

**CATALYTIC HYDROGENATION OF CARBON DIOXIDE BY
REVERSE WATER GAS SHIFT REACTION (rWGS)**

A project report

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DECLARATION

I hereby declare that this thesis submission is my own and that, to the best of my knowledge and belief, it contains no material previously published or written by another person which has been accepted for the award of any other Degree or Diploma of the University or other Institute of Higher learning, except where due acknowledgement has been made in the text.

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CERTIFICATE

This is to certify that the thesis titled “**CATALYTIC HYDROGENATION OF CARBON DIOXIDE BY REVERSE WATER GAS SHIFT REACTION (rWGS)**” submitted by **PRANSHU SUNIL SHENDE (R670215012)**, to the University of Petroleum & Energy Studies, for the award of the degree of **MASTER OF TECHNOLOGY** in Chemical Engineering with specialization in Process Design Engineering is a bonafide record of project work carried out by him under our supervision and guidance. The content of the thesis, in full or parts have not been submitted to any other Institute or University for the award of any other degree or diploma.

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ABSTRACT

The growing concentration of CO₂ in the atmosphere had increased the impact on the environment such as global warming and forcing a climate change. An innovative utilization technologies are greatly needed to reduce the CO₂ released into the atmosphere. But, due to its thermodynamic and kinetic stability, CO₂ is not used to fullest potential by utilization route. For any fruitful utilization of CO₂ to high value and high volume useful chemicals, it is required to develop syngas platform from CO₂. Therefore, catalytic hydrogenation of CO₂ to syngas by reverse water gas shift (rWGS) reaction could be a promising route. Being rWGS a reversible reaction, catalysts active in the water gas shift (WGS) reaction are often active in the reverse reaction. In this work, four catalysts were evaluated at different temperatures (450-650 °C) at a constant CO₂/H₂ ratio (1:3 vol%) and space velocity (50 ml/g_{cat}.min). Among these four catalysts, three catalysts were prepared *in-house* using Fe (III) as an active phase supported on commercial γ -alumina. With an objective to improve catalytic hydrogenation of CO₂, few other components *e.g.* Co-, Ni- phases were incorporated with Fe/Al₂O₃ catalyst in order to assess effects of dopants. All these catalysts were prepared using co-impregnation method. The physico-chemical characterization *e.g.* BET surface area, pore volume, average particle size, X-ray diffraction (XRD), thermo-gravimetric analysis (TGA), coke content, etc. were also performed to evaluate the catalysts properties and correlate with the catalytic activity. Textural properties of the catalysts suggested effective utilization of specific surface area and pore volume, which are predominant for catalytic activity. XRD analysis indicated homogeneous dispersion of Co and Ni with Fe₂O₃ phase on γ -Al₂O₃ support. ICP-OES results also indicated almost complete dispersion of the active components on the support material. Each set of the catalyst were tested under atmospheric pressure and temperature ranging from 450-650 °C in a fixed bed reactor. In comparison with Co-doped Fe/Al₂O₃ catalyst, Ni-doped catalyst showed slight less CO₂ conversion as well as CO yield at 450-550 °C. Possibly, Ni-doped Fe-based catalysts would require higher temperature for higher yield of CO. The rWGS reaction with Co-doped Fe/Al₂O₃ at 550 °C confirms CO₂ conversion and CO yield 53.3% and 42.6% respectively. The CO yield for all catalysts is approx. 79% of the equilibrium CO yield. The methane formation in rWGS reaction was limited to less than 0.1 mol%. Nevertheless, further improvements can be made to increase the yield of CO at lower temperature.

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LIST OF ABBREVIATIONS

BET – Brunauer Emmett Teller
CCS – Carbon Capture and Storage Technologies
DR – Dry Reforming
FTS – Fischer Tropsch Synthesis
GHG – Greenhouse Gas
GHSV – Gas Hourly Space Velocity
HTS-WGS – High Temperature Shift Water Gas Shift
ICP – Inductively Coupled Plasma
MFC – Mass Flow Controller
OES - Optical Emission Spectrometer
PESR – Pre-Experimental Safety Review
rWGS – Reverse Water Gas Shift
SR – Sabatier Reaction
TGA – Thermo gravimetric analysis
TOS – Time on Stream
WGS – Water Gas Shift
XRD – X-Ray Diffraction

CHAPTER 1

1.0 Introduction

The most important greenhouse gas (GHG) emitted into the atmosphere from fossil fuel combustion and other anthropogenic activities are carbon dioxide (CO₂). With increase in the concentration of CO₂ in the atmosphere, the impact on environment also increased. The growing concentration of CO₂ in the atmosphere increased the impact on the environment such as global warming and forcing a climate change. With regard to the last 40 years, CO₂ emissions per year doubled from 16 Gt in 1973 to 32 Gt in 2012, which is expected to grow to 40.3 Gt by 2030 and to 50 Gt by 2050 in the absence of restraining actions [IEA, 2014]. There is a clear mismatch in the scales for CO₂-based chemical production process (urea, derived from CO₂ and NH₃, had a world production of 0.15 Gt in 2008). Recently various carbon capture and storage technologies (CCS) are developed for a significant reduction of CO₂ emissions into the atmosphere. An efficient CO₂ capture and conversion not only mitigates the risks associated with increasing CO₂ concentration in the atmosphere, but also addresses the problem of fossil fuel depletion by providing sustainable production of industrial demanded fuels and chemicals [Song et al., 2006, Aresta et al, 1997]. Transformation of recycled carbon contained in CO₂ into industrially valuable chemicals & fuels has a more promising outlook.

1.1 Options for converting CO₂ *via* hydrogenation

The potential utilization of CO₂, captured at power plants or refineries, should be taken into consideration for sustainability. This CO₂ source, which is potentially a raw material for the chemical industry, will be available at sufficient quality and at gigantic quantity upon realization of on-going tangible capture projects. But, CO₂ is not used to fullest potential by utilization route due to its high thermodynamic and kinetic stability. However, innovative utilization technologies are desperately needed to reduce the CO₂ released into the atmosphere. The two main types of routes for reusing CO₂ to produce commercially valuable products are:

- (i) those reactions incorporating the whole CO₂ moiety in organic or inorganic backbones:- not energy intensive and sometimes may occur spontaneously with low kinetics like in the production of inorganic carbonates;
- (ii) those involve the cleavage of one or more of the C-O bonds:- energy intensive reactions of C-O cleavage require the use of reducing agents (H sources, *e.g.* H₂)

An overview of the different possibilities and routes to convert CO₂ with introduction to renewable energy in the energy and chemical production chains and to monetize CO₂ as a valuable source of carbon are shown in Figure 1.1. In order to chemically reduce the thermodynamically stable CO₂ to low-molecular-weight organic chemicals it requires high chemical-potential reducing agents such as H₂, CH₄, electrons. The biggest share of the energy cost which accounts for reducing agents production and related carbon footprints of carbon dioxide production.

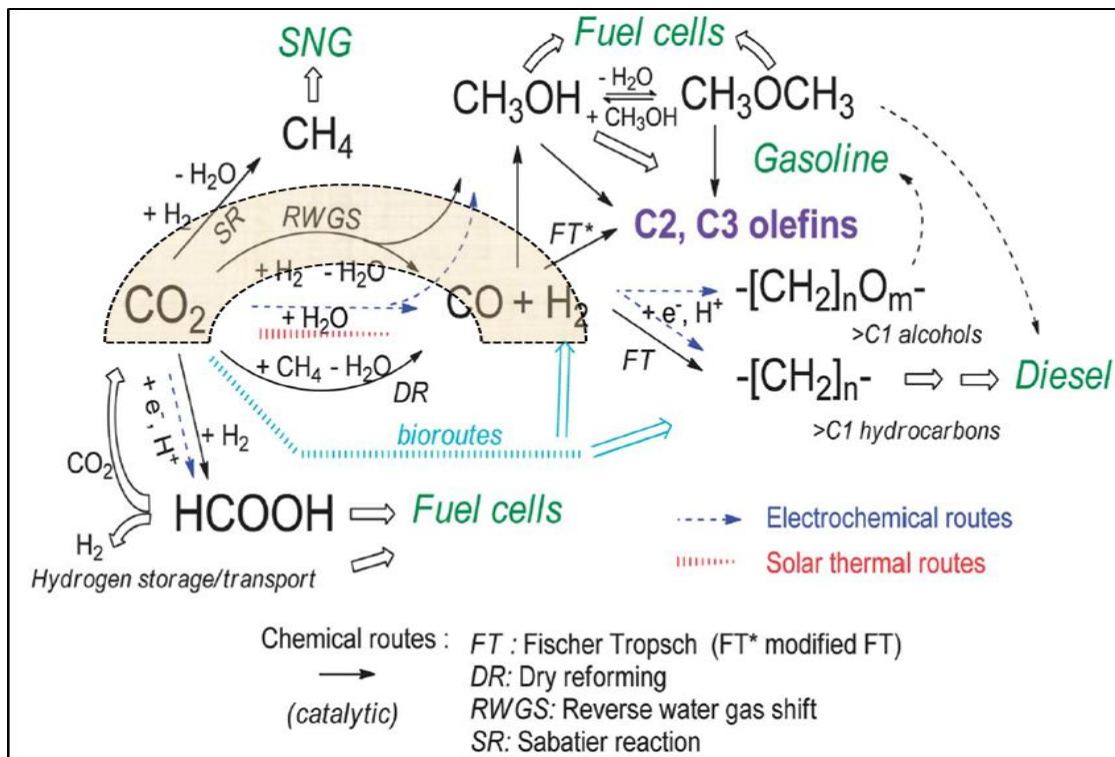


Figure 1.1. Process routes for CO₂ to chemistry and energy products *via* syngas [Centi et al., 2013]

The renewable energy is used either directly (in the solar thermal production of syngas) or indirectly, according to two main possibilities: (i) production of renewable H₂ or (ii) production of electron, or electron/protons (by water photo-oxidation), used in the electrochemical routes [Najafabadi et al., 2013]. The Figure 1.2 elucidates a generic energy cycle of the aforesaid CO₂ chemical conversion. It shows the usage of sustainable electricity derived from renewable resources for water electrolysis, producing hydrogen for fuel synthesis *via* FTS (Fischer-Tropsch Synthesis). The advantages of this ideal ‘carbon-neutral’ fossil-fuel-based energy cycles are enlisted below to achieve:

- (i) liquid fuels with high energy densities well-suited for the industrial applications;
- (ii) the clean fuels with no sulfur as a hazardous environmental pollutant;
- (iii) competitive candidate like methanol as the simplest carbonaceous fuel for both fuel-cell and combustion based power systems.

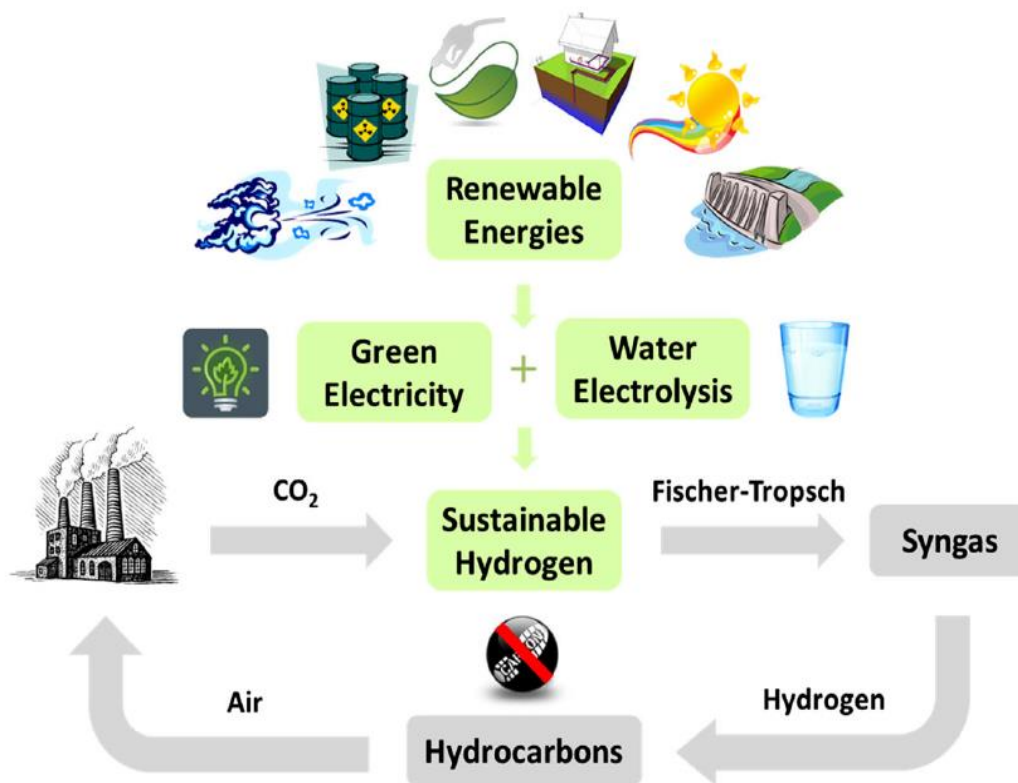


Figure 1.2. Ideal carbon-neutral energy cycle with CO₂ technologies for production of renewable carbonaceous fuel [Najafabadi et al., 2013]

Utilizing renewable energy sources as a means to produce fuels and chemicals is promising as the intermittent energy sources can be converted to stable chemical energy, which can be

transported and used as demanded [Hu et al., 2013, Sa et al., 2014]. The syngas platform which is chemically synthesized mainly focus on the conversion of CO₂ into syngas by reverse water gas shift reaction (rWGS). Here aliphatic acids, hydrocarbons and methanol mainly emerges as the main product. In addition to process route for CO₂ conversion as mentioned in Figure 1.1, CO₂ is also used in the synthesis of several organic compounds, as shown in Figure 1.3. Further, CO₂ conversions to those chemicals wherein, it incorporates CO₂ are:

- (i) organic products, typically used for the fine or specialty chemicals sector;
- (ii) monomers for polymerization.

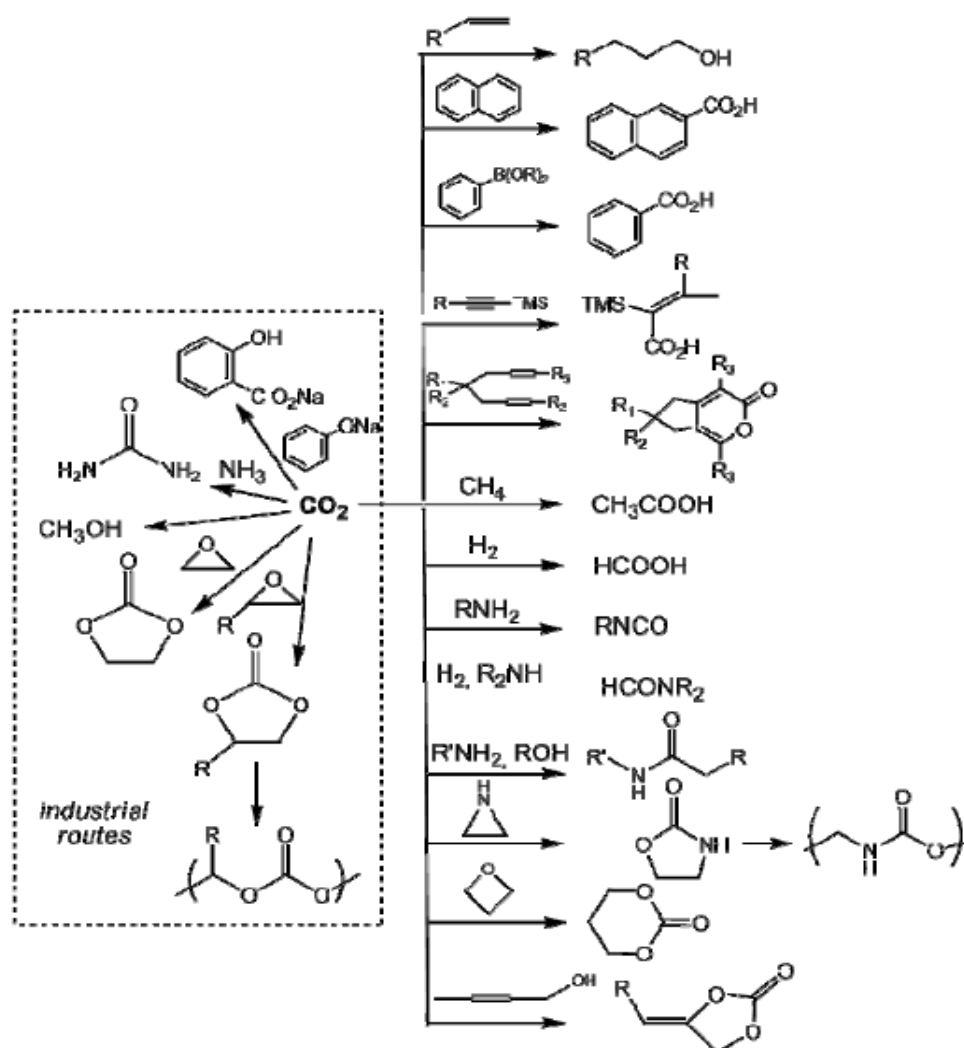


Figure 1.3. Summary of organic chemicals produced from CO₂ [Quadrelli et al., 2011]

In both cases, there is no positive contribution to GHG by considering the full life-cycle assessment based on a pure energetic balance, but process may sound to be attractive in terms of product characteristics, or in terms of advantages in terms of synthesis procedure. In both cases, differently to the routes shown in Figure 1.1, the “CO₂ value” (which may be derived, for example, from avoiding the cost of its disposal) has a minor impact on the overall cost dynamics.

1.2 CO₂ activation: An urgent need for CO₂ conversion chemistry

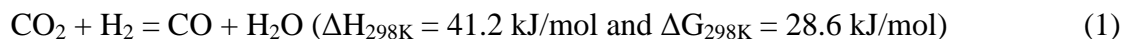
We can also consider CO₂ as a carbon source rather than just a greenhouse gas that needs to be mitigated. It is available as free or even with a financial return if adequate technology is applied for CO₂ capture and recycling. But we must also bear in mind that thermodynamically, water and CO₂ are the stable final product obtained from combustion of hydrocarbon fuels. Often, this stability is commonly misconstrued as if CO₂ is “unreactive” suggesting that any chemical conversion of it will essentially require high energy input. Therefore, it is often believed that the use of CO₂ for chemicals manufacture is not suitable. There are quite a few reactions of CO₂ for which there is no need for any external energy because the co-reactant itself can supply enough energy to facilitate conversion at ordinary temperatures. The reactions of CO₂ with hydroxides, amines or olefins fall into this category. On the other hand, those reactions which requires activation and splitting of CO₂ to convert to valuable chemicals requires considerable amount of external energy. It is well known that CO₂ is classified as a stable, almost inert molecule. It is necessary to overcome its considerable Gibbs energy of formation: $G^{\circ}_{298.15K} = -394.4$ kJ/mol to activate CO₂ [Suib et al., 2013]. Nevertheless, CO₂ use is thermodynamically possible *via* numerous reactions involving its reduction or its incorporation into other compounds. The reduction of CO₂ by the cleavage of the C=O bond(s) and the formation of new C-H or C-C bond(s) can be accomplished using a reductant. The action of an appropriate catalyst can convert CO₂ into a potential energy vector with remarkable surface chemistry of CO₂ through intelligent design of innovative catalytic techniques. On the other hand, the recycling pathway requires a large input of energy and usually H₂ as the reductant, and lead to fuels such as methane and methanol. In this context, two aspects must be taken into account: the production of H₂ and the energy source. If the energy comes from renewable sources and the H₂ does not come from fossil fuels, an extensive merit evaluation of the overall process invites further probe.

1.3 Reverse water gas shift reaction (rWGS)

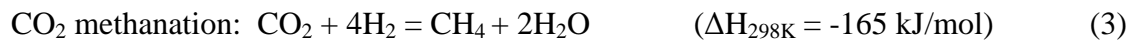
The conversion of CO₂ to syngas by catalytic hydrogenation has been recognized as a very promising process which is capable of large scale industrialization. Since the mid 1800's the rWGS has been known to chemistry, but no experimental work was done to reveal its viability. The WGS equilibrium can be pushed to reverse direction to achieve rWGS reaction. The rWGS technology is a simple and effective way to utilize CO₂ in many industries. The CO₂ hydrogenation reaction has been proposed for use with carbon capture technologies for the production of industrially viable chemicals, such as long chain hydrocarbons, methanol, formic acid, and carbon monoxide [Wang et al., 2011, Vibhatavata et al., 2013]. When CO is selectively formed *via* rWGS reaction and then mixed with excess H₂ in the reaction, the resulting syngas (CO+H₂) is potential feed-stock for the FTS liquid fuels production like gasoline, dimethyl ether etc. The higher feed ratio of CO₂/H₂ (= 2) favors the formation of syngas that can be used for oxygenates production. At elevated temperature (300–400 °C) and atmospheric pressure, CO₂ reacts with H₂ to produces methane and water by Sabatier reaction (SR).

In recent years, various research groups had focused on CO₂ to be the direct source of methanol production but limited yield was major drawback [Edwards et al., 1995, Kharaji et al., 2012]. The CAMERE process has the basis of rWGS reaction which is developed by the Korea Institute of Science and Technology (KIST) and operated by Korea Gas Corporation (KOGAS) and Korean Institute of Energy and Research (KIER). CAMERE process makes use of zinc aluminate and Cu/Zn/Al₂O₃-based catalysts in a two-step process: (i) rWGS, and (ii) CH₃OH synthesis after intermediate H₂O removal. Hence, rWGS reaction (CO₂ + H₂ → CO + H₂O) is an important option create CO / syngas platform and hence, for derived useful chemicals [Joo et al., 1999].

Since the mid 1800's, the rWGS has been known to chemistry, but no experimental work was done to reveal its viability. The WGS equilibrium can be pushed to reverse direction to achieve rWGS reaction. When co-feeding CO₂ and H₂ over a hydrogenation catalyst, there are two main hydrogenation processes that can take place, the reverse water gas shift reaction:



Along with it side reactions are given as:



When CO is selectively formed *via* eq. 1 and mixed with H₂, the resulting syngas can be a feed-stock for the FTS that produces liquid fuels. In contrast, CH₄ formed *via* eq. 2 or 3 is an undesirable by-product that is not convertible to liquid fuels in a FTS. The rWGS reaction has some advantages, including low hydrogen consumption, a high equilibrium conversion rate and, the CO product formed can be utilized for production of major chemical feedstocks. Usually high operating temperatures are required for the endothermic rWGS reaction without considering the end product and undoubtedly require the use of a catalyst. Hence, the development of an efficient catalyst capable of withstanding high temperatures and selective to CO during the rWGS reaction is a necessity if the process is to be used industrially. The process requires standard equipment already available at most processing plants creating a good opportunity to industrialize the hydrogenation of CO₂ through the rWGS reaction.

1.4 Economic status of rWGS

The hydrogenation of CO₂ is an alternative to existing technology like gasification, dry reforming, tri-reforming etc for production of CO/syngas. The rWGS process requires hydrogen and high temperature for hydrogenating CO₂. Currently, hydrogen production is mainly accomplished *via* the steam reforming of methane that is the reverse of the reaction in eq. 3, the entire basis of using the rWGS reaction becomes ineffective when using steam reforming, because the production of CO₂ during this reaction is the opposite of the desired rWGS reaction. In addition, the process uses hydrocarbons and heat. Instead, H₂ should be derived from alternate reaction pathways. The use of biomass, biogas, cyanobacteria and green-algae are all being researched with minimal productivity or efficiency. Using nuclear power or renewable energy like solar or wind power on the other hand, could be a profitable venture. This would be accomplished *via* the electrolysis of water. Electrolyzing water using both solar and wind energy is a topic already being thoroughly researched. Limitations are caused by high over-potential required for the process as well as low overall efficiencies of solar and wind power. Further research in this domain is needed for the rWGS & FTS to become a useful and economical alternative to other energy sources. To analyze the

economic potential of rWGS with reference to hydrogen cost, the Table 1.1 gives economic snapshots.

Table 1.1. Cost of production for CO by rWGS with 60% CO₂ conversion

Particulars	UoM	Norm per ton	Price (\$/ton)	Cost of CO (\$/ton)
Input				
CO ₂	ton	2.756 (based on 60% CO ₂ conv.)	10	27.56
H ₂	ton	0.0714	1200	85.68
Output				
CO	ton			
Conversion cost				25
Feedstock cost				~140

The feedstock cost for CO synthesis by rWGS study was found to be 103 \$/ton. The cost of production specifically depends primarily on hydrogen cost.

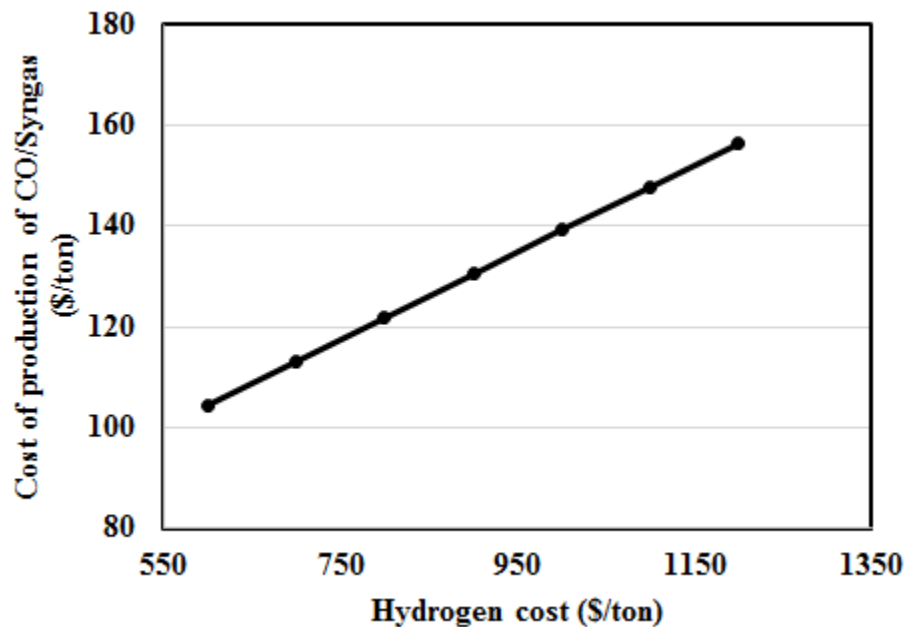


Figure 1.4. Variation of production cost of CO/Syngas with hydrogen price

The typical cost of hydrogen varied from \$ 900-1200/ ton which greatly influence the CO/syngas cost of production. The rWGS economics could become favorable when hydrogen is derived from renewable source, but at very low cost. The Figure 1.4 shows impact of hydrogen price on cost of production for CO/syngas. Anyway the cost comparison needs to be done for all syngas production process like gasification, dry reforming etc. to extract appropriate scenario on rWGS efficacy.

1.5 Reaction kinetics and thermodynamics

As mentioned in section 1.3, CO₂ is a highly stable molecule and therefore, its chemical transformation requires significant amount of input energy (high temperature), effective reaction conditions, and very active catalysts [Song et al., 2002]. The chemical reactions for conversion of CO₂ involve positive change in enthalpy, and thus they are endothermic. It is well known that chemical reactions are driven by the difference in Gibb's free energy between the products and reactants as given by eq 4 given below:

$$\Delta_R G^0 = \Delta H^0 - T \Delta S^0 \quad (4)$$

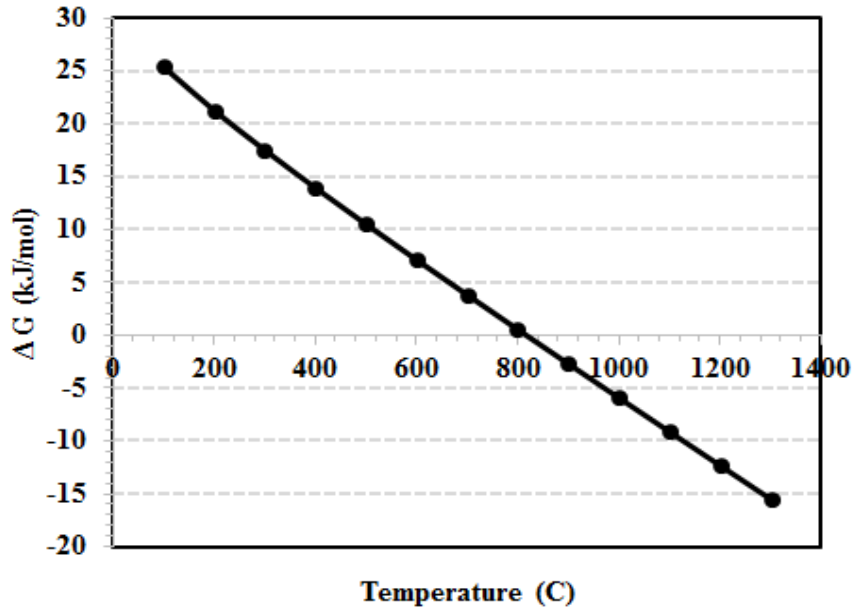
Where $\Delta_R G^0$ is the change in Gibb's free energy (at 1 bar), ΔH^0 is the change in enthalpy, T is the absolute temperature in K, and ΔS^0 is the change in entropy. Being endothermic reaction, rWGS is always thermodynamically favorable at higher temperatures. The Gibb's free energy of CO₂ hydrogenation reaction as a function of temperature is given as:

$$\Delta_R G^0 = 32.197 - 0.03104T(K) + \frac{1774.7}{T(K)}, kJ/mol \quad (5)$$

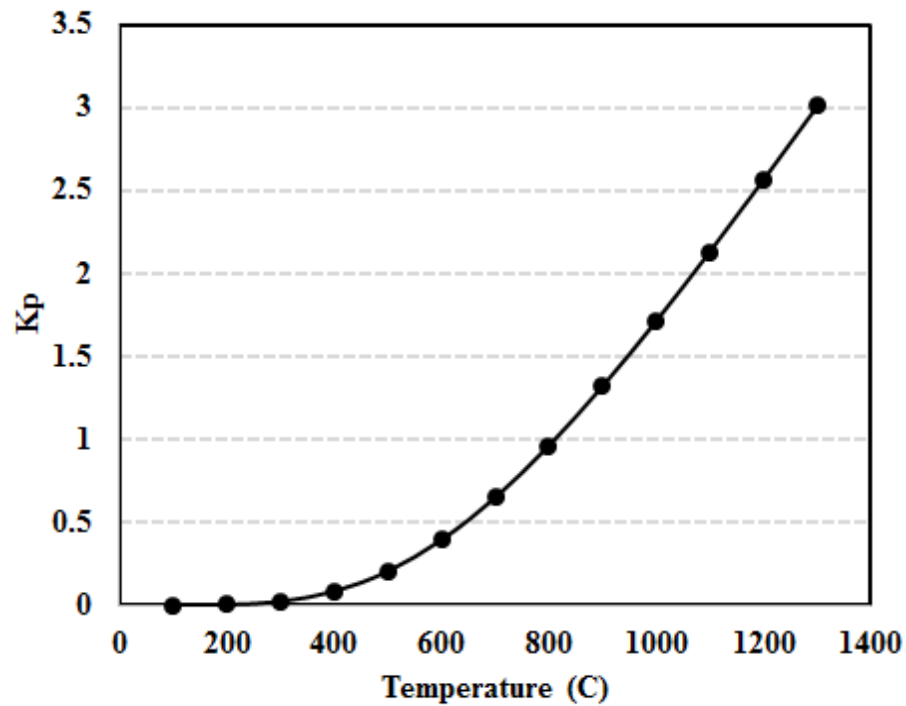
Similarly, the equilibrium constant K_p is defined in terms of the equilibrium partial pressures or concentrations of the reactants and products as given below

$$K_P = \left(\frac{P_{CO} P_{H_2O}}{P_{CO_2} P_{H_2}} \right)_{eq} = \left(\frac{C_{CO} C_{H_2O}}{C_{CO_2} C_{H_2}} \right)_{eq} = \exp \left[\frac{\Delta_R G^0}{RT} \right] \quad (6)$$

The equilibrium conversion of CO₂ may be calculated from the equilibrium constant K_p as a function of temperature. The Gibb's free energy and equilibrium constant of CO₂ hydrogenation reaction as a function of temperature are shown Figure 1.5.



(a)



(b)

Figure 1.5a-b. Thermodynamic equilibrium of CO_2 hydrogenation described by change in (a) Gibbs free energy, (b) Equilibrium constant of the reaction as a function of temperature

$$(y_{\text{CO}_2} = y_{\text{H}_2}, y_{\text{CO}} = y_{\text{H}_2\text{O}} = 0)$$

The Gibb's free energy changes from positive to negative above 800 °C and the equilibrium constant of the reaction increases with increase in temperature. It implies that the reaction is only feasible at higher temperatures. It is important to note that complete conversion of CO₂ to CO can't be achieved even at high temperature (~1000 °C). The calculated equilibrium conversions for the rWGS reaction without methanation and with methanation reaction are shown in Figure 1.6. The rWGS reaction with methanation behaves differently than without methanation and the equilibrium CO₂ conversion decreases with increasing temperature in the low temperature range where methane formation is favored thermodynamically. At higher temperatures, methanation reaction is totally suppressed thermodynamically and the normal rWGS reaction proceeds.

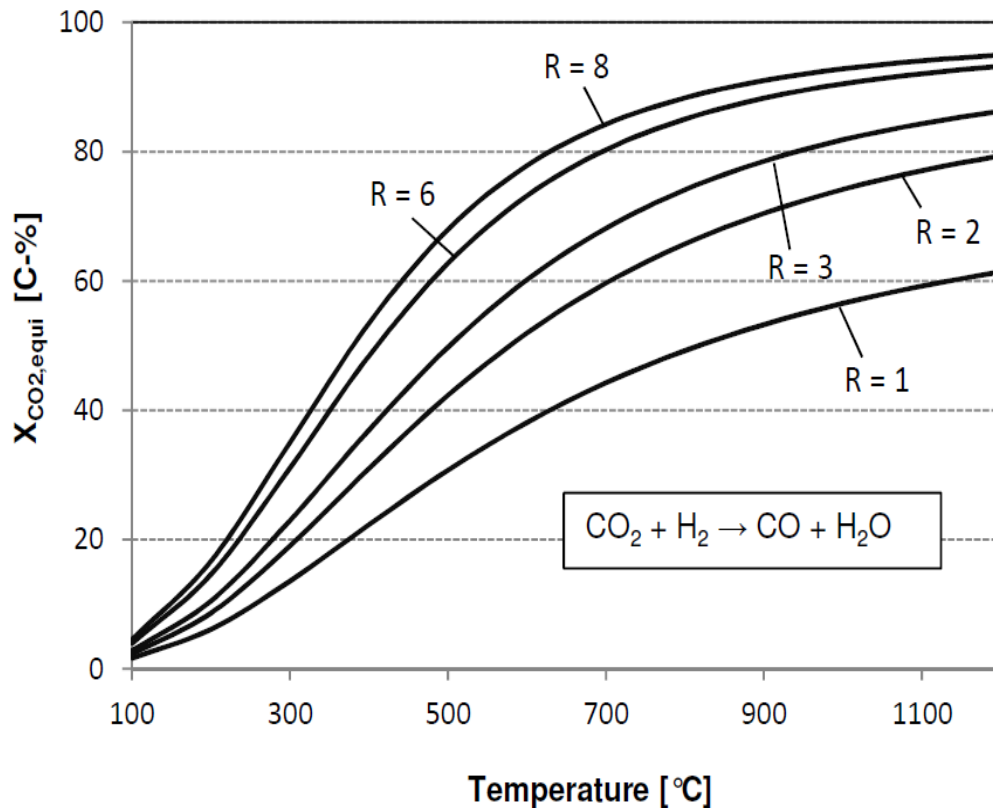


Figure 1.6. Equilibrium conversions of CO₂ hydrogenation with different inlet H₂/CO₂ ratios in rWGS without methanation. (p = 1 atm, R = H₂/CO₂ ratio) [Bajirao et al., 2012]

We know that liquid fuels can be produced from CO₂ by FTS route. At higher temperatures, CO₂ hydrogenation can only produce CO and H₂O as a product. The outlet gas composition

after removal of H₂O from syngas containing small amounts of CO₂ can be further used for the production of fuels *via* FTS. The equilibrium composition of syngas is shown in Figure 1.7. For temperature above 750 °C, atmospheric pressure, and H₂/CO₂ inlet ratio of 2, the CO₂ hydrogenation can give the required ratio of syngas for the production of fuel.

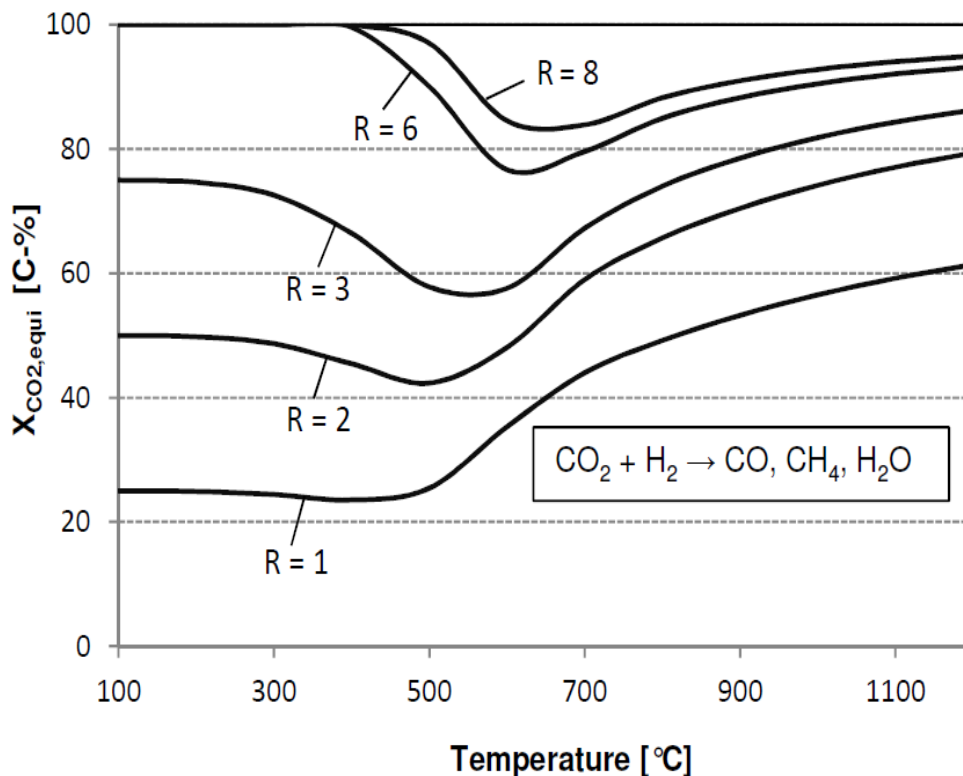


Figure 1.7. Equilibrium composition of syngas after removal of water over temperature in CO₂ hydrogenation reaction with methanation. (p = 1 atm, H₂/CO₂ = 2) [Bajirao et al., 2012]

1.6 Scope and Objectives

As mentioned in the previous section, rWGS is the first step to create syngas platform for further conversion to liquid fuels by FTS. The hydrogenation of CO₂ and H₂ depends upon (i) catalyst selection, (ii) ratio of CO₂/H₂, and (iii) reaction temperature and pressure. Hence, the main motivation of this work was to use an appropriate catalyst and to determine the optimal reaction conditions for CO₂ hydrogenation in a fixed bed reactor.

The experiments were designed such that the rWGS reaction could be examined for Fe-based catalyst in a lab scale fixed bed reactor. In addition to these experiments, the consecutive reaction of CO/CO₂ to methane was also considered. Most available literature reported low

temperature catalytic hydrogenation of CO₂ wherein methane is the byproduct. In this work CO₂ hydrogenation is studied at high temperatures where the rWGS is favored thermodynamically and produces CO and H₂O as main products. The comparative investigations of catalytic activity for alumina supported Fe-based catalyst doped with Ni, Co were carried out. The activity of *in house* catalysts is compared with commercial Fe-based catalyst.

In short, the objective of the work can be summarized as to develop highly stable catalytic system for catalytic hydrogenation of CO₂ by rWGS process that will operate at 450-650 °C to achieve maximum CO₂ conversion and CO yield with minimal or no formation of methane.

The scope of the work was limited to see the efficacy of high temperature WGS catalyst for rWGS and development, characterization and evaluation of Fe-based catalyst doped with Ni and Co and testing at intermediate temperature (450-650 °C) in fixed bed reactor.

The thesis is separated into 4 more chapters. Chapter 2 provides a detailed literature review pertinent to the research conducted during the Master's project. Chapter 3 discusses the methodology comprising of synthesis of the Fe-based catalysts, characterization tools and catalysts evaluation in fixed bed reactor. Chapter 4 further compares evaluation results of *in house* Fe-based catalyst with and without dopant with commercial Fe-based catalyst. Lastly, Chapter 5 summarizes the major findings brought forth in this thesis as well as further suggestions for prospective researchers.

CHAPTER 2

Literature Review

2.0 Introduction

For the separate utilization of the rWGS in processes wherein it first requires reduction of CO₂ to CO, active catalysts for the WGS reaction are generally used. Transition metals (e.g. Cu, Ni, Fe, Co) supported on different metal oxides (e.g. γ -Al₂O₃, CeO₂, SiO₂) have been explored to carry out rWGS reaction [Pekridis et al., 2007]. Few catalytic systems are explained in the below sub-sections.

2.1 Ni-based catalyst

The research work was concentrated on Ni-based catalyst that showed an appropriate performance in catalyzing the rWGS. Currently for CO₂ hydrogenation, Ni-based catalysts are prominently studied because of its high activity and comparatively low cost. Using Ni-based catalyst at low temperature for the CO₂ hydrogenation principally produces CH₄ as a main product. Weatherbee and Bartholomew reported that at temperature between 227 to 327 °C, the activation energy shifts from 89 to 39 kJ/mol when CO₂ hydrogenation carried over Ni/SiO₂ catalyst [Weatherbee et al., 1982]. Aksoylu and IlsenÖnsan studied Ni/Al₂O₃ co-precipitated catalyst and found out that the specific activity of Ni/Al₂O₃ decreases as the metal loading increases whereas, for an impregnated catalyst the activity increases with metal loading [Aksoylu et al., 1997].

Perkas et al investigated Ni supported on ZrO₂ and concluded that the specific activity (related to Ni only) increases with metal loading up to 30% and further decreases [Perkas et al., 2009]. Wang et al and Luhui et al studied Ni supported on CeO₂ that exhibits excellent catalytic activity, selectivity, and stability for the rWGS reaction [Wang et al., 2008, Luhui et al., 2008]. The oxygen vacancies formed in ceria lattice and highly dispersed Ni were reported as key active components for rWGS, and bulk Ni was responsible for methanation of CO₂. At the higher content of Ni, it usually exists as a bulk NiO and promotes CH₄ formation. Suzuki et al concluded that CO₂ conversion at 600 °C and atmospheric pressure with H₂/CO₂ ratio of 1 and higher space velocity of 2 l/g_{cat}/min with 2 wt% Ni/CeO₂ catalyst

reported 35% and 100% CO selectivity. Considering other reverse water gas shift reaction catalyst like 10 wt% NiO/ZnO it shows activity even higher (CO₂ conversion of 38% and CO selectivity of 98%) [Suzuki et al., 1995].

Wolf et al investigated Ni-based catalyst supported on Al₂O₃ at 600-1000 °C and atmospheric pressure and achieved 78% CO₂ conversion at 950 °C. It is also reported that at lower temperature (~700 °C), catalyst deactivation was primarily due to the formation of carbon [Wolf et al., 2016]. Sun et al. studied Ni/Ce–Zr–O catalyst for rWGS and achieved stable conversion of 49.66% at 550–750 °C with equimolar ratio of H₂ and CO₂. It was also found that increasing Ni loading leads to lower CO₂ conversion [Sun et al., 2015]. Liu et al investigated Ni-CeO₂ catalyst at 600 °C and atmospheric pressure at equimolar H₂ to CO₂ ratio and achieved CO₂ conversion of 36%. This performance is mainly due to the lack of exposed NiO on the surface, and also in the uniform meso-porous structure where large amount of O₂ vacancies are present [Liu et al., 2016].

The addition of Ni as promoter to base catalyst was also studied by many researchers to enhance the CO₂ conversion and CO selectivity. The stability of the Ni–Mo/Al₂O₃ catalyst was investigated by Kharaji and Shairati, at 600 °C and GHSV of 30,000 (ml/h·g_{cat}) at equimolar ratio of H₂ and CO₂. The CO₂ conversion, CO yield, and the methane formation were reported as 38%, 34% and 6% respectively at TOS of 60 hrs. The electron deficient state of the Ni species and existence of NiMoO₄ phase showed high activity for rWGS [Kharaji et al., 2012]. Lu et al reported newer catalytic system (bimetallic oxides/SBA-15 catalysts) that works well at 400–900 °C and atmospheric pressure. At temperature range between 600-900 °C and NiO–CeO₂/SBA-15, the CO₂ conversion was found to be in the range of 35-55% whereas the CO selectivity was 100% at high temperature [Lu et al., 2015].

Table 2.1. Summary of prominent Ni-based catalyst for rWGS reaction

Authors {References}	Temp, Press and GHSV (ml/h. g _{cat})	Catalyst	Performance Parameters	Inference

Wolf et al. [Wolf et al., 2016]	600–1000 °C, 1 atm.	Ni/Al ₂ O ₃	CO ₂ conversion= 78% (at 950 °C), 64% (at 800 °C), 58% (at 700 °C)	Stable catalyst at ~900 °C. Carbon formation at lower temp leads to catalyst deactivation.
Luhui et al. [Luhui et al., 2008]	400–750 °C, 1 atm, 120,000 ml/hr gm cat	Ni-CeO ₂	CO yield: 35% (at 600 °C) for CO ₂ /H ₂ = 1.0 for TOS = 9 hrs. CO yield: 45% (at 750 °C) and CH ₄ yield is < 1%	Main active sites are oxygen vacancies in ceria lattice and highly dispersed Ni. At high Ni-content (≥5wt %), it exists mainly as bulk NiO, that leads to high CH ₄ yield.
Sun et al. [Sun et al., 2015]	550 – 750 °C, 1 atm, H ₂ / CO ₂ = 1:1	Ni/Ce-Zr-O	For 3 wt% Ni/Ce-Zr-O: CO ₂ conv = 49.66% and CO selectivity = 93% at 750 °C	Ni/Ce-Zr-O catalyst is stable for 80 hrs. CO ₂ conversion decreases with the increasing Ni loading.
Kharaji et al. [Kharaji et al., 2012]	600 °C, 10 atm, 30,000 ml/h·gcat	Ni–Mo /Al ₂ O ₃	CO ₂ conversion = 38%, at TOS = 60 hrs; CO yield = 34%	Electron deficient state of the Ni species and existence of NiMoO ₄ phase showed high activity for rWGS. No yield data for CH ₄ is given.
Lu et al. [Lu et al. 2015]	400-900 °C, 1 atm	NiO/SBA-15, CuO–NiO/SBA-15, CuO–CeO ₂ / SBA-15, and NiO–CeO ₂ / SBA-15	At 600-900 °C: NiO–CeO ₂ / SBA-15 gives CO ₂ conversion = 35-55%. CO selectivity = 100% at high temp	Bimetallic oxides /SBA-15 catalysts result in the high CO ₂ conversion to CO at low temp due to the presence of the strong interaction between metal (active center) and oxides (promoter).
Liu et al. [Liu et al., 2016]	600 °C, 1 atm, 120,000 /hr, H ₂ /CO ₂ = 1:1	Ni-CeO ₂	Stable CO ₂ conversion = 36% at TOS = 16 hrs	Excellent performance due to lack of exposed NiO on the surface, and the large amount of O ₂ vacancies in the uniform meso-porous structure.

2.2 Fe- and Co-based catalyst

Lee et al and Cubeiro et al studied CO₂ hydrogenation on Fe/Al₂O₃ catalyst and reported 49% CO₂ conversion and selectivity of about 12.4% and 87.6% towards CO and hydrocarbons respectively at 400 °C (2 MPa, space velocity of 31.67 ml/g_{cat}/min) [Choi et al., 1996, Cubeiro et al., 1999]. However, remarkable increase in the catalyst activity and selectivity towards C₂₊ – hydrocarbons was reported on addition of potassium to Fe. But, when molar ratio of K/Fe is increased to 1, the catalyst showed small decrease in activity and hydrocarbon selectivity while the selectivity to CO slightly increased. The addition of alumina itself acts as a promoter for the catalyst Fe-Cu-K/Al₂O₃ is reported by Yan et al [Yan et al., 2000]. Hwang et al demonstrated significant decrease in CO₂ conversion and selectivity to hydrocarbons in long term stability test for Fe-K/Al₂O₃ catalyst [Hwang et al., 2001], wherein the deactivation was attributed mainly due to the carbonaceous deposition on the catalyst surface. A similar behavior was reported by Hong et al for Fe-Cu-K/Al₂O₃ catalyst due the growth of crystallites and hence, decreases in dispersion of catalyst components (promoters) [Hong et al., 2001]. Most of researchers studied binders on the Fe-based catalyst to improve the catalyst strength. The excellent activity and selectivity towards higher hydrocarbons (C₅₊) was observed by the addition of an alumina binder to a Fe-K based catalyst, whereas with silica binder the activity and selectivity dramatically decreased. The reason for this influence found by Lee et al on the activity and selectivity is based on the change in acidity of catalyst, structure and metal-support interaction [Lee et al., 2003]. The catalyst becomes more active and selective towards long chain hydrocarbons and light olefins with strong metal-support interaction between Fe-K/ β -Al₂O₃ as reported by Jun et al [Jun et al., 1998].

The CO₂ hydrogenation was also studied over Co based FTS catalyst. Zhang et al investigated Co/SiO₂ catalyst and reported more than 70% of methane at 210 °C (2.4 MPa, H₂/CO₂ ratio of 4, space velocity of 83.3 ml/g_{cat}/min) and slowly deactivated over time. Osaki et al compared CO₂ hydrogenation on Fe, Co, and Ni catalyst using Al₂O₃ as structural support and showed highest activity over Co/Al₂O₃ catalyst. The selectivity order for CO was in the order of Fe/Al₂O₃ > Co/Al₂O₃ > Ni/Al₂O₃ [Osaki et al., 1997]. Kharaji and Shariati studied Fe doped Mo/Al₂O₃ catalyst for rWGS chemistry [Kharaji et al., 2016]. When the operating condition of 600 °C & GHSV= 80,000 (ml/h·g) with equimolar ratio H₂ and CO₂

under atmospheric pressure, the CO₂ conversion achieved was 22% at TOS = 60 hrs. The performance of the two bimetallic catalysts based Fe-Mo and Co-Mo supported on Al₂O₃ were compared. The existence of Fe₂(MoO₄)₃ phase in the Fe-Mo/Al₂O₃ catalyst was responsible for its stability. At all the temperature level, Co-Mo catalyst showed higher CO₂ conversion. The Fe-Mo/Al₂O₃ catalyst exhibits good stability and Co-Mo/Al₂O₃ gradually deactivated after 50 h of reaction time. The probe on structure of catalytically active surface i.e. metallic Fe for its long-term stability was studied by Kim et al [Kim et al., 2015]. At 600 °C and atmosphere, GHSV = 80,000 ml/hr gm and equimolar ratio of H₂ and CO₂, the CO₂ conversion of 35% further decreases to 31% within first 60 min for unsupported Fe-oxide nanoparticle. The long-term stability test at 600 °C, GHSV = 600,000 mL/(g h) was investigated for Co-CeO₂ catalyst by Luhui et al [Wang et al., 2016]. The Co-CeO₂ catalysts with different Co- contents prepared by co-precipitation method showed excellent rWGS catalytic performance in terms of activity, selectivity and low carbon deposition. High Co loading (≥ 5%) leads to larger size bulk Co₃O₄ that increased carbon-deposition and by-product methane formation. Highly dispersed Co reduced from highly dispersed Co₃O₄ on CeO₂ are the key component for rWGS reaction.

Table 2.2. Summary of prominent Fe-, Co-based catalyst for rWGS reaction

Authors [Reference]	Temp, Press and GHSV (ml/h. g _{cat})	Catalyst	Performance Parameters	Inference
Kharaji and Shariati [Kharaji et al., 2016]	600 °C, 1 atm, 80,000 ml/hr gm, H ₂ /CO ₂ = 1	Fe-Mo /Al ₂ O ₃	CO ₂ conv= 22% at TOS = 60 hrs	Existence of Fe ₂ (MoO ₄) ₃ phase in the Fe-Mo/Al ₂ O ₃ catalyst makes it more stable. CO yield is not mentioned.
Kim et al [Kim et al., 2015]	600 °C, 1 atm, 80,000 ml/hr gm, H ₂ /CO ₂ = 1	Unsupported Fe-oxide nanoparticles	CO ₂ conv= 31 % at TOS = 38 hrs	Structure of catalytically active surface <i>i.e.</i> metallic Fe, was maintained during rWGS reaction, results in a long-term stability of catalytic activity.

Luhui et al. [Luhui et al., 2016]	600 °C, 1 atm, 600,000 ml/gm hr, H ₂ /CO ₂ = 1	Co-CeO ₂	CO ₂ conv= 20 % at TOS = 60 hrs.	High Co loading leads to larger size bulk Co ₃ O ₄ that increased C- deposition and by-product CH ₄ formation. Highly dispersed Co, which is reduced from highly dispersed Co ₃ O ₄ on CeO ₂ , should be the key active for rWGS.
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2.3 Copper based catalyst

Many attempts were directed toward the Cu-based catalysts for CO₂ conversion to CO by rWGS reaction. Nozaki et al studied rWGS reaction with 12 wt % Cu loaded on Al₂O₃ at temperature of 350 °C, atmospheric pressure with H₂/CO₂ feed ratio of 4 and achieved CO₂ conversion of 28% with 100% CO selectivity [Nozaki et al., 1987]. Bando et al studied 5 wt% Cu supported on alumina catalyst at temperature of 220 °C (H₂/CO₂ feed ratio of 3, space velocity of 100 ml/g_{cat}/min, 3 MPa) produces CO and CH₃OH with the selectivity of about 87% and 7.5% [Bando et al., 1997]. The selectivities for CO and CH₃OH are about 87% and 13% for the same amount of Cu on SiO₂, while on TiO₂ the selectivity for CO and CH₃OH are 92.5% and 4.3% and 2.9% for CH₄. Kitayama et al reported CO selectivity of 97% with small amount of CH₄ (<1.5%), C₂H₄ (<0.5%) and C₂H₆ (<0.4%) at 350 °C, 0.2 bar(g), gas recycle loop having a H₂/CO₂ ratio of 4 for 5 wt% Cu/SiO₂ catalyst [Kitayama et al., 1992]. Dubois et al reported enhancement in the catalytic activity with addition of a small amount of Ni to a Cu catalyst, but it also promotes CH₄ formation. When the 5 wt% Cu/SiO₂ used for rWGS (280 °C, 6 MPa, H₂/CO₂ ratio of 3, space velocity of 50 ml/g_{cat}/min), the selectivity of CO decreases and the methanol selectivity increases to 76% and 24% [Dubois et al., 1992]. Nozaki et al reported CO₂ conversion of 28% and CO selectivity > 99% at temperature of 350 °C (1 atm, H₂/CO₂ = 4 and GHSV = 100 ml/g_{cat}/min) with 12 wt % CuO/Al₂O₃ catalyst [Nozaki et al., 1987]. Joo et al probed ZnO/Al₂O₃ catalyst for rWGS reaction (700 °C, 1 bar, GHSV = 150,000 and H₂/CO₂ ratio of 3) and achieved 30% CO₂ conversion for time on stream = 210 hrs, wherein even at high pressure (5 bar) methane was not formed due to non-reducibility of Zn [Joo et al., 2003].

Further various patents reported rWGS for generation of CO/syngas with an objectivity of synthesizing hydrocarbon, oxygenates etc. on different catalytic systems like oxides of Cr-

based, Zn-Cu-based etc. Mamedov and Jodai studied Cr₂O₃ on Al₂O₃ supports (600 °C, pressure = 0.1 - 5 MPa and H₂/CO₂=1–5) and reported 50-57% CO₂ conversion. The targeted syngas composition with H₂/CO = 1 was achieved with feed gas containing CO₂ and H₂ in molar ratio of 1:2. This type of syngas is the feedstock for producing oxygenates, like dimethyl ether. On the other hand, the targeted syngas composition with H₂/CO = 2 was synthesized with feed gas containing CO₂ and H₂ in molar ratio of 1:3. This type of syngas are advantageously used in olefin or methanol synthesis processes [Mamedov et al., 2010]. The iron-free catalysts based on zinc oxide and chromium oxide (77.5% wt ZnO and 21.3% wt Cr₂O₃, NiO: 1.2% wt.) are reported for rWGS by Dupont et al [Dupont et al., 2003]. The CO₂ conversion and CO selectivity over this stable catalyst was reported to be 52% and 48% respectively at 300-520 °C, 10 - 40 bars, 4000 - 6000 Sm³/m³ cat and H₂/CO₂ = 3) and the methane formation was being limited to 3%. Mamedov and co-workers also investigated catalytic system based on Cu (560 °C, pressure = 2 - 4 MPa and H₂/CO₂ = 1 - 5) and achieved CO₂ conversion = 63% and CO yield = 59 – 60% for time on stream (TOS) = 29 days. It was further suggested that feed with H₂/CO₂ = 3 leads to syngas which can be used in olefin/ MeOH synthesis processes [Mamedov et al., 2013].

Table 2.3. Summary on prominent patents on rWGS for Cr-, Zn, Mn-, Cu- based catalyst

Authors	Temp, Pressure & Feed ratio	Catalyst	Performance Parameters	Inference
Agaddin Mamedov and Jodai [Mamedov et al., 2010]	600 °C, 0.1 - 5 MPa, H ₂ /CO ₂ = 1 – 5	13 wt% Cr ₂ O ₃ /Al ₂ O ₃ (pre-treated with H ₂ at 500 – 700 °C, 1 atm)	CO ₂ conv. = 50 – 57 %;	Stable catalyst at 600C for TOS = 150 days. Syngas has SN = ~3.0 that is most suitable for methanol synthesis. Air, CH ₄ in feed have no change in catalyst performance.
Dupont et al. [Dupont et al. 2003]	430 °C, 20 bar, 4000–6000 Sm ³ /m ³ cat, H ₂ /CO ₂ = 3	77.5% wt ZnO & 21.3% wt Cr ₂ O ₃ NiO: 1.2% wt	CO ₂ conv. = 52%; CO yield = 48%; CH ₄ yield = 3%	Stable catalyst for TOS = 50 days. Multi reactor-separator scheme leads to higher CO yield.

Mamedov et al. [Mamedov et al., 2013]	560 °C, 2 – 4 MPa; H ₂ /CO ₂ = 1 - 5	MnO/Cu-Al ₂ O ₃ ; (Mn= 10.45, Cu=4.78);	CO ₂ conv. = 63% (TOS = 29 days); CO yield = 59 – 60%	Stable performance. Feed with H ₂ /CO ₂ = 3, results in syngas that can be used in olefin/MeOH synthesis processes. High temp promote CO ₂ conv.
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CHAPTER 3

EXPERIMENTAL

3.0 Introduction

This chapter introduces the experimental methods and analytical techniques utilized in this research work. A detailed discussion on various catalysts preparation method is included herein. Various physico-chemical characterization techniques, such as Brunauer-Emmett-Teller (BET) surface area analysis, particle size analysis, X-Ray diffraction (XRD), thermogravimetric analysis (TGA), inductively coupled plasma (ICP) with optical emission spectrometer (OES) (ICP-OES), carbon analysis, etc. were used to characterize the catalysts properties. The catalytic performance of various rWGS catalysts was evaluated using a fixed-bed reactor set-up.

3.1 Catalyst Preparation Method

In this research work, one commercial high temperature-water gas shift (HTS-WGS) catalyst is used and three in-house catalysts were prepared to evaluate the catalytic hydrogenation of CO₂. The commercial catalyst was evaluated in both pellet and crushed form to evaluate catalyst performance in terms of CO₂ conversion and CO yield. The in-house developed catalysts were prepared in powder form by co-impregnation method [Li et al., 2006].

3.1.1 Reagents and materials used for in-house catalysts preparation

The following raw materials were used for rWGS catalysts preparation:

- (i) Ni(NO₃)₂ · 6H₂O (Merck, GR)
- (ii) Co(NO₃)₂ · 6H₂O (Merck, AR)
- (iii) Fe(NO₃)₃ · 9H₂O (Labort Fine Chem Pvt Ltd, Surat, AR grade)
- (iv) Gamma alumina (Saint Gobain, Norpro, USA)
- (v) De-mineralized water

The preparation method used for three in-house catalysts are given in a catalyst preparation flow diagram as shown in Figure 3.1.

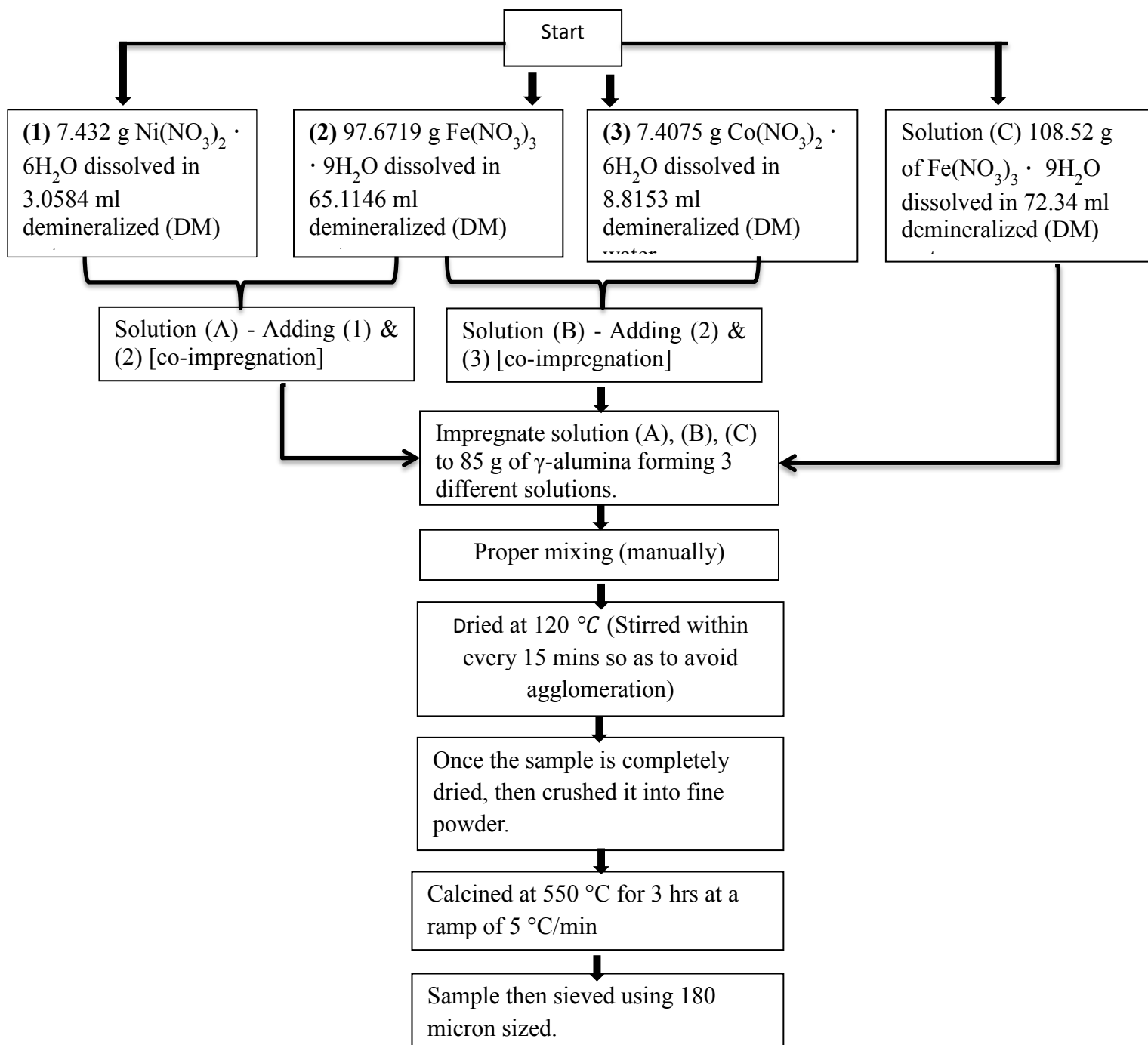


Figure 3.1. Schematic for catalyst preparation steps

3.1.2 Preparation method for Catalyst-2 (Composition: 15 wt% Fe supported on 85 wt% γ -alumina)

500 grams of γ -alumina was kept for overnight drying at 120 °C. Then, 108.52 grams of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in pre-calculated amount of 72.34 ml of demineralized water. On 100-grams scale basis, 85 grams of dried γ -alumina was added to the solution ($\text{Fe}(\text{NO}_3)_3$).

9H₂O + demineralized water) in a beaker and manually stir it well so that proper mixing was ensured. Then, the solution-mixture was dried at 120 °C to make it dry. The solution was stirred every 15 min to avoid agglomeration. Once the free-water in the sample was dried, the mixture was kept in a drier at 120 °C for overnight. The sample was then crushed into fine powder. The powder sample was kept in a furnace at 550 °C for 3 hours at a ramp of 5 °C/min. At last, the sample is sieved to retain 80 mesh size particles (180 μm) for the reaction.

3.1.3 Preparation method for Catalyst-3 (Composition: 1.5 wt% Co + 13.5 wt% Fe supported on 85 wt% γ-alumina)

7.40 grams of Co(NO₃)₂·6H₂O was dissolved in pre-calculated amount of 8.81 ml of demineralized water (solution 1). In a similar method, 97.67 grams of Fe(NO₃)₃·9H₂O was dissolved in 65.11 ml of demineralized water (solution 2). These two solutions of individual reagents were added and mixed manually to obtain an impregnation solution (solution 3). Now 85 grams of dried gamma-alumina was poured in solution 3 and stirred well manually so that it got properly mixed. Then, the solution was kept in a drier at 120 °C for drying. The solution was stirred every 15 minutes to avoid agglomeration as mentioned in catalyst 2 preparation. Once the free solution from the sample was removed, the sample was kept in a drier at 120 °C for overnight. The sample was then crushed into fine powder and kept in a furnace at 550 °C for 3 hours for calcination. The sample was then sieved to retain 80 mesh size particles (180 μm) for reaction.

3.1.4 Preparation method for Catalyst-4 (Composition: 1.5 wt% Ni + 13.5 wt% Fe supported on 85 wt% γ-alumina)

7.432 grams of Ni(NO₃)₂·6H₂O was dissolved in pre-calculated amount of 3.05 ml of demineralized water (solution 1). In a similar method, 97.67 grams of Fe(NO₃)₃·9H₂O was dissolved in 65.11 ml of demineralized water (solution 2). These two solutions of individual reagents were added and mixed manually to obtain an impregnation solution (solution 3). Now 85 grams of dried γ-alumina was poured in solution 3 and stirred well manually so that it got properly mixed. Then, the solution was kept in a drier at 120 °C for drying. The solution was stirred every 15 min so as to avoid agglomeration as mentioned in catalyst 3

preparation. Once the free solution from the sample was removed, the sample was kept in a drier at 120 °C for overnight. The sample was then crushed into fine powder and kept in a furnace at 550 °C for 3 h for calcination. The sample was then sieved to retain 80 mesh size particles (180 µm) for reaction.

3.2 Characterization Methods

Various physico-chemical characteristics of the prepared in-house rWGS catalysts were determined to correlate the catalytic hydrogenation of CO₂. The various characterization methods used in this research work are briefly described below.

3.2.1 BET surface area and pore volume measurement of catalysts

Measuring of the BET surface area and total pore volume of the catalysts was done using N₂ adsorption–desorption experiments in Micromeritics ASAP 2020. Multi-point Brunauer-Emmett-Teller (BET) surface area method was used to estimate the total surface area.

3.2.2 X-Ray diffraction (XRD)

X-ray powder diffraction (XRD) is an analytical technique which is used for phase identification of a crystalline material and can provide information on unit cell dimensions. For the study of crystal structures and atomic spacing, X-ray diffraction is a common technique. X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode-ray tube, filtered to produce monochromatic radiation, collimated to concentrate, and directed toward the sample.

Bragg's law is a simplistic model to understand what conditions are required for diffraction. The Bragg's law is expressed as:

$$\lambda = 2d_{hkl}\sin\theta \quad (7)$$

where, λ = wavelength of X-ray, d = space between diffracting planes, θ = Bragg's angle

For the adsorbent materials, the phase characteristic were performed by X-ray diffraction (XRD, Rigaku Miniflex600) at room temperature by using CuK α radiation.

3.2.3 Average particle size measurement

The average particle size was measured using Malvern Mastersizer 2000 and was found between 120 and 130 μm for various catalysts.

3.2.4 Thermo gravimetric analysis (TGA)

The thermal stability of in-house developed rWGS catalysts was determined by the use of thermo-gravimetric analyser (TGA: Universal V4.5A TA Instruments) where carrier gas used is N_2 at the heating rate of $10\text{ }^\circ\text{C}/\text{min}$. TG analyses provided the thermal stability as well as decomposition species formed during catalyst preparation.

3.2.5 ICP – OES analysis

The elemental analysis in the in-house developed rWGS catalysts was determined using ICP-OES method (iCAP 7000 Series). The catalyst samples were digested in acid media and measured in ICP-OES to determine the loading concentration of active phase in the catalysts.

3.3 Experimental setup

In order to evaluate the rWGS catalysts a fixed bed reactor is set up which is proposed for rWGS reactions. The experimental set-up used for CO_2 hydrogenation is shown below.

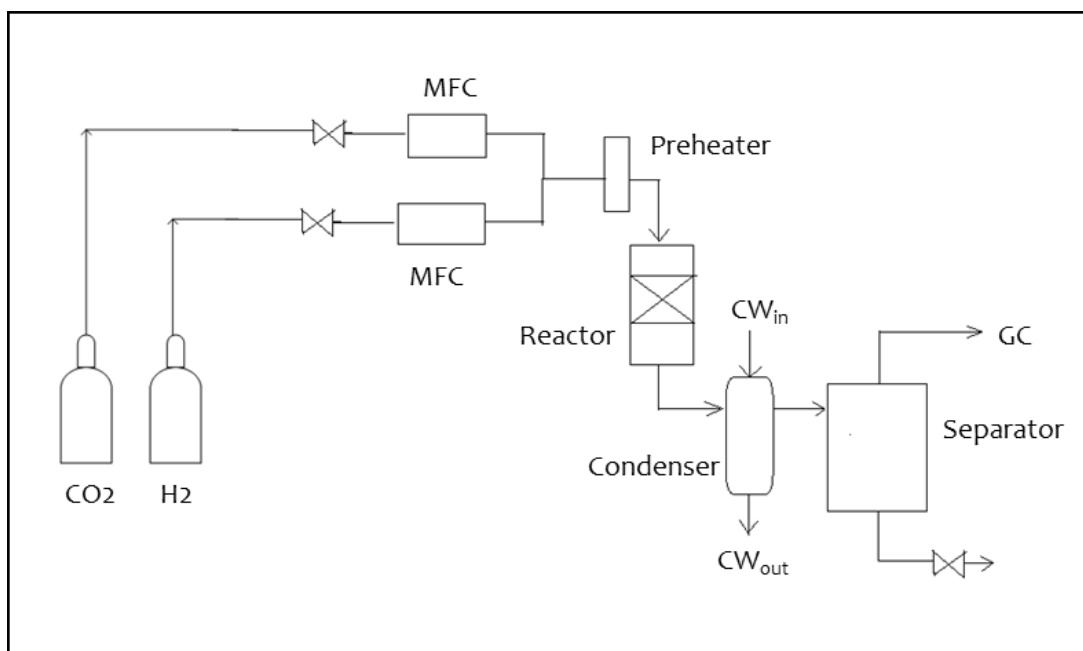


Figure 3.2. Experimental set-up used for CO₂ hydrogenation

A fixed bed reactor (2.1 cm inner diameter and 70 cm length) is used for the experimental studies. K-type thermocouples are installed to measure reactor temperature at different positions. To prevent heat dissipation and maintain the better line temperatures, the gas flow lines (stainless steel tubing) from the reactor outlet to the cooled condenser were wrapped initially with a conventional heating wire and then with insulating tape. In order to measure the bed temperature (reactor internal temperature) along the catalyst bed, a thermocouple is inserted into the radial center of the catalyst bed through the bottom of the reactor. All the gases required for the experimental purpose *i.e.* hydrogen, carbon dioxide, and nitrogen were delivered from the commercial-grade cylinders. Mass flow controllers (MFC, Brooks Co.) were used in order to adjust the desired flow rates. A gas/liquid separator and a conventional condenser were used in order to collect the water produced in the reaction. The product gas will be analyzed using gas-chromatography (GC, Varian 450 GC).

3.4 Catalyst Loading

The selected catalyst comprising 2.3 gm was loaded in the reactor as per loading diagram as shown in Figure 3.3. The space velocity for the entire experimental studies was chosen as 50 ml/g_{cat}.min.

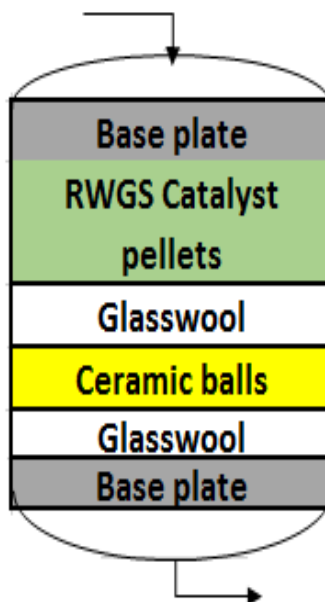


Figure 3.3. Catalyst loading diagram

3.5 Experimental procedure

Before the commencement of catalyst evaluations for selected rWGS catalysts, the safety aspects were taken into consideration through internal audit and mitigation measures as per review exercise of pre-experimental review committee (PESR). All mass flow controllers were calibrated in the range of flow necessary for the desired feed conditions before starting the reaction. Actual flow rates were measured with gas bubblers and compared to the MFC's readout values for each gas. The catalytic hydrogenations of CO₂ were performed at atmospheric pressure in a continuous flow apparatus equipped with a fixed bed reactor. Approximately 2.3 grams of selected rWGS catalysts (crushed/pellets/powder form) was loaded in the reactor at the isothermal temperature zone of the reactor where the maximum temperature was measured by using a quartz frit. After catalyst loading, leak test was conducted at 3 kg/cm²g under N₂ atmosphere for 2 h and continuously monitor to ensure any leakage issue in the experimental set up using soap solution. In the next step, the catalyst was reduced by increasing the temperature (4 °C/min) under a continuous flow of gas mixture containing 50 % H₂ with N₂ at 230 ml/min up to the desired reaction temperature. After reduction, under the same gas flow rates, the reactor was adjusted to the desired reaction temperature. Once the stable temperature was achieved, the reacting gas flow rates for N₂ were set using mass flow controller and switched to feed gases (CO₂ and H₂) at a pre-determined flow rates. The feed stream was then passed to the fixed bed reactor at experimental conditions. The product gas was cooled in a condenser using chilled water (< 4 °C) and separated in a gas-liquid vessel to collect product gas (CO, CH₄, and unreacted H₂ etc.). Gas-chromatography (GC) was used in order to analyze product gases.

3.6 Experimental Plan

The detail experimental plan is tabulated in the given Table 3.1 so as to conduct catalytic hydrogenation of CO₂.

Table 3.1. Detail rWGS experimental plan

Expt.	Catalyst	Catalysts	Experimental Conditions	Pre-treatment
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No.				
01.	Catalyst-1	HTS catalysts (Commercial)	Pellet and Crushed catalysts (1-2 mm) T: 450; 550; 650 °C Feed: CO ₂ : H ₂ = 1: 3 (vol %) Catalyst wt.: 2.3 g H ₂ flow: 173 ml/min, CO ₂ flow: 57 ml/min	Catalyst reduction protocol: 50% H ₂ with N ₂ at 10 °C/min with 230 ml/min up to reaction temperature
02.	Catalyst-2	Fe/Al ₂ O ₃ catalyst (In-house catalyst)	Powder catalyst (120 micron) T: 450 – 550 °C Feed: CO ₂ : H ₂ = 1: 3 (vol%) Catalyst wt.: 2.3 g H ₂ flow: 173 ml/min, CO ₂ flow: 57 ml/min	Catalyst reduction protocol: 50% H ₂ with N ₂ at 10 °C/min with 230 ml/min up to reaction temperature
03.	Catalyst-3	Fe-Co/Al ₂ O ₃ catalyst (In-house catalyst)	Powder catalyst (123 micron) T: 450 – 550 °C Feed: CO ₂ : H ₂ = 1: 3 (vol%) Catalyst wt.: 2.3 g H ₂ flow: 173 ml/min, CO ₂ flow: 57 ml/min	Catalyst reduction protocol: 50% H ₂ with N ₂ at 10 °C/min with 230 ml/min up to reaction temperature
04.	Catalyst-4	Fe-Ni/Al ₂ O ₃ catalyst (In-house catalyst)	Powder catalyst (130 micron) T: 450 – 550 °C Feed: CO ₂ : H ₂ = 1: 3 (vol%) Catalyst wt.: 2.3 g H ₂ flow: 173 ml/min, CO ₂ flow: 57 ml/min	Catalyst reduction protocol: 50% H ₂ with N ₂ at 10 °C/min with 230 ml/min up to reaction temperature

CHAPTER 4

RESULTS AND DISCUSSION

4.0 Introduction

This chapter presents the results of the analytical characterization of the rWGS catalysts such as BET surface area, pore volume, particle size, XRD, TGA and ICP-OES analysis. A detail analysis is performed to examine catalytic hydrogenation of CO₂ in fixed bed reactor for the performance study of each catalyst systems.

4.1 Physico-chemical characterization of catalysts

4.1.1 Surface area, pore volume, pore size

The physical properties like BET surface area, total pore volume and average pore diameter of the fresh in-house developed rWGS catalyst are shown in Table 4.1. In all the catalysts, iron (Fe) was mainly impregnated as an active phase on the support material, γ -Al₂O₃. Three catalysts were prepared in-house by co-impregnation method [Li et al., 2006].

Table 4.1. Structural properties of different in-house developed catalysts

Sr. No.	Catalysts	Description	Surface area (m ² /g)	Pore volume (cm ³ /g)	Average Pore Diameter (Å)	Average particle size (µm)
1	Support material	γ -Al ₂ O ₃	172	0.48	97	80
2	Catalyst-2	15 wt% Fe + 85 wt% γ -Al ₂ O ₃	130	0.32	99	129
3	Catalyst-3	1.5 wt% Co + 13.5 wt% Fe + 85 wt% γ -Al ₂ O ₃	137	0.34	99	115
4	Catalyst-4	1.5 wt% Ni + 13.5 wt% Fe + 85 wt% γ -Al ₂ O ₃	141	0.35	99	123

Cobalt and nickel were used as dopant to study its influence its promoting effect on the CO₂ hydrogenation. It is observed that during active component loading on support material, both

the surface area and pore volume decrease as it was seen for fresh γ - Al_2O_3 . This is due to the blocking of active components in porous structure. It is also seen that the measured average particle size is in between 115 to 129 μm .

4.1.2 XRD analysis

Figure 4.1 represents XRD results that shows the presence of two phases namely, Fe_2O_3 and γ - Al_2O_3 in Fe-based catalysts. The different XRD peaks appeared at 2θ of 24.4, 33.2, 36.6, 49.7, and 54.4 are assigned to hematite (Fe_2O_3) phase (JCPDS 72-6225), which shows a crystalline Fe_2O_3 is impregnated on γ - Al_2O_3 support. Similarly, the peaks appeared at 2θ of 40.4, 46.3, and 67.2 (JCPDS 10-0425) are assigned to be semi-crystalline phase of γ - Al_2O_3 [Sengupta et al., 2015]. The Co_3O_4 and NiO phases were not identified as these two components were used as minimal amount during catalyst preparation and escape the detection limit. It indicates that the dopants like Co and Ni compounds were well-dispersed homogeneously with Fe_2O_3 phase on γ - Al_2O_3 support. The influences of different dopants addition to Fe/ Al_2O_3 on CO_2 hydrogenation are discussed in subsequent section.

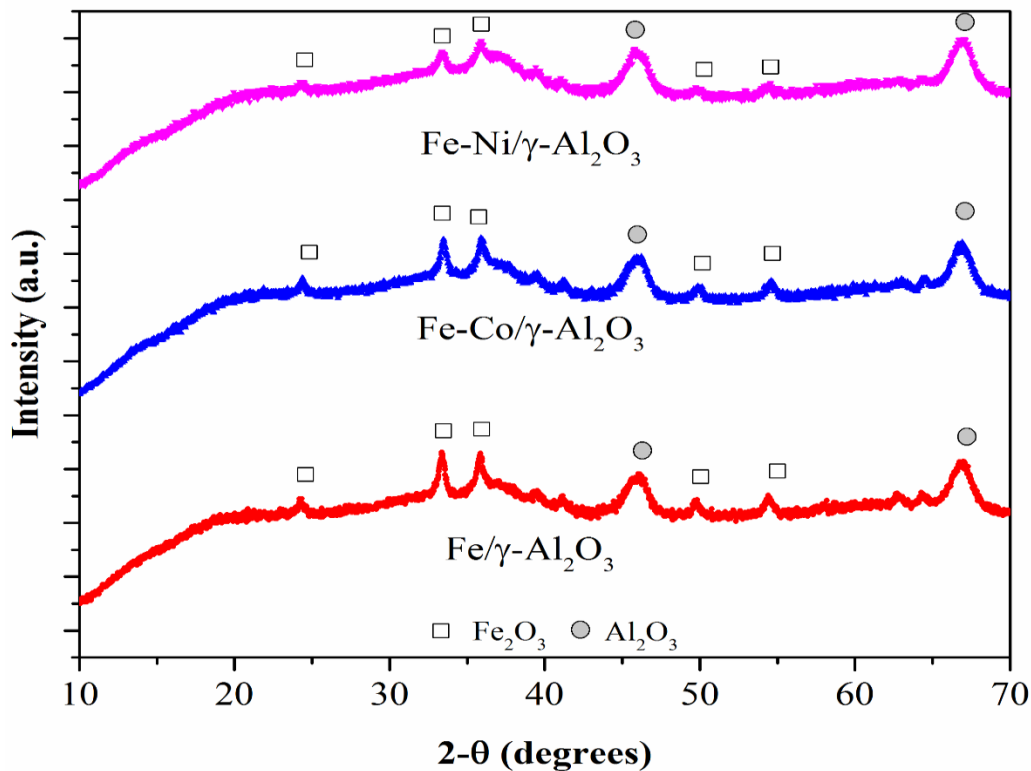


Figure 4.1. XRD pattern for in-house developed rWGS catalysts

4.1.3 TG analysis

The Figure 4.2 shows TG analysis to study the thermal behavior of the in-house developed rWGS catalysts. The TG analysis shows that for three catalysts up to 120 °C from room temperature, there was a loss of weight percent of 2.3%, which is attributed to the removal of free water from the catalysts. In all the three catalysts, there was a loss of ~4 wt% at the temperatures between 120 and 900 °C, which signifies the changes of γ -phase to a mix of theta (θ) and delta (δ) phases [Sengupta et al., 2014]. It also indicates that the formation of crystalline Al_2O_3 from its amorphous phase.

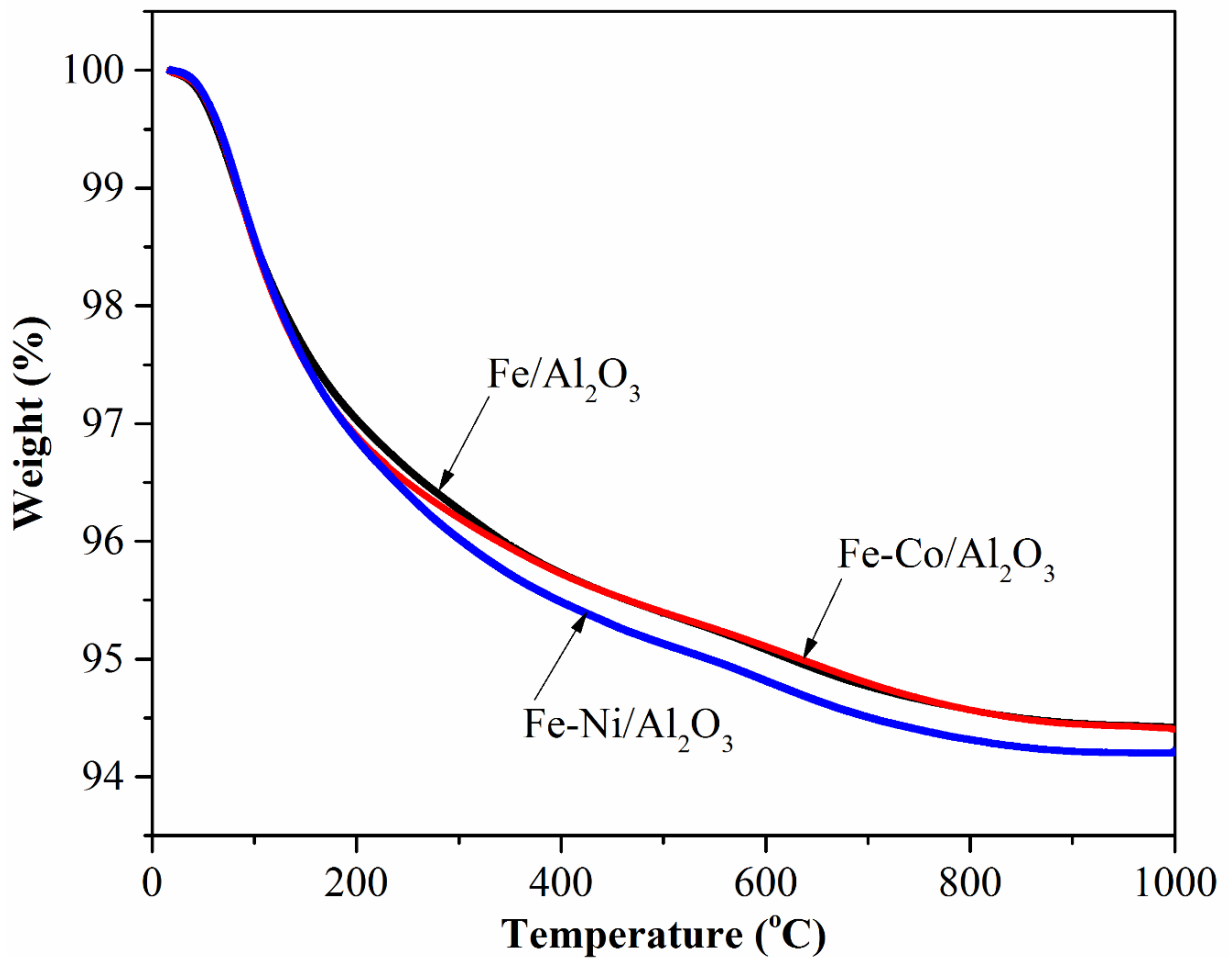


Figure 4.2. TGA for in-house developed rWGS catalysts

4.1.4 ICP-OES analysis

The ICP-OES analysis for the selected rWGS catalysts was performed to evaluate the dispersion of the active phases like Fe, Co, Ni on the γ -alumina. The Table 4.2 shows the loading concentration of the active components employed in the in-house developed catalysts preparation. It shows the active components are homogeneously dispersed on the support material, which is responsible for effective catalytic hydrogenation of CO₂ at the rWGS reaction conditions.

Table 4.2. ICP-OES analysis of different in-house developed catalysts

Catalysts	Fe (wt%)	Co (wt%)	Ni (wt%)
Catalyst-2	12.48	-	-
Catalyst-3	10.59	1.47	-
Catalyst-4	10.62	-	1.08

4.2 Fixed bed reactor evaluation for rWGS

The CO₂ hydrogenation study (CO₂ + H₂ = CO + H₂O) were carried out in a fixed bed reactor over a temperature range (450 – 650 °C) and at atmospheric pressure. Four catalysts were used to study the CO₂ hydrogenation by rWGS. Out of four catalysts, one commercial high temperature shift (Sigma Aldrich, USA) (pellets and crushed) catalyst and 3 in-house developed catalysts were evaluated. These catalysts are named in section 3.6. The following experimental conditions chosen for the entire study is given in Table 4.3.

Table 4.3. Experimental conditions for rWGS

Parameters	Value
Catalyst	Catalysts (1-4)
Temperature	450; 550; 650 °C
Pressure	1 bar(g)
Feed	CO ₂ : H ₂ = 1 : 3 (vol%)
Catalyst weight	2.3 g

Space velocity	50 ml/g _{cat} .min
H ₂ flow	173 ml/min
CO ₂ flow	57 ml/min

4.2.1 Effect of temperature on CO₂ hydrogenation with different catalysts

As per thermodynamic consideration, rWGS reaction is favorable at higher temperatures. The high temperature facilitates reaction producing CO from CO₂. In the subsequent sections, the performance on catalytic hydrogenation of CO₂ for different rWGS catalysts is discussed and correlated with the catalysts properties and characterization.

4.2.2 Performance of high temperature shift (HTS) catalyst (Catalyst-1)

The commercial high temperature shift (HTS) catalyst, namely Catalyst-1 was reduced at three different temperatures (450 °C, 550 °C and 650 °C) and atmospheric pressure. As discussed in earlier section, the catalyst was pretreated prior to CO₂ hydrogenation. Figure 4.3a shows the activity performance of Catalyst-1, which is in pellet form (3-4 mm in size). Both CO₂ conversion and CO yield are described and compared with equilibrium CO₂ conversion. It is observed that on increasing reaction temperature, CO₂ conversion as well as CO yield increased from 22.9% to 55.2% and from 14.9% to 44.1% respectively, which is approximately 70% of the equilibrium CO yield at 650 °C. It is also interesting to see there is very negligible amount of methane (CH₄) formation even at low temperatures (<0.8 mol%), hence selectivity was as high as >99%. It is also noticed that at high temperature e.g. 650 °C, the coke deposition on the Catalyst-1 was measured as 2.3 wt%, which clearly indicates higher temperature exhibits catalyst deactivation resulting in lesser catalyst life.

In the similar way, Figure 4.3b shows catalytic activity of crushed Catalyst-1 (1-2 mm in size). It is observed that on increasing reaction temperature, the CO₂ conversion as well as CO yield increased from 41.9% to 61.7% and from 36.8% to 52.3% respectively, which is approximately 82% of the equilibrium CO yield at 650 °C. The increase in CO₂ conversion and CO yield for crushed Catalyst-1 as compared to pellet Catalyst-1 are due to the utilization of effective surface area and pore volume resulting from crushed samples. In this case, methane formation was also found to be less as <0.1 mol%. The crushed Catalyst-1 was also deactivated more as compared pellet Catalys-1 due to coke deposition (2.8 wt% coke

deposition). The higher deactivation is expected due to more catalytic active sites and hence, higher activity of the catalyst.

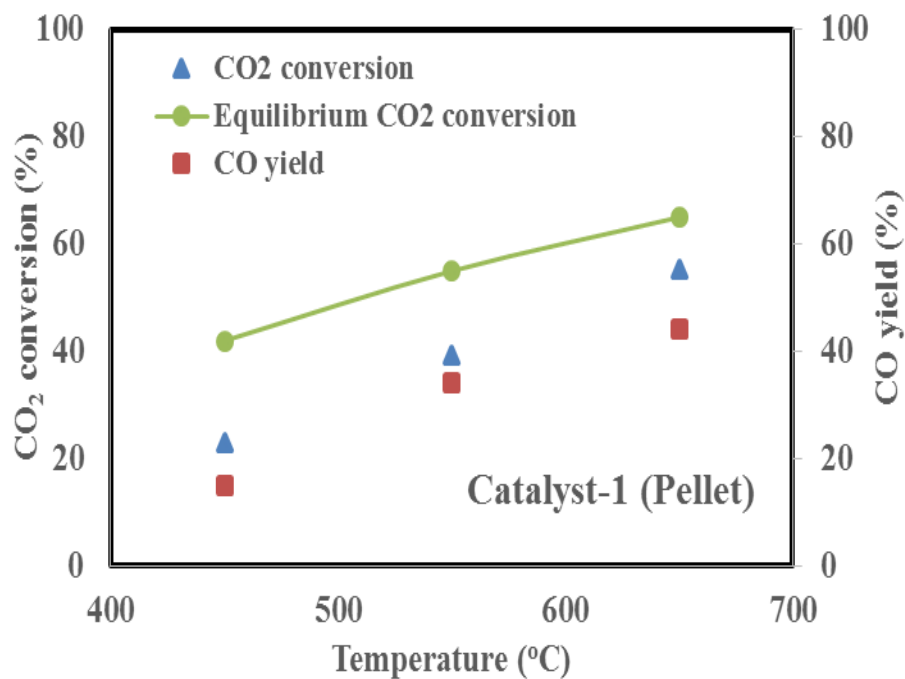


Figure 4.3a. CO₂ hydrogenation of Catalyst-1 (in pellet form) (conditions: CO₂:H₂= 1:3)

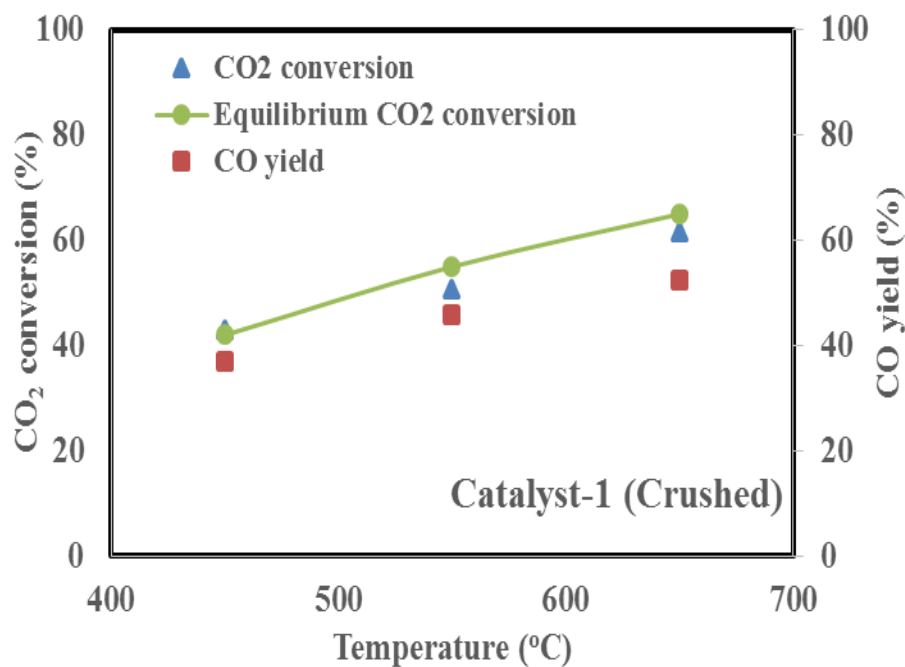


Figure 4.3b. CO₂ hydrogenation of Catalyst-1 (in crushed form) (conditions: CO₂:H₂= 1:3)

4.2.3 Performance of in-house developed catalyst (Catalyst-2)

In order to improve catalytic hydrogenation of CO₂ at the reaction conditions, three catalysts were prepared in-house using co-impregnation method. The preparation of this catalyst was discussed in section 3.1.2.

The Figure 4.4 represents the CO₂ conversion and yield of CO with respect to temperature for Catalyst-2 (15-wt% Fe/Al₂O₃). It is observed that CO₂ conversion increases from 24.8 to 34.7% and CO yield increases from 13.6 to 26.5% with increasing temperatures 450 – 550 °C. It also suggests that higher temperature like 550 °C is favorable to overcome the thermodynamic barriers. It is observed that byproduct methane formation was restricted to less than 0.1 mol%. These experiments were conducted up to 550 °C because of hardware limitation in the reactor used.

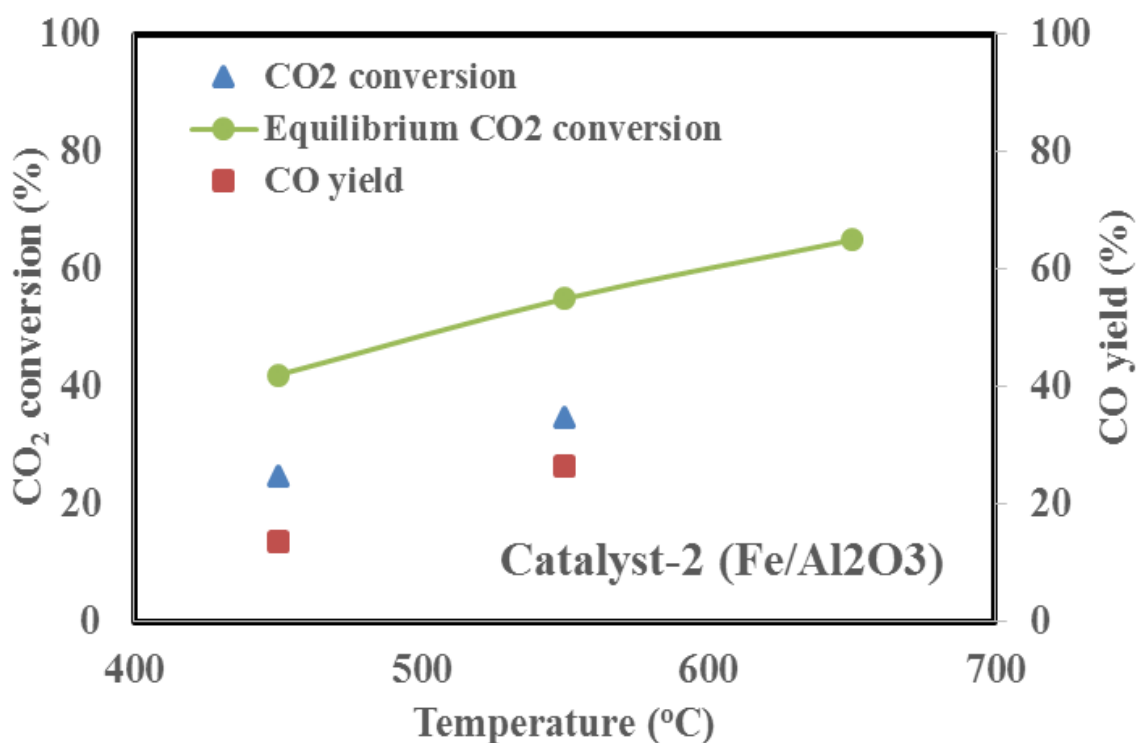


Figure 4.4. CO₂ hydrogenation of Catalyst-2 (Powder) (conditions: CO₂:H₂= 1:3)

4.2.4 Performance of in-house developed catalyst (Catalyst-3)

In this catalyst (Catalyst-3), few concentration of cobalt (1.5-wt%) was incorporated as a dopant to study its impact on CO₂ hydrogenation performance. The Figure 4.5 shows the

variation of CO₂ conversion and CO yield at different temperatures. The CO₂ conversion as well as CO yield increased from 35% to 53.3% and 28.1% to 42.6% respectively, which is 79% of the equilibrium CO yield. CO yield achieved using Catalyst-3 is much higher than reported by [Kharaji et al., 2013]. Herein, CO₂ conversion and CO yield were found to be high as compared to Catalyst-2, which also suggests the effect of dopant like Co₃O₄ has significant role in CO₂ hydrogenation to CO. In this case, very negligible amount of methane was formed at lower temperature.

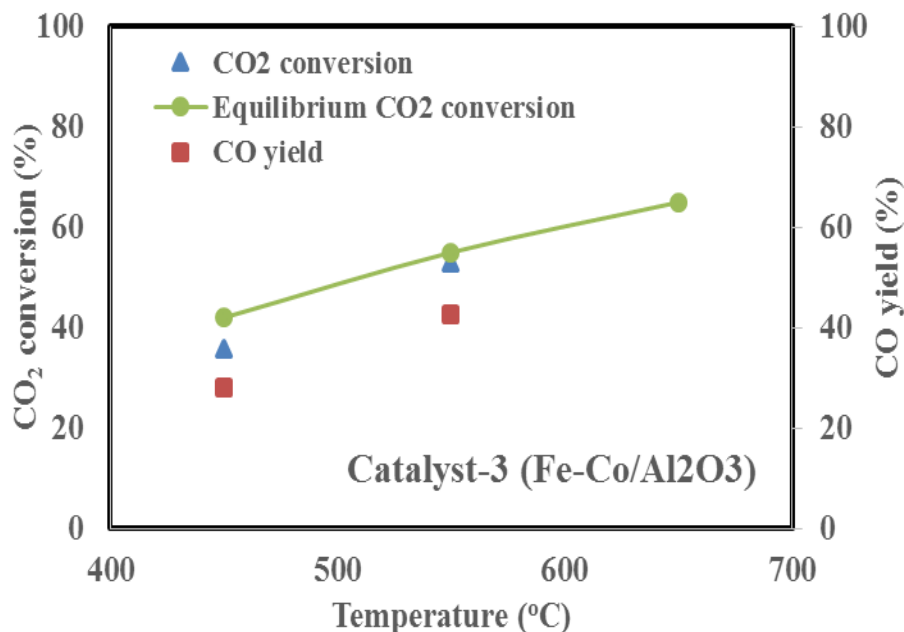


Figure 4.5. CO₂ hydrogenation of Catalyst-3 (in powder form) (conditions: CO₂:H₂= 1:3)

4.2.5 Performance of in-house developed catalyst (Catalyst-4)

In this catalyst (Catalyst-4) similar to Co-doped, very few concentration of Ni (1.5-wt%) was incorporated as a dopant to improve CO₂ hydrogenation performance. The Figure 4.6 shows the trends of CO₂ conversion as well as CO yield at different temperatures. The CO₂ conversion as well as CO yield increased from 28% to 47% and 22% to 40.1% respectively, which is 74% of the equilibrium CO yield. The CO yield achieved using this Catalyst-3 is much higher than as reported by [Kharaji et al., 2012]. It is also seen that CO₂ conversion and CO yield were found to be high as compared to Catalyst-2, which again confirms the significant effect of dopant like NiO on CO₂ hydrogenation. In comparison with Co-doped

Fe/Al₂O₃ catalyst (Catalyst-3), Ni-doped catalyst showed slight less CO₂ conversion as well as CO yield. This also suggest that Ni-doped catalyst is catalytically effective for rWGS reaction at higher temperatures (> 700 °C) [49]. In this case, very negligible amount of methane was formed at lower temperature.

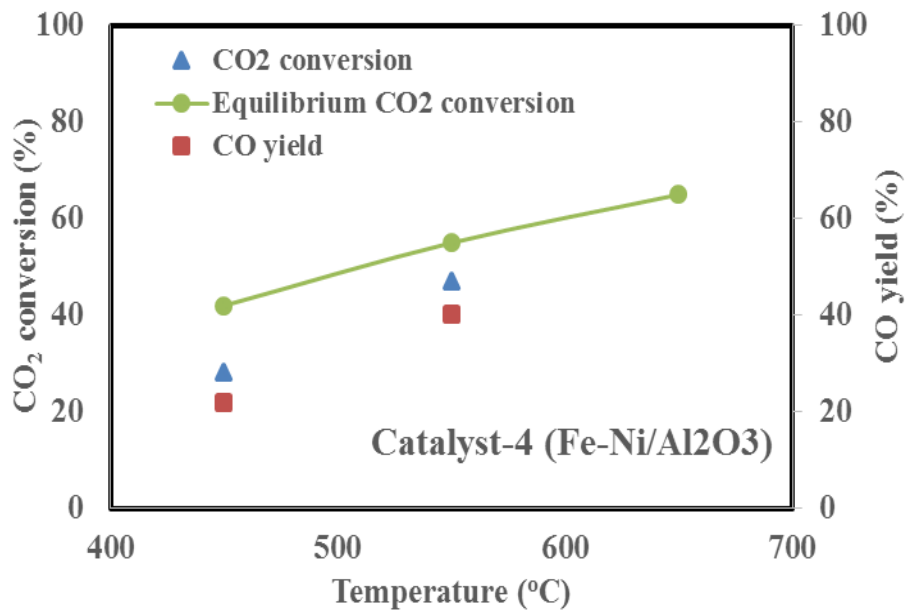


Figure 4.6. CO₂ hydrogenation of Catalyst-4 (Powder) (conditions: CO₂:H₂= 1:3)

4.2.6 Comparison on catalytic performance

The Figure 4.7 shows a comparison between this research work with competitive literature for CO₂ hydrogenation activity in terms of CO yield at different temperatures. It is seen that CO yield increases with increase in temperature.

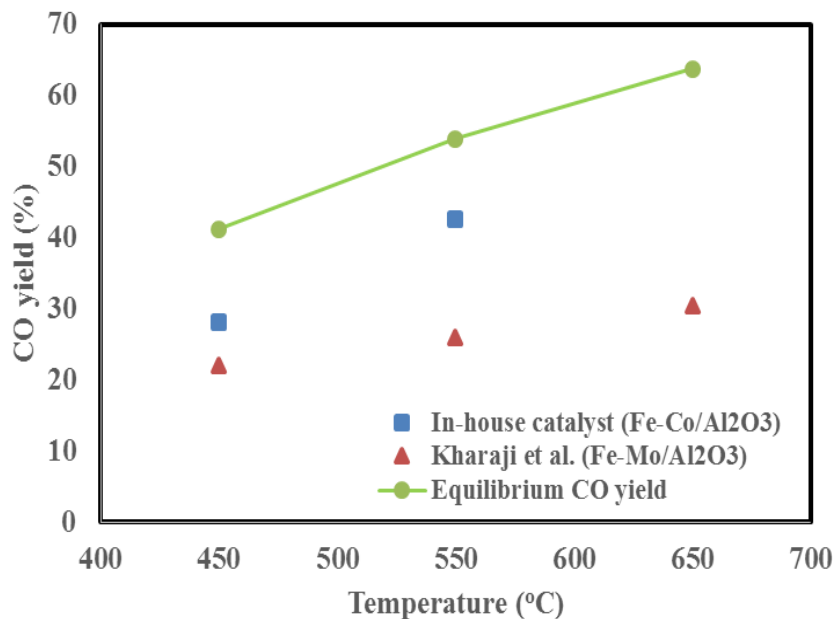


Figure 4.7. Comparison of CO₂ hydrogenation activity with reported literature [36]

The CO yield increases drastically for in-house developed catalyst (Catalyst-3) as compared to Kharaji et al., 2016. At 550 °C, the percent CO yield was found to be higher (42.6%) as compared to Kharaji et al (28%), which is 79% of the equilibrium CO yield. The increase in CO yield is due to the better dispersion of the active components on the porous support material. Thus there is a good agreement between the above observations with textural properties discussed in Table 4.1

CHAPTER 5

CONCLUSIONS AND FORWARD PATH

5.1 Motivation and background of work

The growing concentration of CO₂ in the atmosphere had increased the impact on the environment such as global warming and forcing a climate change. One effective approach to avoid CO₂ accumulation into the atmosphere is the recovery of CO₂ and its recycle by converting to useful chemicals. An efficient and inexpensive conversion of CO₂ into valuable chemicals would simultaneously contribute to reducing CO₂ emission into the atmosphere and lessen the dependence of society on fossil fuels. Hence, innovative utilization technologies are desperately needed to reduce the CO₂ released into the atmosphere. But, due to its thermodynamic and kinetic stability, CO₂ is not used to fullest potential by utilization route. For any fruitful utilization of CO₂ to high value and high volume useful chemicals, it is required to develop syngas platform from CO₂. Therefore, catalytic hydrogenation of CO₂ to syngas (CO+H₂) by reverse water gas shift reaction could be a promising route. The beauty in the rWGS chemistry lies in the fact that it can be applied separately or integrated with processes like steam methane reforming (SMR), or processes for making products like alkanes, aldehydes, acids, or alcohols. The rWGS is as much as competitive to alternate syngas production route like SMR, partial oxidation or methane, dry reforming etc.

Being rWGS a reversible reaction, catalysts active in the water gas shift (WGS) reaction are often active in the reverse reaction. Various types of catalysts are reported for rWGS reaction like those based on Ni-, Fe-, Cu-, noble metal etc. Among those catalytic systems, Ni-based catalyst is found to be appropriate at high temperature (~900 °C), Fe-based at intermediate temperature range (500-600 °C) and Cu-based at low temperature window (~350 °C). In this work, the CO₂ hydrogenation was investigated mainly at intermediate temperatures over Fe-based catalysts, *i.e.* at conditions where the rWGS reaction is favored thermodynamically and CO and H₂O are the main products. The objectives of this research work is divided into two parts, firstly, to develop and characterize Fe-based catalysts with Co- and Ni- as dopant prepared by co-impregnation method and secondly, evaluate in fixed bed reactor to study its

performance at intermediate temperature of 450-650 °C, atmospheric pressure and H₂/CO₂ ratio of 3.0.

5.2 Summary of results

The experimental studies on CO₂ hydrogenation by rWGS reaction over the Fe-based catalyst were carried in a lab-scale fixed bed reactor. The catalysts like Fe-based and Co-, Ni-doped Fe-based catalyst supported on γ -Al₂O₃ were prepared by co-impregnation method. The reactions were carried out in the wide temperature range (450-650 °C) at atmospheric pressure and H₂/CO₂ ratio of 3. The influence of reaction parameters like reaction temperature on the CO₂ conversion and CO yield was studied. The following are the highlights of this research work:

- (i) Textural properties of the catalysts suggested effective utilization of specific surface area and pore volume, which are predominant for catalytic activity.
- (ii) XRD analysis indicated homogeneous dispersion of Co and Ni with Fe₂O₃ phase on γ -Al₂O₃ support.
- (iii) ICP-OES results also indicated almost complete dispersion of the active components on the support material.
- (iv) The catalytic activity of crushed commercial catalyst of 1-2 mm in size showed CO₂ conversion and CO yield increases from 41.9% to 61.7% and from 36.8% to 52.3% respectively with increase in temperature (450-650 °C). The CO yield is approximately 82% of the equilibrium CO yield at 650 °C.
- (v) The Co-doped and Ni-doped Fe-based catalyst showed higher CO₂ conversion and CO yield as compared to un-doped Fe-based catalyst.
- (vi) The rWGS reaction with Co-doped Fe/Al₂O₃ at 550 °C confirms CO₂ conversion and CO yield 53.3% and 42.6% respectively. The CO yield for all catalysts is approx. 79% of the equilibrium CO yield.
- (vii) In comparison with Co-doped Fe/Al₂O₃ catalyst, Ni-doped catalyst showed slightly less CO₂ conversion as well as CO yield at 450-550 °C.
- (viii) The methane formation in rWGS reaction was limited to less than 0.1 mol%.

5.3 Forward Path

It is recommended that the long term stability of the doped Fe-based catalyst supported on Al_2O_3 should be tested with extended time-on-stream. The optimization of H_2 and CO_2 in feed and space velocity are also recommended for appropriate reactor sizing.

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