# Development of Fuel Flexible Reformer for small scale H<sub>2</sub> generation

A thesis

Submitted in partial fulfillment of the requirements

of the degree of

Doctor of Philosophy

of the Indian Institute of Technology Bombay, India and Monash University, Australia

by

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(July 2021)

# DECLARATION

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July 2021

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## **EXECUTIVE SUMMARY**

Hydrogen has a high energy density, which makes it the fuel of choice in the future. However, present hydrogen production cost and lack of a distribution infrastructure prohibits its implementation. Therefore, there is a growing consensus to produce hydrogen on-site to reduce overall costs and increase H<sub>2</sub> usage. This thesis aims to produce hydrogen via oxidative steam reforming of methanol, diesel and gasoline for a potential on-site usage for back-up power generation in a fuel cell as an alternative to diesel gensets.

Oxidative steam reforming of liquid fuels has been widely researched; however, the focus has been on developing catalysts for a single fuel. Studies which report multi-fuel reforming have shown metal sintering due to low sulphur tolerance or low H<sub>2</sub> yields due to poor selectivity. This thesis addresses this research gap. We developed a Ni-Pt bimetallic catalyst supported on highly mesoporous alumina. The alumina support was prepared by pillaring layered clay, Laponite (phyllosilicate), with additional coke mitigation dopants like cerium, potassium and phosphorous. Among these promoters, potassium doped catalyst provide the highest H<sub>2</sub> yields and lowest coke formation rate.

This thesis also evaluates the effects of potassium loading on catalyst activity and selectivity. An optimum potassium loading of 5 wt% was found (Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub>) which gave 88% reduction in carbon formation compared to catalyst with no potassium loading (Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>). Characterisation studies revealed that potassium loading greater than 5 wt% led to increased diffusion of Ni particles onto the support, increasing the metal particle size. Experimental and ReaxFF molecular modelling results showed that the doped potassium binds with Al and Si, leading to KAlSiO<sub>4</sub> formation. It also caused Ni diffusion from the surface to the bulk support, causing part of the surface to become Pt terminated. These two effects were considered as the main reasons for the observed catalyst stability for multi-fuel reforming.

The best performing catalyst (Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub>) was tested for its stability for reforming methanol and commercial diesel and gasoline. It was found to be stable and active for 42 h onstream for all the three liquid fuels. The conversions for diesel, gasoline and methanol remained steady at 85%, 98% and 98%, respectively. Similarly, steady H<sub>2</sub> production rates of 217, 243 and 263 mmol

H<sub>2</sub>/kg<sub>cat</sub>.s for diesel, methanol and gasoline, respectively, were observed over the duration of the test.

Kinetic data from the experimental study was fitted to a power law kinetic model and used for process design and basic techno-economic analysis for the three fuels under consideration. Techno-economic evaluation showed viability at  $4.21/kg-H_2$  for the methanol system for a minimum of 10,000 pan-India locations for hydrogen generation. Similarly, electricity sale price for the methanol system under similar assumptions and a fixed sale price of H<sub>2</sub> at 4/kg were found to be 0.4/kWh, which is slightly lower than diesel gensets. We conclude that the methanol-based reformer gives 47% lower emissions compared to the diesel genset of similar capacity and a 50-60% reduction in water footprint when compared with electrolysers having similar H<sub>2</sub> output. Coupled with CO<sub>2</sub> capture at source, blue hydrogen can be delivered to clients, allowing a smooth transition to hydrogen economy until green hydrogen generation becomes viable.

# SIGNIFICANT OUTPUT FROM THE PRESENT WORK

#### **Journal Papers:**

• Gupta P., Dwivedi S., Srinivas S., van Duin A.C.T. and Tanksale A., Coke resistant catalyst for hydrogen production in a versatile, multi-fuel reformer, submitted to Journal of Catalysis (Under Review)

#### Patents:

• PCT Patent No. 201921024747 titled "Plurimetallic mesoporous catalyst for multi-fuel reforming and method of producing thereof", Indian Patent Office.

#### **Conference Papers:**

- Gupta P., Srinivas S. and Tanksale A., "Oxidative Multi-fuel reforming via Ni-Pt Supported on potassium-doped alumina for small scale H<sub>2</sub> production", Abstract accepted for oral presentation at 17<sup>th</sup> International Congress on Catalysis, June 2020.
- Gupta P., Srinivas S. and Tanksale A., "Mesoporous Alumina supported Pt-Ni Catalysts for Oxidative Reforming of Methanol and Diesel for Hydrogen Production", Poster presented at 26<sup>th</sup> North American Catalysis Society Meeting, June 2019.

### PAPERS UNDER PREPARATION

- Gupta P., Tanksale A., and S. Srinivas, Techno-economic analysis coupled with process modeling and simulation of multi-fuel reforming using novel Ni-Pt bimetallic catalyst for H<sub>2</sub> production, to be submitted to International Journal of Hydrogen Energy.
- Gupta P., S. Srinivas and Tanksale A, Effect of addition of coke mitigation promoters to Ni-Pt bimetallic catalyst for multi fuel reforming for H<sub>2</sub> synthesis, being prepared.

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## NOMENCLATURE

#### **ABBREVIATIONS**

- ADF: Amsterdam Density Functional
- BET: Brunauer-Emmett-Teller
- BJH: Barrett-Joyner-Halenda
- **CEC:** Cation Exchange Capacity
- CO/CO<sub>2</sub> TPD: CO/CO<sub>2</sub> based temperature programmed desorption
- DTG: Differential thermal gradient
- E85: Gasoline blended with 85% ethanol
- EDAX: Energy Dispersive X-ray Analysis
- FID: Flame ionization detector
- GC: Gas chromatography
- GHSV: Gas hourly space velocity, mlsTP/h.gcat
- GW: Gigawatt
- HAADF-STEM: High-angle annular dark field scanning transmission electron microscopy
- HPLC: High pressure liquid chromatography
- JCPDS: Joint Committee on Powder Diffraction Standards
- kW: Kilowatt

kWh: Kilowatt hour

LH: Langmuir – Hinshelwood

LHHW: Langmuir – Hinshelwood Hougen Watson

MD: Reactive Molecular Dynamics

MW: Megawatt

MWh: Megawatt hour

OCR: Oxygen to carbon ratio (mol/mol)

OMR: Oxygen to methanol ratio (mol/mol)

ppmw: parts per million (weight basis)

PSD: Particle Size Distribution

SEM: Scanning Electron Microscopy

SMR: Steam to methanol ratio (mol/mol)

SCR: Steam to carbon ratio (mol/mol)

TCD: Thermal conductivity detector

T: Temperature, °C

TOF: Turn over frequency, s<sup>-1</sup>

TO: Total oxidation

VMD: Visual Molecular Dynamics

w, wt: weight

#### NOTATIONS

 $\Delta H^o$ : Heat of reaction, J/mol

h: hour

δ: delta

γ: gamma

α: alpha

TPH: Tons per hour

TPD: Tons per day

dv: Volume weighted average particle diameter, (nm)

*k*: forward rate constant (mol.g<sub>cat</sub><sup>-1</sup>.s<sup>-1</sup>)

A: pre-exponential factor (mol.g<sub>cat</sub><sup>-1</sup>.s<sup>-1</sup>)

E: activation energy (kJ/mol)

R: Universal gas constant (kJ.mol<sup>-1</sup>.K<sup>-1</sup>)

 $R_j$ : Rate of reaction with j as the reaction subscript indicating the reaction represented by the rate equation.

C: Concentration in mol/m<sup>3</sup>

*K*: Equilibrium constant

W: Catalyst weight in g

 $v_{i,j}$ : stoichiometric coefficient of the reaction j for a particular species i

kWe: Kilowatt electrical

 $C_{BM}$ : Bare module cost, \$

I: Index for the referred year

S: Capacity of the module / system for capex calculations

n: exponent (value is 0.45)

#### **Subscripts**

th: thermal

STP: Standard Temperature and pressure

cat: catalyst

v: volume

eq: equilibrium

SRM: steam reforming of methanol

r: reverse rate reaction

OM: oxidation of methanol

MD: methanol decomposition

WGS: water gas shift reaction

METH: methanation reaction

SRD: steam reforming of diesel surrogate (n-hexadecane)

OD: oxidation of diesel surrogate (n-hexadecane)

SRG: steam reforming of gasoline surrogate (toluene)

OD: oxidation of gasoline surrogate (toluene)

F: molar flow rates at reformer outlet, (mol/s)

M: methanol

W: water

O<sub>2</sub>: oxygen

CO: Carbon monoxide

CO<sub>2</sub>: Carbon dioxide

H<sub>2</sub>: hydrogen

CH<sub>4</sub>: methane

N<sub>2</sub>: nitrogen

To: Total at initial conditions

T: Total at final / exit of reformer

1: Base year

2: Current year

#### 1.1. Background

Growing world population, rapid urbanization and economic development are the drivers for increased energy usage. Two sectors contributing significantly to the energy demand are power generation and transport. The electricity demand-supply gap was 26% in India in 2016-17. It is projected to decrease to 20.5% by 2021-22, 17.4% by 2026-27, 15.46% by 2031-32 and 14.1% by 2036-37 [1]. Also, India has committed to create a cumulative carbon sink of 2.5-3 billion tonnes of  $CO_2$  equivalent by 2030 in the Paris Climate Agreement [2]. Thus, there is an emphasis on decarbonising new capacity additions in the power sector to achieve both the goals. As per a recent report, the low reliability of electricity supply has triggered widespread use of diesel-based backup power and captive power generation systems in the residential and industrial segments [3]. The total capacity of the back-up generators running on diesel was estimated to be 140 GW which is expensive and contributes to greenhouse gas emissions (700 kg CO<sub>2</sub>/MWh) [4]. An alternative for the diesel genset is a fuel cell powered by hydrogen which operates cleanly, reliably and quietly. Fuel cells for back-up power can be installed and operated at new or retrofit sites in urban, rural, remote or unmanned regions [5]. A case study for telecom towers compared a Plug Power based fuel cell with a 30 kW diesel genset for the back-up power requirements of a telecom tower. It was found that using a fuel cell for 160 h resulted in a diesel consumption of 945 litres worth \$1200 while the fuel cell consumed 14 kg of H<sub>2</sub> at a cost of \$119 only. A land saving of 28% with fuel cell was also shown. Other benefits including lower maintenance costs and elimination of noise pollution via fuel cells are also highlighted [6]. Though hydrogen is the most abundant element, it exists almost always chemically combined with other elements, most notably in the form of water or hydrocarbons [7]. Hydrogen as an energy carrier has the highest gravimetric calorific value (120 MJ/kg) compared with the existing fossil fuels (e.g., 17.4-23.9 MJ/kg for coal and 42-55 MJ/kg for natural gas) [8]. However, it has the lowest mass density leading to storage issues [9]. A global push towards hydrogen economy is observed, with Australia, France, Germany, Japan, Korea and Norway developing national hydrogen strategies [10]. However, the present cost of hydrogen production and storage along with the lack of a dedicated distribution infrastructure prohibits large scale implementation globally as well as in India. Therefore, there is a growing consensus to produce hydrogen for on-site consumption.

### 1.2. Reforming technologies for H<sub>2</sub> production

Conventionally, hydrogen has been produced by steam reforming of natural gas (95% of global hydrogen production) [11]. Recently, concerted efforts towards reducing energy consumption and reactor volumes have resulted in technological advancements in the oxidative steam reforming and auto-thermal reforming technologies. Apart from these processes, hydrogen is also produced from thermochemical transformation of biomass through gasification or from electrochemical splitting of water. However, the former is dependent on biomass availability and has scale-up challenges, while the latter is cost intensive, both in terms of capital (specialized electrodes) and operating (electricity consumed) costs [9]. To date, reforming is the cheapest and commercially successful method to produce H<sub>2</sub> despite being carbon intensive. Reforming is a catalytic process and it is very important to judiciously choose the catalyst and process operating parameters for a good reactor performance, based on the reforming feedstock like natural gas, naphtha, heavy oil, etc.

#### **1.3.** Motivation

As discussed in the previous sections, power generation from fuel cells using hydrogen obtained *via* reforming is envisaged to offer the following benefits – using a liquid feedstock that is easy to handle and transport, and on-site H<sub>2</sub> production that avoids H<sub>2</sub> transport. To have flexibility in the feedstock, it is desirable that the reformer can handle different fuels like methanol, gasoline or diesel depending on their availability. However, this is a challenge owing to the requirement of different catalysts (e.g. Cu-based catalyst for methanol reforming, Ni-based catalysts for diesel, gasoline and methane reforming). Therefore, this challenge can be overcome through the development of a suitable catalyst for multi-fuel reforming with the following features – (i) offers good yields of hydrogen; (ii) exhibits good activity and longevity; and (iii) resists coking, especially with regards to higher hydrocarbons. This thesis work focuses on using methanol, diesel and gasoline as the reformer feed. Apart from catalyst development and characterization studies, the work also investigates and reports results from a preliminary techno-economic analysis of the proposed process using the newly formulated catalyst.

#### **1.4.** Organization of the Thesis

This thesis is organized into seven chapters, as follows -

Chapter 2 describes the various reforming processes for producing hydrogen and the advantages of oxidative reforming. A critical review of the various catalysts reported in the literature for reforming methanol, gasoline and diesel is also presented. The chapter concludes with identification of the research gaps which have helped us define the overall objectives of this work.

Chapter 3 summarizes the materials and methods used to synthesize the catalysts and perform the experiments, and the analytical methods used in catalyst and product characterization. It also highlights the modelling approach followed in predicting the experimental observations.

Chapter 4 compares the various catalysts used for diesel, gasoline and methanol reforming during the screening studies and lays the foundation for development of a multi-fuel reforming catalyst. Various characterization techniques are used to analyse and describe the experimental observations. It also investigates the effect of sulphur impurity in the fuel on the catalyst performance.

Chapter 5 investigates the optimized loading for the promoter chosen (viz., potassium) and the effect of different parameters like steam and oxygen flow rates, reactor temperature and space velocity on hydrogen yields. Results from a comprehensive stability test while reforming multiple fuels are also reported and justified using characterization studies. Effects of potassium addition viz. novel kalsilite phase formation and Ni diffusion on bulk support leading to a Pt-terminated surface are proposed as the reasons for the observed catalyst stability.

Chapter 6 reports the modelling and simulation results for the reforming of each fuel. It also includes a preliminary techno-economic analysis for a proposed process using the novel catalyst developed in this work. The evaluation is compared with diesel gensets and electrolysers of similar capacities for hydrogen and power generation. Finally, the key outcomes from this work and the proposed ideas for future work are presented in the last chapter (Chapter 7).

## 2.0. LITERATURE SURVEY

This chapter discusses the present scenario with respect to back-up power generation and need for on-site hydrogen generation through catalytic reforming as a preferred route. Various reforming processes along with a critical review of the catalysts reported are presented in this chapter. The major research gaps in reforming and the objectives identified for this work are also discussed.

#### 2.1. Background

The Indian diesel genset market, estimated at  $1.04 \times 10^9$  in 2018 is projected to reach  $1.52 \times 10^9$ by 2024 [12]. Based on power rating, the diesel genset market is classified into 4-60 kW, 61-300 kW, 301-600 kW and >600 kW segments with the highest market share occupied by the 4-60 kW segment. These gensets are employed in residential and small commercial installations, construction projects, telecom towers, commercial offices, hospitals and hotels. The energy deficits highlighted in Chapter 1 coupled with unreliable electricity supply are the main drivers for the growth in the diesel genset market for back-up power requirements. Unreliable supply from the electrical grid is one of the biggest challenges faced by the rapidly growing telecom industry in India. As on May 2018, 70% of the ~ 4,00,000 telecom towers in India faced electrical outage for more than 8 h per day. According to the Telecom Regulatory Authority of India (TRAI), an estimated 24 L/day of diesel is consumed per tower, which cumulatively amounts to  $2.5 \times 10^9$  L/y, leading to  $6.6 \times 10^6$  tonnes of CO<sub>2</sub> emissions [13]. Post deregulation of diesel prices, the cost of energy has increased with an estimated 90% of the total telecom tower operating expenses being spent on operating and maintaining diesel generators. With the global push towards hydrogen economy, hydrogen powered fuel cells have been proposed as a cleaner, reliable and cost effective alternative to diesel gensets [5,14–16]. Application of fuel cells can also be extended to other diesel genset based applications in India. Fig. 2.1 pictorially describes the usage of hydrogen powered fuel cells as an alternative to diesel gensets in telecom towers. The fuel cell is powered by hydrogen which is produced via reforming of liquid fuels viz. methanol, diesel and gasoline which have established distribution networks. Thus, hydrogen is generated on-site by reacting the liquid fuels (in vapor form) with steam and / or air to form a reformate gas having H<sub>2</sub> mol% between 40 - 70%depending upon the catalyst and process conditions used for reforming. The reformate then undergoes purification to achieve the purity levels suitable for usage in a fuel cell for power generation.



Figure 2.1: Pictorial description of the usage of hydrogen powered fuel cells for telecom towers

The following section discusses the different hydrogen production technologies.

## 2.2. Hydrogen production technologies

Though hydrogen is present in abundance, it is always present in a chemically bound form in the form of hydrocarbons or water. Some of the physical and chemical properties of hydrogen are reported in Table 2.1.

Hydrogen has the highest calorific value of 120 MJ/kg. However, its low energy density necessitates a large storage volume which is the main barrier for its large-scale use as an energy carrier. This storage problem can be circumvented by generating hydrogen on-site by reforming easily available fuels like gasoline and diesel that have a well-established distribution network. The various technologies for hydrogen production are pictorially described in Fig. 2.2.

Parameter	Value	Units
Molecular weight	2.016	g/mol
Freezing point @ 1 bar	-259	°C
Boiling point @ 1 bar	-253	°C
Gas density @ STP	0.09	kg/m <sup>3</sup>
Gas viscosity @ -252.77 °C	0.00085	mPa.s
Heat of vaporization	0.92	kJ/mol
Lower heating value	240	kJ/mol
Autoignition temperature in air	571	°C
Flammability limits in air	4-77	vol%
Energy density	0.011	MJ/dm <sup>3</sup>

# Table 2.1: Physical and Chemical Properties of Hydrogen



**Figure 2.2**: Pictorial description of Hydrogen production Technologies (*Note: PEM stands for Proton electron membrane*)

#### 2.2.1. Electrolysis

Electrolysis of water to produce hydrogen is the most widely reported method for green hydrogen production. Electrolysis is done predominantly by alkaline electrolysis (AE) or proton exchange membrane (PEM) electrolysis. The most commonly used technology is alkaline electrolysis in which KOH or NaOH is used as an electrolyte solution and negatively charged ions (hydroxyl ions) are used as charge carriers [17]. The input water quality determines the overall efficiency of the AE process. Small amounts of Ca, Mg or NaCl, if present, form deposits and reduce the overall surface area available for electrolysis. Moreover, presence of NaCl can lead to formation of chlorine gas at anode instead of oxygen which can lead to extensive corrosion [17]. PEM electrolysers are an improvement over AE electrolysers in terms of reducing the electrical consumption (12.5%) and water consumption (12.5%) [18–20]. PEM electrolysers use acidic electrolytes in which positively charged ions act as energy carriers. The conversion efficiency is ~80% when operated between 60 to 80°C. In addition to improved membrane designs, a Pd or Pt coating on electrolytes is also needed to avoid damage due to corrosion since the medium is acidic [21]. In view of the gap in technical maturity and high cost, the electrolyser technology is not yet competitive for decentralized production of hydrogen.

#### 2.2.2. Biomass Gasification

Since decades, thermochemical conversion of biomass *via* gasification is considered as the most mature technology for syngas (H<sub>2</sub>+CO) production from biomass using different feedstocks like wood, rice husk, bagasse, etc. [9]. Biomass pyrolysis is another thermochemical process that produces bio-oil as the main product and H<sub>2</sub> as the secondary product [22]. Since the yield of H<sub>2</sub> is lower in pyrolysis compared to gasification, it is not discussed further. Biomass gasification for hydrogen production has been extensively reported for large scale systems. A complete 1 MW<sub>th</sub> gasification system with downstream purification gave a hydrogen production cost of \$11.5/kg H<sub>2</sub>\* - the higher costs are attributed to the down-stream purification process [23,24]. A techno-economic analysis for a 100 kW<sub>th</sub> system indicated that a 50% reduction in the capital cost of the purification system coupled with a 50% increase in the steam input should lead to a decrease in the H<sub>2</sub> production cost from 17.67 to 13.17 (\$/kg) [25]. The cost was still higher than the target price of \$6.93/kg indicated in the study. Further, large-scale biomass gasification is associated with problems of feedstock supply, land use, handling of tar in the syngas and cost of the biomass.

Another study showed viability for a minimum household demand of 2 kWh per house using a cluster of 300 households for a decentralized dedicated biomass gasification system with a support price of \$2650/ton for the biochar produced [27]. A small-scale biomass based H<sub>2</sub> generation system is, therefore, techno-commercially unviable and it would be prudent to consider these systems for a semi-centralized or centralized generation applications (> 1 MW<sub>th</sub> systems).

#### 2.2.3. Reforming

There are three major reforming technology options to produce hydrogen from fossil fuels: steam reforming (SR), partial oxidation (POX) and auto-thermal reforming (ATR). Eqns. 2.1 to 2.3 list the principal reactions encountered in each process [28,29]. Based on these three reactions, it can be inferred that the highest  $H_2$  yield can be obtained from the steam reforming reaction.

Steam reforming is an endothermic process that requires heat which is supplied by combusting the fossil fuel in an auto-thermal process. Excess steam is used in this catalytic process to limit coke deposition and hot spot formation.

$$C_x H_y + x H_2 \mathbf{0} \rightarrow x C \mathbf{0} + \left(x + \frac{1}{2}y\right) H_2, \quad \Delta H^o > 0$$
 2.1

Partial oxidation is an exothermic process that utilizes oxygen or air as a reactant for hydrogen production (Eq. 2.2). A major advantage with POX is that higher operating temperatures can be realized from the exotherm making it more sulphur tolerant. However, the higher operating temperatures lead to a decrease in hydrogen selectivity. High rates of carbon formation, sintering of catalyst as well as deactivation along with hot spot formation are the other problems frequently encountered [28].

$$C_x H_y + \frac{x}{2} (O_2 + 3.76N_2) \rightarrow xCO + \left(\frac{y}{2}\right) H_2 + \frac{x}{2} 3.76N_2, \quad \Delta H^o < 0$$
 2.2

Auto-thermal reforming or oxidative steam reforming is a combination of steam reforming and partial oxidation as seen in Eq. 2.3. During ATR, the exotherm released during the partial oxidation is used to sustain the endothermicity of the steam reforming reaction. ATR results in higher  $H_2$  yields and low carbon formation depending upon the process conditions utilized. Studies have shown that ATR is a dynamic and energy efficient process capable of handling the frequent startups and shutdowns occurring in back-up power applications [30–32]. The technology is versatile as it combines the advantages of both steam reforming and partial oxidation resulting in a small, compact reformer. ATR is more energy efficient compared to SR due to lower steam requirements [33]. However, downstream purification cost increases due to dilution of the reformate gas with nitrogen leading to lower  $H_2$  yields than SR [34–36]. Heat integration is also quite complex making the design of the reformer challenging.

$$C_x H_y + \frac{x}{4} (O_2 + 3.76N_2) + \frac{x}{2} H_2 O \rightarrow x CO + \left(\frac{x}{2} + \frac{y}{2}\right) H_2 + \frac{x}{4} 3.76N_2$$
 2.3

In this thesis, auto-thermal reforming or oxidative steam reforming was used as the reforming methodology for reforming three fuels, viz. gasoline, diesel and methanol. The following section details the various catalysts which have been reported in literature for ATR of each fuel.

#### **2.3. Reforming Catalysts**

Though methane has not been considered as a potential fuel in our study, a short review of the methane reforming catalysts is presented owing to their wide-spread use. Also, various promoters have been investigated in methane reforming to lower the carbon formation rate. Following the section on SMR catalysts, the remaining sub-sections review the catalysts reported for ATR of methanol, diesel and gasoline.

#### 2.3.1. Methane

A summary of the catalysts used for ATR of methane is tabulated in Table 2.2.

Different supports (Ce-ZrO<sub>2</sub>, ZrO<sub>2</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, MgO and MgAl<sub>2</sub>O<sub>4</sub>) on Ni were tested for methane reforming [37]. BET surface area for single oxide supports were in the range of 3-16 m<sup>2</sup>/g with the highest surface area obtained for Ce-ZrO<sub>2</sub> (40 m<sup>2</sup>/g). Consequently, highest conversions and H<sub>2</sub> production rates were obtained for Ni/Ce-ZrO<sub>2</sub> catalyst. The superior activity was attributed to the high oxygen storage capacity with the formation of free Ni species on the surface and their interaction with the support. Addition of Al<sub>2</sub>O<sub>3</sub> to tetragonal Ce-ZrO<sub>2</sub> was shown to have a positive effect on Ni/Ce-ZrO<sub>2</sub> for methane reforming [38]. Addition of Al<sub>2</sub>O<sub>3</sub> favoured the formation of smaller Ni particles and increased the metal dispersion. The presence of Ce-ZrO<sub>2</sub> helped avoid carbon deposits by providing an additional path for adsorption and dissociation of oxygen and steam, forming O<sup>2-</sup> and OH<sup>-</sup> on the support surface which reacted with carbon at the metal support interface.

Catalyst Conversion		Test	Key reasons for the observed catalyst activity	Reference
		Duration, h		
Ni/Ce-ZrO <sub>2</sub>	99.1%	$NA^*$	Easy reducibility, access to mobile lattice oxygen via redox	[37]
			reaction due to presence of Ce	
Ni/Ce-ZrO <sub>2</sub> -	65%	24	Alumina addition favoured higher Ni dispersion and	[38]
Al <sub>2</sub> O <sub>3</sub>			formation of smaller Ni particles compared to Ce-ZrO2 only	
Ni/Ce-ZrO <sub>2</sub>	96%	NA	Higher Ni reducibility due to weak metal support	[39]
			interaction when compared with Ni/La <sub>2</sub> O <sub>3</sub>	
Pt/Ce-ZrO <sub>2</sub>	78%	24	Presence of Ce helped in oxygen transfer at the metal	[40]
			support interface thereby eliminating coke formation	
Rh/Ce-ZrO <sub>2</sub>	55%	10	Emulsion method led to the formation of a single cubic	[41]
			phase of Ce-Zr leading to enhanced oxygen transfer	
Ni-Pt/Al <sub>2</sub> O <sub>3</sub>	80%	NA	Pt presence helped in bringing a large number of Ni species	[42]
			to the surface via H <sub>2</sub> spill-over mechanism	
Ni-Ag/Ce-ZrO <sub>2</sub>	60%	24	Ag addition improved Ni reducibility and enhanced redox	[43]
			reaction capability of Ce	
Ni-Pt/ Al <sub>2</sub> O <sub>3</sub>	90%	NA	Promotion of H <sub>2</sub> spill over mechanism due to Pt presence	[44]
Pt/Ce-Al <sub>2</sub> O <sub>3</sub>	100%	2400	Using $\alpha$ -phase of alumina which is more stable compared	[45]
			to the $\gamma$ -phase along with Ce promoted redox reaction	

Table 2.2: Sumn	nary of catalysts	used for ATR	of methane
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\*-NA (Not reported)

Note: Hydrogen production rates and corresponding yields were not reported for above references in Table 2.2
Three different supports, La<sub>2</sub>O<sub>3</sub>, Ce doped with Gadolinium and Ce-ZrO<sub>2</sub>, with Ni as active metal species were tested for methane reforming [39]. Yields of 35% H<sub>2</sub> and 41% CO with 76% conversion were observed for La<sub>2</sub>O<sub>3</sub> while the yields improved to 49% and 66%, respectively for H<sub>2</sub> and CO with conversion nearly 96% for Ni/Ce-ZrO<sub>2</sub>. Comparable activities were obtained when 10 wt% Ni was replaced by 1 wt% Rh. Strong interaction of Ni with La<sub>2</sub>O<sub>3</sub> leading to formation of LaNiO<sub>3</sub> and La<sub>2</sub>NiO<sub>4</sub> led to reduction in active sites for reforming. The activity improved with Ce-ZrO<sub>2</sub> as the support. Pt/CeZr prepared using co-precipitation method showed superior activity for methane at 800 °C [40]. This was attributed to a balance in oxygen transfer ability of the support and metal dispersion with oxygen transfer occurring at the metal-support interface which helped in removing the carbon deposits. Different catalyst preparation methods (reverse micro-emulsion, urea combustion and sol-gel) for Rh/CeZr were evaluated [41]. The best activity was reported for the emulsion method owing to the single cubic phase of the Ce-Zr which enhanced the oxygen storage capacity and reducibility of the catalyst. Adding 0.1 wt% Pt to 15 wt% Ni on Al<sub>2</sub>O<sub>3</sub> was shown to be beneficial for methane reforming resulting in higher conversions and H<sub>2</sub> formation [42]. The addition of Pt was shown to increase the number of Ni species available for reduction due to H<sub>2</sub> spillover effect leading to an increase in the active metal area. Effect of different promoters (Ag, Fe, Pt and Pd) in Ni/Ce-ZrO<sub>2</sub> in methane reforming was studied [43]. Amongst the different promoters, Ag gave the highest conversion and H<sub>2</sub> yields compared to monometallic Ni catalyst owing to increased reducibility and redox capability due to Ag addition. It was also shown that addition of Ag and Ni in co-impregnation mode rather than sequential impregnation mode was beneficial for retaining catalyst performance. Addition of Pt, Pd and Ir to Ni/Al<sub>2</sub>O<sub>3</sub> was shown to increase the conversion of methane with addition of Pt showing highest conversions for the same operating conditions [44]. Enhancement in activity was attributed to the H<sub>2</sub> spillover mechanism wherein more Ni sites were available for reaction due to presence of Pt. Consequently, the conversion improved from 40% for Ni/Al<sub>2</sub>O<sub>3</sub> to nearly 90% while the H<sub>2</sub> mol fraction improved from 7 mol% to 28 mol% at 600 °C with Pt addition. A 2% Pt on CeO<sub>2</sub>-α- $Al_2O_3$  catalyst was shown to be stable for reforming commercial natural gas (majorly methane) with a conversion of 99% and H<sub>2</sub> concentration of 62% for more than 2400 h in operation [45]. Formation of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> from  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> led to a decrease in the surface area from 175 to 60 m<sup>2</sup>/g which was further reduced to 20 m<sup>2</sup>/g with a coating of CeO<sub>2</sub> to the support. However, the loss in surface area is reasoned to be a better approach compared to doping of the support. The CeO<sub>2</sub> coating layer is shown to eliminate coke due to its oxygen storage capacity releasing oxygen and oxidizing the adsorbed carbon on catalyst surface. Majorly, compared to monometallic catalysts (Ni/Pt), bimetallic combination (Ni-Pt/Ni-Pd/Ni-Ag) showed higher activities primarily due to more active species made available for reforming due to the H<sub>2</sub> spillover mechanism. Similarly, modified supports with Ce-ZrO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> addition to Ce-ZrO<sub>2</sub> was shown to favour formation of smaller metal particles compared to Ce/Al<sub>2</sub>O<sub>3</sub> based supports. Following section reviews the various catalysts reported for methanol reforming.

## 2.3.2. Methanol

The catalysts used in ATR of methanol are summarized in Table 2.3.

ATR of methanol over Cu/ZnO was shown to provide higher H<sub>2</sub> production rates compared to steam reforming [46]. Also, catalyst (Cu) sintering was avoided by maintaining a reactor temperature of 250 °C to overcome the exotherm generated during the oxidation reactions. In another study, Cu-Zn/Al<sub>2</sub>O<sub>3</sub> gave high methanol conversions where primary combustion products were produced [47]. Over the course of the reaction, it was found that part of the Cu metal particle size increased due to high temperatures resulting from the exothermic oxidation reactions. Part of the catalyst surface, however, remained active for hydrogen production. With further progress in run times, the proportion of sintered Cu metal surface increased leading to complete catalyst deactivation.

Catalyst	Conversion	Test	Key Reasons for the observed catalyst activity	Reference
		Duration, h		
Cu <sub>20</sub> -Zn <sub>80</sub> /Al <sub>2</sub> O <sub>3</sub>	48%	1	The process conditions were compared	[46]
Cu60-Zn25/Al2O3	99.5%	15	Over the reaction time on stream, Cu particle sintered leading	[48]
			to the observed deactivation in unreduced form in start/stop	
			experiments	
Cu32-Zn42/Al2O3	99.5%	4	Co-precipitation led to a lowering of the reduction temperature	[49]
			for Cu, thereby leading to the availability of a larger number of	
			active sites	
Cu <sub>6</sub> -Zn <sub>9</sub> /Al <sub>2</sub> O <sub>3</sub>	87%	24	Higher Cu reducibility observed	[50]
Cu31-Zn50-	60%	18	Decrease in conversion observed due to a progressive increase	[51]
$Zr_{14}/Al_2O_3$			in the Cu particle size and segregation of Zn from the bulk	
Ni6-Cu24/Al2O3	91%	46	Formation of a Cu core with Ni in nanoparticle form till Ni/Cu	[52]
			loading of 15 wt%. Beyond 15 wt%, Ni-Cu alloy formed	
			leading to a decrease in H <sub>2</sub> yield.	
Rh1/Ce10-Al2O3	72%	1.67	Higher selectivity towards methanol decomposition due to the	[53]
			presence of Rh	

## Table 2.3: Summary of different catalysts used for ATR of methanol

\*-NA (Not reported)

Similar observations were reported for Sud-Chemie based Cu-Zn/Al<sub>2</sub>O<sub>3</sub> catalyst which deactivated rapidly upon temperatures exceeding 300 °C due to sintering of the metal particles [48]. In a separate study, catalyst preparation method was shown to influence the catalyst performance [49]. Cu-Zn/Al<sub>2</sub>O<sub>3</sub> prepared *via* co-precipitation method improved the H<sub>2</sub> concentrations (71-76 mol%) with very low CO concentrations (0.15 mol%) at a steam to methanol ratio of 1.43 and oxygen to methanol ratio of 0.158 (mol/mol). The effect of promoter addition to Cu-Zn catalysts was also shown to have an influence on the catalyst activity. Addition of Zn, Zr and Cr to Cu/Al<sub>2</sub>O<sub>3</sub> was studied on methanol reforming [50]. It was found that the Cu-Zn/Al<sub>2</sub>O<sub>3</sub> combination gave the highest methanol conversion (nearly 100%) with lower CO concentrations in ATR mode compared to its use in the steam reforming mode. The catalyst effectiveness was attributed to the easier reducibility of copper and the reduction temperature was the lowest for the Cu-Zn combination. However, extended runs were not possible since prolonged exposure to oxidizing environments oxidized Cu to CuO – this lowered the catalyst activity and required  $H_2$  pre-treatment for regaining its activity. In another study, a Cu/ZnO-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> combination tested on methanol was found to be superior in catalytic activity compared to Cu/ZnO [51]. The combined mixed oxide catalyst was also found to be stable when subjected to multiple oxidation-reduction cycles. During oxidation,

it was hypothesized that there is an increase in the Cu particle size as it is well dispersed in the support and the metallic surface is easily oxidized. Upon reduction, the catalyst regains its activity. During this process of simultaneous oxidation and reduction cycles, a distinct increase in the Cu particle size coupled with segregation of zinc from the bulk is observed. This phenomenon was responsible for the stability of the catalyst in an oxidative steam reforming environment. Sintering of the Cu particles at temperatures greater than 350 °C led to efforts where noble metals were tried out. Pd/ZnO was tested for methanol reforming and it showed good selectivity towards H<sub>2</sub> with low CO formation in the product gas (8.4 mol%) [54]. However, with the addition of Ni to Zn, the CO formation increased to 41 mol% with a corresponding decrease in H<sub>2</sub> yields. Similar results were reported for addition of Co and Mg. Addition of Al, Zr, La, Ce, Ru and Mn also resulted in a significant increase in the CO concentration suggesting an increase in the selectivity towards methanol decomposition on addition of these metals. Contrastingly, addition of Cr, Fe or Cu to Zn decreased the CO formation and increased the H<sub>2</sub> concentration. However, sintering of ZnO particles was observed due to the high reduction temperatures of 500 °C, especially with Cu. Pt-Ru/SiO<sub>2</sub> supported catalyst exhibited superior activity compared to monometallic variants (Pt/SiO<sub>2</sub> and Ru/SiO<sub>2</sub>) for methanol reforming [55]. The formation of solid solution of Pt and Ru with Ru addition to Pt/SiO<sub>2</sub> led to high H<sub>2</sub> yields and low CO concentrations. The reaction proceeded through HCOOCH<sub>3</sub> and HCOOH while CO<sub>2</sub> formation did not proceed via HCHO decomposition. The catalyst was not found to be very active for methanol decomposition reaction. Bimetallic Ni-Cu/ZrO<sub>2</sub> prepared by successive impregnation was shown to be a stable catalyst for methanol reforming at 400 °C [52]. This is due to the formation of a Cu core with Ni nanoparticles till a Ni/Cu loading of 15 wt%, which led to high H<sub>2</sub> selectivities. However, the formation of a Ni-Cu alloy within the Cu core with an increase in Ni/Cu loading from 15 wt% to 30 wt% led to a decrease in H<sub>2</sub> selectivity and a corresponding increase in CO concentration. The catalyst was found to be stable for 46 h on-stream. Ce-ZrO<sub>2</sub> impregnated with Rh showed higher methanol decomposition rates compared to reforming thereby providing higher CO concentrations in the reformate gas [53]. Cu-Zn based catalysts showed higher H<sub>2</sub> yields with lower CO concentrations compared to noble metal based catalysts (Rh/Pt) due to their lower selectivities for methanol decomposition reaction [53]. However, Cu-Zn based catalysts are also prone to sintering above 350 °C and hence are not suitable for high temperature reforming especially fuels like diesel and gasoline. Following section details the catalysts reported in literature for diesel reforming.

# 2.3.3. Diesel

Most of the studies on ATR of diesel are concentrated on reporting stable performance of the catalyst used and coke formation tendency which is the main reason for catalyst deactivation. Since commercial diesel is a complex mixture of hydrocarbons, the studies use surrogate components. Table 2.4 summarizes the various catalysts reported for either commercial diesel or surrogates.

Catalyst	Conversion	Test	Key Reasons for the observed Catalytic Activity	Reference
		Duration, h		
Rh1/Ce10-Al2O3	96%	1.67	The Ce-Al combination showed high oxygen transfer due to	[53]
			redox reaction which led to decreased coke formations.	
Mo <sub>2</sub> C	100%	6	Exhibited resistance to coking and oxidation in low steam	[56]
	(hexadecane)		environments. However, low H2 yields obtained	
Pt/CeO <sub>2</sub>	80%	55	Deactivation observed in the presence of sulphur	[57]
Pt/Gd-CeO <sub>2</sub>	100%	54	Enhancement in redox behaviour observed due to the	[58]
	(dodecane)		presence of Gd in the CeO <sub>2</sub> matrix	
Rh/ZrO <sub>2</sub>	100%	2	Experimental evaluation of carbon free regime was found	[59]
Rh-Pt/CeO2-	97.6%	3	Higher metal dispersion and higher reducibility of Rh	[60]
$ZrO_2$			observed with Pt presence	

 Table 2.4: Summary of catalyst performance reported for ATR of diesel

\*-NA (Not reported)

Note: H<sub>2</sub> production rates were not reported for any of the references mentioned in Table 2.4

Rh/Ce-ZrO<sub>2</sub> gave high conversions for commercial diesel reforming with high H<sub>2</sub> selectivity [53]. Bulk Molybdenum carbide as a catalyst (surface area < 5 m<sup>2</sup>/g) was reported for oxidative steam reforming of hexadecane (diesel surrogate) [56]. Though the catalyst was found to be stable (upto 2 wt% aromatic content), the H<sub>2</sub> yields were low due to the lower surface area at 885 °C and the low steam to carbon ratios (0.71 mol/mol) used. Pt/CeO<sub>2</sub> (surface area of 68 m<sup>2</sup>/g) was used for reforming of synthetic diesel (surrogate mixture to mimic commercial diesel) [57]. Stable performance was reported for a steam to carbon ratio of 2.5 mol/mol, oxygen to carbon ratio of 0.5 mol/mol and GHSV of 17000 h<sup>-1</sup> with feed fed at 400 °C. Overall, the reforming was demonstrated to be sustained adiabatically resulting in auto- thermal conditions.

Ni/Al<sub>2</sub>O<sub>3</sub> wherein Nickel aluminate (NiAl<sub>2</sub>O<sub>4</sub>) spinel formation prepared via wet impregnation showed higher stability for diesel reforming compared to spinel prepared via co-precipitation [61]. It was inferred that the impregnation method led to the presence of more Ni species on the surface which contributed to the catalyst stability. Co-precipitation method led to the presence of Ni

species in the bulk due to stronger metal-support interaction and decreased the Ni species available for reaction. A Rh/ZrO<sub>2</sub> catalyst was tested for reforming commercial diesel and a relatively carbon free regime were reported [59]. It was also observed that the presence of napthenes and aromatics in diesel can also act as precursors for carbon formation in addition to the ethylene produced during the reaction. The performance of Pt on modified Gd-CeO2 was optimized on dodecane and hexadecane (surrogate fuels for diesel) [58]. The stability of the catalyst was investigated in the absence of any aromatic content in the fuel. Performance of monometallic (Pt/Al<sub>2</sub>O<sub>3</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>) as well as bimetallic (Pd-Pt/Al<sub>2</sub>O<sub>3</sub>) were evaluated on synthetic diesel and the performance of the bimetallic catalyst was found to be superior to the monometallic catalysts [62]. The superior performance was due to the improved metal-support interactions and increased reducibility due to the presence of the noble metal. Similar observations were reported with Ni-Pt/CeO<sub>2</sub> as compared to Ni/CeO<sub>2</sub> and Pt/CeO<sub>2</sub>. Different supports like Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>-ZrO<sub>2</sub>, SiO<sub>2</sub> and TiO<sub>2</sub> on Rh-Pt were tested for reforming of commercial diesel [60]. Rh-Pt/CeO<sub>2</sub>-ZrO<sub>2</sub> showed the highest conversion of 98% with the activity increasing in the following order: Rh-Pt/SiO<sub>2</sub>< Rh-Pt/TiO<sub>2</sub>< Rh-Pt/Al<sub>2</sub>O<sub>3</sub>< Rh-Pt/CeO<sub>2</sub>-ZrO<sub>2</sub>. Various promoters such as MgO, Y<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub> and ZrO<sub>2</sub> ranging from 4 to 10 wt% were also added. In most cases, negligible impact was seen on the catalyst performance except for the addition of La<sub>2</sub>O<sub>3</sub> to Rh-Pt/Al<sub>2</sub>O<sub>3</sub> in which case the hydrogen concentration was enhanced from 24 vol% to 36 vol% in the reformate. The superior performance is ascribed to the higher reducibility of Rh species with high metal dispersion. Rh was found mainly on Ceria and zirconia while Pt was dispersed mainly on Ceria in the form of Pt-O-Ce bond. A Rh/δ-Al<sub>2</sub>O<sub>3</sub> with Ce and La doped on the support was tested on commercial diesel and was found to be stable for 60 minutes of time on-stream [63]. The conversion was ~95% and CO<sub>2</sub>, H<sub>2</sub> and CH<sub>4</sub> were the major constituents in the product gas which had negligible CO content. In summary, bimetallic combinations showed superior activity compared to monometallic catalysts.

#### 2.3.4. Gasoline

Gasoline is also a complex mixture of hydrocarbons with varying aromatic content. This section briefs about the catalysts reported for auto thermal reforming of gasoline or simulated fuels mimicking gasoline properties. Table 2.5 lists the various catalysts tested for ATR of gasoline or its surrogates.

Catalyst	Conversion	Test	Key Reasons for Observed Catalytic Activity	Reference
		duration, h		
Rh <sub>1</sub> /Ce <sub>10</sub> -Al <sub>2</sub> O <sub>3</sub>	99%	1.67	The Ce-Al combination showed high oxygen transfer due to	[53]
			redox reaction which led to reduced coke formation.	
Pt/CeO <sub>2</sub> -ZrO <sub>2</sub>	80% (iso-	15	Pt gave higher thermal stability at 850-900 $^{\circ}\mathrm{C}$ compared with	[64]
	octane)		Rh. Ce-Zr showed high oxygen transfer	
La0.8Ce0.2NiO3	100% (n-	220	Homogenous dispersion of Ni particles coupled with	[65]
perovskite	octane)		enhanced oxygen transfer due to Ce presence	

Table 2.5: Summary of catalysts performance reported for ATR of gasoline

Rh/Ce-ZrO<sub>2</sub> gave high conversions for commercial gasoline reforming with high H<sub>2</sub> selectivity [53]. In a study on simulated gasoline where the aromatic fraction was varied between 14 and 38 wt%, it was found that Pt/ZrO<sub>2</sub> and Rh/ZrO<sub>2</sub> had lesser coke formation compared to Ni [66]. Among the Pt and Rh promoted catalysts, the Pt promoted catalyst showed better performance. It was concluded that the volatile rhodium compounds vaporized at the high reforming temperatures of 850-900 °C leading to lower thermal stability of the catalyst when compared with Pt/ZrO<sub>2</sub>. Pt/Ce-ZrO<sub>2</sub> combination was tested for optimizing the process conditions of iso-octane (gasoline surrogate fuel) reforming [64]. Highest H<sub>2</sub> production and nearly thermoneutral conditions were achieved at steam to carbon ratio of 2.4 (mol/mol) and oxygen to carbon ratio of 0.75 (mol/mol). Though sintering in Pt particles was observed at such high oxygen to carbon ratios, it did not lead to any decrease in conversion since the catalyst was tested for shorter durations. Ni/MgO-Al<sub>2</sub>O<sub>3</sub> (hydrotalcite) was tested for iso-octane (surrogate for gasoline) reforming and compared with variants where a fourth element Fe/Co or Mo was added to Ni [67]. It was found that the Ni-Fe/MgO-Al<sub>2</sub>O<sub>3</sub> combination gave the highest H<sub>2</sub> selectivity (65% mol/mol) and lowest CO selectivity (11.3% mol/mol). The authors reported the catalyst to be stable for 800 h on-stream when 5 ppmw sulphur was added to iso-octane. Addition of Fe increased the BET surface area from 28 (for Ni/MgO-Al<sub>2</sub>O<sub>3</sub>) to 74 m<sup>2</sup>/g which helped in maintaining Ni dispersion and was cited as the main reason for the catalyst stability. La-Ce-NiO<sub>3</sub> perovskite (Ce substituted La) was tested on n-octane (gasoline surrogate compound) and was found to be thermally stable for 220 h of operation [68]. However, the catalyst reported rapid deactivation when sulphur content was increased beyond 5 ppmw in the fuel feed. The catalyst stability was attributed to the homogenous dispersion of Ni metallic particles over the perovskite matrix coupled with enhanced oxygen mobility of cerium to oxidize any carbon accumulated during the reaction. A study on commercial gasoline using Rh/Al<sub>2</sub>O<sub>3</sub> was reported and it was concluded that the catalyst deactivated due to

the presence of sulphur in the feed which led to initiation of carbon formation [69]. In summary, Pt/Rh based catalysts or bimetallic combinations with Ni as the main metal showed higher activities for gasoline reforming. However, there are very few studies wherein the same catalyst has been tested for multiple fuels. Following section discusses about multi- fuel reforming catalysts.

# 2.3.5. Multi-fuel Reforming Catalysts

It is evident that most studies have focused on developing a stable catalyst for a single type of fuel which limits the catalyst applicability. To make significant progress towards the hydrogen economy, a multi-fuel reforming catalyst is needed which can treat a wide range of liquid hydrocarbons. One of the earliest publications on multi-fuel reforming was reported on a proprietary Pd/ZnO formulation developed primarily for methanol reforming; results on JP-8, synthetic diesel and iso-octane were also reported [70]. However, the catalyst deactivated in this study due to low sulphur tolerance, which led to sintering and high carbon deposition. A Rh-based Ce/La doped  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst for reforming diesel, gasoline, dimethyl ether, ethanol, E85 and methanol showed higher selectivity for methanol decomposition instead of reforming reaction, thereby lowering hydrogen yields for methanol [53]. One of the major issues in diesel and gasoline reforming is the tendency of coke formation on the catalyst surface leading to metal sintering and deactivation. Hence, additional promoters have been added to the catalyst structure to increase the coking resistance by altering the acid-base properties of the support to avoid sintering and promote catalyst activity. The most versatile supports reported were Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, CeO<sub>2</sub>-ZrO<sub>2</sub> or a combination of Al<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> with Zr added in some cases. CeO<sub>2</sub> based supports offer lower surface area compared to Al<sub>2</sub>O<sub>3</sub> based supports. Therefore, Al<sub>2</sub>O<sub>3</sub> was chosen as the base support for our case. The following section discusses the various coke mitigation promoters reported with Al<sub>2</sub>O<sub>3</sub> as the base support.

#### 2.3.6. Coke Mitigation Promoters

Addition of Ce led to partial coverage of Ni and increased the CO<sub>2</sub> adsorption in dry reforming of methane owing to increased basicity. This led to the formation of surface carbonate species resulting in removal of carbon precursors from the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst surface [71]. Enhanced catalyst activity and coke resistance were reported when Ce was added to alumina with co-impregnation of Ni and potassium on the mixed support oxide of CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. The catalyst

stability was attributed to oxidation of the surface carbon species due to the oxygen storage capacity of Ce. However, increased ceria loading led to coverage of Ni sites leading to lower activities [72]. Another study showed that the presence of Ce on the surface *via* co-impregnation led to the formation of NiO aggregates of greater sizes due to the competition generated by the anchorage sites dependent on Ce content. Coke formation, however, was reported to be reduced with Ce addition [73]. Higher stabilities and activities were registered when Rh/Al<sub>2</sub>O<sub>3</sub> was doped with Ce due to the ability of Ce to store, release and exchange oxygen within their lattice structure in methane steam reforming. This ability to release oxygen thereby oxidized deposited carbon on the catalyst surface and contributed to the catalyst stability [74]. The presence of Ce on Rh/Ce-Zr led to thermal stability of the support, higher Rh dispersion and lower carbon formation on the support [75].

Another coke mitigation promoter commonly used in dry reforming of methane is potassium. Increase in basicity of support by potassium addition reduced coking tendency by increasing adsorption of CO<sub>2</sub> and decreasing CO disproportionation via reverse Boudouard reaction [71]. Promotional effects of K on Ni/MgO showed that potassium induced electronic enrichment of Ni resulted in stronger interaction between Ni and electron acceptor intermediates thereby affecting morphology of carbon by inhibiting carbon dissolution and nucleation process across Ni particles [76]. An optimum potassium loading of 1 wt% was reported for CO<sub>2</sub> and steam reforming of coke oven gas when added to Ni/MgAl<sub>2</sub>O<sub>4</sub>. Potassium presence led to higher reduction temperatures, enhanced metal support interaction, lower coking tendency and greater catalyst stability [77]. Addition of potassium was also shown to control the Ni ensemble size. Smaller Ni particles favoured CO<sub>2</sub> reforming of methane and reduced carbon formation [78]. Another study showed that potassium preferentially adsorbs on the step sites of the Ni surface resulting in decrease in catalytic activity – this shows the importance of potassium addition to the support rather than to the metal impregnated on the support in order to retain catalytic activity as well as reduce coke formation [79].

By using phosphorous, the selectivity towards carbon formation can be altered by tuning the acidity of the alumina support. 2 wt% addition of phosphorous to Ni/Al<sub>2</sub>O<sub>3</sub> resulted in high carbon resistance with satisfactory catalyst activities. Slight acidity due to phosphorous addition leads to easy adsorption of CO<sub>2</sub> molecules thereby leading to easy removal of carbon via reverse

Boudoaurd reaction [80]. Phosphorous addition proved crucial in inhibiting sulphur adsorption thereby lowering S surface coverage on alumina support and retaining activity of Rh/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [81]. Contrastingly, phosphorous addition (2.5 wt%) to Rh/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> led to formation of carbon filaments with large rhodium particles at the support tip which increased in size with increase in phosphorous content [82]. It is evident that tuning of acid-base properties of the support plays a crucial role in making the catalyst coke resistant. Hence, coke mitigation promoters like Ce / K / P are effective however, the final loading of these promoters should be optimized in terms of achieving highest yields and lowest carbon formation.

Another interesting approach employs usage of clays as a medium to form mesoporous supports having higher surface areas to develop the reforming catalysts. Mesoporous supports are known to facilitate smaller metal particles and therefore is another approach to mitigate coke formation [83]. Following section discusses these aspects along with a brief on clay and the mechanism of support preparation via intercalation.

# 2.3.7. Phyllosilicate Materials (Clay)

Historically, clays are formed by the weathering process of rocks. The characteristics of clay deposits are dependent on the source rocks, the weathering process, transportation and environmental conditions. Besides, some forms of natural clays can be synthetically manufactured to modify their properties based on end use such as catalyst, adsorbent, ion exchange, decolouration agent, etc [84,85]. Clay minerals belong to the phyllosilicate or layered silicates family. Most of the clay minerals belong to the triclinic or monoclinic system. The basic structure of clay minerals can be obtained by stacking of two sheets: Tetrahedral (a tetrahedron which contains one Si<sup>4+</sup> in the centre with four O<sup>2-</sup> at the corners) and Octahedral (an octahedron which contains mainly Al<sup>3+</sup> or Mg<sup>2+</sup> surrounded by 6 oxygen atoms or hydroxyl groups) sheets. The tetrahedra are linked to neighbouring tetrahedra by sharing three oxygen atoms each to form a hexagonal mesh pattern. The octahedral and tetrahedral sheets are covalently linked through sharing of the apical oxygen atoms of the tetrahedral sheet with the octahedral sheet creating the metal cation (octahedral)– O–Si (tetrahedral) link as seen in Fig. 2.3.



**Figure 2.3**: Arrangement within the clay structure showing the linkage due to sharing of the apical oxygen from the tetrahedral layer and unshared ions normal to the octahedral sheet [84]

If only 1 tetrahedral sheet is linked to an octahedral sheet, it is a 1:1 type of clay. If the octahedral sheet is sandwiched between two tetrahedral sheets, it is a 2:1 type of clay. Table 2.6 lists the various types of clays reported in literature.

Two important properties of clays need mention, i.e. isomorphic substitution and cation exchange capacity. Isomorphic substitution refers to the substitution of either the tetrahedral or octahedral cations by lower valency cations of approximately similar ionic radius. For instance,  $Al^{3+}$  can substitute  $Si^{4+}$  in the tetrahedral layer in four coordination and can substitute  $Mg^{2+}$  in octahedral layer in six coordination. Because of this substitution, a net negative charge develops on the clay layers which is balanced by the cations and keeps the adjacent clay layers together.

The number of exchangeable cations present in the interlayer space determines the cation exchange capacity (CEC) of the clay layer. This phenomenon has been exploited extensively for tuning the properties of clays for various applications. For our study, we have used laponite as the material for support preparation and hence, we will restrict the discussion to Laponite, a synthetic form of hectorite under saponites. Laponite is chemically pure and free from crystalline quartz impurities and transition metals found in natural clays. It also has a uniform particle size since it is synthesized under controlled chemical conditions. Laponite has many distinct advantages over natural minerals. It disperses easily to give colourless, transparent and highly thixotropic gels. The amount of Laponite required is 3 to 5 times lesser than natural clays, making it cost effective.

Layer Type	Group	Interlayer	Di/trioctahedral	Species	
		type			
1:1	Serpentines	None	Trioctahedral	Chrysotyle, Antigorite	
	Kaolinites		Dioctahedral	Kaolinite, Dickite	
2:1	Talcs	None	Trioctahedral	Talc, Willemseite	
	Pyrophyllites		Dioctahedral	Pyrophylite	
	Smectites	Hydrated cations	Trioctahedral	Saponite, Hectorite	
			Dioctahedral	Montmorillonite, Beidellite, Nontronite	
	Vermiculites	Hydrated cations (mostly Mg <sup>2+</sup> )	Trioctahedral	Trioctahedral Vermiculites	
			Dioctahedral	Dioctahedral Vermiculites	
	Micas	Unhydrated cations (usually K <sup>+</sup> )	Trioctahedral	Biodite, Lepidolite	
			Dioctahedral	Muscovite, Paragonite	
	Brittle micas	Unhydrated	Trioctahedral	Clintonite, Anadite	
		cations (divalent)	Dioctahedral	Margarite	
2:2 or 2:1:1	Chlorites	Octahedral	Trioctahedral	Clinochlore, Nimite	
		Hydroxy layer	Dioctahedral	Donbassite, Cookeite, Sudoite	
2:1 (inverted ribbons)	Sapiolites	Any	Trioctahedral	Sepiolite, Loughlinite	
	Palygorskites		Dioctahedral	Palygorskite	

# Table 2.6: Types of clays reported in literature [85]

To ensure porosity is maintained under thermal treatment, clays are subjected to a pillaring process where the clay layers are propped open by introduction of stable pillars in the interlayer space. The

pillared interlayer clay maintains its porosity during the overall treatment process. The most common pillaring agent used is Locron,  $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$  containing Al<sub>13</sub> polyoxycations, and is a Al<sub>13</sub> complex consisting of a central tetrahedral aluminium cation surrounded by 12 edges linked to octahedrally coordinated aluminium cations. The first step in the intercalation is to mix Locron solution with clay (Laponite). After the cation exchange reaction between the ions in the clay framework and polyoxycations, the suspension is washed, centrifuged, dried and calcined to convert the complex into intercalated mixed metal oxide pillars in the clay interlayers [86]. The overall process is schematically depicted in Fig. 2.4. A highly porous Al<sub>2</sub>O<sub>3</sub> based support having a high surface area (200-400  $\text{m}^2/\text{g}$ ) is obtained from this process which can therefore be used as a support material in lieu of commercial alumina having a lower surface area. Effective use of surfactants during pillaring for increasing porosity has been demonstrated [87]. The positively charged surfactant micelles enter the galleries of negatively charged clay layers to form mesophase assemblies with the sol-particles and clay layers. Heat treatment removes surfactants thereby leading to high porosity. Polyethoxide (PEO) surfactants introduced during Al pillaring of Laponite greatly reduces the water content of the framework and the surfactant micelles create the template due to dehydration of alumina precursors. Calcination removes the surfactants which can be recovered leading to a porous framework of alumina. Along with Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and MgO are also present in the support structure thereby retaining the overall properties associated with a stable support.

Following sub-section discusses the usage of clays as support materials for some important reactions like oxidation, reforming and other industrially relevant reactions involving hydrocarbons.



Figure 2.4: Representation of the pillaring process with change in interlayer distance [84]

## 2.3.7.1. Catalysts based on clay as support material

Activity of a hydroisomerization catalyst based on Montmorillonite with Pt and Re impregnated on the support was reported at 350 °C [88]. The catalyst was reported to be stable for the tested duration. It was found that the increased porosity allowed easy access of the C<sub>6</sub> and C<sub>7</sub> paraffins which contributed to the observed catalytic activities. Dry reforming of methane as an application for clay (montmorillonite) based nickel catalyst was reported [83]. The pillared clays exhibited stability for methane reforming at reaction temperatures of 800 °C. Addition of Lanthanum to increase basicity of the support was shown to enhance the catalyst activity further compared to only Ni based catalyst. However, the amount of coke formation increased 6 times in the presence of La compared to only Ni based catalyst. Thus, the importance of tuning the acid-base characteristics of the support for reforming reactions coupled with thermal stability at high reforming temperatures was demonstrated. Hydrocarbon cracking and deposition of coke led to an overall decrease in pore volume due to pore filling and pore blocking on Ti pillared and Al pillared Montmorillonite [89]. It was shown that toluene adsorption on Ti pillared clay led to irregular coke deposition and reduced the micropore volume (pore filling effect). High Lewis acidity and large pores wherein the coke molecules could deposit within the pores was the main reason attributed to the observations. However, pore blocking was observed in case of Al pillared Montmorillonites which do not allow pore filling due to the smaller pores. Under oxidation conditions, removal of coke from the Al pillared clays was at a lower temperature compared to the Ti pillared sample. In another study, the method of addition of materials to clay structure was shown to have an important effect on the overall yields and stability [90]. A Mn (III) based complex was immobilized on Laponite surface using three methods: direct immobilization on Laponite (method A), covalent anchoring through cyanuric chloride addition (Method B) and covalent anchoring through cyanuric chloride addition on a modified Laponite (APTES based) (Method C). It was found that the highest yields and selectivity for heterogenous epoxidation of styrene was for method A followed by methods B and C. However, the material based on Methods B and C could be reused 4 times with the highest stability observed for material based on Method B while the material prepared by method A deactivated after 2 runs. The characterization results showed that the immobilization of manganese was at the edges of the clay particles via methods B and C and homogenously distributed throughout the clay surface using method A. Selective oxidation of H<sub>2</sub>S was studied on alumina prepared from Laponite pillaring with iron impregnated onto the support as the active metal species [91]. A high surface area of 518 m<sup>2</sup>/g was reported for the prepared mesoporous alumina support with Pd as the metal impregnated on it. The catalyst showed high catalytic activities in the range of 120-200 °C with the stability demonstrated for 100 h on-stream for oxidation of benzene. Thermal stability was enhanced by replacing alumina with Ce/Zr with Zr showing the longest thermal stability of 70 h for an optimized calcination temperature of 600 °C [92]. The mesoporous supports thus prepared using Laponite showed pore diameters greater than 4 nm with the Pd crystallite size remaining similar for the entire reaction duration [92]. Ce-Al mixed pillared structures as an alternative to Al pillared structures using Montmorillonite as clay were reported for 2-propanol conversion to di-isopropyl ether [93]. It was found that the sample when calcined between 400 to 800 °C showed sintering when only aluminium pillars were present. The Ce-Al sample were composed of two intercalated species with interlayer spacings of 1.9 and

2.6 nm with the two phases showing stability upto 600 °C upon calcination. Beyond 600 °C, a single phase corresponding to 1.8 nm was evident which was attributed to Ce-Al mixed pillars. Selectivity to diisopropyl ether was highest for the Ce-Al case suggesting that only sites presenting Ce-Al pillars provide the low coordination aluminium atoms required for the reaction. Different pillaring species (Al, Fe, Ti, Zr) which determine the type of pillars incorporated was shown to determine the porosity features of pillared clays [94]. Langmuir type isotherms were obtained for Al and Zr pillared clays with more uniform pore size distribution (narrow range) for Al compared to Zr, Type II isotherm (non-porous) for Fe pillared clay while a Type IV isotherm for Ti pillared clay (mixture of micro and mesopores). The study also showed that new catalytic properties could be derived with the addition of Zr and Cr to Fe pillared clays as pillaring species. More meso and macroporosity was achieved when Laponite was used instead of Montmorillonite. Usage of amines for ordered stacking of clay layers in Laponite was suggested to further increase the pore volumes which lead to increased surface area also [94].

Based on the literature review, Al<sub>2</sub>O<sub>3</sub> based support using Laponite as the clay material is proposed for the catalyst synthesis. Since bi-metallic catalysts offer higher activity and stability compared to monometallic catalysts, a combination of Ni and Pt will be used as the active metals in the catalyst. Therefore, the proposed catalyst is envisaged to be a Ni-Pt/Al<sub>2</sub>O<sub>3</sub> catalyst using a clay support and a coke inhibition promoter from among K, P, or Ce for our work to reform three commercial fuels (methanol, diesel and gasoline).

To feed a H<sub>2</sub> stream as per the fuel cell specifications, the impurities in the reformate gas like CO, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub> and water vapor need to be removed. To separate these, water gas shift (WGS) reactors, a Preferential oxidation reactor (PROX) and membrane separation units are employed. The following section discusses these processes.

# **2.4.** H<sub>2</sub> Purification

The water gas shift is a mildly exothermic reaction that usually takes place in two successive adiabatic reactors. The first reactor is the high temperature shift (HTWGS) reactor that operates between 300-400 °C typically using iron/chromium oxides as catalysts and is sulphur tolerant. The outlet gas from HTWGS is cooled and fed to a low temperature shift reactor (LTWGS) which operates between 200-250 °C using copper/zinc oxides as catalyst. The CO content at the end of

the two shift reactors is usually 1 mol% with an increase in H<sub>2</sub> concentration by ~20%. Eq.2.4 depicts the water gas shift reaction [95,96].

$$\boldsymbol{CO} + \boldsymbol{H_2O} \leftrightarrow \boldsymbol{CO_2} + \boldsymbol{H_2}$$

The shift reactor is usually followed by a PROX reactor which reduces the CO concentrations to below 10 ppm. The reaction is carried out under slightly excess air conditions at 120-150 °C using Ru/SiO<sub>2</sub> catalysts or other noble metals like Pt and Rh [97–99]. Highly selective catalysts prevent parasitic loss of H<sub>2</sub> due to its oxidation as a side reaction. The overall reaction scheme is depicted in Eq. 2.5 for CO oxidation and Eq. 2.6 for H<sub>2</sub> oxidation.

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$
 2.5

$$H_2 + \frac{1}{2}O_2 \to H_2O$$
 2.6

After the removal of CO, other gases present in the reformate gas are separated from hydrogen using pressure swing adsorption (PSA). Typically, the reformate gas at the outlet of PROX is sent through an adsorbent column at high pressure where impurities (gases other than hydrogen) are adsorbed while hydrogen passes through with very limited adsorption. When the adsorbent gets saturated, it is regenerated by lowering the pressure and purging with pure hydrogen [100]. For hydrogen purification, multiple adsorbents (layered beds) are used like silica gel, alumina, activated carbon and zeolite. The units are typically operated at ambient temperatures and high pressures (20-60 atm). The hydrogen produced from the PSA system is typically at a lower pressure (accounting for pressure drop of 1 bar) while the off gas is at a relatively low pressure of 1.1-1.7 atm. The recovery of hydrogen from the PSA system typically ranges between 60-95% depending on the feed gas composition and its purity is >99.999% [100,101].

One of the objectives of our work is to perform a process simulation for a reformer using the developed catalyst. Hence, the following section briefly reports the modelling and simulation studies on reforming of methanol, diesel and gasoline.

# 2.5. Modelling and Simulation studies on reforming

The kinetic model of the reforming catalyst is the most important part of the process to predict the hydrogen yield and selectivity for a given set of reformer operating conditions. The details of the

kinetic studies reported in literature for the three fuels under consideration are presented in the next few sub-sections.

## 2.5.1. Methanol

Early studies on methanol reforming proposed methanol decomposition as the rate determining step followed by the water gas shift reaction [102,103]. Later studies using Cu-based catalysts have experimentally proven that methanol and water react directly to produce carbon dioxide and hydrogen via a methyl formate intermediate. These catalysts are also highly selective towards steam reforming, operate at lower temperatures and do not promote methanol decomposition [104– 106]. There are only a few studies on oxidative reforming of methanol (ORM). In one such study, a power law based model was fitted for a Cu/ZnO catalyst [47]. The model showed a positive dependence on methanol and oxygen consumption with steam shown to suppress the reforming reaction. The authors concluded that the Cu/ZnO catalyst favors methanol oxidation till oxygen is completely consumed. The catalyst remains in oxidized state till the completion of combustion reaction. With further time on stream, hydrogen present in the products stream reduces the Cu catalyst, thereby improving the selectivity towards methanol reforming. Usage of Group VIII metals for methanol reforming showed that the reaction mechanism favored CO formation at higher temperatures via methanol decomposition reaction [52,55]. Hence, it is imperative to choose the right model based on the catalyst chosen and the products formed from the experimental conditions.

# 2.5.2. Diesel

Diesel is a complex mixture composed of many hydrocarbon species including paraffins, olefins, cycloparaffins and aromatics [107]. Hence, most of the studies have used n-hexadecane ( $n-C_{16}H_{34}$ ) and n-tetradecane ( $n-C_{24}H_{50}$ ) as the representative compound for modelling since the paraffins have the highest concentration in diesel [63,107–109]. A power law model based on experimental data for auto thermal reforming of low sulphur diesel was proposed using four reactions. These were steam reforming, total oxidation, water gas shift and methanation reaction *via* fuel decomposition for a Rh/Al<sub>2</sub>O<sub>3</sub> with Ce and La doped on the catalyst [63]. A combination of an Eley-Rideal model for steam reforming kinetics [107]. Kinetics of tetradecane reforming was developed using three independent reactions i.e. total oxidation as a power-law kinetic model, and

steam reforming and water gas shift using LHHW model [108] – An elementary surface reaction mechanism for  $C_1$  species linked with a global reaction equation for dissociative adsorption of hexadecane was developed [109]. However, the model failed to predict the carbon dioxide selectivity which was attributed to failure in predicting the equilibrium between CO and CO<sub>2</sub> at the reaction conditions due to the water gas shift reaction.

## 2.5.3. Gasoline

Gasoline is a complex mixture of many hydrocarbons such as n-alkanes, cycloalkanes, olefins and aromatics with the aromatic content significantly higher than diesel [110]. Most of the studies have modelled gasoline using iso-octane as a surrogate [111–113] or as a mixture of compounds such as 2,2,4-trimethylpentane, methylcyclohexane, 1,2,4-trimethylbenzene, hexane and 1-octene [114]. The kinetics of iso-octane were predicted using a power law model as well as a LH based model in which the rate determining step was found to be the reaction between dissociatively adsorbed isooctane and steam [111]. A pseudo-homogenous model including reaction kinetics and intraparticle mass transfer resistance was developed for auto thermal reforming of iso-octane using a LHHW formulation for the reaction network. The proposed model was able to predict experimental data generated for temperatures between 600 to 800 °C and space velocities between 15000 to 150000 h<sup>-1</sup> [112]. The kinetics of partial oxidation of gasoline (surrogate considered was a mixture of 5 compounds) as a function of oxygen molar flow rates and reaction temperatures was studied using a dual site mechanism based on LHHW model. Similarly, a power law model was also proposed to predict the observed experimental data [114]. In summary, it was observed that both power law models to represent the global reaction and LH based models based on the mechanistic details involved in the reaction scheme have been used to model the kinetics of ATR of the three fuels under consideration.

Based on the kinetic models, the overall process (reforming with downstream purification) can be simulated to arrive at a process design providing basic equipment sizes for each unit operation. A basic techno-economic analysis can be done to arrive at the delivered cost of hydrogen which is another objective of the present work. A brief discussion on the studies reporting techno-economic analysis for auto-thermal reforming of the three fuels of interest is provided in the following section.

# 2.6. Techno-economic analysis

Biogas based auto thermal reforming was studied for H<sub>2</sub> production capacity of 100 Nm<sup>3</sup>/h and it was concluded that the final cost of  $H_2$  is \$3.05/kg over a 10-year amortization period [115]. Analysis of methanol and natural gas as feedstock for H<sub>2</sub> production of 1500 kg/day using steam reforming showed that the return on investment was favourable for natural gas compared to methanol, primarily due to the lower fuel cost of natural gas [116]. Another study reported comparison between steam reforming and auto-thermal reforming of natural gas for a 18.9 TPH  $H_2$  production capacity [117]. The  $H_2$  selling price was \$1.07/kg for steam reforming and \$1.15/kg for ATR process since the savings due to higher efficiency and lower reactor volume in the ATR are offset by its need for high purity oxygen from an air separation plant which is energy and capital intensive. Another study reported performance of an integrated ATR based hydrogen generation (590 TPD) coupled with electricity generation where the cost of hydrogen was found to be between \$1.8 to \$2.3/kg of H<sub>2</sub> depending upon electricity supply, cogeneration potential and CO<sub>2</sub> capture [118]. Amongst smaller capacity plants, ATR of biogas obtained from anaerobic digestor was found to be cheaper compared to landfill gas primarily because of the smaller volumes of biogas to be processed for the same H<sub>2</sub> output [119]. The levelized cost of hydrogen was \$ 7.8/kg for a 100 kg/h H<sub>2</sub> generation unit at 20 bar and \$ 8.7/kg for H<sub>2</sub> generation at 700 bar. Economies of scale play a huge role in the overall cost of hydrogen. A recent study analysed H<sub>2</sub> costs on the basis of an average from natural gas reforming coupled with CO<sub>2</sub> capture and renewable hydrogen from renewable power generation and electrolysis [4]. On the stationary front,  $H_2$  price at \$2.5/kg and \$1.8/kg will serve 8% and 18% of the global energy demand, respectively [4].

# 2.7. Research Gaps

To enable on-site hydrogen generation and provide fuel flexibility, it is imperative that a single catalyst capable of reforming multiple fuels be developed. Unfortunately, to-date, none of the catalysts reported in the literature have shown a stable performance giving low H<sub>2</sub> productivity and high coking resistance when tested on multiple fuels. Common issues encountered include catalyst deactivation due to coke deposition on the catalyst or sintering due to the harsh operating conditions (high temperature or oxidizing environments) leading to lowering of product (hydrogen) yields. Frequent regeneration or complete replacement of the catalyst therefore

becomes the need of the hour. Hence on-site reforming to produce hydrogen widely depends on the availability of fuel and its distribution infrastructure.

# 2.8. Research Hypothesis

We have proposed a bimetallic Ni-Pt based catalyst where the support is prepared from a phyllosilicate (Laponite) to obtain highly mesoporous alumina-based support. Further, there is a need for the addition of a coke mitigation promoter to obtain stable catalyst performance for longer durations and thereby either eliminate or minimize coke deposition. This research is an effort to provide a multi fuel stable reforming catalyst and test the effect of addition of cerium, potassium and phosphorous as coke mitigation promoters. Our literature review has shown that addition of these coke mitigation promoters has proved beneficial in retaining the catalyst activity and reducing the coke deposition when compared with un promoted catalysts.

The literature review also shows that higher capacities for  $H_2$  production offer viable scenarios which may not be true for the distributed generation scenario. In this context, an effort to simulate the reforming process using the results of the experimental data to perform a techno-economic analysis is made. The reformer system delivers pure hydrogen for consumption in a fuel cell to cater to the back-up power requirements of telecom towers. Sensitivity analysis of various scenarios for making the proposed system viable and competitive when compared with diesel gensets and electrolysers is also presented. With this study, we hope to bridge the gap related to the development of multi-fuel reforming with respect to catalyst development followed by process design and techno-economic analysis.

# 3.0. Materials and Methods

This chapter has details of the materials used in the catalyst preparation and the synthesis procedure in the first few sections. The various analytical techniques used to characterize the catalyst (both fresh and spent) are discussed in the next few sections. The last section of the chapter describes the experimental set-up used to test the catalyst performance, the analytical methods used to determine the product composition and the equations used to calculate the conversions and yields for the various reforming experiments.

# **3.1.** Materials

Laponite RD (M/s BYK-Chemie GmbH, Germany) with a cation exchange capacity of 55 meq per 100 g clay and BET surface area of 370  $m^2/g$  was used as the base material. Its chemical composition (wt%) is: 59.5% SiO<sub>2</sub>, 27.5% MgO, 0.8% Li<sub>2</sub>O and 2.8% Na<sub>2</sub>O. The clay consists of many single or bilayer particles coupled with bigger tactoids stacked parallel to each other. Grain dimensions estimated from SEM in literature suggested an average thickness of 10-14 nm for the plate type particles and a plate width of 30-200 nm [120,121]. The pillaring agent was a solution of aluminium hydroxychloride (Locron L from M/s Omega Chemicals, Australia) containing polyoxycations of aluminium hydrate with an Al<sub>2</sub>O<sub>3</sub> content of 23±1 wt%, OH/Al ratio of 2.5 and pH in the range of 2.8 to 4. Potassium Chloride (KCl) and potassium nitrate (KNO<sub>3</sub>) (M/s Merck) were used as the precursors for potassium, cerium chloride heptahydrate (CeCl<sub>3</sub>.7H<sub>2</sub>O) and cerium nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O) (M/s Sigma Aldrich) for cerium and ammonium dihydrogen phosphate ((NH<sub>4</sub>)H<sub>2</sub>PO<sub>4</sub>) and phosphorous trichloride (PCl<sub>3</sub>) for phosphorous. Tergitol 15-s-9 (M/s Sigma Aldrich) was used as the surfactant in the pillaring process. Nickel nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2.6</sub>H<sub>2</sub>O), 10 wt% chloroplatinic acid solution (H<sub>2</sub>PtCl<sub>6.6</sub>H<sub>2</sub>O) (M/s Sigma Aldrich), Rhodium (III) nitrate hydrate Rh(NO<sub>3</sub>)<sub>3</sub>.xH<sub>2</sub>O, ~36wt% Rhodium basis) and ammonium perrhenate (NH<sub>4</sub>ReO<sub>4</sub>) (M/s Sigma Aldrich) were used as the metal precursors for nickel, platinum, rhodium and rhenium, respectively.

Commercial gasoline and diesel were obtained locally (Caltex and United Petroleum, respectively, in Victoria, Australia), while anhydrous methanol (99.8%) was purchased from M/s Sigma Aldrich.

# **3.2.** Preparation of Support

Pillared alumina support (without any promoter) was prepared using a published method [86], whereas the promoter doped supports were prepared by modifying the published method. The desired amount of KCl or CeCl<sub>3</sub>.7H<sub>2</sub>O or PCl<sub>3</sub> (to get a final loading of 2 wt% for each promoter) was mixed with Locron L and distilled water, and stirred for 2 h. The mixture was then kept in a Teflon coated stainless steel vessel for 100 h at 120 °C (Solution A). Laponite (10 wt% of the amount of Locron used) was added to 80 mL of distilled water and the mixture was stirred till homogeneity was achieved, followed by Tergitol 15-s-9 addition and stirring for 2 h (Solution B). Solution A was then added to Solution B dropwise with continuous stirring. The mixture was stirred vigorously for 2 h after addition of Solution A. The contents were then transferred to a Teflon coated stainless steel vessel and aged for 48 h at 100 °C followed by centrifuging and washing with distilled water to remove free Cl<sup>-</sup> ions. The precipitate thus obtained was dried overnight at 100 °C in an oven and calcined at 500 °C for 20 h at 2 °C/min. The supports were labelled as K0-Al<sub>2</sub>O<sub>3</sub> (no promoter), K2-Al<sub>2</sub>O<sub>3</sub> (2 wt% potassium doped in alumina), Ce2-Al<sub>2</sub>O<sub>3</sub> (2 wt% cerium doped in alumina) and P2-Al<sub>2</sub>O<sub>3</sub> (2 wt% phosphorous doped in alumina).

The effect of potassium was evaluated in detail for which the supports were prepared by varying potassium loadings. The desired amount of KCl (with K/Al molar ratio of 0.1, 0.45 and 0.7 to get the desired potassium loadings of 2, 5 and 8 wt%, respectively) was mixed with Locron L and distilled water and stirred for 2 h. The mixture was then kept in a Teflon coated stainless steel vessel for 100 h at 120 °C. This solution was termed as Solution A and was used in preparation of the potassium doped supports using the same procedure listed for K2-Al<sub>2</sub>O<sub>3</sub>. The supports thus prepared were labelled as K0-Al<sub>2</sub>O<sub>3</sub> (no promoter), K2-Al<sub>2</sub>O<sub>3</sub> (2 wt% potassium doped in alumina), K5-Al<sub>2</sub>O<sub>3</sub> (5 wt% potassium doped in alumina) and K8-Al<sub>2</sub>O<sub>3</sub> (8 wt% potassium doped in alumina).

# **3.3.** Catalyst Preparation

Nickel nitrate hexahydrate and chloroplatinic acid were dissolved in deionized water along with the supports prepared in the previous step. The final concentrations of Ni and Pt in the bimetallic catalyst were 10% (w/w) and 1% (w/w), respectively. The mixture was stirred at 60 °C for 5 h followed by drying at 100 °C (overnight) in an oven. The dried material was then directly reduced *in-situ* prior to the catalyst testing, using 10% H<sub>2</sub>/N<sub>2</sub> at 550 °C for 5 h followed by N<sub>2</sub> purge at 550

°C for 1 h to remove any traces of hydrogen. The effect of removing calcination step prior to reduction is discussed in chapter 4 of this thesis. The catalysts thus prepared were labelled as Ni-Pt/Al<sub>2</sub>O<sub>3</sub> (uc\*), Ni-Pt/Al<sub>2</sub>O<sub>3</sub> (c\*\*), Ni-Pt/K<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (uc), Ni-Pt/Ce<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (uc) and Ni-Pt/P<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (uc). To study the effect of different noble metals, Pt was replaced by Rh and Re such that the final concentrations were 1 wt%. The catalysts thus prepared were labelled as Ni-Rh/K<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (uc) and Ni-Re/K<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (uc). For comparison purposes, the above procedure was repeated by taking unpromoted support (Al<sub>2</sub>O<sub>3</sub>) and mixing appropriate quantities of nickel nitrate hexahydrate, chloroplatinic acid and promoter (potassium nitrate / cerium nitrate hexahydrate / ammonium dihydrogen phosphate) in co-impregnation mode to arrive at the final concentrations of Ni (10% w/w), Pt (1% w/w) and promoter (2% w/w). The catalysts thus formed were labelled as Ni-Pt-K<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (uc), Ni-Pt-Ce<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (uc) and Ni-Pt-P<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (uc).

The effect of removing calcination step after metal impregnation was evaluated using methanol reforming. The effect of different coke mitigation promoters and noble metals was investigated through reforming of diesel and gasoline, respectively. These details are presented in chapter 4.

The supports prepared with different potassium loadings were co-impregnated with Ni-Pt and the resulting catalysts were labelled as Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub> (All the samples were uncalcined which means post drying and metal impregnation, the material was directly reduced and used *in-situ* for testing the catalyst activity). Figs. 3.1 and 3.2 depict the catalyst preparation method for the various uncalcined samples. Fig. 3.3 depicts the catalyst preparation method for the calcined sample.

\*Note: uc stands for uncalcined wherein the dried sample post metal impregnation was directly reduced for reaction purposes

<sup>\*\*</sup>c stands for calcined sample wherein the dried sample post metal impregnation was calcined at 500 °C for 5 h at a ramp rate of 5 °C/min.



**Figure 3.1:** Catalyst preparation method for Ni-Pt/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub> and Ni-Pt-P2/Al<sub>2</sub>O<sub>3</sub> (All uncalcined samples)



**Figure 3.2**: Catalyst preparation method for Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/P2-Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub>, Ni-Rh/K2-Al<sub>2</sub>O<sub>3</sub> and Ni-Re/K2-Al<sub>2</sub>O<sub>3</sub> (All uncalcined samples)



Figure 3.3: Catalyst preparation method for Ni-Pt/Al<sub>2</sub>O<sub>3</sub> (calcined sample)

# 3.4. Catalyst Characterization Techniques

The catalyst samples prepared were characterized to determine the surface area, number of active metal sites, reducibility, structure and morphology as well as the oxidation states of the various metals on the support surface. The following sub-sections provide a summary of the various catalyst characterization techniques used in this work.

# 3.4.1. X-Ray Diffraction (XRD)

Powder X-Ray Diffraction of the supports, and the reduced and spent catalysts were performed using Rigaku Miniflex powder diffractometer with mono-chromatized Cu K- $\alpha$  ( $\lambda = 0.154$  nm) radiation at 40 KV and 15 mA. Scherrer equation was used for calculating the metal particle diameter from XRD using the following formula (Eq. 3.1)

$$D(nm) = \frac{K \times \lambda}{\beta \times \cos \theta}$$
3.1

Where D is the metal particle diameter, K is the geometrical shape factor taken as 0.92 (cubic shape),  $\beta$  is the value of FWHM (in radian) obtained from the XRD plot for the corresponding Bragg's angle  $\theta$  (in radian).

#### 3.4.2. TPR/TPO/TPD/Pulse Chemisorption

The analysis was performed using Thermo Scientific TPDRO 1100. For CO pulse chemisorption, a quartz reactor was loaded with 0.1 g catalyst and reduced using 5% (v/v) H<sub>2</sub>/Ar at 550 °C for 5 h. The sample was then flushed with Ar for 1 h and cooled to room temperature under Ar flow. A CO pulse (0.34 mL of 10% CO/He) was then introduced during each injection. A TCD detector was used to quantify the adsorbed CO. The dispersion was calculated according to the procedure published in literature [122]. Metal dispersion was calculated assuming a stoichiometry of metal:CO = 1:1 wherein the two metals were Ni and Pt [122,123]. The weight loadings for the catalyst samples were derived from XRF results (X-ray fluorescence), while the turn-over frequency (TOF) was calculated as per Eq. 3.2.

$$TOF = \frac{Rate of the reaction (mol.g.catalyst^{-1}min^{-1})}{Moles of CO(mol.g.catalyst^{-1})}$$
3.2

The metal surface area and particle diameters were not calculated from the chemisorption studies since it is difficult to estimate the surface composition due to the bimetallic nature of the catalyst [124].

For TPR (temperature programmed reduction) studies, 0.1 g of the sample was placed in a quartz tube and the temperature ramped at 10 °C/min under 10 mL/min (10% H<sub>2</sub>/Ar) flow from 30 °C to 900 °C. From the TPR profiles obtained, the H<sub>2</sub> uptake for each catalyst sample was quantified.

For CO<sub>2</sub>-TPD, 0.1 g of the sample was loaded at room temperature and kept under Argon flow for 1 h followed by reducing the sample at 550 °C for 5 h under 5% (v/v) H<sub>2</sub>/Ar flow. The sample was then cooled under Argon flow followed by flushing under Argon for 1 h to remove any residual hydrogen. 99.99% CO<sub>2</sub> was introduced for 1 h at 30 °C. The sample was then flushed with Argon for 2 h and subsequently heated under Argon flow from 30 to 900 °C at 10 °C/min. A TCD was used to quantify the desorbed CO<sub>2</sub>.

For CO-TPD, 0.1 g of the sample was loaded at room temperature and kept under Argon flow for 1 h followed by reducing the sample at 550 °C for 5 h under 5% (v/v) H<sub>2</sub>/Ar flow. The sample was then cooled under Argon flow followed by flushing under Argon for 1 h to remove any residual hydrogen. CO flow (0.34 mL of 10% CO/He) was then introduced for 10 minutes followed by Ar

flushing for 1 h at room temperature before ramping up the temperature under Ar flow from 30 to 900 °C at 10 °C/min to obtain the CO desorbed profile as a function of temperature.

## 3.4.3. Nitrogen Physisorption

The catalyst specific surface area, pore diameter and pore volume were measured by nitrogen physisorption in a Micromeritics 3Flex instrument. The surface area was characterized using the Brunauer-Emmett-Teller (BET) method. The pore diameter, pore size distribution and pore volume were measured using the Barrett-Joyner-Halenda (BJH) desorption isotherm curve. Micropore volumes were reported using the t-plot (De Boer's method).

## 3.4.4. X-Ray Fluorescence (XRF)

XRF analysis to identify elemental compositions was carried out with a Rigaku ED XRF (model NEX DE Analyzer) using a shuttered 50 KV X-ray tube.

## 3.4.5. Thermo-gravimetric analysis (TGA)

TGA of the spent catalysts was carried out using a Shimadzu DTG-60H, wherein 10 mg of the sample was placed onto the crucible and heated to 900 °C at a ramp rate of 50 °C/min under air at 100 mL/min. Post reaction, the catalyst sample was recovered, dried and analyzed. Three independent analyses of the catalyst samples were conducted. The carbon evolution obtained from the DTG curve was normalized as a function of carbon converted and was reported as g C/(g<sub>cat</sub>.g C converted).

## 3.4.6. Transmission Electron Microscopy (TEM)

Both the fresh and spent catalysts were analyzed using FEI Tecnai G2 T20 and JEOL HR-TEM 300 KV to obtain their TEM images. High resolution TEM images (HRTEM) and selected area electron diffraction (SAED) patterns were also obtained. The TEM resolution was kept at 1 Å while the magnification was kept in the range of 89000x to 150000x. For HRTEM imaging, the magnification was always above 250000x. SAED patterns for high resolution images (HRTEM) could not be obtained due to instrument limitations and chance of sample damage due to beam intensity. Ni, Pt, Al, K, Si and Mg were mapped using energy dispersive spectroscopy and the HAADF-STEM methodology. Freshly reduced and spent catalyst samples were prepared by grinding and suspending the particles in iso-butanol using sonication for 15 minutes before drop-casting the suspended samples on a holey carbon grid. The grid was dried under an Infrared lamp

for 10 minutes before loading for analysis. Imaging was done on different particles on the grid and the particle size distribution was obtained using ImageJ software.

# 3.4.7. X-Ray Photoemission Spectroscopy (XPS)

The catalyst sample (reduced) in case of catalyst and support were ground before analysis. The samples were analysed on an AXIS Supra from Kratos using monochromatic Al X-ray (600 W with a 1486.6 eV source). The analysis was conducted wherein the binding energy was calibrated using the characteristic peak of Ag3d at 368.3 eV with an instrument tolerance of  $\pm$  0.1 eV. XPS peaks were analysed by fitting a mixed Gaussian-Lorentzian function with 30% Lorentzian contribution. The contribution was based on the instrument setting used for XPS analysis. The analysis chamber pressure was kept less than  $2*10^{-7}$  Pa while pass energies were 20 eV for high resolution scans with the resolution being 0.5 eV.

# **3.5.** Evaluation of Catalyst Performance

# 3.5.1. Experimental Setup

The catalytic activity was evaluated by using a bench scale reactor setup shown in Fig. 3.4. It consisted of an Inconel based reactor tube (500 mm long with an OD of 25 mm from M/s Amar Equipments Private Limited), two Alltech HPLC pumps (model 426) – one each for the reactant (methanol/diesel/gasoline) and water, one Teledyne Hasting mass flow controller for nitrogen, one Swagelok based metering valve for controlling oxygen flow, a Labec vertical split tube furnace, a custom-built vaporizer and a Swagelok based gas liquid separator.



Figure 3.4: Reaction setup for reforming experiments (fuel used – diesel, methanol or gasoline)

For catalytic activity evaluation, 0.4 g of the catalyst was loaded in the reactor and supported at the centre by quartz wool. Appropriate operating conditions were chosen based on the fuel used in the experiments, e.g. diesel or gasoline flow rate was kept at 0.1 mL/min and the reaction conditions were – steam to carbon ratio (SCR, (mol/mol)) = 4, oxygen to carbon ratio (OCR, (mol/mol)) = 0.2, reforming temperature (T) = 700 °C and GHSV = 5000 ml<sub>STP</sub>/(h.g<sub>cat</sub>). The reforming temperature was chosen based on thermodynamic studies which suggested 600 to 800 °C as the preferred range for carbon free operation [125,126]. Further, experimental evidence also reports temperatures exceeding 650 °C for diesel reforming [60,126]. For methanol, the reaction conditions were as follows: steam to methanol ratio (SMR) = 1.0 mol/mol, Oxygen to methanol ratio (OMR) = 0.1 mol/mol, reforming temperature (T) = 420°C and GHSV = 6350 ml<sub>STP</sub>/(h.g<sub>cat</sub>). Apart from the temperature, the other operating conditions (molar ratio of reactants and GHSV) were derived based on some screening experiments (not reported) and observations from the literature reported in Chapter 2. These operating conditions were used for catalyst screening for the three fuels to arrive at a suitable combination for further analysis.

#### 3.5.2. Catalyst Performance Evaluation

For all the reforming experiments, the dried catalyst was directly reduced ( $10\% H_2/N_2$  at 550 °C for 5 h) and post completion of 5 h, an additional 1 h of N<sub>2</sub> flow is continued at the same

temperature to flush out any hydrogen present within the system. Thereafter under  $N_2$  flow, the reforming temperature via the furnace is reached. Thus, the catalyst is used in-situ and hence there is no chance of oxygen ingress to oxidize the active metallic species. Once, the vaporizer and the reformer were at the desired temperatures, fuel and water flows (using calibrated HPLC pumps) were started and continued for 10 minutes to achieve a steady state. Once a steady flow was measured at the outlet of the reactor (using a pre-calibrated bubble flow meter), oxygen flow was commenced using a calibrated metering valve (M/s Swagelok). The gas flows at the outlet of the reactor were measured at intervals of 10 minutes. On an average, steady gas flows at the outlet of the reactor were observed after 30-40 minutes indicating achievement of steady state. Thereafter, the resulting reformate gas was passed through a gas-liquid separator to separate the condensable gases from the non-condensables. The outlet gas flow rate was measured and its composition was analysed by a gas chromatograph equipped with a 5 Å molecular sieve column (60/80 mesh, 1/8 in. O.D., 6 ft length) using TCD and FID detectors (Shimadzu, GC-2014, column temperature: 40 °C, oven temperature: 390 °C, detector temperature: 250 °C using ramp rate of 10 °C/min, total runtime of 25 minutes with a carrier gas (Argon) flow of 15 mL/min). The condensed liquid samples for diesel and gasoline had two phases - aqueous and organic, (a photo of the sample from one of the runs with diesel is shown in Fig. 3.5) and the organic phase was analysed using a FID detector in 7820A GC (M/s Agilent, column temperature: 50 °C, oven temperature: 300 °C, detector temperature: 300 °C using ramp rate of 10 °C/min, total runtime of 26 minutes with carrier gas (Nitrogen) flow of 120 mL/min) equipped with a 7650A Autosampler and VF-5HT column (diameter: 250 µm, Length: 30 m) for the total organic content in the recovered liquid samples.



Figure 3.5: Photo of the samples collected after diesel reforming experiment

The condensed liquid samples for methanol (single phase) were analysed using the capillary column installed in Shimadzu GC-2014 using a FID detector (column temperature: 40 °C, oven temperature: 250 °C, total runtime of 3 minutes with a carrier gas (Argon) flow of 330 mL/min).

Only the steady state performance of the catalyst is reported. Conversion was calculated using the following formula (Eq. 3.3).

$$Conversion = \frac{(mol \ of \ Carbon)_{in,liquid} - (mol \ of \ Carbon)_{out,liquid}}{(mol \ of \ Carbon)_{in,liquid}} 3.3$$

For estimating the moles of carbon in diesel, eight most prominent compounds present in commercial diesel ( $C_{10}H_{22}$ ,  $C_{12}H_{26}$ ,  $C_{14}H_{30}$ ,  $C_{16}H_{34}$ ,  $C_{18}H_{38}$ ,  $C_{20}H_{42}$ ,  $C_{22}H_{46}$ ,  $C_{24}H_{50}$ ) were calibrated in Agilent 7820A GC. The conversion of diesel as per Eq. 3.3 was estimated using these compounds. The associated procedure for calculating conversions along with the calibration studies for each of the compounds are detailed in Appendix A for diesel.

Similarly, six prominent compounds present in commercial gasoline (Benzene, Toluene, o-xylene, p-xylene, pseudocumene and 1,3,5-trimethyl benzene) were used for its calibration and carbon conversion calculations. The associated procedure for calculating conversions along with the calibration studies for each of the compounds are detailed in Appendix A for gasoline.

The carbon collected on the catalyst was estimated using TGA. The carbon balance over all the runs was within  $\pm 5\%$  of experimental error. No carbon formation was observed in the methanol experiments. The apparent mass of the gas was estimated using ideal gas law at 25°C and 1 atm. The gas phase mole fractions were all reported in terms of N<sub>2</sub> free basis. The product gas yields (H<sub>2</sub>, CO and CO<sub>2</sub>) were estimated from the gas flows obtained by the bubble flow meter measurements and the mol% values obtained from GC analysis. Gas yields were estimated based on the following formulae:

$$H_2 Yield = \frac{(mol of H_2)}{(mol of C)_{feed}}$$
3.4

$$CO Yield = \frac{mol \ of \ CO}{(mol \ of \ C)_{feed}}$$
3.5

$$CO_2 Yield = \frac{mol \, of \, CO_2}{(mol \, of \, C)_{feed}}$$
3.6

Catalyst performance was reported in terms of carbon conversion and  $H_2$  production rate (mmol  $H_2/kg_{cat.}s$ ). Chapter 4 details the catalyst screening results for oxidative steam reforming of methanol, diesel and gasoline.

# 4.0. CATALYST EVALUATION FOR MULTI-FUEL REFORMING

This chapter details the results obtained from the screening tests of various catalysts on reforming of methanol, diesel and gasoline. Firstly, the metal (Ni and Pt) loadings are optimized and the effect of calcination on the catalyst is evaluated using methanol. Thereafter, the effect of adding different coke mitigation promoters is evaluated using diesel as the fuel. Finally, the effect of different noble metals on the catalyst performance is evaluated using gasoline. The objective in each set of experiments was to find out the most stable and active catalyst. The following sections present the various insights derived from the catalyst screening work.

# 4.1. Methanol

In this section, activity results for different Ni and Pt loadings and effect of calcination after metal impregnation are discussed.

# 4.1.1. Effect of Pt Loading

To evaluate the effect of Pt loading, four catalysts were tested with different Pt loadings (0.05, 0.3, 1 and 1.2 wt%) while keeping the Ni loading fixed at 10 wt%. The catalyst conversion and  $H_2$  production rates for oxidative steam reforming of methanol are reported in Figs. 4.1a and 4.1b, respectively. (*Note: All samples were directly reduced post metal impregnation*)



**Figure 4.1**: Effect of Pt loading on a) Conversion and b) H<sub>2</sub> production rates for oxidative steam reforming of methanol; Operating Conditions (SMR: 1.2, OMR: 0.05, T: 320 °C and GHSV: 6500 ml<sub>STP</sub>/h.g<sub>cat</sub>);  $\blacksquare$  – Pt (0.05 wt%),  $\circ$  - Pt (0.3 wt%),  $\blacktriangle$  – Pt (1 wt%) and  $\square$  – Pt (1.2 wt%) with 10 wt% Ni

It can be seen from Fig. 4.1a that conversion increases with increase in Pt loading till 1 wt% and remains constant thereafter. However, the  $H_2$  production rate shows a maximum at 1 wt% Pt loading. Literature studies have shown an optimum Pt loading of 0.3 wt% and 1 wt% for Nickel loading of 10 wt% [122,127,128]. From our experimental studies, the optimum was found to be 1 wt%. Since the objective was to investigate the multi fuel reforming capability, hence, the Pt loading was fixed at 1 wt% for all experiments performed henceforth.

# 4.1.2. Effect of Ni loading

After fixing the Pt loading at 1 wt%, the effects of Ni loading on methanol conversion and  $H_2$  production rates were evaluated by varying the Nickel loading as 7.5, 10 and 12.5 wt%. Figs. 4.2a and 4.2b depict the effect of variation in Ni loading on methanol conversion and  $H_2$  production rates for oxidative steam reforming of methanol. (*Note: All samples were directly reduced post metal impregnation*)



**Figure 4.2**: Effect of Ni loading on a) Conversion and b) H<sub>2</sub> production rates for oxidative steam reforming of methanol; Operating Conditions (SMR: 1.2, OMR: 0.05, T: 320 °C and GHSV: 6500 ml<sub>STP</sub>/h.g<sub>cat</sub>);  $\Box$ - Ni (7.5 wt%), • - Ni (10 wt%), ▲ - Ni (12.5 wt%) with 1 wt% Pt

It can be seen from Fig. 4.2a that conversion increases with increase in Ni loading till 10 wt% beyond which it remains constant. However, the  $H_2$  production rate is maximum at 10 wt% Ni loading. Various studies have reported Ni loading at 10 wt% to be ideal in a Ni-Pt combination [42,44,122,129–131]. Hence, our results are in line with those reported in literature. Therefore, the Ni loading was fixed at 10 wt% in all future experiments.

#### 4.1.3. Effect of calcination on catalyst activity

For evaluating the effect of calcination (post metal impregnation and before catalyst activation through reduction), two samples were tested for their activity for methanol oxidative steam reforming. One sample was directly reduced post metal impregnation (labelled as "uncalcined") and the second sample was calcined following metal impregnation, and then reduced (labelled as calcined). Fig. 4.3 shows the variation in conversion and H<sub>2</sub> production rates with time on stream for these two catalyst samples. With calcination, both conversion and H<sub>2</sub> production rates tend to decrease indicating catalyst deactivation. The probable cause of deactivation could be increase in metal particle size due to heat treatment (calcination) which is consistent with literature[132]. Some characterization studies were conducted to validate this finding.


**Figure 4.3**: Comparison of Catalysts – a) Conversion, and b)  $H_2$  productivity v/s time on- stream Operating parameters: SMR: 1.0, OMR: 0.1, T: 420 °C and GHSV 6350 ml<sub>STP</sub>/h.g<sub>cat</sub> (- $\Box$ -calcined, -•- uncalcined)

Estimation of the Ni particle size using Scherrer Equation confirmed an increase in the Ni crystallite size for the calcined case (Table 4.1). The XRD graphs of fresh and spent samples (calcined and uncalcined) in Fig. 4.4 show sharper intensities for the Ni peaks in the calcined case indicating an increase in particle size.

It can be inferred that the heat treatment (calcination) led to an increase in the metal particle size, which is the cause for deactivation in the calcined case.

<b>Table 4.1</b> : N	i (111) crystal	size estimation	using Scherrer	Equation fo	r the reduced	and spent
catalysts						

Catalyst	Ni- Pt/Al2O3(uncalcined)	Ni- Pt/Al2O3(calcined)
Reduced (fresh) (d <sub>p</sub> , Ni (111), nm)	3.1	4.5
Spent (d <sub>p</sub> , Ni (111), nm)	3.1	6.3

Further evidence on increase in the particle size was obtained provided from the TEM images and nitrogen adsorption isotherms of the two catalysts (Fig. 4.5 and Table 4.2).



**Figure 4.4**: XRD of Ni-Pt/Al<sub>2</sub>O<sub>3</sub> a) Uncalcined fresh *vs.* spent b) Calcined fresh *vs.* spent (i – Laponite, ii – Ni (111), iii – Ni (220) and iv – Ni (200)

Sample	Sbet (m <sup>2</sup> /g)	BJH	BJH	<b>d</b> <sub>v</sub> ( <b>nm</b> ) <sup>a</sup>
		Desorption	Desorption	
		average pore	cumulative	
		diameter (nm)	pore volume	
			(cm <sup>3</sup> /g)	
Al <sub>2</sub> O <sub>3</sub> support	401	5.8	0.65	-
Ni-Pt/Al <sub>2</sub> O <sub>3</sub>	221	4.5	0.38	$5.01 \pm 0.39$
uncalcined				
Ni-Pt/Al <sub>2</sub> O <sub>3</sub>	229	4.4	0.42	$6.17 \pm 0.45$
calcined				

**Table 4.2**: BET Surface area, pore diameter and particle size for reduced Ni-Pt catalysts

 (calcined and uncalcined)

<sup>a</sup> diameter values reported are the volume weighted average diameters calculated from the TEM images of the 2 fresh catalysts (calcined and uncalcined, refer Fig. 4.5). Diameter is calculated using the following formula  $d_v = \frac{\sum_i n_i d_i^4}{\sum_i n_i d_i^3}$ 

It can be seen from the TEM images (Figs. 4.5a-d) that there is an increase in the metal particle size for the calcined sample compared with the uncalcined sample. The volume weighted average particle diameter (Table 4.2) also corroborates the observed increase. The nitrogen adsorption isotherms are of the same type (IUPAC Type IV) indicative of mesoporous nature having  $H_2$  type hysteresis loop (Figs. 4.5e and 4.5f) [133]. The surface areas, pore volumes and pore diameters are relatively similar. The uncalcined sample shows a bimodal pore distribution centered at 3.5 and 4.5 nm while the calcined sample shows an unimodal pore distribution centered at 4.5 nm. The pore distribution indicates an increase in pore diameter for some percentage of the pores which maybe due to pore collapse due to heat treatment via calcination (Fig. 4.5f). Since the best results were obtained with an uncalcined sample, all the catalysts in the rest of our work are uncalcined, i.e. the sample is directly reduced and tested for its activity after metal impregnation and drying. This catalyst was then tested for its activity on diesel to check for sulphur tolerance and gasoline for other noble metals. The next sections detail the findings from these experiments.



**Figure 4.5**: Ni-Pt uncalcined, a) TEM image, b) Particle size distribution, Ni-Pt calcined, c) TEM image, d) Particle size distribution, e) BET adsorption isotherms and f) Pore volume distribution

## 4.2. Diesel

#### 4.2.1. Effect of coke mitigation promoters

Since the objective is to develop a multi-fuel reforming catalyst, the combination found effective for methanol was tested for diesel oxidative reforming and the performance was compared with other catalysts doped with different coke mitigation promoters – K, Ce and P. The catalyst activity and the H<sub>2</sub> production rates along with the DTG analysis of each catalyst and the amount of coke formed are plotted in Fig. 4.6.



**Figure 4.6**: a) Conversion b) H<sub>2</sub> Production rate for oxidative reforming of diesel, c) Carbon evolution for the tested catalysts and d) DTG v/s Temperature for oxidative reforming of diesel (SCR = 4; OCR = 0.2; T = 700 °C and GHSV = 5000 ml<sub>STP</sub>/(h.g<sub>cat</sub>)

As seen in Fig. 4.6a, the conversion for the unpromoted catalyst (Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>) decreases drastically after about 250 minutes of operation while the conversions for the promoted catalysts (except phosphorous based) remain stable for the reaction duration. Comparing the potassium and

cerium promoters, Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub> are superior to Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub> and Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>. In fact, the reforming activity and H<sub>2</sub> production rates are substantially increased when compared with the unpromoted catalyst (Figs. 4.6a and 4.6b). The conversion and H<sub>2</sub> production rates increased by 55% and 2.14 times as we switched from Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub> to Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, respectively. Similarly, the increase in conversion and H<sub>2</sub> production rates were 112% and 2.26 times as we switched from Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub> to Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub>, respectively. The primary reason for the catalyst deactivation and reduction in catalyst activity was due to coke formation as evidenced from the TGA results (Figs. 4.6c and 4.6d). Carbon formation was found to be the highest for the phosphorous promoted (Ni-Pt-P2/Al<sub>2</sub>O<sub>3</sub>) followed by the unpromoted (Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>) and other co-impregnated catalysts. The least carbon formation was observed in the Ce and K doped alumina-based catalysts (Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>). The coke reduction was highest for Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> (80%) followed by Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub> (76%), Ni-Pt-K2/Al2O3 (60%) and Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub> (45%) when compared with Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>. It is expected that the promoters which are added in the co-impregnation mode compete for active sites with Ni and Pt and lead to reduced catalyst activities. However, promoters added to the alumina support during intercalation are evenly dispersed in the clay layers within the pillar templates leading to availability of more active sites for reforming. It has been reported that phosphorous helps in inhibiting sulphur adsorption thereby retaining catalyst activity [80,81]. However, it has also been reported to form carbon filaments with increase in metal particle size [82]. Hence, for our work, since the activity was poor for the phosphorous promoted catalysts hence, they were not considered for further evaluation. Further investigations into the observed catalyst performance were done using characterization studies. The results from the nitrogen adsorption isotherms are reported in Table 4.3 with the adsorption isotherms shown in Fig. 4.7.

Sample	Sbet	BJH Desorption average	BJH Desorption cumulative
	(m²/g)	pore diameter (nm)	pore volume (cm <sup>3</sup> /g)
SUPPORTS			
Al <sub>2</sub> O <sub>3</sub>	401	5.80	0.65
K2-Al <sub>2</sub> O <sub>3</sub>	349	5.71	0.71
Ce2-Al <sub>2</sub> O <sub>3</sub>	324	8.52	0.47
<b>REDUCED CATA</b>	ALYSTS		
Ni-Pt/Al <sub>2</sub> O <sub>3</sub>	221	4.5	0.38
Ni-Pt-K2/Al <sub>2</sub> O <sub>3</sub>	175	7.6	0.15
Ni-Pt-Ce2/Al <sub>2</sub> O <sub>3</sub>	266	4.7	0.21
Ni-Pt/K2-Al <sub>2</sub> O <sub>3</sub>	296	5.48	0.42
Ni-Pt/Ce2-Al <sub>2</sub> O <sub>3</sub>	256	5.91	0.33

Table 4.3: BET surface area and pore diameter for the supports and reduced catalysts



Figure 4.7: N<sub>2</sub> adsorption isotherms for a) promoted supports b) promoted catalysts

It can be inferred from Table 4.3 that the unpromoted support (Al<sub>2</sub>O<sub>3</sub>) had the highest surface area compared to the other two supports (K2-Al<sub>2</sub>O<sub>3</sub> and Ce2-Al<sub>2</sub>O<sub>3</sub>). The higher ionic radii of both potassium and cerium compared to Mg and Si in the clay sheets leads to partial blockage of pores during intercalation. Hence, there is a decrease in the surface area observed for the promoted supports compared to the Al<sub>2</sub>O<sub>3</sub> support. The reduced catalysts exhibit lower surface areas compared to the corresponding supports – this is as expected since metal impregnation leads to pore blockage. Amongst the promoted catalysts, Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> gave the highest surface area while Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub>. In the case of potassium promoted catalysts, the addition of potassium plays a crucial role in retaining the mesoporous structure created during intercalation. When potassium is added in co-impregnation mode along with Ni and Pt, it competes for active sites and leads to partial pore blockage of pores.

Table 4.4 shows the Ni crystal size corresponding to  $d_{111}$  reflection for the spent catalysts while Fig. 4.8 compares the XRD plots between the fresh and spent catalysts for Ce and K promoted catalysts. There is a relative increase in the Ni crystal size after reaction for all the promoted catalysts. However, the increase is substantially lower compared to the unpromoted catalyst.

**Table 4.4**: Ni (111) crystal size estimation using Scherrer Equation for the reduced and spent

 catalysts

Catalyst	Ni-Pt-	Ni-Pt-	Ni-Pt/K2-	Ni-Pt/Ce2-	Ni-
-	<b>K2/Al<sub>2</sub>O<sub>3</sub></b>	Ce2/Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Pt/Al <sub>2</sub> O <sub>3</sub>
Reduced (fresh)	4.5	4.4	4.5	2.9	4.5
(d <sub>p</sub> , Ni (111), nm)					
Spent (d <sub>p</sub> , Ni (111), nm)	6.0	6.4	6.4	4.4	11.0

TEM images of the promoted catalysts (fresh reduced) viz. Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub> are shown in Fig. 4.9. The corresponding TEM images of the spent catalysts are shown in Fig. 4.10. Higher number of particles in the 2-12 nm range were observed in Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub> (Fig. 4.9a) while similar particle sizes between 3-9 nm were observed in the Ce promoted catalysts (Figs. 4.9b and 4.9c). A narrow particle size distribution was observed (2-6 nm) for Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> (Fig. 4.9d). The volume weighted average particle diameter was found to be 8.64  $\pm$  0.25 nm, 8.44  $\pm$  0.49 nm, 7.87  $\pm$  0.36 nm and 5.88  $\pm$  0.34 nm for Ni-Pt-

K2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, respectively. Evidently, the promoters added along with Ni and Pt gave higher particle sizes than the promoters added during intercalation. Lattice spacing at 0.208 nm, 0.196 nm, 0.209 nm and 0.196 nm were observed in the HRTEM images of the fresh catalysts (refer Figs. 4.9e, 4.9f, 4.9g and 4.9h for, Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, respectively).

These lattice spacings were close to the interplanar distance (0.206 nm) reported for Ni nanoparticles having d<sub>111</sub> orientation [134]. Adjacent to the Ni lattice, Pt nanoparticles with lattice spacing at 0.228 nm, 0.219 nm, 0.229 nm and 0.219 nm were measured corresponding to fresh catalysts (refer Figs. 4.9e, 4.9f, 4.9g and 4.9h for, Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, respectively) which is consistent with the lattice spacing corresponding to d<sub>111</sub> of Pt cubic phase [135,136]. Such interfaces forming adjacent to each other enhance catalytic properties due to H<sub>2</sub> spillover. The SAED pattern in Fig. 4.9i confirms the crystalline nature of Ni (111) and Pt (111) phases consistent with the HRTEM observations and XRD results. The other catalysts showed similar interphases of Ni (111) and Pt (111) from the SAED patterns in Figs. 4.9j, 4.9k, 4.9l for Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, respectively. An increase in the particle sizes was observed for all the promoted catalysts upon reaction in Fig. 4.10. The volume weighted average particle diameter was found to be  $9.78 \pm 0.45$ nm,  $10.89 \pm 0.55$  nm,  $9.28 \pm 0.16$  nm and  $6.72 \pm 0.45$  nm for the spent catalysts - Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, respectively. Relatively, the particle size increase was found to be the least for Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> amongst the catalysts analysed. The lattice spacings observed in the HRTEM images of the fresh catalysts were also observed in the spent catalysts (refer Figs. 4.10e, 4.10f, 4.10g and 4.10h for, Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, respectively). Similarly, the SAED patterns showed Ni (111) and Pt (111) crystalline phases in the spent samples similar to the fresh catalysts (refer Figs. 4.10i, 4.10j, 4.10k and 4.10l for Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, respectively).

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**Figure 4.8**: XRD of Ni-Pt promoted catalysts a) Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub> fresh vs. spent b) Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub> fresh vs. spent (c) Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> fresh vs. spent (d) Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub> fresh vs. spent e) Ni-Pt/Al<sub>2</sub>O<sub>3</sub> fresh vs. spent



**Figure 4.9**: Characterization of promoted catalysts (fresh) with PSD as inset of a) Ni-Pt-K2-Al<sub>2</sub>O<sub>3</sub>, b) Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, c) Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub>, d) Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>; HRTEM for e) Ni-Pt-K2-Al<sub>2</sub>O<sub>3</sub>, f) Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, g) Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub>, h) Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>; SAED for i) Ni-Pt-K2-Al<sub>2</sub>O<sub>3</sub>, j) Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, k) Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub>, l) Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>(PSD inset x-axis: 1-13 nm for Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub>, 1-9 nm for Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> and 1-12 nm for remaining catalysts)



**Figure 4.10**: Characterization of promoted catalysts (spent) with PSD as inset of a) Ni-Pt-K2-Al<sub>2</sub>O<sub>3</sub>, b) Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, c) Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub>, d) Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>; HRTEM for e) Ni-Pt-K2-Al<sub>2</sub>O<sub>3</sub>, f) Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, g) Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub>, h) Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>; SAED for i) Ni-Pt-K2-Al<sub>2</sub>O<sub>3</sub>, j) Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, k) Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub>, l) Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>(PSD inset x-axis: 1-13 nm for Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub>, 1-15 nm for Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub> and 1-12 nm for remaining catalysts)

Further analysis of the metal particle sizes was performed using HAADF-STEM analysis. Figs. 4.11, 4.12, 4.13 and 4.14 showed the HAADF-STEM results for Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, respectively. The metal particles (Ni and Pt) showed homogenous dispersion in all the four catalysts. However, the volume weighted average particle diameters ( $d_v$ ) for Ni were relatively higher compared to Pt in all the four catalysts. The  $d_v$  values for Ni particles were 7.14 ± 0.35 nm, 8.12 ± 0.19 nm, 6.55 ± 0.44 nm and 5.58 ± 0.24 nm for Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, respectively. The  $d_v$  values for Pt particles ranged between 4-6 nm for all the four catalysts. This result confirms that the increase observed is for Ni particles with the least effect on particle size observed for Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>.



Figure 4.11: EDAX result and spectrum for fresh Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub>



Figure 4.12: EDAX result and spectrum for fresh Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub>



Figure 4.13: EDAX result and spectrum for fresh Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub>



Figure 4.14: EDAX result and spectrum for fresh Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>

To understand the influence of the promoter on the metal-support interactions, H<sub>2</sub>-TPR studies were conducted and the results from the same are plotted in Fig. 4.15. The unpromoted catalyst shows a reduction peak at 232 °C attributed to the reduction of bulk Pt species [137] and a broad peak at 348 °C suggesting the reduction of bulk Ni species due to spillover effect of Pt [42,44,122,138].



Figure 4.15: Temperature Programmed Reduction (TPR) curves for the various catalysts

The peaks at 383 °C and 446 °C suggest reduction of Ni species having weak and strong interactions with the support, respectively [130]. TPR of Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> shows peaks corresponding to bulk Pt and Ni species at relatively elevated temperatures (279°C and 350°C). When compared with the unpromoted catalyst, the Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub> catalyst shows reduction peaks

corresponding to bulk Pt reduction, reduction of Ni species due to spillover effect, Ni species weakly interacting with the support and Ni species strongly interacting with the support at lower temperatures. This seems to suggest easier reducibility with more Ni-Pt species available for reduction than the unpromoted catalyst. Also, the presence of potassium due to its basic nature ensures some degree of stability in the catalyst performance which is consistent with literature [78,79]. However, the potassium competes with Ni-Pt for active sites due to its addition in the coimpregnation mode and leads to reduction in reforming activity. For the Cerium based catalysts, multiple peaks are recorded above 450 °C for Ni-Pt-Ce2/Al<sub>2</sub>O<sub>3</sub> suggesting the presence of Ni strongly interacting with the support. The peak is evidently broad which continues till 900 °C suggesting the possibility of NiAl<sub>2</sub>O<sub>4</sub> spinel formation and reduction of bulk ceria which appears at 875 °C [139]. The NiAl<sub>2</sub>O<sub>4</sub> spinel was not detected in the XRD and its formation can be ruled out. A similar profile is observed for Ni-Pt/Ce<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> with a broad peak starting at 450 °C which continues till 900 °C. At temperatures  $\geq$  300 °C in a reducing environment, it has been reported that Ce can induce migration of the metal oxides from the reduced support to the metal phase generating decoration or encapsulation effect on supported metal nanoparticles [140]. Higher decoration leads to higher coverage of metal particles by Ce which leads to lower availability of active metal sites and an increase in the reduction temperatures. Consequently, the reforming activity decreases due to the lower number of active metal sites. Characterization studies depicting the effect on dispersion (CO pulse chemisorption) due to the different promoters as well as the method of addition can be performed to ascertain this further. Also, the variations in acid-base characteristics could be estimated through CO<sub>2</sub>-TPD experiments.

From the studies on different promoters, the highest activity and stability was observed for Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>. Characterization studies showed that the stability in the metal particle size (Ni and Pt) is the major reason for the least carbon formation rates observed. It is also evident that the method of promoter addition plays an important role in the observed catalyst performance. This K-doped catalyst and Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub> were then compared with Ni-Rh/K2-Al<sub>2</sub>O<sub>3</sub> and Ni-Re/K2-Al<sub>2</sub>O<sub>3</sub> for gasoline oxidative reforming, which is elaborated in the following section.

# 4.3. Gasoline

#### 4.3.1. Effect of noble metal

Different noble metals namely, Pt, Rh and Re were investigated for gasoline reforming to check their efficacy in coke mitigation, especially when handling aromatic rich fuels like gasoline. The conversion and  $H_2$  production rates along with the TGA and DTG analysis of each catalyst showing the amount of coke formed are plotted in Fig.4.16.



**Figure 4.16**: Comparison of Catalysts for gasoline oxidative reforming – a) Conversion, b) H<sub>2</sub> productivity *vs*. time on-stream c) C evolution from TGA analysis and d) DTG curves; Operating parameters: SCR: 4, OCR: 0.2, T: 700 °C and GHSV 5000 ml<sub>STP</sub>/h.g<sub>cat</sub> (- $\blacksquare$ - Ni-Pt/K<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>,- $\square$ - Ni-Pt/Ce<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, - $\blacktriangle$ - Ni-Rh/K<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and - $\blacklozenge$ -Ni-Re/K<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>)

There is a sharp decrease in the conversion and  $H_2$  production rates for the other catalysts when compared with Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> as shown in Figs. 4.16a and 4.16b. The initial activity is high which results in higher H<sub>2</sub> production rates, especially in case of Ni-Rh/K2-Al<sub>2</sub>O<sub>3</sub>. All the four catalysts show a reduction in the H<sub>2</sub> production rate with only Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> showing stable trends after 250 minutes on-stream which indicates that all the other catalysts had deactivated. The Ce based catalyst which showed stable trends in diesel reforming also deactivated as shown in Fig. 4.16a. Evaluation of TGA results reveals coke formation (Figs.4.16c and 4.16d) in varying amounts on all the four catalysts with the highest coke formation observed for Ni-Re/K2-Al<sub>2</sub>O<sub>3</sub> followed by Ni-Rh/K2-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub>. The least amount of coke was formed over Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>. From the DTG curves (Fig. 4.16d), it can be seen that all the four catalysts show major peaks associated with the formation of graphitic carbon ranging between 550 and 590 °C [141]. Fig. 4.17 reports the XRD micrographs for all the four catalysts comparing the fresh and spent samples while Table 4.5 reports the Ni crystal size corresponding to (111) reflections calculated using Scherrer equation. It can be seen from Fig. 4.17 and Table 4.5 that there is a distinct rise in the Ni crystal size after the reaction for all the catalysts except Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> which can be attributed to coke formation. The rate of carbon formation is found to be the least in the Ni-Pt-K combination and it tends to retain the catalytic activity compared to the other catalysts tested. It has been reported that sulphur present in the fuel tends to preferentially adsorb on Ni this reduces the number of active sites available for reforming while protecting Rh from sulphur poisoning [142]. Also, addition of Rh increases the acidity and alters the desired selectivity towards hydrogen formation via reforming [143]. Similarly, Re is reported as an effective promoter for sulphur adsorption [144]. These observations can be verified for the bi-metallic catalysts that we prepared using Rh and Re also through other characterization methods like pulse chemisorption, CO<sub>2</sub> TPD, etc.

Based on the foregoing discussions, it can be concluded that the most suitable catalyst for the three fuels under consideration in terms of activity and stability is Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>. Further studies need to be performed to ascertain the tolerance limits with respect to sulphur since the sulphur limits in commercial diesel and gasoline vary between 10 ppm to 50 ppm depending on the fuel standards followed. The following section details the investigations conducted with respect to sulphur tolerance of the selected catalyst, i.e., Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>.



**Figure 4.17**: XRD of Ni-Pt promoted catalysts a) Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub> fresh *vs*. spent b) Ni-Pt/Ce2-Al<sub>2</sub>O<sub>3</sub> fresh *vs*. spent (c) Ni-Rh/K2-Al<sub>2</sub>O<sub>3</sub> fresh *vs*. spent (d) Ni-Re/K2-Al<sub>2</sub>O<sub>3</sub> fresh *vs*. spent

**Table 4.5**: Ni (111) crystal size estimation using Scherrer Equation for the reduced and spent catalysts

Catalyst	Ni-Pt-	Ni-Pt/Ce2-	Ni-Rh/K2-	Ni-Re/K2-
	K2/Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>
Reduced (fresh)	4.5	4.4	3.0	2.9
(d <sub>p</sub> , Ni (111), nm)				
Spent (d <sub>p</sub> , Ni (111), nm)	4.3	7.0	4.8	5.7

## 4.4. Sulphur tolerance of the catalyst

Owing to difficulties in measuring the ppm levels of sulphur in commercial diesel, a synthetic mixture mimicking diesel was prepared with different sulphur loadings.

#### 4.4.1. Experimental methodology for sulphur tolerance test

Model compounds for diesel (tetradecane and hexadecane) were procured from M/s Sigma Aldrich. A 50:50 (wt/wt) mixture to mimic diesel properties was prepared and termed as 'base case'. To add sulphur to the base case, Benzothiophene was procured from M/s Sigma Aldrich. For obtaining 10 ppmw, 50 ppmw and 100 ppmw sulphur loadings, equivalent amounts of benzothiophene were added to the base case. The operating conditions chosen were as follows – SCR: 4, OCR: 0.2, T: 780 °C and GHSV: 6100 (ml<sub>STP</sub>/h.g<sub>cat</sub>). The catalyst used for the test was Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>. This catalyst was uncalcined and directly reduced before being used in situ for reforming.

### 4.4.2. Results for Sulphur Tolerance of Catalyst

Figs. 4.18a and 4.18b compare the conversion and  $H_2$  production rates for different sulphur loadings and the base case. The catalyst was found to be stable for the base case and for a sulphur loading of 10 ppmw. As the sulphur loading was increased to 50 ppmw, the catalyst deactivated with the rate of deactivation increasing with sulphur loading. To check for carbon formation, TGA analysis was done – Figs. 4.18c and 4.18d confirm carbon formation as the reason for catalyst deactivation with the rate of carbon formation increasing with sulphur loading with sulphur loading beyond 10 ppmw.



**Figure 4.18**: Sulphur Tolerance test for Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> for different sulphur loadings, a) Conversion b) H<sub>2</sub> production rate c) C evolution for different sulphur loadings d) DTG Curve from TGA Analysis; Operating conditions for reforming experiments: SCR: 4, OCR: 0.2, T: 700 °C and GHSV 5000 ml<sub>STP</sub>/(h.g<sub>cat</sub>);  $\blacksquare - 0$  ppmw sulphur loading,  $\Delta - 10$  ppmw sulphur loading,  $\bullet - 50$  ppmw sulphur loading and  $\blacktriangledown - 100$  ppmw sulphur loading

These results clearly indicate that the catalyst can withstand sulphur up to a limit of 10 ppmw which complies with the Euro VI norms followed globally. Hence, fuels following Euro VI norms can be reformed using this catalyst without the need for a desulfuriser upfront of the reformer. Since the objective was to develop a stable catalyst, the deactivation mechanism leading to C formation was not studied in detail. The best catalyst found from this study, Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, was selected for further experimental investigations to study the kinetics and perform a longer duration stability test.

# 5.0. EFFECT OF POTASSIUM ON CATALYST STABILITY AND ACTIVITY

In this section, experimental findings related to optimization of potassium loading and operating conditions are discussed in detail. The findings are supported with characterization studies investigating the effect of potassium addition on overall catalyst performance. This discussion is followed by a stability test for the best performing catalyst based on the methodology described in the experimental section.

Following section details the experimental findings with respect to optimization of potassium loading on the catalyst.

# 5.1. Effect of potassium loading

For evaluating the effect of potassium loading, four different catalysts were tested for oxidative steam reforming of diesel. These were Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub> (K/Al molar ratio of 0.1, 0.45 and 0.7 to get the desired potassium loadings of 2, 5 and 8 wt%, respectively was chosen) and these catalysts were tested for their performance against unpromoted Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>. Following section details the catalyst performance of the four catalysts under consideration. (*Note: The unpromoted catalyst is denoted as Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub> to emphasize on no potassium present*).

#### 5.1.1. Catalyst activity results for different potassium loadings

The effects of K loading on catalyst performance are plotted in Fig. 5.1. For comparison purposes, the result obtained for Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub> (discussed in chapter 4) is also plotted in Fig. 5.1a for conversion and Fig. 5.1b for H<sub>2</sub> production rates. Fig. 5.1a shows that the catalyst without K loading (Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>) deactivated after 275 min and provided low H<sub>2</sub> yield (Fig. 5.1b). The conversion and H<sub>2</sub> yield improved with potassium addition however, a marked difference was observed depending upon how potassium was introduced. The conversion and H<sub>2</sub> yield both were higher for Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> than Ni-Pt-K2/Al<sub>2</sub>O<sub>3</sub> suggesting that addition of potassium during alumina synthesis allows homogenous dispersion of the potassium along the clay interlayers. When potassium was added via co-impregnation along with Ni and Pt, potassium competes for active sites and gets preferentially deposited on Ni step sites thereby reducing

reforming activity [79,145]. Although, there was an increase in activity when compared with Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>, the activities were still lower compared to the case when potassium was added during alumina preparation. This strategy of adding potassium exclusively to alumina support thereby enhancing potassium-alumina interactions has been highlighted in previous studies [79] however, to the best of our knowledge has not been demonstrated. TGA analysis of the spent catalysts revealed highest coke formation over Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub> and lowest for Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub>, an 88% reduction in coke deposition (Fig. 5.1c). The DTG plots exhibit carbon peaks ranging between 500 to 570°C (Fig. 5.1d), indicating formation of graphitic carbon [146]. The peaks at lower temperatures correspond to moisture loss. In this chapter only the alumina doped potassium catalysts and K0-Al<sub>2</sub>O<sub>3</sub> are considered for further analysis and discussion.



**Figure 5.1**: a) Conversion b) H<sub>2</sub> Production rate for oxidative reforming of diesel, (SCR = 4; OCR = 0.2; T = 700 °C and GHSV = 5000 ml<sub>STP</sub>/(h.g<sub>cat</sub>) c) Specific coke deposition over the spent catalysts and d) DTG curve of the spent catalysts

XRD micrographs of fresh and spent catalysts (Fig. 5.2, and Table 5.1) show that Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub> had the highest increase in Ni crystallite size after the reaction. All the K-doped catalysts were comparatively stable, with Ni- Pt/K5-Al<sub>2</sub>O<sub>3</sub> catalyst showing a similar Ni crystallite size after reaction. Therefore Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> was considered the best catalyst for further analysis in our study.



**Figure 5.2**: XRD of fresh v/s spent catalysts (tested on Diesel) A) Ni-Pt/Al<sub>2</sub>O<sub>3</sub> B) Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> C) Ni-Pt/K5- Al<sub>2</sub>O<sub>3</sub> D) Ni-Pt/K8- Al<sub>2</sub>O<sub>3</sub>; (i) – Laponite (ii)  $\gamma$ - Al<sub>2</sub>O<sub>3</sub> (iii) Ni (111) (iv) Ni (200) (v) Ni (220) (vi) Pt (111) (vii) Pt (200) (viii) Pt (311)

Catalyst	Ni-Pt/K0- Al2O3	Ni-Pt/K2- Al <sub>2</sub> O <sub>3</sub>	Ni-Pt/K5- Al2O3	Ni-Pt/K8- Al2O3
Reduced (fresh) (d <sub>p</sub> , Ni (111), nm)	4.5	4.5	5.3	8.4
Spent (d <sub>p</sub> , Ni (111), nm)	11.0	6.4	5.5	8.7

**Table 5.1**: Ni (111) crystal size estimation using Scherrer Equation for the reduced and spent

 catalysts

5.1.2. Characterization Studies on Potassium promoted catalysts

XRD of samples (Figs. 5.3a and 5.3b) shows characteristic peaks of Laponite at  $2\theta = 20^{\circ}$ ,  $28^{\circ}$ ,  $35^{\circ}$ ,  $54^{\circ}$ ,  $61^{\circ}$  and  $72^{\circ}$  which correspond well with the literature [147]. Following intercalation, laponite peaks were retained, while new peaks at  $37.5^{\circ}$  and  $65.8^{\circ}$  corresponding to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (JCPDS No: 10-0425) appeared for all the supports suggesting successful intercalation. Basal spacings based on a d<sub>001</sub> diffraction peak for each support after calcination are reported in Table 5.2 with the corresponding XRD micrograph shown in Fig. 5.4. The increase in the basal spacing with addition of potassium till K5-Al<sub>2</sub>O<sub>3</sub>, compared to laponite, indicates successful intercalation of Al and K, without altering the clay sheet structure. This suggests a homogenous anchoring of the species within the clay layers. Beyond 5 wt%, a decrease in basal spacing was observed suggesting limited intercalation. On closer observation of the XRD of K8-Al<sub>2</sub>O<sub>3</sub>, minor peaks of K<sub>2</sub>O at 25.3, 29.3 and 41.9° (JCPDS 01-077-2176) [148] (Fig. 5.5) were observed suggesting deposition of excess K ions outside the interlayers, thus no longer participating in intercalation.



**Figure 5.3**: XRD of a) Supports b) Reduced Catalysts (i – Laponite, ii – Al<sub>2</sub>O<sub>3</sub>, iii – Ni (111); iv-Ni(220); v-Ni(200); vi-Pt(111); vii-Pt(200); viii-Pt(311)

Sample	d001 (Interplanar
	spacing), (Å)
Supports	
Laponite	13.9
K0-Al <sub>2</sub> O <sub>3</sub>	19.4
K2-Al <sub>2</sub> O <sub>3</sub>	22.1
K5-Al <sub>2</sub> O <sub>3</sub>	22.7
K8-Al <sub>2</sub> O <sub>3</sub>	17.8

**Table 5.2**: Comparison of basal spacings (d<sub>001</sub>) for supports



**Figure 5.4**: XRD of supports to view the d<sub>001</sub> interplanar spacing peak



Figure 5.5: XRD of K8-Al<sub>2</sub>O<sub>3</sub> (i – Laponite, ii – Al<sub>2</sub>O<sub>3</sub>, iii – K<sub>2</sub>O)

During intercalation and pillaring, reduction in Al with a simultaneous increase in K weight fraction was observed with K addition (XRF results, Table 5.3). However, homogenous distribution of K and Al was seen within the support framework (HAADF-STEM images Figs. 5.6, 5.7, 5.8, 5.9 for K0-Al<sub>2</sub>O<sub>3</sub>, K2-Al<sub>2</sub>O<sub>3</sub>, K5-Al<sub>2</sub>O<sub>3</sub> and K8-Al<sub>2</sub>O<sub>3</sub>, respectively). This strongly suggests the presence of both Al and K based intercalated species within the support upon potassium addition until 5 wt% K loading, beyond which excess K deposits on the surface outside the interlayers. After metal impregnation and reduction, Ni<sup>0</sup> peaks at 44° (111), 51° (220) and 76° (200) (JCPDS 87- 0712) were detected for all the catalysts, while Pt<sup>0</sup> peaks at 40.6° (111), 46.2° (200) and 81.3° (311) (JCPDS 04-0802) were detected for Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> (Fig. 5.3b). Minor intensity peaks corresponding to Pt<sup>0</sup> at 40.6° and 81.3° were also detected for Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub> thereby suggesting Ni-Pt phase segregation for potassium loadings  $\geq$  5 wt%. Higher Ni<sup>0</sup> peak intensities were observed in Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub> also suggesting an increase in Ni particle size.

Element	Ni	Pt	Al	Si	Mg	K
Supports						
K0-Al <sub>2</sub> O <sub>3</sub>	-	-	24.61±0.9	50.21±0.4	25.11±0.1	-
K2-Al <sub>2</sub> O <sub>3</sub>	-	-	22.80±0.3	50.42±1.1	24.81±0.5	1.86±0.2
K5-Al <sub>2</sub> O <sub>3</sub>	-	-	19.12±0.2	47.82±0.8	28.54±0.1	4.80±0.5
K8-Al <sub>2</sub> O <sub>3</sub>	-	-	16.62±0.1	45.22±0.5	29.61±0.3	8.63±0.1
Reduced Ca	atalysts					
Ni-Pt/K0-	10.39±0.1	0.98±0.01	22.04±0.3	44.98±0.5	22.49±0.1	0
$Al_2O_3$						
Ni-Pt/K2-	9.91±0.1	$1.08 \pm 0.01$	20.55±0.2	45.43±0.5	22.35±0.1	1.67±0.02
$Al_2O_3$						
Ni-Pt/K5-	10.17±0.1	0.98±0.01	17.04±0.2	42.87±0.1	25.06±0.1	4.81±0.3
$Al_2O_3$						
Ni-Pt/K8-	10.14±0.1	$0.98 \pm 0.02$	14.89±0.2	40.56±0.3	26.56±0.2	7.77±0.1
Al <sub>2</sub> O <sub>3</sub>						

Table 5.3: Elemental composition of the catalysts (wt%) determined by XRF analysis

Temperature programmed reduction profiles (TPR) of the four catalysts were studied to study the metal-support interaction. The TPR profile is plotted in Fig. 5.10a while the deconvoluted peaks corresponding to each catalyst is plotted in Fig. 5.10b. Three peaks were deconvoluted (Figs. 5.10a and 5.10b) for Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub> corresponding to bulk Pt (250 °C) reduction [137], Ni species brought to the surface due to H<sub>2</sub> spillover effect (360 °C) and Ni species strongly interacting with the support (610 °C), respectively [122,149]. The likelihood of spinel (Ni-Aluminate) formation was ruled out since the catalyst preparation method involves direct reduction post metal impregnation and hence calcination step is avoided. Besides, the characteristic peaks deconvoluted at 610 °C for Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub> was attributed to Ni species interacting strongly with the support exhibiting monometallic character typical of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts [61,150]. The profile for Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> showed four reduction peaks with the peak corresponding to bulk Pt reduction (250 °C), Ni species brought to the surface due to H<sub>2</sub> spillover effect (320 °C).





Figure 5.6: EDAX\_STEM image and spectrum of K0-Al<sub>2</sub>O<sub>3</sub> support



Figure 5.7: EDAX\_STEM image and spectrum of K2-Al<sub>2</sub>O<sub>3</sub> support

Det: Octane Elite TW 55

8.0

6.0

12.0

14.0

16.0

18.0

10.0

КΚ

12.500 keV

4.0

2.0

68 Cnts

36.4K 27.3K 18.2K 9.1K

0.0K

Lsec: 892.9



Figure 5.8: EDAX\_STEM image and spectrum of K5-Al<sub>2</sub>O<sub>3</sub> support



Figure 5.9: EDAX\_STEM image and spectrum of K8-Al<sub>2</sub>O<sub>3</sub> support

interacting weakly with the support (390 °C) and Ni species interacting strongly (700 °C) with the support (Figs. 5.10a and 5.10b). An increase in temperature was observed for peaks attributed to Ni interaction with support for Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>. With further increase in potassium loading, a distinct change in the TPR profile was observed for Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub>. A higher intensity peak corresponding to bulk Pt reduction at 250 °C for Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> and at 260 °C for Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub> were observed. While the peak positions corresponding to bulk Pt reduction and

Ni species interacting strongly with the support remained constant for the potassium doped catalysts, there was an increase in temperatures observed corresponding to Ni reduction on surface and interacting weakly with the support for Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> (Figs. 5.10a and Fig. 5.10b). With further increase in potassium loading, slight decrease in reduction temperature for peaks corresponding to Ni species on surface and Ni species interacting weakly with the support were observed (Figs. 5.10a and 5.10b). Three conclusions which can be derived from the TPR results is that with potassium loading  $\geq$  5 wt%, distinct Pt phase can be identified thereby confirming Ni-Pt phase segregation as observed in XRD results. Secondly, the segregation may be partial with part of the Ni species available at the surface migrating on the support thereby leading to stronger Nisupport interactions as evidenced by increase in reduction temperatures. Thirdly, as potassium loading is increased from 5 wt% to 8 wt%, the Ni interaction with the support decreases due to observed decrease in reduction temperatures which might be due to the limited intercalation observed for Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub>. The H<sub>2</sub> consumed/uptake during the TPR runs has been reported in Table 5.4 and the maximum  $H_2$  consumption was reported for Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> thereby suggesting presence of higher reducible sites than other catalysts. A distinct drop in H<sub>2</sub> consumption for Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub> was observed thereby suggesting decrease in reducible sites which may be attributed to increase in metal particle size leading to lowering of active metal surface area. Indeed, the CO uptake values (refer Table 5.4) obtained from CO-pulse chemisorption experiments followed similar trend as seen in H<sub>2</sub> consumption values with the maximum obtained for Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub>. Corresponding dispersion and TOF values (Table 5.4) calculated from the CO uptake values and as per the published procedure [122] also showed a maximum for Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub>. Few studies have reported effect of potassium on CO adsorption in monometallic Ni and Pt based catalysts. Presence of potassium was found to have an insignificant effect on CO adsorption with the adsorption predominantly observed on potassium free Ni surfaces [151]. Contrastingly, CO adsorption decreased with increase in potassium loadings from 1 wt% to 10 wt% on Ni/Al<sub>2</sub>O<sub>3</sub> catalyst mainly due to the coverage of potassium on Ni species thereby hindering the reforming ability of the catalyst with potassium presence [152]. Potassium addition to  $Pt/Al_2O_3$  led to greater electron deficiency of Pt species [153] which was supported by a DRIFTS-MS study [154]. It was observed that potassium presence led to weakening of C-O bond and strengthening of Pt-C bond leading to hindrance of CO desorption while facilitating reaction of CO with OH to form CO<sub>2</sub>. In another study [155], 4 wt% potassium addition to Pt/CeO<sub>2</sub> led to decrease in CO uptake since
potassium was found to weaken Pt-Ce interaction thereby reducing activity with respect to H<sub>2</sub> production. The studies reported above add potassium either in co-impregnation mode or in sequential impregnation mode thereby altering the properties of the metals (Ni or Pt). However, in our work, the potassium is added during support preparation essentially limiting the interactions to Al-K thereby the effects observed in monometallic catalysts are absent in our case. However, we must add that the uncertainty in stoichiometry and surface compositions commonly observed with bimetallic catalysts limit the accuracy of the dispersion and TOF values reported in Table 5.4 however, a qualitative analysis of each catalyst can be made from the reported values. The TOF reported for Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> was 2.6 times higher compared to Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>, indicating a promoting effect of potassium addition. The amount of adsorbed CO however, distinctly quantifies the number of active sites among the four catalysts [60,156]. K loading greater than 5 wt% resulted in a drop in H<sub>2</sub> uptake, CO uptake, dispersion and TOF values, which is likely due to the increase in Ni crystallite size as seen in XRD results.

Catalyst	Metal loading (% w/w) <sup>a</sup>	H2 uptake (mmol/g)	CO uptake (mmol/g)	% Dispersion	<b>TOF</b> (s <sup>-1</sup> ) <sup>b</sup>	<b>d</b> <sub>v</sub> ( <b>nm</b> ) <sup>c</sup>
Ni-Pt/K0-Al <sub>2</sub> O <sub>3</sub>	Ni: 10.39±0.1 (10) Pt: 0.98±0.01 (1)	2.09	8.11×10 <sup>-4</sup>	4.82	22.67	5.55
Ni-Pt/K2-Al <sub>2</sub> O <sub>3</sub>	Ni: 9.91±0.1 (10) Pt: 1.08±0.01 (1)	2.18	1.23×10 <sup>-3</sup>	7.21	28.12	5.88
Ni-Pt/K5-Al <sub>2</sub> O <sub>3</sub>	Ni: 10.17±0.1 (10)	2.29	2.47×10 <sup>-3</sup>	14.02	59.04	6.38
Ni-Pt/K8-Al <sub>2</sub> O <sub>3</sub>	Ni: 10.14±0.1 (10) Pt: 0.98±0.02 (1)	1.33	1.10×10 <sup>-3</sup>	6.23	37.79	9.19

**Table 5.4**: H<sub>2</sub> and CO uptake, metal dispersion and particle size, BET surface area and TOF for the 4 catalysts

<sup>a</sup>The values of metal loading were measured using XRF; the values in parenthesis are the nominal values. XRF values for all elements are reported in Supplementary Table S1

<sup>b</sup> The TOF values have been calculated based on the CO uptake values from chemisorption experiments and initial activity results for the four catalysts based on  $H_2$  production rates reported in Fig. 1b

<sup>c</sup> diameter values reported are the volume weighted average diameters calculated from the TEM images of the four catalysts (reduced). The particle size distributions along with the TEM images are reported in Fig. 5. Diameter is calculated using the following formula  $d_v = \frac{\sum_i n_i d_i^2}{\sum_i n_i d_i^2}$ 



**Figure 5.10**: a) Temperature Programmed Reduction Profiles for promoted and unpromoted catalysts; b) Deconvolution of peaks in TPR profiles for Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K2- Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K5- Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K8- Al<sub>2</sub>O<sub>3</sub>

Referring to Table 5.4 and Fig. 5.11 (showing TEM images of the four catalysts), a distinct increase in particle size with increase in potassium loading was observed. The  $d_v$  calculated from the

particle size distribution (refer inset Fig. 5.11) was calculated as  $5.55 \pm 0.38$  nm,  $5.88 \pm 0.34$  nm,  $6.38 \pm 0.37$  nm and  $9.19 \pm 0.74$  nm for catalysts having 0,2,5 and 8 wt% potassium loading respectively. When compared with the particle sizes calculated for the supports, there is a rise in particle size for Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub> when the support (K8-Al<sub>2</sub>O<sub>3</sub>) undergoes metal impregnation and heat treatment in the form of reduction. To further check on the increase in particle size, HAADF STEM results for Ni and Pt for the four catalysts are shown in Fig. 5.12 with the other elements mapped and reported in Figs. 5.13, 5.14, 5.15 and 5.16 for Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub>, respectively.

Fig. 5.12 shows a rise in Ni particle size with increase in potassium loading, while the Pt particle size remains largely unaffected. Further evidence was obtained by calculating the observed particle sizes from the Ni and Pt elemental maps. The  $d_v$  of Ni particles was found to be  $4.64 \pm 0.59$  nm,  $4.87 \pm 0.6$  nm,  $5.28 \pm 0.79$  nm and  $9.05 \pm 1.07$  nm for Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub>, respectively. Similar analysis for Pt particle however revealed a size ranging between 4.5 to 5.5 nm for all the four catalysts.

Table 5.5 reveals that the pore surface area of Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> were higher than other catalysts. All the catalysts show similar isotherms (IUPAC Type IV) indicative of mesoporous nature having H<sub>2</sub> type (Fig. 5.17) hysteresis loop [157].



**Figure 5.11**: TEM images of a) Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>, b) Ni-Pt/K2- Al<sub>2</sub>O<sub>3</sub>, c) Ni-Pt/K5- Al<sub>2</sub>O<sub>3</sub> and d) Ni-Pt/K8- Al<sub>2</sub>O<sub>3</sub> and inset particle size distribution of four catalysts (PSD inset x-axis scale: Particle size (1-12 nm)



**Figure 5.12**: HAADF image and EDAX-mapping of Ni, Pt in a) Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>, b) Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, c) Ni-Pt/K5- Al<sub>2</sub>O<sub>3</sub> and d) Ni-Pt/K8- Al<sub>2</sub>O<sub>3</sub>



**Figure 5.13**: STEM-EDAX Images of Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub> a) HAADF image a1) Mg elemental map a2) Al elemental map a3) Si elemental map a4) Spectrum for Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>



**Figure 5.14**: STEM-EDAX Images of Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> a) HAADF image a1) Mg elemental map a2) Al elemental map a3) Si elemental map a4) K elemental map a5) Spectrum for Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>



**Figure 5.15**: STEM-EDAX Images of Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> a) HAADF image a1) Mg elemental map a2) Al elemental map a3) Si elemental map a4) K elemental map a5) Spectrum for Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub>



**Figure 5.16**: STEM-EDAX Images of Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub> a) HAADF image a1) Mg elemental map a2) Al elemental map a3) Si elemental map a4) K elemental map a5) Spectrum for Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub>

Sample	SBET (m <sup>2</sup> /g)	ВЈН	BJH	Micropore	
		Desorption	Desorption	volume (cm³/g)	
		average pore	cumulative		
		diameter (nm)	pore volume		
			(cm <sup>3</sup> /g)		
Supports					
K0-Al <sub>2</sub> O <sub>3</sub>	401	5.80	0.65	9.11×10 <sup>-4</sup>	
K2-Al <sub>2</sub> O <sub>3</sub>	349	5.71	0.71	2.59×10 <sup>-3</sup>	
K5-Al <sub>2</sub> O <sub>3</sub>	331	5.07	0.76	1.03×10 <sup>-2</sup>	
K8-Al <sub>2</sub> O <sub>3</sub>	247	7.23	0.36	$1.00 \times 10^{-3}$	
Reduced Catalysts					
Ni-Pt/K0-Al <sub>2</sub> O <sub>3</sub>	221	4.50	0.38	2.21×10 <sup>-4</sup>	
Ni-Pt/K2-Al <sub>2</sub> O <sub>3</sub>	296	5.48	0.42	$1.41 \times 10^{-3}$	
Ni-Pt/K5-Al <sub>2</sub> O <sub>3</sub>	280	4.23	0.48	1.93×10 <sup>-3</sup>	
Ni-Pt/K8-Al <sub>2</sub> O <sub>3</sub>	191	5.21	0.26	0.87×10 <sup>-3</sup>	

Table 5.5: BET Surface area and pore diameter for Ni-Pt catalysts and supports

A sharp decrease in surface area for both K8-Al<sub>2</sub>O<sub>3</sub> and the corresponding reduced catalyst can be attributed to the higher particle sizes observed in the TEM analysis thereby further confirming the observed trends. Compared to K0-Al<sub>2</sub>O<sub>3</sub>, there is a substantial reduction in BET surface area of Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>. Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> shows a BET surface area of 296 m<sup>2</sup>/g while Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub> show a BET surface area of 280 m<sup>2</sup>/g and 191 m<sup>2</sup>/g, respectively. Correspondingly, the supports show a BET surface area of 349 m<sup>2</sup>/g, 331 m<sup>2</sup>/g and 247 m<sup>2</sup>/g for K2-Al<sub>2</sub>O<sub>3</sub>, K5-Al<sub>2</sub>O<sub>3</sub> and K8-Al<sub>2</sub>O<sub>3</sub>, respectively. The process of intercalation involves pillaring and is known to improve the porosity of the support [84,85]. This is evident from the high surface areas obtained which show Type IV isotherms indicative of mesoporous character. Upon Ni-Pt impregnation followed by reduction under H<sub>2</sub> environment, due to the heat treatment, substantial amounts of pores are destroyed which are evident from the decrease in the cumulative pore volume in the reduced catalysts (Table 5.5). Potassium has an higher ionic radii hence due to potassium addition there is a possibility of some of the pores being blocked due to potassium deposition which explains the decrease in surface area of the potassium doped supports compared to K0-Al<sub>2</sub>O<sub>3</sub> [158]. However, potassium addition till 5 wt% also leads to an increase in pore volumes

(refer BJH pore volumes in Table 5.5 for K2-Al<sub>2</sub>O<sub>3</sub> and K5-Al<sub>2</sub>O<sub>3</sub> relative to K0-Al<sub>2</sub>O<sub>3</sub>). Hence the amount of pores formed also increases with increase in potassium addition till 5 wt%. Cumulatively, upon Ni-Pt impregnation followed by reduction under H<sub>2</sub>, the extent of decrease in surface area is offset by the presence of more pores in potassium doped catalysts. Further, a sharp decrease in both surface area and pore volume for both K8-Al<sub>2</sub>O<sub>3</sub> and the corresponding reduced catalyst were observed. The increase in particle size as observed in TEM analysis coupled with incomplete intercalation leading to pore blocking due to larger size potassium cation are probable reasons for the observed decrease for catalysts having potassium loading greater than 5 wt%.



**Figure 5.17**: a) Nitrogen adsorption Isotherms and b) Pore Size distribution for K0-Al<sub>2</sub>O<sub>3</sub>, K2-Al<sub>2</sub>O<sub>3</sub>, K5- Al<sub>2</sub>O<sub>3</sub> and K8- Al<sub>2</sub>O<sub>3</sub>; c) Nitrogen adsorption Isotherms and d) Pore Size distribution for Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K2- Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K5- Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K8- Al<sub>2</sub>O<sub>3</sub>

Pillared clays exhibit both Lewis and Brönsted acid sites, however, K promoted catalysts are expected to have higher basicity as seen in CO<sub>2</sub>-TPD results (Fig. 5.18a). Two peaks were observed

for all the four catalysts, with the lower temperature peak assigned to weak basic sites and the higher temperature peak assigned to strong basic sites [71]. The peak corresponding to strong basic sites shifted to higher temperatures with increasing potassium loading. Expectedly, the amount of  $CO_2$  desorbed (Table 5.6) increased with increasing potassium loading, confirming the presence of basic sites, which adsorb  $CO_2$  and mitigate CO disproportionation via the reverse Boudouard reaction. To illustrate the role of acid-base sites, gas phase composition of the reformate was plotted in Fig. 5.18b with changes in catalyst selectivity captured with increase in potassium loading. H<sub>2</sub> concentration increases with increase in K loading up to 5 wt%, whereas methanation, reverse water gas shift and coke forming reactions are dominant over Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub> leading to Ni deactivation.

Therefore, higher methane and CO concentrations are dominant in Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>. K doping enhanced the metal support interaction, promoted H<sub>2</sub> formation via water gas shift and methane reforming reactions, and hindered the reverse Boudouard reaction. Beyond 5 wt% K loading, increased diffusion of Ni particles on the support caused them to agglomerate, thereby lowering the number of active sites. Thus, higher Ni particle sizes contributed to enhanced carbon formation as well as promoted methanation and reverse water gas shift reactions thereby leading to higher methane and CO concentrations with corresponding decrease in H<sub>2</sub> concentration when compared with Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub>.



**Figure 5.18**: a) CO<sub>2</sub>-TPD profiles for the four catalysts b) Effect of K doping on reformate gas composition during oxidative reforming of diesel. (SCR= 4; OCR=0.2; T= 700 °C and GHSV= 5000 ml<sub>STP</sub>/(h.g<sub>cat</sub>)

CO <sub>2</sub> desorbed mmol/g
4.29
4.37
6.33
6.42

Table 5.6: CO<sub>2</sub>-TPD results for promoted and unpromoted catalysts

Fig. 5.19 shows the XPS spectra of Ni 2p for the reduced catalysts. Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub> catalyst exhibits Ni  $2p_{3/2}$  main peak at 855.42 eV with a shoulder at 860.7 eV and a spin orbit coupling energy gap of 17.3 eV, corresponding to Ni<sup>2+</sup> species, with a small peak at 852.68 eV attributed to metallic Ni<sup>0</sup> species [159]. The Ni  $2p_{3/2}$  and Ni<sup>0</sup> peaks red-shifts by 1.4 eV and 1.85 eV, respectively, after K loading (Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>) due to enhanced Ni-K interactions. Similar red-shifts of 0.54 eV and 0.72 eV were observed for Ni  $2p_{3/2}$  and Ni<sup>0</sup>, respectively, for 5 wt% K loading. Beyond 5 wt% loading we observed a blue shift in binding energy for Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub> relative to other K loaded catalysts. Stronger metal-support interaction led to the growth of Ni particle size with increasing K loading, and while the XPS results showed presence of Ni<sup>2+</sup> species on the

surface, XRD did not show evidence of NiO in the bulk. Therefore, the presence of Ni<sup>2+</sup> is likely to be due to surface passivation only during sample storage in inert atmosphere and preparation for XPS analysis.

Al2p spectrum which is characteristic of pillared clays, show two peaks (Fig. 5.20a) corresponding to Al present in four coordination in tetrahedral sheets (Si) (72.78 eV) and in six coordination, present in the octahedral sheet (Mg) (73.57 eV). The peaks are spaced at 0.8 eV as reported in other literature [84]. A sharp reduction in peak intensity associated with Al in the tetrahedral sheet was observed for K<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, which reduced further with increasing K loading, suggesting the formation of K-Al-Si mixed oxides. An additional peak at 76.01 eV for K0-Al<sub>2</sub>O<sub>3</sub> and 75.79 eV for K8-Al<sub>2</sub>O<sub>3</sub>, corresponds to the extra framework Al and K, Al, respectively. Based on the cation exchange capacity (CEC) calculation procedure [85] (Table 5.7), we found that for K0-Al<sub>2</sub>O<sub>3</sub> and K8-Al<sub>2</sub>O<sub>3</sub> supports, the actual loading exceeds the maximum CEC, leading to deposition of extra cations (Al<sup>3+</sup> and K<sup>+</sup>) outside the framework. Higher binding energies for these peaks suggest a higher oxidation state. Similar observations for incomplete intercalation and deposition of Al outside the clay layers have been reported [160]. Additional XRD results confirm the presence of K<sub>2</sub>O in K8-Al<sub>2</sub>O<sub>3</sub> (Fig. 5.5) thereby supporting the observation of excess potassium deposition outside the interlayer space. The trend is similar for reduced catalysts (Fig. 5.20b), with further red shifts due to metal impregnation and reduction.

O1s of Laponite showed bulk oxygen (Fig. 5.21) at 530.56 eV from the clay structure, a hydroxyl group at 532.94 eV and adsorbed water at 534.75 eV [161], whereas for K0-Al<sub>2</sub>O<sub>3</sub>, an additional O1s peak, characteristic of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, was observed at 531.69 eV [162] (Fig. 5.22). These peaks red shift for K2-Al<sub>2</sub>O<sub>3</sub> and K5-Al<sub>2</sub>O<sub>3</sub> while a blue shift with an additional peak at 529.2 eV corresponding to K<sub>2</sub>O for K8-Al<sub>2</sub>O<sub>3</sub> was observed [163]. Fig. 5.23 shows K2s spectra for potassium-doped supports with peaks at a lower binding energy than the characteristic peak at 377-379.2 eV [164,165], confirming the shift in K peaks due to interaction with clay. Pt4f and Pt4d peaks coincided with Al2p and Mg Auger peaks at 74 eV and 313 eV, respectively. Hence, Pt peaks could not be recorded for the scanned region [166].



Figure 5.19: XPS of Ni 2p for reduced catalysts



Figure 5.20: XPS of Al 2p for a) supports b) reduced catalysts

Support	Actual	Maximum*
K0-Al <sub>2</sub> O <sub>3</sub>	8.92	8.45
K2-Al <sub>2</sub> O <sub>3</sub>	9.14	10.53
K5-Al <sub>2</sub> O <sub>3</sub>	9.8	10.53
K8-Al <sub>2</sub> O <sub>3</sub>	10.71	10.53

 Table 5.7: Cation Exchange Capacity (CEC, g precursor / g clay) for 4 supports



Figure 5.21: XPS of O1s for Laponite



Figure 5.22: XPS of O 1s for a) supports b) reduced catalysts



Figure 5.23: XPS of K 2s for a) supports b) reduced catalysts

Oxidative reforming of diesel and gasoline proceeds through a series of complex reactions on the catalyst surface resulting in the formation of CO, CO<sub>2</sub>, H<sub>2</sub> and H<sub>2</sub>O. The acid-base characteristics of the catalyst and the reforming conditions determine the final reformate composition. Through CO<sub>2</sub>-TPD experiments, the role of basicity due to potassium addition in altering the catalyst H<sub>2</sub> selectivity has been demonstrated. The improved reforming activity is attributed to the novel catalyst synthesis method, in which addition of potassium during intercalation resulted in a K-Al-Si mixed metal oxide framework. The Materials Project database [167] lists KAlSi<sub>3</sub>O<sub>8</sub> (space group  $P\overline{1}$ ) and KAlSiO<sub>4</sub> (space group P6<sub>3</sub>) as two of the most stable K-Al-Si mixed oxide structures. Characteristic XRD peaks of KAlSiO<sub>4</sub> from literature [168] corresponded well with our supports (Fig. 5.24).



Figure 5.24: XRD of Supports (i – Laponite, ii – Al<sub>2</sub>O<sub>3</sub>, iii – KAlSiO<sub>4</sub>)

To further elucidate the presence of KAlSiO<sub>4</sub> structure in a collaborative work, my colleague Mr. Swarit Dwivedi under the supervision of Prof. Adrianus Van Duin validated the experimental observations using ReaxFF based Molecular dynamics simulations. Details of the simulations and the results from the same are reported in Appendix B. Based on these preliminary reactive MD simulations, we conclude that it is possible to form lattice sites like KAlSiO<sub>4</sub> by mixing  $Al_2O_3$ , SiO<sub>2</sub>, and K<sub>2</sub>O oxides in a similar composition as listed in Table 5.3.

The cations (K<sup>+</sup> and Al<sup>3+</sup>) introduced into the clay layers during intercalation are likely to access the octahedral sites through the hexagonal cavity formed by the arrangement of silica tetrahedron in the tetrahedral layer, leading to KAlSiO<sub>4</sub> formation. The cations crossing the tetrahedral layer intercalate in the octahedral layer substituting Mg<sup>2+</sup>, thereby forming pillared oxides during calcination. Increasing potassium loading (up to 5 wt%) caused an increase in pillars, simultaneously increasing the number of pores as evidenced from the increase in pore volume (Table 5.5) [160]. At above 5 wt%, the extra-framework K limited intercalation, thereby decreasing the pore volume and pillaring. Unfortunately, it was not possible to quantify the amount of KAlSiO<sub>4</sub> formed. Metamorphic Kalsilite or KAlSiO<sub>4</sub> exists as P31c symmetry at ambient conditions [169], which undergoes irreversible phase transformation to P63 symmetry upon calcination at 500 °C [170], explaining the match with P6<sub>3</sub> symmetry (Fig. 5.24). Formation of KAlSiO<sub>4</sub> is highly likely to increase catalyst stability. Historically, some naptha steam reforming catalysts have incorporated KAlSiO<sub>4</sub> to suppress coke formation [171]. At the reforming temperatures used in this study, Kalsilite is stable, maintaining alkalinity of the catalyst during the reaction. It is postulated that potassium acts as an electron donor resulting in adsorbed hydrocarbon reacting with steam and CO<sub>2</sub> to form H<sub>2</sub>. The lattice sites combine with the proton from steam (H<sup>+</sup>), producing an active hydroxyl ion (OH<sup>-</sup>), which reacts with hydrocarbon or carbon thereby accelerating water gas shift and coke removal, respectively.

Potassium also causes nickel diffusion on the support, which became more dominant beyond 5 wt% K loading leading to formation of larger Ni particles due to agglomeration. The addition of potassium does not affect Pt particle size however, there is a distinct segregation of Pt and Ni with potassium loadings  $\geq$  5 wt%. In order to understand this phenomenon, CO-TPD experiments were conducted as shown in Figs. 5.25a, 5.25b, 5.25c and 5.25d for Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K2- Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K5- Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K8- Al<sub>2</sub>O<sub>3</sub>, respectively. The profiles indicated in Figs. 5.25a and 5.25b corresponding to Ni-Pt/K0- Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K2- Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K2- Al<sub>2</sub>O<sub>3</sub> and Sieptite of Ni [122,124]. However, a new peak close to 100 °C was observed for both Ni-Pt/K5- Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K8- Al<sub>2</sub>O<sub>3</sub> which closely resembles  $\alpha_1$  single site CO desorption mode on Pt based sites [122,124]. We hypothesize that the Ni-Pt/K0- Al<sub>2</sub>O<sub>3</sub>

and Ni-Pt/K2- Al<sub>2</sub>O<sub>3</sub> catalysts upon reduction resemble a Ni-terminated surface with presence of bimetallic character as evidenced from TPR results.



**Figure 5.25**: CO-TPD profiles for a) Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>, b) Ni-Pt/K2- Al<sub>2</sub>O<sub>3</sub>, c) Ni-Pt/K5- Al<sub>2</sub>O<sub>3</sub> and d) Ni-Pt/K8- Al<sub>2</sub>O<sub>3</sub>

With further potassium addition, part of the Ni diffuses from the surface on the bulk support, thereby causing part of the surface to become Pt terminated, which might be the reason for Ni-Pt phase segregation observed in XRD and TPR results. Presence of Pt on the surface inhibits large scale diffusion of carbon atoms across the Ni terrace sites while Pt atoms near step edges of Ni may destabilize C nucleation thereby inhibiting coking [124]. Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> thus is the best catalyst wherein the Ni diffusion due to potassium presence in the support is partial thereby not leading to an excessive increase in particle size (unlike Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub>). Presence of Pt on the surface coupled with formation of KAlSiO<sub>4</sub> is suggested to be the main reasons for the observed

catalyst stability giving highest  $H_2$  selectivity and lowest carbon formation rates amongst the various catalysts tested. The above phenomenon has been described in the form of a proposed schematic as illustrated in Figure 5.26.



**Figure 5.26**: Schematic illustration of the proposed hypothesis on potassium addition to the catalysts (Ni-Pt/K0-Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>, Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> and Ni-Pt/K8-Al<sub>2</sub>O<sub>3</sub>)

We therefore selected Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> as the catalyst for further reforming experiments as our choice of multi-fuel reforming catalyst. Next section reports the studies done on optimizing the process conditions for each fuel.

## 5.2. Optimization of Process Conditions

Following section details the experimental results using Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> for optimizing the process conditions for each fuel.

## 5.2.1. Diesel

Effect of SCR (varying from 1 to 5) on catalyst performance was reported in Fig. 5.27. Increase in SCR increased the conversion till an optimum value of 4 and then remained constant with further

increase in SCR. H<sub>2</sub> production rate however decreased with SCR beyond 4 indicating an equilibrium for water gas shift reaction at the optimal value. Correspondingly CO and  $CO_2$ increased slightly with SCR beyond 4. Effect of OCR (varying between 0.1 to 0.65) on catalyst performance was reported in Fig. 5.28. An increase in conversion, H<sub>2</sub> production rates and H<sub>2</sub> yield was observed till OCR of 0.2 followed by a sharp decrease with further increase in OCR for H<sub>2</sub> production rate and H<sub>2</sub> yield while conversion remained constant. Increase in CO and CO<sub>2</sub> yields were observed as OCR was increased from 0.2 to 0.3 suggesting oxidation reactions gaining precedence at higher OCR's. Further increase in OCR did not cause any change in the observed trends for desired product. Effect of temperature was studied by varying temperature from 650 to 820 °C with catalyst performance reported in Fig. 5.29. A steady increase in conversion was observed till 780 °C which remained constant with further increase in temperature. However, the H<sub>2</sub> production rate and H<sub>2</sub> yields were nearly doubled as the temperature was increased from 700 to 780 °C. Beyond 780 °C, a drop in CO<sub>2</sub> and H<sub>2</sub> yields and an increase in CO yield suggest shift in selectivity towards reverse water gas shift reaction. These results indicate that temperature beyond 780 °C favour lower H<sub>2</sub>/CO ratio while reverse trend dominates below 780 °C. Due to reactor material limitations, temperatures beyond 820 °C could not be tested. GHSV was varied between 4600 to 12,600 ml<sub>STP</sub>/(h.g<sub>cat</sub>) by varying the catalyst weight with catalyst performance reported in Fig. 5.30. A decrease in conversion, H<sub>2</sub> production rate and H<sub>2</sub> yield beyond GHSV of 6100 was observed. Correspondingly, the yields of CO and CO<sub>2</sub> also show a decrease clearly indicating that the residence time provided inside the reactor was not enough for GHSV values greater than 6100. The optimized values of conversion, H<sub>2</sub> production rate, H<sub>2</sub> yield, CO yield and CO<sub>2</sub> yield for SCR: 4, OCR:0.2, T: 780 °C and GHSV: 6100 ml<sub>STP</sub>/(h.g<sub>cat</sub>) were 99%, 356 mmol H<sub>2</sub>/kg<sub>cat</sub>.s, 2.36 mol H<sub>2</sub>/mol C, 0.43 mol CO/mol C and 0.73 mol CO<sub>2</sub>/mol C, respectively.



**Figure 5.27**: Effect of SCR on: A) Conversion B)  $H_2$  production rate C) Product Yield D) Gas phase mol fraction, for diesel oxidative reforming (OCR: 0.2, T: 700 °C and GHSV: 5000  $ml_{STP}/(h.g_{cat})$ )



**Figure 5.28**: Effect of OCR on: A) Conversion B)  $H_2$  production rate C) Product Yield D) Gas phase mol fraction, for diesel oxidative reforming (SCR: 4, T: 700 °C and GHSV: 5000  $ml_{STP}/(h.g_{cat})$ )



**Figure 5.29**: Effect of temperature on: A) Conversion B)  $H_2$  production rate C) Product Yield D) Gas phase mol fraction, for diesel oxidative reforming (SCR: 4, OCR: 0.2 and GHSV: 5000  $ml_{STP}/(h.g_{cat})$ )



**Figure 5.30**: Effect of GHSV on: A) Conversion B) H<sub>2</sub> production rate C) Product Yield D) Gas phase mol fraction, for diesel oxidative reforming (SCR: 4, OCR: 0.2 and T: 780 °C)

Similar procedure was repeated for gasoline reforming. Starting operating conditions were set based on previous reforming experience with diesel. Following section reports the results obtained from gasoline using Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> as catalyst for optimizing the process conditions.

## 5.2.2. Gasoline

Gasoline having more concentration of aromatics compared to diesel would require further tuning of operational parameters from the optimum values obtained during diesel experiments. On expected lines, the trends obtained were like diesel with slight variation in operational parameters. The optimum values of SCR (Fig. 5.31), OCR (Fig. 5.32), temperature (Fig. 5.33) and GHSV (Fig. 5.34) following similar methodology to diesel were 6, 0.3, 780 °C and 6100 ml<sub>STP</sub>/(h.g<sub>cat</sub>), respectively. The optimum conversion, H<sub>2</sub> productivity, H<sub>2</sub> yield, CO yield and CO<sub>2</sub> yields were 97.6%, 376 mmol H<sub>2</sub>/kg<sub>cat</sub>.s, 2.51 mol of H<sub>2</sub>/mol of C , 0.71 mol of CO/mol of C and 0.71 mol of CO<sub>2</sub>/mol of C, respectively.



**Figure 5.31**: Effect of SCR on: A) Conversion B) H<sub>2</sub> production rate C) Product Yield D) Gas phase mol fraction, for gasoline oxidative reforming (OCR: 0.3, T: 780 °C and GHSV: 6100  $ml_{STP}/(h.g_{cat})$ )



**Figure 5.32**: Effect of OCR on: A) Conversion B)  $H_2$  production rate C) Product Yield D) Gas phase mol fraction, for gasoline oxidative reforming (SCR: 6, T: 780 °C and GHSV: 6100  $ml_{STP}/(h.g_{cat})$ )



**Figure 5.33**: Effect of temperature on: A) Conversion B)  $H_2$  production rate C) Product Yield D) Gas phase mol fraction, for gasoline oxidative reforming (SCR: 6, OCR: 0.3 and GHSV: 6100  $ml_{STP}/(h.g_{cat})$ )



**Figure 5.34**: Effect of GHSV on: A) Conversion B) H<sub>2</sub> production rate C) Product Yield D) Gas phase mol fraction, for gasoline oxidative reforming (SCR: 6, OCR: 0.3 and T: 780 °C)

Similar experimental studies in optimizing the process conditions for methanol using Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> as the catalyst are reported in the following section.

## 5.2.3. Methanol

Methanol being a simpler compound to reform compared to diesel and gasoline would require a different set of operational parameters (lower reforming temperatures) and hence preliminary experimental runs (results not reported) were done to arrive at a range for operating parameters using the catalyst. The operating region narrowed using preliminary experiments thus were steam to methanol ratio, SMR (1 to 1.7), oxygen to methanol ratio, OMR (0.05 to 0.3), temperature (250 to 550 °C) and GHSV (2000 to 15000 ml<sub>STP</sub>/(h.g<sub>cat</sub>)).

Figs. 5.35A, 5.35B and 5.35C show the effect of SMR on conversion, H<sub>2</sub> production rate and product yields, respectively. An increase in H<sub>2</sub> yield till SMR value of 1.25 was observed, while beyond 1.25, the H<sub>2</sub> yield drops off. Stoichiometrically water reacts with methanol to give the desired reforming reaction which was further enhanced by the water gas shift reaction till SMR of 1.25 but beyond 1.25, water gas shift reaction does not cause any further increase in  $H_2$  or  $CO_2$ . Figs. 5.36A, 5.36B and 5.36C show the effect of OMR on catalyst performance. Additionally, effect on gas phase molar concentration of water and  $CO_2$  is also shown in Fig. 5.36D. With an increase in OMR, although the conversions remained constant, the  $H_2$  production rate decreases with a corresponding increase in CO<sub>2</sub> and water indicating the oxidation reactions start dominating beyond OMR of 0.1. Increase in methane fractions indicate onset of methanation reaction with OMR > 0.2. Figs. 5.37A, 5.37B and 5.37C report effects of temperature variation on conversion, H<sub>2</sub> production rate and product yields, respectively. The selectivity changes from higher H<sub>2</sub>/CO ratio to increase in CO<sub>2</sub> and CH<sub>4</sub> formation as temperature was increased beyond 420 °C suggesting water gas shift reaction dominating the low temperature regime (250 to 420 °C) and methanol decomposition reaction favoured in the high temperature regime (> 420 °C) [172]. Fig. 5.38 depicts effect of GHSV on conversion, H<sub>2</sub> production rates and gas yields. For low GHSV's, the conversion remains constant but starts decreasing as GHSV increases beyond 6350 ml<sub>STP</sub>/(h.g<sub>cat</sub>). H<sub>2</sub> production rate increased with increase in GHSV but starts dropping beyond 6350 ml<sub>STP</sub>/(h.g<sub>cat</sub>). GHSV had little effect on conversion between 2000 to 6350 ml<sub>STP</sub>/(h.g<sub>cat</sub>) but had significant effect on hydrogen production rates since the hydrogen formation reaction (reforming) was not in equilibrium at lower GHSV values leading to an increase in H<sub>2</sub> production. Beyond 6350 ml<sub>STP</sub>/(h.g<sub>cat</sub>), the contact time of the reactants with the catalyst decreases thereby causing a drop in conversion and yields. The optimized conditions thus derived were SMR: 1.25, OMR: 0.1, Temperature: 420 °C and GHSV: 6350 mlsTP/(h.gcat) for which the catalyst performance was reported as conversion 94%, H<sub>2</sub> production rate 230 mmol H<sub>2</sub>/kg<sub>cat</sub>.s and H<sub>2</sub> yield 1.68 mol of  $H_2$ /mol of C.



**Figure 5.35**: Effect of SMR on A) Conversion B) H<sub>2</sub> Production rate C) Product Yield D) Mol fraction, gas phase, (T: 420 °C, OMR: 0.1, GHSV: 6350 ml<sub>STP</sub>/(h.gcat))



**Figure 5.36**: Effect of OMR on A) Conversion B) H<sub>2</sub> Production rate C) Product Yield D) Mol fraction, gas phase for methanol oxidative reforming (SMR: 1.25, T: 420 °C, GHSV: 6350  $ml_{STP}/(h.g_{cat})$ )



**Figure 5.37**: Effect of temperature on: A) Conversion B)  $H_2$  production rate C) Product Yield D) Mol fraction gas phase, for methanol oxidative reforming (SMR: 1.25, OMR: 0.1, GHSV: 6350  $ml_{STP}/(h.g_{cat})$ )


**Figure 5.38**: Effect of GHSV on: A) Conversion B) H<sub>2</sub> production rate C) Product Yield, D) Mol fraction gas phase, for methanol oxidative reforming (SMR: 1.25, OMR: 0.1 and T: 420 °C)

These optimized parameters were then used to study the stability of the catalyst for each fuel. Subsequent section details the experimental findings from the stability test for the catalyst (Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub>).

# 5.3. Stability Test

Fig. 5.39 shows that the conversion of gasoline remained constant (c.a. 98 %) for the duration of the entire test, with the H<sub>2</sub> production rate dropping from the initial rate of 380 mmol H<sub>2</sub>/kg<sub>cat</sub>.s to 263 mmol H<sub>2</sub>/kg<sub>cat</sub>.s after 10 h on stream, remaining steady thereafter. Although Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> displayed high H<sub>2</sub> production rates, <9 mol% methane composition was observed after 8 h, which explains the observed drop in H<sub>2</sub> yields (Fig. 5.40A).

Diesel conversion displayed a gradual drop (98% to 85%), with H<sub>2</sub> yield also decreasing from c.a. 350 mmol H<sub>2</sub>/kg<sub>cat</sub>.s to c.a. 310 mmol H<sub>2</sub>/kg<sub>cat</sub>.s after 8 h on stream and remaining constant at ~217 mmol H<sub>2</sub>/kg<sub>cat</sub>.s for the remaining test duration (Fig. 5.39). The initial drop in conversion could be due to irreversible coverage of catalyst sites by foulants. However, as catalyst samples could not be collected intermittently, there is no data to conclusively state the reason for the decrease in conversion. The catalyst, however, stabilized after the initial loss of activity. An increase in CO concentration was observed, which stabilized after 30 h of operation indicating a slight change in selectivity to reverse water gas shift reaction (Fig. 5.40B).

Methanol conversion was steady at 98% with H<sub>2</sub> production rate stabilizing after 8 h to remain at 243 mmol H<sub>2</sub>/kg<sub>cat</sub>.s for the duration of the test (Fig. 5.39). The morphology of the fresh and spent Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> catalyst (after 42 h time-on-stream) was analyzed using TEM (Fig. 5.41). Particle size distribution (PSD) for the fresh and spent catalysts showed a narrow size distribution between 2 and 9 nm with the maximum particles showing size ranging between 2 - 5 nm (Refer inset in Figs. 5.41a, 5.41b, 5.41c and 5.41d for fresh reduced and spent catalysts for diesel, gasoline and methanol, respectively). The volume weighted average particle diameter (d<sub>v</sub>) for the fresh catalyst was found to be 6.38  $\pm$  0.37 nm. Similar, d<sub>v</sub> was found for the spent catalysts (5.86  $\pm$  0.45 nm,  $5.75 \pm 0.36$  nm and  $6.18 \pm 0.66$  nm for spent catalysts used for diesel, gasoline and methanol runs, respectively). Lattice spacing at 0.204 nm, 0.206 nm, 0.208 nm and 0.207 nm were observed in the HRTEM images of the fresh and spent catalysts (refer Figs. 5.41e, 5.41f, 5.41g and 5.41h for fresh and spent catalysts for diesel, gasoline and methanol, respectively). These lattice spacings were close to the interplanar distance (0.206 nm) reported for Ni nanoparticles having [111] orientation [134]. Adjacent to the Ni lattice, Pt nanoparticles with lattice spacing at 0.222 nm, 0.227 nm, 0.221 nm and 0.222 nm were measured corresponding to fresh and spent catalysts for diesel, gasoline and methanol runs, respectively, which is consistent with lattice spacing corresponding to d<sub>111</sub> of Pt cubic phase [135,136]. Such interfaces forming adjacent to each other enhance catalytic properties due to H<sub>2</sub> spillover. The SAED pattern in Fig. 5.41i confirms the crystalline nature of Ni (111) and Pt (111) phases consistent with the HRTEM observations and XRD results. The spent catalysts showed similar interphases of Ni (111) and Pt (111) from the SAED patterns in Fig. 5.41j, 5.41k, 5.41l for diesel, gasoline and methanol, respectively, further supporting the evidence for catalyst stability.

The catalyst performance results were compared to the literature (Table 5.8), which clearly shows the state-of-art performance of Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub>. Apart from the current work, only  $Rh_1/Ce_{10}-Al_2O_3$  [53] reported in Table 5.8 was tested for reforming all the fuels.



**Figure 5.39**: Stability test for Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> for gasoline, diesel and methanol,  $\blacksquare$  – Conversion v/s time,  $\circ$  – H<sub>2</sub> production rate v/s time (gasoline- SCR 6, OCR 0.3, T 780 °C, GHSV 6100 (ml<sub>STP</sub>/h.g<sub>cat</sub>); diesel- SCR 4, OCR 0.2, T 780 °C, GHSV 6100 (ml<sub>STP</sub>/h.g<sub>cat</sub>); Methanol- SMR 1.25, OMR 0.1, T 420 °C, GHSV 6350 (ml<sub>STP</sub>/h.g<sub>cat</sub>))



**Figure 5.40**: Stability test for Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> for gasoline, diesel and methanol, mol fraction, gas phase v/s time for (A) Gasoline, (B) Diesel and (C) Methanol; Operating Conditions (diesel-SCR 4, OCR 0.2, T 780 °C, GHSV 6100 (ml<sub>STP</sub>/h.g<sub>cat</sub>); gasoline- SCR 6, OCR 0.3, T 780 °C, GHSV 6100 (ml<sub>STP</sub>/h.g<sub>cat</sub>); Methanol- SMR 1.25, OMR 0.1, T 420 °C, GHSV 6350 (ml<sub>STP</sub>/h.g<sub>cat</sub>))



**Figure 5.41**: Characterisation of Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> catalyst by TEM, with PSD as inset of a) fresh catalyst b) diesel-spent c) gasoline-spent d) methanol (spent); HRTEM for e) fresh catalyst f) diesel-spent, g) gasoline-spent and h) methanol-spent; and SAED pattern for (i) fresh catalyst, (j) Diesel-spent (k) gasoline-spent and (l) methanol-spent (PSD inset x-axis: Particle size (1-10 nm)

Catalyst	Conversion*	H2	H <sub>2</sub> yield,	Stability	Reference
		Production	mol H <sub>2</sub> /mol	test, h	
		rate, mmol	C*		
		H2/kgcat.S*			
Methanol					
Cu <sub>6</sub> -Zn <sub>9</sub> /Al <sub>2</sub> O <sub>3</sub>	87%	161	NA	24	[50]
$Cu_{32}$ - $Zn_{42}/Al_2O_3$	100%	NA	1.9	1	[49]
$Cu_{31}$ - $Zn_{50}$ - $Zr_{14}$ / $Al_2O_3$	60%	NA	NA	18	[51]
Ni <sub>6</sub> -Cu <sub>24</sub> /Al <sub>2</sub> O <sub>3</sub>	91%	NA	0.63	46	[52]
Rh <sub>1</sub> /Ce <sub>10</sub> -Al <sub>2</sub> O <sub>3</sub>	72%	90	1.3	1.7	[53]
Ni-Pt/K5-Al <sub>2</sub> O <sub>3</sub>	98%	250	1.68	42	This work
Gasoline					
Rh <sub>1</sub> /Ce <sub>10</sub> -Al <sub>2</sub> O <sub>3</sub>	99%	NA	1.62	1.7	[53]
Pt/CeO <sub>2</sub> -ZrO <sub>2</sub>	80% (iso-octane)	68	NA	15	[64]
La <sub>0.8</sub> Ce <sub>0.2</sub> NiO <sub>3</sub>	100% (n-octane)	NA	1.93	220	[68]
perovskite					
Rh/Gd-CeO <sub>2</sub>	100%	NA	NA	3	[173]
Ni-Pt/K5-Al <sub>2</sub> O <sub>3</sub>	98%	262	1.7	42	This work
Diesel					
Rh <sub>1</sub> /Ce <sub>10</sub> -Al <sub>2</sub> O <sub>3</sub>	96%	NA	1.5	1.7	[53]
Pt/Gd-CeO <sub>2</sub>	100% (dodecane)	NA	1.41	54	[174]
Rh/ZrO <sub>2</sub>	100%	NA	1.25	2	[175]
Rh-Pt/CeO <sub>2</sub> -ZrO <sub>2</sub>	97.6%	NA	NA	3	[60]
Mo <sub>2</sub> C	100%	14	NA	6	[56]
	(hexadecane)				
Ni-Pt/K5-Al <sub>2</sub> O <sub>3</sub>	85%	235	1.8	42	This work

**Table 5.8**: Comparison of other catalysts reported in literature with our work for oxidative reforming of methanol, gasoline and diesel

\* Values are reported at the end of the stability test; If model compounds for diesel and gasoline are used, they have been explicitly mentioned

This catalyst was then used for kinetics studies to simulate the reformer performance.

# 6.0. Modelling, Simulation and Techno-Economic Analysis of Reforming Process

In order to model a reforming process based on the novel catalyst formulated, a power-law based kinetic model is developed. The following sections detail the methodology followed in developing and validating the kinetic model using MATLAB and Aspen Plus, respectively. The process model helps to predict the overall hydrogen yield and fuel requirements based on the chosen capacity of the PEM-based fuel cell. Finally, results from a preliminary techno-economic analysis for the different scenarios evaluated are presented.

# 6.1. Modelling Studies (MATLAB)

# 6.1.1. Experimental Data

The experimental data was taken from our studies on Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> which was proven to be stable for all the three fuels, i.e methanol, diesel and gasoline. The major reaction products observed were  $H_2$ , CO, CO<sub>2</sub>, and CH<sub>4</sub> in addition to water, unreacted fuel and oxygen in the reformate gas. For the purpose of kinetic studies, a total of 17, 17 and 15 experiments were performed for methanol, diesel and gasoline, respectively. The parameters varied are listed in Table 6.1.

Parameter	Methanol	Diesel	Gasoline
SCR, (mol/mol)	1, 1,25, 1.4 and 1.7	1, 2, 3, 4 and 5	4, 5, 6 and 7
OCR, (mol/mol)	0.05, 0.1, 0.2 and 0.3	0.1, 0.2, 0.3 and 0.65	0.2, 0.3 and 0.4
Temperature, °C	230, 350, 420 and 550	650, 700, 780 and 820	700, 740, 780 and 820
GHSV, ml <sub>STP</sub> /(h.g <sub>cat</sub> )	1661, 2375, 6350, 10000 and 14750	5000, 6100, 10000 and 12600	4067, 6100, 8000 and 10000

Table 6.1: Kinetic model experimental	l parameters for the three fuels
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#### 6.1.2. Model Development

#### 6.1.2.1.Methanol

For the purposes of developing the kinetic model, steam reforming (Eq. 6.1), partial oxidation (Eq. 6.2), methanol decomposition (Eq. 6.3), water gas shift (Eq. 6.4) and methanation (Eq. 6.5) have been considered. Methanol decomposition has been considered since CO is present in the reformate gas and noble metal based catalysts have shown high selectivity for methanol decomposition [53]. Oxidation reactions are usually fast and are therefore considered irreversible in our analysis. All the other reactions are reversible in nature.

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \tag{6.1}$$

$$CH_3OH + \frac{1}{2}O_2 \rightarrow CO + H_2 + H_2O \tag{6.2}$$

$$CH_3OH \leftrightarrow CO + 2H_2 \tag{6.3}$$

$$\boldsymbol{CO} + \boldsymbol{H_2O} \leftrightarrow \boldsymbol{CO_2} + \boldsymbol{H_2} \tag{6.4}$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \tag{6.5}$$

#### 6.1.2.2.Diesel

Diesel reforming consists of thousands of gas phase and surface reactions comprising cracking, isomerization, dehydrogenation, hydrogenolysis and hydrocyclisation occurring simultaneously[108]. Since the aim is to predict the reformate gas composition, only the major reactions such as steam reforming (Eq. 6.6), total oxidation (Eq. 6.7), water gas shift (Eq. 6.4) and methanation (Eq. 6.5) were considered[176]. Methanation reaction was considered since a small amount of methane was detected in the reformate gas during experimental studies. To model diesel, a surrogate compound (n-hexadecane) was chosen and the model equations were based on the stoichiometry of n-hexadecane. The basis for choosing n-hexadecane is documented in Appendix C.

$$C_{16}H_{34} + 16H_2O \leftrightarrow 16CO + 33H_2$$
 6.6

$$C_{16}H_{34} + \frac{49}{2}O_2 \rightarrow 16CO_2 + 17H_2O$$
 6.7

#### 6.1.2.3.Gasoline

Gasoline reforming also consists of numerous reactions including cracking, isomerization, dehydrogenation and ring-breaking reactions that occur simultaneously. However, only the major reactions such as steam reforming (Eq. 6.8), total oxidation (Eq. 6.9), water gas shift (Eq. 6.4) and methanation (Eq. 6.5) were considered as they suffice to predict the product gas composition[176]. Based on the GCMS analysis (Appendix A) of commercial gasoline used in our experiments, a molecular weight distribution analysis (Appendix C) revealed an average molecular weight of 95.6 with the major compound identified as toluene ( $C_7H_8$ ). Hence, toluene with a molecular weight of 92 was chosen as the surrogate compound for modelling gasoline.

$$C_7H_8 + 7H_2O \leftrightarrow 7CO + 11H_2 \tag{6.8}$$

$$\boldsymbol{C_7H_8} + \boldsymbol{90_2} \to \boldsymbol{7C0_2} + \boldsymbol{4H_2O} \tag{6.9}$$

The forward and backward reactions are modelled separately in each case and are coupled using the equilibrium constant of the reversible reaction. Therefore, a total of 9 reactions for methanol, 7 reactions for diesel and 7 reactions for gasoline were considered.

#### 6.1.3. Kinetic Model

Power law models were considered to capture the reaction scheme. Accordingly, the forward rate constants were defined as per Eq.6.10.

$$k_{SR} = A_{SR} * exp^{\left(\frac{-E_{SR}}{R*T}\right)} \tag{6.10}$$

where  $A_{SR}$  is the pre-exponential factor (mol.g<sub>cat</sub><sup>-1</sup>.s<sup>-1</sup>),  $E_{SR}$  is the activation energy (kJ.mol<sup>-1</sup>), R is the gas constant (kJ.mol<sup>-1</sup>.K<sup>-1</sup>) and T is the temperature in K. Subscript *SR* refers to the steam reforming reaction. Similarly, other subscripts were defined as O for oxidation, *WGS* for water gas shift reaction, *METH* for methanation and *MD* for methanol decomposition reaction.

The reverse rate constants were expressed as per Eq. 6.11.

$$k_{SRr} = \frac{k_{SR}}{K_{SR(eq)}} \tag{6.11}$$

where  $K_{SR(eq)}$  corresponds to the equilibrium constant for the steam reforming reaction and subscript *SRr* refers to the backward steam reforming reaction. Accordingly, subscripts for the other backward reactions were defined as *WGSr*, *METHr* and *MDr* for water gas shift, methanation and methanol decomposition, respectively. This approach helps in reducing the number of constants to be determined since the backward rate constant is expressed in terms of the forward rate constant and also helps in maintaining the thermodynamic consistency. The values of the reaction equilibrium constants at different temperatures were obtained from Aspen Plus by simulating an equilibrium-based reactor model (REquil) for each of the reactions and are tabulated in Table 6.2.

Reaction				
Temperature,	Steam	Water-gas shift	Methanation	Methanol
°K	reforming			Decomposition
Methanol				
503	2.47 x 10 <sup>4</sup>	130.58	8.07 x 10 <sup>9</sup>	189.69
593	2.14 x 10 <sup>5</sup>	31.34	3.22 x 10 <sup>6</sup>	6849.41
623	3.91 x 10 <sup>5</sup>	21.47	3.84 x 10 <sup>5</sup>	1.82 x 10 <sup>4</sup>
693	1.34 x 10 <sup>6</sup>	10.18	5.37 x 10 <sup>3</sup>	1.31 x 10 <sup>5</sup>
823	8.07 x 10 <sup>6</sup>	3.67	12.46	2.21 x 10 <sup>6</sup>
Diesel				
923	1.19 x 10 <sup>60</sup>	2.07	0.36	-
973	5.25 x 10 <sup>67</sup>	1.63	0.08	-
1053	2.82 x 10 <sup>78</sup>	1.18	9.01 x 10 <sup>-3</sup>	-
1093	1.69 x 10 <sup>83</sup>	1.02	3.79 x 10 <sup>-3</sup>	-
Gasoline				
973	1.14 x 10 <sup>18</sup>	1.63	0.08	-
1013	$1.05 \ge 10^{20}$	1.38	0.03	-
1053	6.84 x 10 <sup>21</sup>	1.18	9.01 x 10 <sup>-3</sup>	-
1093	3.29 x 10 <sup>23</sup>	1.02	3.79 x 10 <sup>-3</sup>	-

 Table 6.2: Equilibrium Constants for various reactions at different temperatures

The reaction rates considered in the kinetic model have been defined as per Eqs.6.12-6.26.

$$R_{SRM} = k_{SRM} \times \left(\frac{C_{To} \times F_M}{F_T}\right) \times \left(\frac{C_{To} \times F_W}{F_T}\right)$$

$$6.12$$

$$R_{SRMr} = k_{SRMr} \times \left(\frac{C_{To} \times F_{CO2}}{F_T}\right) \times \left(\frac{C_{To} \times F_{H2}}{F_T}\right)$$

$$6.13$$

$$R_{OM} = k_{OM} \times \left(\frac{C_{To} \times F_M}{F_T}\right) \times \left(\frac{C_{To} \times F_{O2}}{F_T}\right)$$

$$6.14$$

$$R_{MD} = k_{MD} \times \left(\frac{C_{To} \times F_M}{F_T}\right)$$

$$6.15$$

$$R_{MDr} = k_{MDr} \times \left(\frac{C_{To} \times F_{CO}}{F_T}\right) \times \left(\frac{C_{To} \times F_{H2}}{F_T}\right)$$

$$6.16$$

$$R_{WGS} = k_{WGS} \times \left(\frac{C_{To} \times F_{CO}}{F_T}\right) \times \left(\frac{C_{To} \times F_W}{F_T}\right)$$

$$6.17$$

$$R_{WGSr} = k_{WGSr} \times \left(\frac{C_{To} \times F_{CO2}}{F_T}\right) \times \left(\frac{C_{To} \times F_{H2}}{F_T}\right)$$

$$6.18$$

$$R_{METH} = k_{METH} \times \left(\frac{C_{To} \times F_{CO}}{F_T}\right) \times \left(\frac{C_{To} \times F_{H2}}{F_T}\right)$$

$$6.19$$

$$R_{METHr} = k_{METHr} \times \left(\frac{C_{To} \times F_{CH4}}{F_T}\right) \times \left(\frac{C_{To} \times F_W}{F_T}\right)$$

$$6.20$$

$$R_{SRD} = k_{SRD} \times \left(\frac{C_{To} \times F_{HD}}{F_T}\right) \times \left(\frac{C_{To} \times F_W}{F_T}\right)$$

$$6.21$$

$$R_{SRDr} = k_{SRDr} \times \left(\frac{C_{To} \times F_{CO}}{F_T}\right) \times \left(\frac{C_{To} \times F_{H2}}{F_T}\right)$$

$$6.22$$

$$R_{OD} = k_{OD} \times \left(\frac{C_{TO} \times F_{HD}}{F_T}\right) \times \left(\frac{C_{TO} \times F_{O2}}{F_T}\right)$$

$$6.23$$

$$R_{SRG} = k_{SRG} \times \left(\frac{C_{To} \times F_{TG}}{F_T}\right) \times \left(\frac{C_{To} \times F_W}{F_T}\right)$$

$$6.24$$

$$R_{SRGr} = k_{SRGr} \times \left(\frac{C_{To} \times F_{CO}}{F_T}\right) \times \left(\frac{C_{To} \times F_{H2}}{F_T}\right)$$

$$6.25$$

$$R_{OG} = k_{OG} \times \left(\frac{C_{To} \times F_{TG}}{F_T}\right) \times \left(\frac{C_{To} \times F_{O2}}{F_T}\right)$$

$$6.26$$

where R<sub>SRM</sub>, R<sub>OM</sub>, R<sub>MD</sub>, R<sub>WGS</sub>, R<sub>METH</sub>, R<sub>SRD</sub>, R<sub>OD</sub>, R<sub>SRG</sub> and R<sub>OG</sub> denote the forward reaction rates; the subscripts M, D and G represent methanol, diesel, and gasoline, respectively. The order with

respect to each reactant in the reaction set has been assumed as 1 and was kept out of the regression function. The reaction rates have units of mol/( $g_{cat.s}$ ). F<sub>M</sub>, F<sub>w</sub>, Fo<sub>2</sub>, F<sub>H2</sub>, F<sub>CO2</sub>, F<sub>CO</sub>, F<sub>CH4</sub>, F<sub>HD</sub> and F<sub>To</sub> represent the molar flow rates at steady state for each experiment for methanol, water, oxygen, hydrogen, CO<sub>2</sub>, CO, methane, hexadecane and toluene, respectively. C<sub>TO</sub> represents the initial total concentration of the reactants in mol/m<sup>3</sup> while F<sub>T</sub> represents the total molar flow rate (mol/s) at steady state, e.g. refer Eq.6.27 for methanol experiments.

$$F_T = F_M + F_W + F_{O2} + F_{C0} + F_{H2} + F_{CO2} + F_{CH4}$$

$$6.27$$

Similarly,  $F_T$  is defined for diesel and gasoline experiments by taking the sum of the individual component molar flow rates at steady state for each experiment.

To fit the experimental dataset, only the pre-exponential factor and activation energy corresponding to the rate constants of the forward reactions (defined by Eq.6.12-6.26) were regressed. Thus, a total of 10, 8 and 8 parameters were regressed for methanol, diesel and gasoline, respectively.

Assuming isothermal operation, the following set of differential equations is solved using ODE15s in MATLAB (Eq. 6.28).

$$\frac{dF_i}{dW} = \sum_{j=1}^{j=M} v_{i,j} R_j \qquad for \ i = 1, \dots, n$$
6.28

where F refers to the molar flow rate at reformer outlet (mol/s) of species i, W is the catalyst weight (g),  $v_{i,j}$  is the stoichiometric coefficient, j is the reaction number (e.g.  $R_{SRM}$ ) and n refers to the number of components.

The calculated outlet flow rate for all the components was fitted to the experimental flow rates using "*LSQNONLIN*" function in MATLAB. For predicted outlet molar flow rates of  $H_2$ , CO, CO<sub>2</sub>,  $H_2O$ ,  $O_2$  and fuel (methanol/diesel/gasoline), mean square regression test was applied to check whether the model picked up significant trend (Eq. 6.29).

$$Test Ratio = \frac{MSR}{MSE}$$

$$6.29$$

where MSR is the Mean Square Regression error and MSE is the Mean Square Error. The ratio was then compared with the value given from F-test ( $F_{(p-1),(n-p),0.05}$ ). The model was considered to

pick up significant trend when the test ratio given by Eq. 6.29 exceeded the value given by the F-test [108]. The analysis was done in MS Excel using ANOVA tool.

# 6.2. Simulation studies (Aspen Plus)

The kinetic model developed was used to simulate the reformer in Aspen Plus using the "RPlug" module. The reactions defined by Eqs. 6.1-6.5 for methanol, Eqs. 6.4-6.7 for diesel and Eqs. 6.4, 6.5, 6.8 and 6.9 for gasoline were used with the power-law kinetics developed in section 6.2. The operating parameters and catalyst loading chosen for the reformer simulation were based on our experimental studies. To increase the H<sub>2</sub> yield, two water gas shift (WGS) reactors were used in the process after the reformer – a high temperature (HTWGS) reactor operating at 300 °C followed by a low temperature (LTWGS) reactor operating at 150 °C (both modelled using "REquil" module in adiabatic mode since they are known to operate close to equilibrium) [177–179]. The high temperature shift followed by the low temperature shift is a common way to reduce CO concentrations to levels acceptable for further processing after the shift reactors [180]. The excess steam added to the reformer takes care of the water requirement in both the adiabatic WGS reactors. The shift reactors also help in decreasing the CO concentration by converting it into CO<sub>2</sub>. Since CO is a known poison for the fuel cell anode, its concentration needs to be reduced to 10 ppm in the outlet H<sub>2</sub> stream [95]. Hence, a preferential oxidation reactor (PROX) operating adiabatically (modelled as "RPlug") was added after the LTWGS reactor to include the CO and H<sub>2</sub> oxidation reactions (Eqs. 6.30 and 6.31) [97]. An air stream (stoichiometric) was added to take care of the combustion.

$$\boldsymbol{CO} + \frac{1}{2}\boldsymbol{O}_2 \rightarrow \boldsymbol{CO}_2 \tag{6.30}$$

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \tag{6.31}$$

Some penalty on hydrogen was incurred due to  $H_2$  oxidation taking place in PROX (Eq. 6.31). Further purification of  $H_2$  was achieved through a PSA (pressure swing adsorption) system which produces  $H_2$  stream at 99.995% purity. The PSA system was modelled as a splitter operating at 20 barg with the specifications of 99.995%  $H_2$  purity and 80% recovery from the incoming feed (based on details shared by a PSA system vendor). The purified  $H_2$  stream was then compressed to 139 barg and stored in a  $H_2$  bottle. The heat requirements of the system were taken care of by the exothermic heat of reaction from the HTWGS, LTWGS and PROX reactors. Surplus heat was generated using the off gas (unrecovered hydrogen from PSA) in a combustor which was then used to fulfil the heat requirements of the system (namely, the vaporizer and the reformer). The combustor was modelled through the "RStoic" module. A sequential modular approach with PSRK as the equation of state was used to solve the mass and energy balances. After validating the simulation results of the flowsheet with the experimental observations, the flowsheet was used to simulate a scaled-up process for the desired H<sub>2</sub> generation capacity. The scale-up parameters considered are tabulated in Table 6.3 (derived from our experimental studies) and were kept constant during scaling up. H<sub>2</sub> output at the battery limit was fixed to delivering H<sub>2</sub> equivalent to producing 10 kWe in a PEM fuel cell operating at 47% efficiency [181]. The H<sub>2</sub> storage conditions were derived from the specification sheet of the standard H<sub>2</sub> bottles sold by M/S Praxair. The input parameters were derived for each fuel based on the values reported in Table 6.3.

Table 6.3: Scale up paramet	ers for the reformer sy	stem generating H <sub>2</sub> equ	vivalent to fuelling a 10
kWe fuel cell			

Parameters	Methanol	Diesel	Gasoline
$H_2$ purity at the battery limit	99.995% pure (molar)	99.995% pure (molar)	99.995% pure (molar)
H <sub>2</sub> storage condition	Temperature: 50 °C	Temperature: 50 °C	Temperature: 50 °C
	Pressure: 139 bar	Pressure: 139 bar	Pressure: 139 bar
$H_2$ output at the battery limit	0.6 kg/h (Actual can vary)	0.6 kg/h (Actual can vary)	0.6 kg/h (Actual can vary)
Steam to Carbon ratio (mol/mol)	1.25	4	6
Oxygen to Carbon ratio (mol/mol)	0.1	0.2	0.3
Temperature, °C	420	780	780
GHSV, (ml <sub>STP</sub> /h.g <sub>cat</sub> )	6350	6100	6100

Once the process simulation was completed for each fuel for the defined capacity, a costing analysis was performed. The methodology followed in developing the cash flows is detailed in the next section.

# 6.3. Costing Analysis

For predicting the process economics, a MS Excel spreadsheet was used. The capex (capital expenditure) was estimated based on the quotes obtained from vendors for the equipment sizes derived from the process simulation. To obtain the quotes for the fixed bed reactors, the catalyst bed volumes were estimated. In the case of reformer and PROX, the catalyst bed volume was obtained directly from the process simulation. In the case of HTWGS and LTWGS, the catalyst bed volume was estimated based on the procedure mentioned using recommended space velocities for an Fe-Cr catalyst in HTWGS and Cu-Zn catalyst in LTWGS [178,180]. Similarly, the heat exchanger areas were obtained from the process simulation based on which the vendor quotes were obtained. The compressor type quoted was a multi-stage reciprocating compressor while the PSA system was a 9-bed adsorption unit. Chemical Engineering Plant Cost Index (CEPCI) was used to account for the effects of inflation as reported in Eq. 6.32 [182]

$$C_{BM2} = C_{BM1} * \binom{I_2}{I_1}$$
6.32

where  $C_{BM}$  refers to bare module cost and I refer to the index derived from CEPCI. Subscript 2 refers to current year while subscript 1 refers to the year in which the quote was obtained. Since, the plant location will be India based, 18% Goods and Service Tax (GST) on the base modules were considered. The operating costs were summed up by deriving the costs of raw materials, catalyst, utilities and manpower while depreciation (book and tax), interest costs on loan (debt: equity ratio of 80:20) and income taxes were added to the cash flow to arrive at the consolidated net revenue. The revenue was based on two models i.e. sale of H<sub>2</sub> only (Model 1) and sale of two products in Model 2 (power produced through fuel cells and excess H<sub>2</sub> which could not be consumed). The cash flows were then accrued for 20 years to arrive at an economic internal rate of return (EIRR). The calculations were continued in Excel spreadsheet by varying the sale prices of H<sub>2</sub> in Model 1 and electricity price in Model 2 with a fixed sale price of H<sub>2</sub> at \$2.5/kg till the solver returned a net present value of 0 for an EIRR of 16%. An EIRR of 16% is considered as a

standard yardstick for measuring economic performance of an investment industrially. The next section discusses the results obtained.

# 6.4. Modelling, Simulation and Costing Results

### 6.4.1. Kinetic Parameters

This section discusses the regression results for each fuel starting with methanol followed by diesel and gasoline.

#### 6.4.1.1.Methanol

The regression estimation procedure resulted in estimation of 10 parameters (five pre-exponential factors and 5 activation energies). The calculated ratio, MSR/MSE, was much greater than  $F_{(p-1),(n-1)}$ p),0.05. The ratio was calculated to be 29916055 which was much higher than the F value from the F table (3.84 for 95% significance interval) with the MSR value as 4236 (degrees of freedom as 1) and the MSE value as 0.0001 (degrees of freedom as 116). Hence, the null hypothesis that MSR and MSE were equal was rejected and it implies that the model could pick up significant trend. Fig. 6.1 compares the experimental values with the predicted conversions and Hydrogen production rates from the model for different SMR, OMR, temperature and GHSV. The model could predict the maxima observed with respect to experimental data at SMR of 1.25 (Fig. 6.1a) and OMR value of 0.1 (Fig. 6.1b) with some deviation observed with conversion values at OCR value of 0.05. However, the anomaly observed was within the tolerance limits and is attributed to experimental error. The conversion (Fig. 6.1c) was predicted correctly by the model with slight deviation at a temperature of 550 °C. The model predicts the trends with GHSV variations accurately (Fig. 6.1d). Similarly, the trends were captured accurately for H<sub>2</sub> production rates with respect to all the variables - SMR, OMR, temperature, and GHSV (see Figs. 6.1a to 6.1d) and were within 10% tolerance limits with respect to the experimental data. The parity plots for the global rates of reaction of methanol and hydrogen formation are depicted in Figs. 6.1e and 6.1f, respectively, which also show a good agreement. The parity plots with respect to the other species can be seen in Figs. 6.2a, 6.2b, 6.2c, 6.2d and 6.2e for water, oxygen, CO, CO<sub>2</sub> and CH<sub>4</sub>, respectively). It can be seen from the parity plots that the model predictions are within  $\pm 10\%$  of the experimental values.



**Figure 6.1**: Comparison of Experimental and model predicted values for conversion and H<sub>2</sub> production rates of methanol for various parameters, a) SMR b) OMR c) Temperature and d) GHSV; ■ – experimental conversion, ▲ -experimental H<sub>2</sub> production rates, — (predicted); Parity plots for global rates of reaction for e) Methanol f) hydrogen (*Note: SMR and OMR stand for steam to methanol ratio and oxygen to methanol ratio, respectively. Since methanol has 1 carbon atom hence, SCR and OCR is similar to SMR and OMR*)



**Figure 6.2**: Parity plots for global rates of various species for methanol oxidative steam reforming system, a) Water b) Oxygen c) CO d) CO<sub>2</sub>, e1) Methane and e2) Methane with parity values at lower values

The regressed parameters are compared with values reported in the literature in Table 6.4. The estimated activation energy from our work agrees well with literature values for steam reforming (74 to 115 kJ/mol). The activation energy for water gas shift reaction also is close to the values in literature. However, there is a mismatch observed in the case of methanol decomposition [183]. This is attributed to the differences in the catalyst combination (Cu-Zn) which is not selective for methanol decomposition compared to Ni-Pt which is selective for methanol decomposition [53,183].

Reaction Scheme	Model Type	Activation energy (kJ/mol)	Reference
Steam reforming	Power law	105	[105]
Steam reforming	Power law	74	[184]
Steam reforming	Power law	103	[185]
	LHHW	111	
Steam reforming	LHHW	108	[186]
Oxidative reforming	Power law	115	[47]
Steam reforming	LHHW	SR: 103	[183]
		WGS: 88	
		MD: 170	
Oxidative reforming	Power law	SR: 115	Our work
		WGS: 110	
		MD: 23	

|--|

#### 6.4.1.2.Diesel

In the case of diesel, 8 parameters (4 pre-exponential factors and 4 activation energies) were estimated with a good fit, and the MSR/MSE was much greater than  $F_{(p-1),(n-p),0.05}$ . The ratio was calculated to be 172793 which was much higher than the F value from the F table (3.84 for 95% significance interval) with the MSR value as  $7.33*10^{-7}$  (degrees of freedom as 1) and the MSE value as  $4.25*10^{-12}$  (degrees of freedom as 117). Hence, it can be concluded that the model was able to pick up significant trend. The comparison of experimental data with the predicted rates were reported in Figs. 6.3 and 6.4.

The conversions and  $H_2$  production rates for diesel were plotted as a function of SCR, OCR, temperature and GHSV in Fig. 6.3 to check the accuracy of the model with respect to variation in the operating parameters. The plots show a good accuracy in all the cases. Further, the parity plots shown in Fig. 6.4. show that the model captures the trends quite well within a tolerance of 10%. The regressed kinetic parameters were compared with the literature values and are reported in Table 6.5.

The estimated values of the activation energy from our work for the steam reforming, WGS and total oxidation reactions agreed with the reported literature values. However, there was a mismatch in the predicted value for the methanation reaction with the reported values, which is attributed to the different catalyst combination used in our work. Low methane concentrations at the reformer exit were observed experimentally indicating low selectivity of the developed catalyst towards methane formation.



Figure 6.3: Comparison of Experimental and model predicted values for conversion and H<sub>2</sub> production rates of diesel for various parameters, a) SCR b) OCR c) Temperature and d) GHSV;
– experimental conversion, ▲ -experimental H<sub>2</sub> production rates, — (predicted); Parity plots for e) global rate of reaction of diesel f) global rate of hydrogen formation



**Figure 6.4**: Parity plots for global rates of various species for diesel oxidative steam reforming system, a) Water b) Oxygen c) CO d) CO<sub>2</sub>, e) Methane

Reaction Scheme	Model Type	Activation energy (kJ/mol)	Reference
Auto-thermal reforming (tetradecane	Power law	SR: 117	[63]
used as surrogate for diesel)		WGS: 54	
		TO: 108	
		METH: 122	
Auto-thermal reforming (tetradecane	LHHW	SR: 103	[108]
used as surrogate for diesel)		TO: 47	
		WGS: 141	
Steam reforming of diesel	Power law for TO	TO: 44	[107]
(hexadecane used as surrogate for diesel)	Reduced Eley-Rideal Model for SR	SR: 99	
Auto-thermal reforming (hexadecane	LHHW	TO: 86	[187]
used as surrogate for diesel)		SR: 240	
		WGS: 55	
Oxidative reforming	Power law	SR: 147	Our work
		WGS: 135	
		METH: 185	
		TO: 110	

# Table 6.5: Comparison of the regressed parameters with literature values for diesel

# 6.4.1.3.Gasoline

Similar to diesel, the regression was used to estimate 8 kinetic parameters, and the calculated ratio, MSR/MSE, was much greater than  $F_{(p-1),(n-p),0.05}$ . The ratio was calculated to be 557 which was much higher than the F value from the F table (3.84 for 95% significance interval) with the MSR value as  $1.37*10^{-8}$  (degrees of freedom as 1) and the MSE value as  $2.47*10^{-11}$  (degrees of freedom

as 111). Hence, the null hypothesis that MSR and MSE were equal was rejected and the model could pick up significant trend. Figs. 6.5 and 6.6 compare the experimental data with the predicted rates at the reactor exit. The predicted conversions and H<sub>2</sub> production rates were plotted as a function of SCR, OCR, temperature and GHSV in Fig. 6.5, and showed good agreement with the experimental values. In all the parity plots in Figs. 6.5e, 6.5f and 6.6, the experimental and predicted rates are within a tolerance of  $\pm 10\%$ . The regressed parameters obtained were compared with the values from literature in Table 6.6. The estimated activation energy for steam reforming, WGS and methanation reactions were in the range of the reported literature values. Slight anomaly was observed in the predicted activation energy for oxidation reaction which could be due to the different surrogate compounds used to mimic gasoline.



**Figure 6.5**: Comparison of Experimental and model predicted values for conversion and  $H_2$  production rates of gasoline for various parameters, a) SCR b) OCR c) Temperature and d) GHSV;  $\blacksquare$  – experimental conversion,  $\blacktriangle$  -experimental  $H_2$  production rates, — (predicted); Parity plots for e) gasoline f) hydrogen



**Figure 6.6**: Parity plots for various species for gasoline oxidative steam reforming system, a) Water b) Oxygen c) CO d) CO<sub>2</sub>, e) Methane

Reaction Scheme	Model Type	Activation	Reference
		energy (kJ/mol)	
Steam reforming (iso-octane used as surrogate for gasoline)	Power law	SR: 44	[111]
Steam reforming (iso-octane used as surrogate	LHHW	SR: 240	[112]
for gasoline)		TO: 166	
		WGS: 67	
Partial oxidation (iso-octane used as surrogate	LHHW model	PO: 19	[114]
for gasoline)	Power law model	PO: 19	
Partial oxidation (iso-octane used as surrogate for gasoline)	Power law	PO: 50	[113]
Oxidative reforming (toluene used as surrogate	Power law	SR: 135	Our work
for gasoline)		WGS: 130	
		METH: 220	
		TO: 80	

#### Table 6.6: Comparison of the regressed parameters with literature values for gasoline

The pre-exponential factors obtained from regression are reported separately in Table A3 in Appendix C. The kinetic parameters obtained from the regression in MATLAB were used in modelling the reformer in Aspen Plus. The reformer outlet compositions obtained from the process simulations were compared with the experimental mole fractions. The following section elaborates the process simulation studies for each fuel.

### 6.4.2. Process Simulation Results

A common flowsheet for each fuel was developed for the process simulations (Fig. 6.7). The flowsheet for each fuel consists of two liquid streams (fuel and water as per the SCR ratio defined in Table 6.3) which are vaporized, and sent to a reformer. The reformer is modelled as a plug-flow

reactor using the "RPlug" module and the kinetic model developed in the previous section. An air stream containing pre-defined oxygen concentration (based on OCR from Table 6.3) was added to the reformer. The reformer was operated at a specified temperature for each fuel (Table 6.3). The reformate gas from the reformer outlet was cooled to 110 °C to recover heat without water condensation. This is followed by a multi-stage compressor to compress the reformate gas from atmospheric pressure to 20 barg. The compressor was a 3-stage compressor with inter-cooling and without an after-cooler. The reformate gas temperature rises adiabatically to 300 °C at the compressor outlet. The compressed reformate gas was then fed to a HTWGS followed by a LTWGS (both modelled using the "REquil" module as equilibrium reactors) in adiabatic mode. In between the two shift reactors, a cooler reduces the temperature of the reformate gas to 150 °C. The reformate gas is cooled to 120 °C after leaving the LTWGS. It then enters the PROX where CO levels were reduced to ppm levels (Eq. 6.30 and 6.31). A small hydrogen penalty was incurred which was consistent with the trends indicated in literature for catalytic PROX [97]. The PROX reactor was modelled as a plug-flow reactor using the "RPlug" module and the kinetic rate expressions obtained from literature for the two oxidation reactions (Eqs. 6.30 and 6.31) [188]. The air flow rate was fed to maintain an O<sub>2</sub>/CO ratio of 1.2 with the catalyst loading varied till the desired CO levels at the exit of the PROX reactor were achieved [188]. The process gas from the outlet of the PROX was then fed to a PSA system where 80% of the hydrogen was recovered at 99.995 mol% purity – this is based on specifications provided by a vendor. The PSA was modelled as a splitter for the sake of simplicity. However, it may be noted that it is a 9-bed system in industrial application. Each bed has different adsorbents, e.g. alumina for water removal, activated carbon for CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub> removal, and zeolite for CO removal [189]. A multi-stage compressor pressurizes the recovered H<sub>2</sub> to the desired storage pressure of 139 barg). The off-gas from the PSA was fired in a combustor to generate the heat needed to maintain the reformer temperature. A utility stream (water) was passed through each cooler to do pre-heating. The pre-heated water is converted into steam by recovering the reaction exotherm from the PROX. The steam so generated meets the vaporizer heat load. In the case of gasoline, a small percentage of the fuel in addition to the PSA off gas was combusted to account for the reformer heat loads. The mole fractions (N2 free basis) at the outlet of the reformer, shift reactors and PROX are reported in Figs. 6.8a, 6.8b and 6.8c for methanol, diesel and gasoline, respectively. The comparison of the reformate composition

with the experimental values was reported in Fig. 6.9a for methanol, Fig. 6.9b for diesel and Fig. 6.9c for gasoline.

The H<sub>2</sub> yields increase downstream (Fig. 6.8a) of the reformer in the shift reactors followed by a slight decrease in the PROX reactor owing to the H<sub>2</sub> oxidation reaction (Eq. 6.31). Similar trends were observed for diesel and gasoline (Figs. 6.8b and 6.8c). Water present in the off-gas from the PSA was separated and recycled in the case of methanol. Hence, the overall steam to carbon ratio at the reformer inlet increased from 1.25 to 1.6 - this excess steam is favourable for the shift reaction and increased the yields of H<sub>2</sub>. In case of diesel and gasoline, excess steam was fed to the shift reactors which increased the steam to carbon ratio to 8 (from 4 and 6 in the case of diesel and gasoline, respectively). The predicted mole fractions for each fuel (Fig. 6.9) were in good agreement with the experimental mole fractions at the reformer outlet. The methane mole fractions were not plotted as the values were negligible, both experimentally as well as from predictions. Similarly, the conversions predicted from the process simulation were in good agreement with the experimental values (Fig. 6.9). A summary of the process simulation results is given in Table 6.7. To meet the delivered hydrogen requirement, additional fuel needs to be reformed leading to an increase in the CO<sub>2</sub> emissions (Table 6.7). The least CO<sub>2</sub> emissions and highest thermal efficiencies were obtained for methanol. The H<sub>2</sub> yields were highest for diesel followed by gasoline and methanol while the CO<sub>2</sub> emissions were slightly lower for diesel compared to gasoline. The difference is due to the small percentage of fuel used for combustion purposes in case of gasoline.



Figure 6.7: Process flow diagram of the simulated Flowsheet in Aspen Plus



**Figure 6.8**: Predictions of gas composition ( $N_2$  free basis) downstream of reformer from the process simulation for a) Methanol b) Diesel c) Gasoline



**Figure 6.9**: Experimental *vs*. Aspen Plus predictions of reformate gas composition (N<sub>2</sub> free basis) at exit of reformer and conversion for a) Methanol b) Diesel c) Gasoline; Experimental conditions for a) Methanol – SCR: 1.25, OCR: 0.1, Temperature: 420 °C and GHSV: 6350 (ml<sub>STP</sub>/h.g<sub>cat</sub>) b) Diesel – SCR: 4, OCR: 0.2, Temperature: 780 °C and GHSV: 6100 (ml<sub>STP</sub>/h.g<sub>cat</sub>) and c) Gasoline - SCR: 6, OCR: 0.3, Temperature: 780 °C and GHSV: 6100 (ml<sub>STP</sub>/h.g<sub>cat</sub>)

Parameter	Methanol	Diesel (n-	Gasoline (Toluene)
		hexadecane)	
Actual H <sub>2</sub> output, kg/h	0.72	0.72	0.74
Specific $H_2$ output, g of $H_2/g$ of fuel	0.14	0.24	0.24
H <sub>2</sub> yield, mol of H <sub>2</sub> /mol of fuel	2.15	26.72	10.97
CO <sub>2</sub> yield, mol of CO <sub>2</sub> /mol of fuel	1	14.53	6.45
CO <sub>2</sub> emission, kg CO <sub>2</sub> /kg H <sub>2</sub>	10.23	11.96	12.93
Thermal efficiency, (based on NCV) <sup>1</sup>	80.5%	61.2%	66.4%
Catalyst requirement, kg	0.28	0.31	0.25

**Table 6.7**: Performance Summary of the process simulation models for methanol, diesel and gasoline

1. Thermal efficiency =  $\left(\frac{m_{H2}*NCV_{H2}}{m_{fuel}*NCV_{fuel}}\right)$  where m<sub>H2</sub> and m<sub>fuel</sub> refer to the mass flow rates of hydrogen and input fuel, respectively and NCV refers to the net calorific value.

Based on the process simulation results, an economic analysis considering various scenarios for each fuel was performed and is discussed in the next section.

### 6.4.3. Costing Analysis Results

For the analysis, two models were considered – Model 1 considers a stand-alone reformer producing only hydrogen for sale while Model 2 considers sale of power from a fuel cell using hydrogen and sale of excess hydrogen not consumed in the fuel cell. In both the cases, the reformer output was fixed at producing hydrogen equivalent to powering a 10 kWe PEM fuel cell. For model 2, it was assumed that the reformer was located next to the fuel cell location and would produce hydrogen and be stored in H<sub>2</sub> bottles. As and when the demand for back-up power arises in telecom towers, the fuel cell would draw hydrogen from the H<sub>2</sub> bottles. Each fuel cell was assumed to be located onsite as an alternative to a diesel genset used to provide back-up power.

The reformer was assumed to be operating for 7680 h annually (320 days in operation and 24 h/day). The fuel cell was assumed to be operating for 12 h/day for a total of 4380 h annually. This assumption creates surplus hydrogen in Model 2, which helps in selling hydrogen apart from its use for power production in fuel cells. All cost numbers were reported in USD with the conversion rate assumed as 1 USD = 73.62 INR (last accessed on 17/9/2020). Table 6.8 lists the various equipments, their suppliers and the cost quoted for the various equipments in the reformer system. Operating costs estimated include cost of fuel, electricity, catalyst, water, manpower; annual plant maintenance was assumed to be 4% of the base module capex [178]. Table 6.9 lists the various operating cost components. The capex for the fuel cell was assumed to be \$5700/kW (bare equipment cost) and the installed cost (inclusive of piping and installation (5% of bare module cost), contingency (10% of total capex) and local taxes (18% of total capex) is \$7660/kW [5]. Based on the values mentioned in Tables 6.8 and 6.9, a cash flow analysis for a period of 20 years

was conducted for the two models under consideration. The cash flow analysis was done for a single location only initially with the reformer and fuel cell capacities as mentioned in above section. Table 6.10 lists the results of the cash flow analysis for the three fuels. The sale prices for the pilot plants in both models were extremely high which was expected for a single location. To identify the factors affecting the economics, a sensitivity analysis was also performed. These factors are: (i) fuel price fluctuations, (ii) capex costs (either technology advancement leading to reduction in capital cost, or cost overruns contributing to increase in capital costs), (iii). variation in interest rates and (iv) electricity costs. Since the cash flow analysis considered revenue escalation year on year as 3 %, the effect of variation in revenue escalation was also considered. Figs. 6.10a, 6.10b and 6.10c depict the effects of various parameters on H<sub>2</sub> sale price for methanol, diesel and gasoline, respectively. Figs .6.10d, 6.10e and 6.10f depict the effects of various parameters on electricity sale price keeping H<sub>2</sub> sale price fixed at \$2.5/kg which is the price suggested in order to serve 8% of energy demand globally [4].

Equipment	Description	Vendor	Cost, USD
Reformer,	5 Tubular reactors, SS316 (material of	M/s Amar Equipments	13,600 (total cost for 5
HTWGS, LTWGS,	construction)	Private Limited	tubular reactors)
PROX and			
Combustor			
Vaporizer	Shell and Tube type, SS316 (material of		29,340 (total cost for
Coolers	construction), (5 heat exchangers))		all heat exchangers)
Compressors	Diaphragm type multi stage compressor (2	M/s Indian Compressors	21,460 (total cost for 2
	compressors)	Limited	compressors)
Pressure Swing	Cyclic PSA, 9 bed system with layered	M/s MVS Engineering	37510
Adsorption System	adsorbent. Skid mounted with control panel	Private Limited	
Instrumentation	Includes pressure gauges, temperature sensors, Isolation Valves, needle valves	M/s Amar Equipments Private Limited	10,850
Miscellaneous	Skid mounted structure. Fittings, tubing, PID	M/s Amar Equipments	6.385
	based control panel	Private Limited	- ,
Demineralized Water	Type 2, 10 LPH water purification system	M/s Pulse Life Science	2,235
system			
Installation and	5% of base equipment capital cost		5,750
Commissioning			
Contingency @ 10% o	f the overall capex (excluding taxes)		12,713
Goods and Services Ta	ax (GST) @ 18%		21,848
Total (Capex)			1,61,691

**Table 6.8**: Equipment list, supplier list and capex for the various components of the reformer

 plant
Item	Description / Usage	Vendor / Link for price	Cost, USD/unit
Methanol	Raw material	Methanol.Org[190]	0.34/kg (landed cost)
Diesel	Raw Material	Commercial price[191]	1.18/kg (at pump)
Gasoline	Raw Material		1.43/kg (at pump)
Electricity	Utility	The Tata Power Company Limited (LT II (A) Commercial 0-20 kW)[192]	0.09/kWh + 0.17/day (fixed charge)
Water	Utility and Process	Local Municipal Corporation[193]	0.81/m <sup>3</sup>
Air (Pressurized cylinder)	Process	Maharashtra Gas	0.03/kg
Catalyst for Reformer	Nickel Nitrate hexahydrate	Merck Group	66.4/kg
	Chloroplatinic Acid hexahydrate		34,825/kg
	Potassium chloride		95/kg
	Tergitol-15-s-9		87.34/kg
	Laponite	M/s IMCD India Private Limited	23.88/kg
	Locron	M/s Innova Corporate India[194]	1.2/kg

## Table 6.9: Operating Cost Components for the reformer plant along with source of supply

<b>Table 6.10</b> : Economic analysis results for model 1 and model 2 for the three fuels (single	¢
ocation)	

Parameter	Model 1	Model 2
Capex, \$	161,691	2,38,299
Products for sale (common to	H <sub>2</sub> : 5516 kg/year	H <sub>2</sub> : 2885 kg/year
all the three fuels considered)		Electricity: 43,800 kWh/year
Internal Rate of Return	16%	16%
Net present value, \$	0	0
Methanol		
Operating cost <sup>1</sup> , \$/year	31,196	34,300
H <sub>2</sub> sale price, \$/kg	10.91	2.5
Electricity sale price, \$/kWh	-	1.90
Diesel		
Operating cost <sup>1</sup> , \$/year	51,267	54,371
H <sub>2</sub> sale price, \$/kg	14.63	2.5
Electricity sale price, \$/kWh	-	2.46
Gasoline		
Operating cost <sup>1</sup> , \$/year	55,361	58,465
H <sub>2</sub> sale price, \$/kg	15.04	2.5
Electricity sale price, \$/kWh	-	2.56

1: Operating cost includes raw materials cost (fuel, process water), utility cost (electricity, utility water), catalyst cost, operation and maintenance and manpower



**Figure 6.10**: Sensitivity analysis for effect of various parameters on H<sub>2</sub> sale price (Model 1) for a) methanol, b) diesel and c) gasoline and on electricity sale price (Model 2) with H<sub>2</sub> sale price fixed at \$2.5/kg for d) methanol, e) diesel and f) gasoline.  $\blacksquare$  – Electricity,  $\bullet$  – revenue escalation,  $\blacktriangle$  – Capex,  $\Box$  – Rate of interest on loan,  $\circ$  – Fuel price (Methanol, diesel and gasoline)

In Fig. 6.10, the 0% on the x-axis refers to the base case for which the economic analysis was depicted in Table 6.10. For every parameter evaluated, a discounting pattern was created. For example, a 10% discount on electricity price would lead to a reduction in electricity price by 10% from the base scenario while a -10% discount would mean an increase in electricity price by 10%. Thus, the overall variations for electricity and fuel price were worked out from -30% to 60% to consider price fluctuations over the course of the plant life. Similarly, capex was varied from -50% to 60% of the base case scenario. The interest rates on loans were only likely to come down from the current value – hence, the interest rates were discounted from 0% to 100% where 100% represents an interest free grant from a funding agency. For revenue escalation parameter, the discounting varied from -60% to 30% where the negative discount indicated an increase in escalation (year on year) and a positive discount indicated a decrease in revenue escalation percentage (year on year).

A 50% reduction (Fig. 6.10a) in capex resulted in H<sub>2</sub> sale price reduction by  $\sim 30\%$  (\$10.91 to \$7.66/kg) while a similar reduction in methanol fuel price reduced H<sub>2</sub> sale price by ~12% (\$10.91) to \$9.65/kg) only. The reductions were not so significant for the other parameters which showed that the capex and the fuel prices were the two most important parameters affecting the cash flows. Similar observations were made with respect to diesel and gasoline (Figs. 6.10b and 6.10c) and for model 2 (Fig. 6.10d for methanol, Fig. 6.10e for diesel and Fig. 6.10f for gasoline). Based on initial discussions with each vendor, it was concluded that the quoted prices in Tables 6.8 and 6.9 were budgetary estimates with a significant scope for reduction depending upon volumes and capacities. The fuel cell production costs could reduce by 45% by scaling the fuel cell production from 10,000 to 2,00,000 units without any major technological breakthroughs [4]. Similar analogy could be used for calculating the capital costs for both the models with an increase in the production capacities. The revenue sale prices for both the models were therefore evaluated considering economies of scale where multiple locations utilize similar capacities for the fuel cells and the reformer (Table 6.10 for single location as the base case). Thus, for Model 1, the number of reformers (each producing  $H_2$  equivalent to powering 10 kWe fuel cell) were varied from 1 to 2,00,000 and its effect on H<sub>2</sub> sale price was captured in Fig.6.11a for all the three fuels. Similarly, the number of fuel cells (10 kWe each) and corresponding number of reformers (10 kWe equivalent H<sub>2</sub> producing capacity) were varied for Model 2, and the result was plotted in Fig. 6.11b for all the fuels.



**Figure 6.11**: Effect of capacity variation on a) Model 1 and b) Model 2;  $\blacksquare$  – Methanol,  $\bullet$  – Diesel and  $\Delta$  – Gasoline; H<sub>2</sub> sale price for model 2 fixed at \$2.5/kg

The capex calculation was based on Eq. 6.33 with the index value taken as 45% [4,182].

$$C_{BM2} = C_{BM1} * \left(\frac{S_2}{S_1}\right)^n \tag{6.33}$$

where S refers to the capacity (calculated as capacity of 1 location\*number of locations) while subscript 2 refers to new capacity and subscript 1 refers to base case (single location). Exponent n value taken is 0.45 based on the published study [4]. The basic assumption made in model 2 was that the secondary revenue component i.e. Hydrogen sale price was kept at \$ 2.5/kg in line with published studies [4]. Figs. 6.11a and 6.11b show an exponential drop in the sale price of  $H_2$  and electricity with increase in numbers from 1 to 10,000 beyond which the decrease was minimal indicating 10,000 locations as an optimum number for replication of similar capacities. These results clearly indicate the effect of capital cost on the plant economics. Thus, for an optimum capacity of 10,000 reformers, the sale price of H<sub>2</sub> for methanol was observed to be \$4.21/kg; for diesel and gasoline, it was found to be \$7.87/kg and \$8.55/kg, respectively. At \$4/kg at the nozzle,  $H_2$  could meet 50% of the mobility sector's demand and therefore provides a great impetus in the move towards adopting hydrogen economy [4]. It should be noted that the sale price of H<sub>2</sub> was still lower than the delivered cost of hydrogen reported (7.8 \$/kg) for a 100 kg/day H<sub>2</sub> generation plant based on biogas [119]. Fig. 6.11b shows that a similar optimum number of 10,000 locations was derived for Model 2 with the electricity sale price observed to be \$0.52/kWh, \$1.06/kWh and \$1.17/kWh for methanol, diesel and gasoline, respectively – these are higher than the prevalent electricity prices in India. Since the sale price of H<sub>2</sub> in model 2 was fixed, a sensitivity analysis for each fuel was done by varying the  $H_2$  sale price for the optimum capacity of 10,000 locations. The range considered was \$1.5-4/kg which was the predicted range for hydrogen to be adopted globally for various applications [4]. The corresponding change in electricity sale price for each fuel was reported in Fig. 6.12. It was concluded that the effect of variation in electricity sale price was prominent with a decrease of 22% for methanol, 11% for diesel and 10% for gasoline as the H<sub>2</sub> sale price was increased from \$2.5/kg to \$4/kg. Hence, the H<sub>2</sub> sale price was revised to \$4/kg and the fuel cell kWe output was varied. The capacity variation accounted for back-up power capacities ranging from 2.5, 5, 7.5 kW for telecom towers, 10, 20 and 50 kW for microgrids, 100, 1000 and 2000 kW for large scale back-up power applications. The number of locations for each fuel cell capacity was assumed as 10,000 and correspondingly, the number of reformers were calculated with the minimum reformer capacity producing H<sub>2</sub> equivalent to running a 10 kWe fuel cell. Therefore, higher amount of excess hydrogen would be available for sale in a smaller fuel cell (< 10 kWe) and number of reformers would exceed 10,000 numbers for fuel cell capacities > 10 kWe. The corresponding results were plotted in Fig. 6.13a and the electricity sale price was higher for a lower fuel cell capacity, i.e. 2.5 kW compared to 10 kW for all the three fuels. The electricity price, however, decreases rapidly as the fuel cell capacity was increased. Beyond 10 kWe, the decrease was minimal. The revenue share analysis for the values in Fig. 6.13b reveals that the hydrogen revenue share decreased with an increase in the fuel cell capacity as more hydrogen was consumed in generating electricity, thereby, lowering hydrogen available for sale. Correspondingly, with an increase in the electricity revenue fraction, the corresponding electricity sale price decreased. With the growing impetus on hydrogen economy, governments globally are dishing out incentives to setup hydrogen generating stations. In this context, for the case of 10,000 locations, H<sub>2</sub> sale price of \$4/kg and fuel cell capacity of 10 kWe, models 1 and 2 were evaluated for fuel price variations with a sensitivity analysis like that reported in Fig. 6.10. The results from the sensitivity analysis were plotted in Fig. 6.14 and the H<sub>2</sub> sale price drops from \$4.21/kg to \$1.96 /kg for a 90% discount to the methanol price (Fig. 6.14a). Similarly, the drop was substantial for diesel (\$7.87-3.41/kg) and gasoline (\$8.55-3.17/kg) with a 90% discount in fuel price. At current diesel and petrol prices in USA (\$0.634/litre for diesel and \$0.67/litre for gasoline), the H<sub>2</sub> sale price is \$6/kg for diesel and at \$6.75/kg for gasoline which was still higher than



**Figure 6.12**: Effect of H<sub>2</sub> sale price variation on Model 2;  $\blacksquare$  – Methanol,  $\bullet$  – Diesel and  $\Delta$  – Gasoline; (Case: 10,000 reformers and equivalent fuel cells)



**Figure 6.13**: a) Effect of fuel cell capacity (kW) on electricity sale price;  $\blacksquare$  – Methanol,  $\bullet$  – Diesel and  $\Delta$  – Gasoline; H<sub>2</sub> sale price fixed at \$4/kg b) Corresponding revenue share fraction as a function of fuel cell capacity, kW;  $\blacksquare$  – Methanol,  $\bullet$  – Diesel and  $\blacktriangle$  – Gasoline  $\Box$  – Methanol,  $\circ$  – Diesel and  $\varDelta$  – Gasoline



**Figure 6.14**: Effect of fuel price variation on a) Model 1 and b) Model 2;  $\blacksquare$  – Methanol,  $\bullet$  – Diesel and  $\Delta$  – Gasoline; (Case: 10,000 reformers and equivalent fuel cells), For Model 2 – H<sub>2</sub> sale price fixed at \$4/kg

the recommended prices for H<sub>2</sub> to be competitive[4]. Fig. 6.14b shows that for similar discounting in fuel prices, the electricity sale price drops to \$0.04/kWh for methanol, \$0.39/kWh for diesel and \$0.34/kWh for gasoline. At current diesel and petrol prices in USA, the electricity sale price was \$0.79/kWh for diesel and \$0.89/kWh for gasoline. The prices observed from the three fuels lead to the conclusion that only methanol should be considered as a potential fuel for generating hydrogen. Diesel and gasoline need massive subsidies in the form of price waivers to be economically viable as per current market trends., Therefore, only the methanol based model was considered for further analysis where the price trends obtained were compared with diesel genset and electrolyser systems. The electrolyser systems considered were an alkaline and a PEM based system. The commercial details of the electrolyser and diesel genset considered for comparison were tabulated in Table 6.11. For evaluation purposes, electricity needed by the electrolysers is provided by means of solar PV panels. Detailed analysis with respect to the number of panels needed has been well documented [195]. Similar analysis and assumptions have been done in our calculations. The study also details the land needed for solar panels installation. However, the location considered is Mumbai where the land cost is very high and it will not be right to consider the same land cost pan-India as the land cost is relatively cheaper. Therefore, it has been assumed that the land is available free of cost for solar panels installation. Quote for PEM based electrolyser was obtained from MVS Engineering Private Limited while the cost and performance numbers for

alkaline electrolyser were taken from literature [18,20,195]. Similarly, quote for diesel genset having the make of Ashok Leyland was obtained from the manufacturer.

Model type	Alkaline electrolyser coupled	PEM based electrolyser	Diesel genset
	with solar PV for electricity	coupled with solar PV for	
	supply	electricity supply	
H <sub>2</sub> generation capacity	0.72 kg/h	0.72 kg/h	Not applicable
kW rating	Not applicable	Not applicable	10 kWe
Capex, \$	2,78,083	8,06,167	3,970 (quote obtained from GMDT Marine and Industrial Engineering Private Limited)
Water consumption	12.46 kg water / kg H <sub>2</sub> (process) and 87 L/min cooling water requirement	10.2 kg water / kg H <sub>2</sub> (process) and 87 L/min cooling water requirement	Not applicable
Electricity consumption	73.08 kWh/kg H <sub>2</sub>	62.36 kWh/kg H <sub>2</sub>	Not applicable
Diesel consumption	Not applicable	Not applicable	0.345 L/kWh
Operation and Maintenance costs, \$/year	4% of capex	4% of capex	\$353/year (quoted by GMDT Marine and Industrial Engineering Private Limited)
Reference	[18,20,195]	[195], Quote obtained from MVS Engineering Pvt Ltd for electrolyser	QuoteobtainedfromGMDTMarineandIndustrialEngineering Private Limited)

 Table 6.11: Techno-commercial data for diesel genset and electrolysers

Table 6.12 lists the results of our evaluation between diesel genset, electrolyser and methanol based reformer from our work. Table 6.12 shows that the diesel genset turns out to be the cheapest amongst the options being considered. For both the pilot and commercial case, the methanol based reformer solution turns out to be cheaper compared to both the electrolyser systems. The hybrid model 2 in our case also turns out to be marginally cheaper than diesel gensets. In terms of  $CO_2$ 

emissions, the methanol based reformer emits 0.368 kg CO<sub>2</sub>/kWh which was 47% lower than a diesel genset (0.7 kgCO<sub>2</sub>/kWh) but much higher when compared to the electrolyser systems which produce green hydrogen [4]. In terms of water footprint, the water consumption values for the alkaline electrolyser system, PEM-based electrolyser and methanol-based reformer were 12.46 kg/kg H<sub>2</sub>, 10.2 kg/kg H<sub>2</sub> and 5 kg/kg H<sub>2</sub>, respectively Thus, the methanol reformer based system has a significantly lower water footprint compared to the electrolyser systems. The methanol reformer was viable only in certain scenarios when compared with diesel genset primarily because the technical maturity needed for a decentralized small-scale hydrogen generating system is not fully developed. For instance, there is a penalty incurred in the pressure swing adsorption system since the hydrogen recovery rates were 80% leading to increased fuel consumption. An increase in recovery or an alternative technology needs to be explored to improve the overall system efficiency. Also, substantial reduction in the fuel cell capital cost from the current prices is needed for stationary systems. Similarly, the fuel cell efficiency considered in our analysis was 47% while the target fuel cell efficiency by 2020 as per DOE is 60% [196]. Factoring in the increase in fuel cell efficiency, the electricity sale price drops to \$0.35/kWh for a 10 kWe capacity working at 10,000 locations with H<sub>2</sub> sale price at \$4/kg. This proposition makes the overall solution more competitive to alternatives for back-up power applications. Due to lower fuel cost, natural gas based system for the catalyst developed in our work could be even more favourable compared to methanol. However, this scenario needs to be investigated in detail supported with experimental evidence that the catalyst can yield high quantities of hydrogen like that obtained for liquid fuels. Therefore, there is scope for reduction in the overall sale price for both models and thereby an alternative to diesel genset in terms of cleaner energy and overall viability in the form of methanol based reformer using the novel catalyst developed in this study should be explored.

Table 6.12: Price Comparison for methanol based reformer (our work), electrolyser and diesel
genset (Model 2)

Parameter	Reformer with fuel cell (using methanol as fuel)	Alkaline electrolyser with fuel cell	PEM electrolyser with fuel cell	Diesel genset
(Pilot case – Single location)				
H <sub>2</sub> sale price, \$/kg	2.5	2.5	2.5	Not applicable
Electricity price, \$/kWh	1.91	2.34	6.67	Not applicable
(Commercial case – 10,000 locations, Fuel cell capacity 10 kWe)				
H <sub>2</sub> sale price, \$/kg	4	4	4	Not applicable
Electricity price, \$/kWh	0.4	0.44	0.54	0.42

Based on these results, we can conclude that the methanol based reformer system is competitive compared to existing back-up power generation solutions and can be considered as a solution till the green hydrogen systems become technically mature and commercially viable.

## 7.1. Conclusions

A novel mesoporous bimetallic catalyst with potassium as the promoter was developed in this work for multi-fuel reforming. The best catalyst formulation was Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> with 10 wt% nickel, 1 wt% platinum and 5 wt% potassium. The efficacy of adding potassium and its role in enhancing the stability of the catalyst for high hydrogen yields is demonstrated. The novel catalyst developed was stable and active in the reforming experiments with three commercial fuels, viz. methanol, diesel and gasoline for ~ 42 hours. The hydrogen yield for all the three fuels was ~ 1.7 mol of H<sub>2</sub>/mol of C, which was comparable to the reported values in literature for different catalysts. Our work fills an important research gap wherein no other catalyst has been shown to be active and stable for multiple fuels. The catalyst combination Ni-Pt/K5-Al<sub>2</sub>O<sub>3</sub> was found to be stable and active for three liquid fuels viz. methanol, diesel and gasoline

The simple hydrothermal method used for catalyst preparation is easily replicable and the materials used for catalyst development are available commercially. We demonstrated that the addition of potassium during the synthesis of the alumina support allows the potassium to be evenly dispersed within the clay framework. It was shown that part of the potassium attaches with the silica layer in the clay framework to form a kalsilite type structure which helps in improving the catalyst stability. However, this type of structure formation is demonstrated to happen until an optimum potassium loading of 5 wt% only, above which the potassium tends to pull Ni deep onto the support matrix owing to its strong electropositivity. This leads to Ni agglomeration and an increase in the metal particle diameters which was observed from characterization of the different potassium promoted catalysts. At the optimum loading of 5 wt% potassium, the catalyst showed highest reducibility, dispersion, TOF, H<sub>2</sub> yield and lowest carbon deposition. Amongst the various coke mitigating promoters tried out, potassium gave the highest catalyst activity for all the three fuels.

Commercially available gasoline and diesel have ppm level sulphur concentration despite the purification. Therefore, it is important for the developed catalyst to have high sulphur tolerance when such fuels are used. We conclusively established that the novel catalyst is capable of reforming fuels with sulphur content up to 10 ppm (w/w). Higher sulphur loadings deactivated the

catalyst primarily due to catalyst poisoning leading to excessive carbon deposition. The catalyst can, therefore, be used without a desulfuriser for fuels complying with Euro VI norms.

A techno-economic analysis of the process with a reformer using the novel developed catalyst and operating in a decentralized mode was evaluated. In our analysis, two models were considered – the first model consisted of hydrogen distribution while the second model consisted of powering fuel cells for backup power generation thereby mimicking diesel gensets. The hydrogen production was found to be viable (EIRR 16%) at a sale price of \$4.21/kg for the methanol system when a minimum of 10,000 locations are available pan-India at similar capacities (equivalent H<sub>2</sub> produced to power a 10 kWe equivalent fuel cell). Similarly, electricity sale price for the methanol system under similar assumptions and a fixed sale price of H<sub>2</sub> at \$4/kg was found to be \$0.4/kWh which is slightly lower when compared with diesel gensets. In terms of CO<sub>2</sub> emissions, the methanol-based system was ~47% less CO<sub>2</sub> intensive compared to diesel gensets.

Thus, the novel multi-fuel reforming catalyst developed in this work is envisaged to increased use of on-site catalytic reforming and thereby eliminate dependence on availability of fuels. This versatile system eliminates the costs incurred in distributing hydrogen and is expected to make hydrogen production viable.

## 7.2. Future Work

The novel catalyst developed has given high yields of hydrogen which can make onsite reforming feasible. Hence, efforts should be made to make the reformer system utilizing the novel catalyst commercially viable. For that purpose, a summary of future work covering these aspects is suggested in the following points.

- For each liquid fuel (methanol, diesel and gasoline), the catalyst needs to be tested for longer runtimes (2000-4000 h) to check for catalyst degradation and deactivation due to coke formation. Based on the observations, a cost-effective (oxygen treatment at 400-600 °C) regeneration mechanism should also be devised to avoid frequent catalyst top-ups. Morphological changes in the catalyst structure during the test runs would also need to be studied in detail to understand the cause of degradation and deactivation.
- 2. For the commercial capacities, a standard practise is to use monoliths or pellets instead of powder to avoid pressure build-up in the system. However, larger particle sizes of the

catalyst introduce heat and mass transfer limitations which may affect the overall  $H_2$  yields. Hence, an effective design coupled with optimization of catalyst particle size and loadings for each fuel needs to be verified experimentally.

- 3. The reactor was heated in the experiments using an external electrical furnace. However, the scaled-up process requires a burner (fired with off-gas coming from the PSA unit) to heat the reformer therefore, methodologies for effective heat transfer also need to be evaluated for a good and economic reformer design.
- 4. Operation of the completely integrated system with the reformer, downstream purification and power generation in a PEM fuel cell would conclusively establish the various assumptions used in our techno-economic study.
- 5. Extend the usability of the catalyst to other fossil fuels such as natural gas, ethanol blended gasoline, kerosene, biogas, and dimethyl ether to conclusively establish the multi-fuel reforming capability of the catalyst.
- 6. Conduct a detailed LCA coupled with techno-economic study for coupling CO<sub>2</sub> capture with the methanol reforming system to arrive at the true cost of the delivered blue hydrogen as an alternative to green hydrogen.

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# **APPENDIX** A

A GCMS analysis of diesel showed an alkane distribution in the range of  $n-C_9H_{20}$  to  $n-C_{25}H_{52}$ . The GCMS snapshot is shown in Fig. A1.



Figure A1: GCMS snapshot of diesel (commercial sample)

Diesel standard procured from Agilent contained a mixture of  $C_{10}H_{22}$ ,  $C_{12}H_{26}$ ,  $C_{14}H_{30}$ ,  $C_{16}H_{34}$ ,  $C_{18}H_{38}$ ,  $C_{20}H_{42}$ ,  $C_{22}H_{46}$ , and  $C_{24}H_{50}$ . This was used to create calibration curves in order to estimate the molar content of these compounds in diesel. The calibration curves were created by using ethyl acetate as a diluent. The standard and ethyl acetate were pre-mixed in different concentrations to create the calibration curves. The calibration equations so derived are listed below:

Y1 = 0.0002X1 - 0.011

Y2 = 0.0001X2 - 0.0193

Y3 = 0.0001X3 - 0.0508

Y4 = 0.00008X4 - 0.0317

Y5 = 0.00008X5 - 0.0238

Y6 = 0.00007X6 - 0.004

Y7 = 0.00007X7 - 0.0016

Y8 = 0.00008X8 - 0.0021

Where Y1-Y8 are the weight fraction of the various components ( $C_{10}H_{22}$ ,  $C_{12}H_{26}$ ,  $C_{14}H_{30}$ ,  $C_{16}H_{34}$ ,  $C_{18}H_{38}$ ,  $C_{20}H_{42}$ ,  $C_{22}H_{46}$ ,  $C_{24}H_{50}$ , respectively) while X1-X8 are the area recorded by the GC for the retention time of the compound. The GC initially yielded mole fraction which was then converted into weight fraction based on the molecular weight of each compound. When the experiment was run, the total weight of the liquid sample (organic) was measured for each sample collected. The liquid sample was then analysed in a GC to find the area under the peak for each retention time measured. The areas for each sample were then used along with the calibration equations to calculate the weight fraction of each compound. Multiplication of the weight fraction with the total weight of the sample gives the weight of the corresponding compound. Knowing the initial weight of these compounds in the diesel sample, the conversion was then calculated by the following formula by converting the weights in molar form:

$$Conversion = \frac{(mol \ of \ Carbon)_{in,liquid} - (mol \ of \ Carbon)_{out,liquid}}{(mol \ of \ Carbon)_{in,liquid}}$$

In order to check for carbon balance, the amount of Carbon in diesel feed sample and unconverted diesel was estimated based on the above procedure. Carbon in gas phase was estimated by collecting the gas sample and analysing it in a GC. The areas under the peaks were obtained from the GC and the calibration equations for each gas were used to calculate the mole fraction of each component in the gas phase. Knowing the volumetric flow rate of the gas, the molar flow rate of each component was estimated and used to complete the carbon balance in the gas phase. The carbon content in the solid phase was estimated from the TGA analysis after the experiment was over. Thus, the carbon balance was completed as per the following formula:

$$C_{diesel} = C_{gas \, phase} + C_{liquid \, phase} + C_{solid \, phase}$$

A Sample calculation showing the carbon balance has been shown below:

The calculations shown here (refer Table A1) pertain to diesel run done on Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> (refer results reported in Fig. 5.1a).

Time,	C in, g	C in gas	C in liquid	C in solid phase, g	Conversion, %
minutes		phase, g	phase, g		
0	0	0	0	Measurement done at	
15	0.67	0.65	0.01	the end of the analysis	98.7%
60	1.9	1.88	0.01	using TGA hence	99.62%
101	1.81	1.80	0.01	only total is shown	99.53%
138	1.64	1.63	0.01		99.59%
184	2.04	1.99	0.05		97.41%
226	1.86	1.42	0.41		77.81%
272	2.03	1.56	0.47		76.94%
315	1.9	1.39	0.49		73.92%
355	1.77	0.68	0.45		74.64%
396	1.81	1.36	0.45		75.23%

Table A1: Carbon balance (sample calculation) for diesel for the catalyst Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>

429	1.46	0.73	0.36		75.71%	
Total	18.89	15.09	2.72	0.017	74.86%	(Average
					of steady	values)*

\* - The average conversion reported is for the steady conversions observed.

Total C measured from the experiments is 17.8 g. The corresponding error is 5.63%

The C in gas phase is calculated based on the GC observations made in the FID. A GC snapshot of the FID is shown below (Fig. A2):



**Figure A2**: GC snapshot of the FID of the components in the gas phase during diesel reforming using the catalyst Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub>

The areas under the peaks are calibrated and therefore mol% of the components in the gas phase from FID and TCD are obtained. Using a pre calibrated bubble flow meter, the total volumetric flow rate at the outlet of the reformer is measured. The molar flow rates of each component (CH<sub>4</sub>,

 $CO_2$ , CO,  $H_2$ ,  $O_2$ ,  $N_2$  and if any ethane present) is quantified. The total C from the gas phase is then summed up. There is no representative image of the TCD to show the  $H_2$ ,  $O_2$  and  $N_2$  peaks.

For the liquid phase C calculation following sample calculation is followed:

A sample GC snapshot of the diesel being fed (Fig. A3) and the liquid phase collected (aqueous and organic) (Fig. A4) is shown below:



Figure A3: GC snapshot of the commercial diesel



**Figure A4**: GC snapshot during diesel reforming using Ni-Pt/K2-Al<sub>2</sub>O<sub>3</sub> of the a) organic phase and b) aqueous phase

The distribution of the hydrocarbons in the diesel is shown in Fig. A3. As per the procedure listed, the primary compounds as per the diesel standard are identified as  $C_{10}H_{22}$ ,  $C_{12}H_{26}$ ,  $C_{14}H_{30}$ ,  $C_{16}H_{34}$ ,

 $C_{18}H_{38}$ ,  $C_{20}H_{42}$ ,  $C_{22}H_{46}$ ,  $C_{24}H_{50}$ , respectively corresponding to the peak retention times (in minutes) of 5.4, 8.4, 11.17, 13.57, 15.7, 17.6, 19.4 and 21.04, respectively. The calibration equations were used to account for the mole distribution based on which the overall carbon content in the diesel being fed and the carbon content in the liquid phase were estimated. The retention peak of 2.1 seen in Fig. A4b refers to ethyl acetate which is used as a diluent in the runs.

A similar analysis for gasoline was conducted. Based on the GCMS analysis of commercial gasoline (snapshot shown in Fig. A5), the major components present in commercial gasoline were identified as Benzene, Toluene, o-xylene, p- xylene and pseudo-cumene (1,2,4-trimethyl benzene and 1,3,5-trimethyl benzene).



Figure A5: GCMS snapshot of gasoline (commercial sample)

Gasoline standard from Agilent consisted of these compounds and a calibration procedure similar to diesel was followed. The calibration equations used are described below:

Y1 = 3E-11X1 + 1E-9

Y2 = 4E-11X2 + 2E-9

Y3 = 2E-11X3 + 2E-9

Y4 = 4E-11X4 + 2E-9

Y5 = 3E-11X5 + 1E-9

Y6 = 3E-11X6 + 2E-9

where Y1-Y6 are the weight fractions for Benzene, Toluene, o-xylene, p-xylene, 1,2,4-trimethly benzene and 1,3,5-trimethyl benzene, respectively and X1-X6 represent the areas under the peaks recorded at the retention times of these compounds in GC. Rest of the procedure remained similar to diesel for estimating the conversion.

## **APPENDIX B**

The details of the ReaxFF simulations are detailed in this appendix.

#### **Simulation Procedure**

Molecular dynamic (MD) simulations were performed to understand the formation of K-Al and K-Si sites in a thermally treated K<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system by comparing the resulting structure with those of standard KAlSiO<sub>4</sub> and KAlSi<sub>3</sub>O<sub>8</sub> mixed oxides. The ReaxFF Cu/zeolite forcefield was used in the ADF Modelling Suite to perform the reactive MD simulations. The molecular coordinates were visualized using VMD (Visual Molecular dynamics) software package. The DFT optimized structures of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, K<sub>2</sub>O, KAlSiO<sub>4</sub>, and KAlSi<sub>3</sub>O<sub>8</sub> were obtained from the Materials Project Database. The forcefield was able to reproduce the density of these structures within ±5% of the DFT values. A mixture of K<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub> clusters with concentrations mimicking their elemental ratio in experimentally reported structures (Table 5.3) was simulated using an NPT ensemble. The timestep of an iteration was 0.25 fs at low temperatures (< 2200 K) and 0.1 fs at high temperatures (> 2200 K). The Berendsen thermostat was used with a damping constant of 100 fs, whereas the Berendsen barostat with a damping constant of 1500 fs, was used during the NPT simulation. The system was kept at 300 K for 100 ps and then the temperature was ramped with a rate of 4 K/ps to 2800 K. Subsequently, the system was kept at 2800 K for 200 ps. Thereafter, the structure was cooled down to 300 K with a rate of 4 K/ps and kept at room temperature for another 100 ps. This temperature scheme was essential for accelerating the bond breaking and formation process as the experimental timescale of the formation of mixed oxide was not feasible computationally. The present study focused on the position of K in the final structure and we compared our results with Al<sub>2</sub>SiO<sub>5</sub>, KAlSiO<sub>4</sub> and KAlSi<sub>3</sub>O<sub>8</sub> structures simulated (NPT) for 100 ps at 300 K.

#### **RESULTS**

In order to confirm the KAlSiO<sub>4</sub> structure we thermally annealed a K/Al/Si/O mixed oxide structure using ReaxFF MD-simulations. Figure A3 shows the final structure of the thermally annealed mixed oxide. The presence of a lattice site matching the DFT optimised structure of standard KAlSiO<sub>4</sub> was found in the simulated mixed oxide. Although the present temperature

scheme and simulation time were not enough for complete crystallization, a short-range order was apparent in the final structure. The radial pair distribution functions (g(r)) between Al-K (Figure A3(b)) and Si-K (Figure A3(c)) show that the peak positions closely matched with KAlSiO<sub>4</sub> than KAlSi<sub>3</sub>O<sub>8</sub>. Their ratio of the first and second peak height in the Si-K g(r) (Figure A3(c)) was 1.86, which matched closely with the ratio in the g(r) of KAlSiO<sub>4</sub> (1.94). However, this was not the case for the Al-K g(r) as the first peak height was significantly shorter. The low height of the first peak of Al-K g(r) can be attributed to the relatively low number of Al and K atoms present inside the simulation box. The g(r) for the Al-Si framework (Figure A3(d)) in the mixed oxide is compared against Al<sub>2</sub>SiO<sub>5</sub>, KAlSiO<sub>4</sub>, and KAlSi<sub>3</sub>O<sub>8</sub> structures. The number of K atoms in the simulation box is stoichiometrically insufficient for a complete KAlSiO<sub>4</sub> lattice, therefore the excess Al-Si-O framework could lead to mixed oxides and/or Al<sub>2</sub>SiO<sub>5</sub>. The first and second peak positions in the Al-Si g(r) (Figure A3(d)) match with the  $Al_2SiO_5$  structure. However, due to the formation of lattice sites like KAlSiO<sub>4</sub>, the relative intensity of the second peak increases. However, since the focus was to ascertain the position of K in the support framework hence, further investigations were not conducted. Based on these preliminary reactive MD simulations, it was concluded that it is possible to form lattice sites like KAISiO<sub>4</sub> by mixing Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, and K<sub>2</sub>O oxides in a 0.26/0.64/0.09 composition, which is similar to experimental support composition (Table 5.3).



**Figure A3**: ReaxFF MD results of a orthogonal simulation box size of 8.6 nm<sup>3</sup> a) simulated structure of thermally treated mixed oxide of K-Al-Si, the inset shows position of K in the lattice structure of standard KAlSiO<sub>4</sub> and the simulated mixed oxide; Radial Pair Distribution Function of simulated mixed oxide, KAlSiO<sub>4</sub> and KAlSi<sub>3</sub>O<sub>8</sub> in between pairs of (b) Al-K, (c) Si-K, and d) Al-Si.

# **APPENDIX C**

Table A1 lists the molecular weight distribution of diesel sample from the calibration procedure described in Appendix A.

Compound	Molecular weight (g/mol)	Weight %	
n-C <sub>10</sub> H <sub>22</sub>	142	6.89	
$n-C_{12}H_{26}$	170	9.42	
$n-C_{14}H_{30}$	198	24.03	
$n-C_{16}H_{34}$	226	24.20	
$n-C_{18}H_{38}$	254	16.73	
n-C <sub>20</sub> H <sub>42</sub>	282	9.68	
n-C <sub>22</sub> H <sub>46</sub>	310	5.66	
n-C <sub>24</sub> H <sub>50</sub>	338	3.39	

Table A1:	Molecular	weight	distribution	for diesel	sample
		0			

Average Molecular weight obtained = 226.83 g/mol, which is very close to C<sub>16</sub>H<sub>34</sub>. Hence, n-hexadecane was chosen as the surrogate compound for modelling diesel.

Table A2 lists the molecular weight distribution of gasoline sample from the calibration procedure described in Appendix A.

Compound	Molecular weight (g/mol)	Weight %
Benzene	78	1.87
Toluene	92	70.15
o-xylene	106	11.01
p-xylene	106	5.04
1,2,4-trimethyl benzene	120	4.73
1,3,5-trimethyl benzene	120	7.22

### Table A2: Molecular weight distribution for gasoline sample

Average Molecular weight obtained = 97.35 g/mol which is close to toluene. Hence, toluene was chosen as the surrogate compound for modelling gasoline.

Table A3 lists the pre-exponential factors predicted from the kinetic model for the three fuels under consideration

Table A3: Pre-exponential factors (in  $mol/g_{cat}$ .s) predicted from the kinetic model for the three

fuels i.e. methanol,	diesel and	gasoline
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Reaction	Methanol	Diesel	Gasoline
Steam reforming	5.02*10 <sup>17</sup>	$2.4^{*}10^{16}$	5.37*10 <sup>16</sup>
Oxidation	5*10 <sup>19</sup>	4.25*10 <sup>14</sup>	8.5*10 <sup>14</sup>
Water gas shift	1.13*10 <sup>8</sup>	5.06*10 <sup>8</sup>	1.13*10 <sup>8</sup>
Methanation	5.50*10 <sup>8</sup>	5.05*10 <sup>8</sup>	$4.58*10^{10}$
Methanol decomposition	1.09*10 <sup>9</sup>	Not applicable	Not applicable

## **APPENDIX D**

This appendix lists the stream tables for each fuel starting with methanol.

Flowsheet is attached for reference (Same flowsheet is shown in Chapter 6 (refer Fig. 6.7))



Figure A4: Process flow diagram of the simulated Flowsheet in Aspen Plus

Stream Name	S1	S2	S3	S4	S5	<b>S6</b>	S7	<b>S8</b>	<b>S9</b>	S10	S11	S12	S13	S14	S15
Temperature, °C	25	25	30	25	170	25	154	420	110	297	402	150	189	120	25
Pressure, bar	1	1	1	1	1	1	1	1	1	20	20	20	20	20	1
Total flow, kmol/h	0.17	0.152	0.44	0.152	0.44	0.08	0.52	0.84	0.84	0.84	0.84	0.84	0.84	0.84	0.05
Methanol, kmol/h	0.17		0.17		0.17		0.17	0	0	0	0	0	0	0	
Water, kmol/h		0.152	0.27	0.152	0.27		0.27	0.25	0.25	0.25	0.16	0.16	0.14	0.14	
Oxygen, kmol/h						0.017	0.017	0	0	0	0	0	0	0	0.01
CO, kmol/h								0.11	0.11	0.11	0.03	0.03	0.002	0.002	
CO <sub>2</sub> , kmol/h								0.06	0.06	0.06	0.14	0.14	0.166	0.166	
H <sub>2</sub> , kmol/h								0.36	0.36	0.36	0.44	0.44	0.468	0.468	
CH4, kmol/h								0	0	0	0	0	0	0	
N <sub>2</sub> , kmol/h						0.063	0.063	0.063	0.063	0.063	0.063	0.063	0.063	0.063	0.04

 Table A3:
 Stream table for methanol

Stream	S16	S17	S18	S19	S20	S21	S22	S23	U1	U2	U3	U4	U5	U6
Name														
<sup>°</sup> C	120	214	135	40	40	40	25	58	25	99.57	99.57	99.57	185	63
Pressure, bar	20	20	20	20	20	1	1	1	1	1	1	1	1	1
Total flow, kmol/h	0.89	0.87	0.87	0.36	0.39	0.12	0.11	0.49	0.45	0.45	0.45	0.45	0.45	0.45
Methanol, kmol/h	0	0	0		0									
Water, kmol/h	0.14	0.157	0.157		0.037	0.12		0.087	0.45	0.45	0.45	0.45	0.45	0.45
Oxygen, kmol/h	0.01	0	0		0		0.024	0						
CO, kmol/h	0.002	0	0		0			0						
CO <sub>2</sub> , kmol/h	0.166	0.168	0.168		0.168			0.168						
H <sub>2</sub> , kmol/h	0.468	0.45	0.45	0.36	0.09			0.042						
CH4, kmol/h	0	0	0		0			0						
N <sub>2</sub> , kmol/h	0.103	0.103	0.103	0	0.103		0.09	0.19						

<b>Table A4:</b> Stream table for Diese
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Stream Name	<b>S1</b>	S2	<b>S</b> 3	S4	S5	<b>S6</b>	<b>S</b> 7	<b>S8</b>	S9	S10	S11	S12	S13	S14	S15
Temperature, °C	25	25	25	25	300	25	216	780	110	331	339	150	173	120	25
Pressure, bar	1	1	1	1	1	1	1	1	1	20	20	20	20	20	1
Total flow, kmol/h	0.013	0.11	0.124	0.11	0.124	0.014	0.128	0.688	0.688	0.688	0.694	0.694	0.698	0.698	0.23
n-hexadecane, kmol/h	0.013		0.014		0.014		0.014	0.012	0.012	0.012	0.012	0.012	0.012	0.012	
Water, kmol/h		0.1	0.11	0.11	0.11		0.11	0.023	0.023	0.023	0.018	0.018	0.002	0.002	
Oxygen, kmol/h						0.003	0.003	0	0	0	0	0	0	0	0.048
CO, kmol/h								0.11	0.11	0.11	0.103	0.103	0.086	0.086	
CO <sub>2</sub> , kmol/h								0.1	0.1	0.1	0.108	0.108	0.125	0.125	
H <sub>2</sub> , kmol/h								0.43	0.43	0.43	0.44	0.44	0.46	0.46	
CH4, kmol/h								0.001	0.001	0.001	0.001	0.001	0.001	0.001	
N2, kmol/h						0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.012	0.19

Stream Name	S16	S17	S18	S19	S20	S21	S22	S23	U1	U2	U3	U4	U5	U6
Temperature, °C	120	830	120	40	40	35	25	47	25	99.57	99.57	99.57	440	99.57
Pressure, bar	20	20	20	20	1	1	1	1	1	1	1	1	1	1
Total flow, kmol/h	0.924	0.874	0.874	0.36	0.56	0.001	0.19	0.65	0.9	0.9	0.9	0.9	0.9	0.9
n-hexadecane, kmol/h	0.012	0.012	0.012		0	0.001		0						
Water, kmol/h	0.002	0.011	0.011		0.011			0.09	0.9	0.9	0.9	0.9	0.9	0.9
Oxygen, kmol/h	0.048	0	0		0		0.04	0						
CO, kmol/h	0.086	0	0		0			0						
CO <sub>2</sub> , kmol/h	0.125	0.21	0.21		0.21			0.21						
H <sub>2</sub> , kmol/h	0.46	0.45	0.45	0.36	0.09			0.009						
CH <sub>4</sub> , kmol/h	0.001	0.001	0.001	0	0.001			0.001						
N <sub>2</sub> , kmol/h	0.19	0.19	0.19		0.19		0.15	0.34						

Stream Name	<b>S1</b>	S2	<b>S3</b>	S4	S5	<b>S6</b>	<b>S7</b>	<b>S8</b>	S9	S10	S11	S12	<b>S13</b>	S14	S15
Temperature, ℃	25	25	25	25	400	25	353	780	110	278	341	150	185	120	25
Pressure, bar	1	1	1	1	1	1	1	1	1	20	20	20	20	20	1
Total flow, kmol/h	0.033	0.25	0.283	0.25	0.283	0.06	0.343	0.74	0.74	0.74	0.74	0.74	0.74	0.74	0.18
Toluene, kmol/h	0.033		0.033		0.033		0.033	0.001	0.001	0.001	0.001	0.001	0.001	0.001	
Water, kmol/h		0.25	0.25	0.25	0.25		0.25	0.066	0.066	0.066	0.025	0.025	0.003	0.003	
Oxygen, kmol/h						0.01	0.01	0	0	0	0	0	0	0	0.038
CO, kmol/h								0.134	0.134	0.134	0.09	0.09	0.07	0.07	
CO <sub>2</sub> , kmol/h								0.09	0.09	0.09	0.13	0.13	0.15	0.15	
H <sub>2</sub> , kmol/h								0.398	0.398	0.398	0.44	0.44	0.46	0.46	
CH4, kmol/h								0.001	0.001	0.001	0.001	0.001	0.001	0.001	
N <sub>2</sub> , kmol/h						0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.14

**Table A5**: Stream table for Gasoline

Stream Name	S16	S17	S18	<b>S19</b>	S20	*Extra	S22	S23	U1	U2	U3	U4	U5	U6
						Gasoline								
<sup>°</sup> C	120	771	120	40	40	25	25	126	25	99.57	99.57	99.57	553	99.57
Pressure, bar	20	20	20	20	1	1	1	1	1	1	1	1	1	1
Total flow, kmol/h	0.913	0.87	0.87	0.36	0.509	0.003	0.28	0.74	0.7	0.7	0.7	0.7	0.7	0.7
Toluene, kmol/h	0.001	0.001	0.001		0.001	0.003		0.003						
Water, kmol/h	0.003	0.007	0.007		0.007			0.1	0.7	0.7	0.7	0.7	0.7	0.7
Oxygen, kmol/h	0.038	0	0		0		0.06	0						
CO, kmol/h	0.07	0	0		0			0						
CO <sub>2</sub> , kmol/h	0.15	0.22	0.22		0.22			0.23						
H <sub>2</sub> , kmol/h	0.46	0.45	0.45	0.36	0.09			0						
CH <sub>4</sub> , kmol/h	0.001	0.001	0.001	0	0.001			0.001						
N <sub>2</sub> , kmol/h	0.19	0.19	0.19		0.19		0.22	0.41						

\* - S21 is not there in the gasoline flowsheet since there is no recovery possible and extra gasoline is needed to fuel the combustor along with hydrogen present.