Registration Seminar Report
on
Development of efficient Ni-based alloy catalysts by comparing activity with transition noble metals for CO_2 methanation

Under the esteemed guidance of

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Certificate

This is to certify that the **Ph.D. Registration Report** titled **"Development of efficient Ni-based alloy catalysts by comparing activity with transition noble metals for CO_2 methanation"**, submitted by **RAHUL KUMAR (Roll No. 19CH91R08)** to Indian Institute of Technology, Kharagpur, is approved for submission.

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Declaration

I joined the Department of Chemical Engineering as a PhD student and enrolled in PhD on the 9th of July, 2019 under the guidance of Dr. Koustuv Ray. The broad area of my research work is “Catalyst”. I am presenting below the course work completed and the work done during the period of my stay from 9th of July, 2021 till date.

Course Work Completed

I have completed the following courses and also passed the **Comprehensive Viva Examination dated 30/12/2020.**

Sl No.	Subject Name	Subject No.	Credit	Grade
1	Industrial Pollution Control	CH62007	3	C
2	Chemical Reactor Analysis	CH62016	4	C
3	Petroleum Refinery Engineering	CH62009	4	A
7	English for Technical Writing	HS63002	4	C

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1. Introduction

Catalytic hydrogenation of CO_2 to methane (CH_4) has been focused for the past several years because of energy and environmental concern [1]. Increased CO_2 concentration in the atmosphere is alarming and attention is being paid by many researchers to sequester and utilize this molecule. Again, due to rapid emergence of renewable energy resources the generation of hydrogen is now more favorable whereas the storage and utilization of excess hydrogen need a suitable way. It is the very occurrence in CO_2 methanation that renewably produced hydrogen can be fed with oxides of carbon to produce hydrocarbons serving as fuels and chemicals [2]. The hydrogenation of CO_2 leads to the formation of C_1 molecules such as methanol (CH_3OH), formaldehyde (HCHO), methane (CH_4). Moreover, C_2 and higher hydrocarbons can also be produced depending on desired process conditions [3]. According to the published reports, CO_2 methanation typically occurs within a range of 300-450℃ and at atmospheric pressure of 1 atm. If methanation is conducted under high temperature conditions, sintering of metallic particles and carbon deposition are inevitable [32]. Therefore, in order to perform CO_2 methanation, it requires the development of more selective and a stable heterogeneous catalyst. Transition metals such as Ni, Co and Fe are known to be catalytically active for CO hydrogenation to CH_4 or CO methanation for past many years [4,13,34]. Moreover, these metals also possess catalytic activity for CO_2 methanation. However, it is already proven that noble metals such as Rh, Ru, Pt, Pd have superior activity than those of the non-noble metals. The superior activity of noble metals is always attractive but high price and limited availability almost directs for the search of an alternate catalyst which could equally promising to them. The group VIII 3d transition metals and noble metals have been recognized as the most active in the CO_2 methanation process. Because of its exceptional activity and selectivity to methanation, as well as its low cost, Ni is one of the most intensively examined transition metal possibilities [6]. Ni based catalysts serve a good balance between high catalytic activity and low price, which is favourable in the chemical industry. Nickel catalysts on the other hand have a limited activity at low temperature compared to the noble metals such as Rh, Ru for CO_2 hydrogenation reaction. Such as phenomena like sintering and/or coke deposition can quickly deactivate the catalyst at high temperature. Moreover, it is susceptible to sulphur poisoning [32]. These drawbacks are generally alleviated by making better catalysts using a suitable support, catalytic promoters, forming bimetallic alloys or spinel structures. This has a direct consequence on catalytic activity enhancement and catalyst life improvement as founded in the past studies [2,5,7]. One of the most commonly used noble metals to form bimetallic alloy is ruthenium. In CO_2 methanation, Ru possesses better catalytic activity as compared to Ni at low temperature owing to the increased reducibility and dispersion on the catalyst surface [5]. However, the higher cost and limited availability are the demerits for developing a low-cost Ni-based catalyst. That's why the aim of this research is basically to synthesize Ni and Ni-based bimetallic catalysts (Ni-Fe, Ni-Co, Ni-Cu) and compare the catalytic properties and performances of these four catalysts with the noble metals (Pt, Pd, Rh and Ru). The effective comparison will open up the new possibilities to achieve the desired low-cost yet effective catalyst for the CO_2 methanation process. In our study, Nickel and Nickel based Ni-Fe, Ni-Co and Ni-Cu catalysts would be synthesized, characterized and tested for CO_2 methanation. In addition to that, noble metal-based catalysts such as Rh, Ru, Pt, Pd would also be synthesized, characterized and tested for the effective comparison. The γ-Al_2O_3 will be considered as support or carrier material for synthesis of these catalysts. Incipient wetness impregnation (IWI) synthesis method will be used initially for comparing these catalysts [8]. Later, the sol-gel method will be employed to understand the effect of particle size using the most active noble and non-noble catalyst on the catalytic turnover frequency (TOF). Thus, a meaningful comparative study could be envisaged in our whole work for the purpose of developing a superior Nickel-based bimetallic catalyst. In the current report a part of the literature survey has been presented followed by the details of catalysts synthesis using IWI technique.

2. LITERATURE REVIEW

2.1. CO_2 METHANATION

In 1897, hydrogenation of CO_2 to methane (CH_4) was first studied by Sabatier and Senderens. That is why this reaction is also known as Sabatier reaction [9]. The reaction involved during hydrogenation of CO_2 is: -

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \qquad \Delta H^0_R = -165 \text{ kJ/mol} \qquad (1)$$

where, carbon dioxide (CO_2) and hydrogen (H_2) are used as reactant gases. As the enthalpy change is negative, the above hydrogenation reaction is exothermic in nature. The mechanism behind the hydrogenation reaction is the combined form of reverse water gas shift reaction (RWGS) which is endothermic in nature and CO methanation reaction which is exothermic in nature as shown in equation (2) and (3) respectively.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta H^0_R = +41 \text{ kJ/mol} \qquad (2)$$

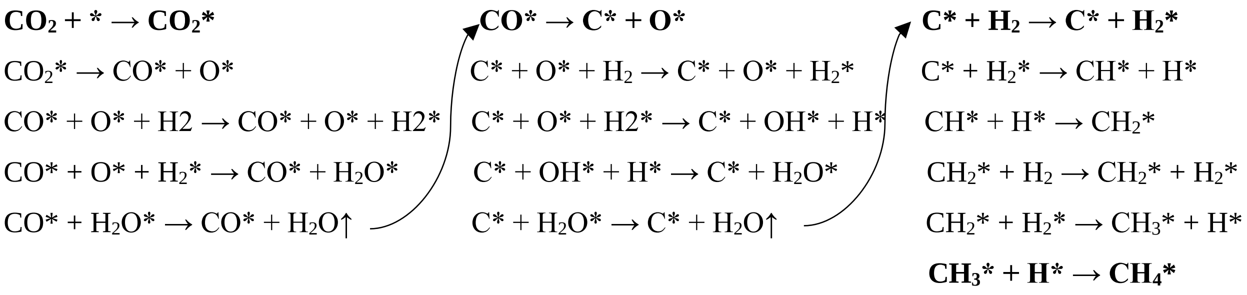
$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad \Delta H^0_R = -206 \text{ kJ/mol} \qquad (3)$$

CO_2 methanation can be carried out in a fixed bed reactor or two-stage catalytic reactor at relatively low temperature i.e., 523 K and operated at atmospheric pressure (1 atm.). The working range of temperature and pressure for CO_2 methanation is generally between 373 to 573 K and pressure is greater than 1 atm [10]. From thermodynamic point of view, CO_2 methanation processed at low temperature reaction is an advantage from the standpoint of lower energy consumption, lesser possibility of metals sintering. On the other hand, catalytic rates for Ni based catalysts are very low at low temperature operation. Moreover, it suffers from carbon deposition due to Boudouard reaction leading to catalyst deactivation. Thus, it is almost imperative to test catalytic activity not at lower temperature which favours only the noble metals for high rates of methane formation

2.2. Reaction mechanism and kinetics

Much effort has gone into determining the mechanism of CO_2 methanation, however there is still no consensus in the field on the kinetics and mechanism. The difference of view stems from the nature of the intermediate substance used in the rate-determining step for the methane formation.

The proposed CO_2 methanation method can be divided into two groups. The first and more widely accepted approach involves converting CO_2 to CO, which is then transformed to CH_4 using the same mechanism as CO methanation, which lacks unanimity. The other hypothesized method converts CO_2 directly to CH_4 without forming a CO intermediate. So, in case of CO intermediate involved, at first, CO_2 is chemisorbed on the surface of the catalyst. After that, the gaseous CO_2 is dissociated into CO and O, so that CO can act as an intermediate and remain consistent for this pathway. This dissociation process is an exothermic in nature. In the next step, the dissociated CO will further undergo dissociation into C and O on the metal sites and at the same time H_2 dissociation also take place, which is further hydrogenated into CH_4 by the combination with dissociated hydrogen. The rate determining step of the CO_2 methanation reaction is the dissociation of the adsorbed CO into C and O atoms on the metallic sites [19]. Initially, Fitzharris et al. originally proposed this mechanism of CO dissociation. [25]. The stepwise reaction schematic view and the picturized representation of the above mentioned pathways of CO_2 methanation is shown in figure 1 and 2 respectively. Figure 1, shows the stepwise reaction procedure, where, at first CO_2 is adsorbed and then dissociated into CO and O. After that, step 1 to step 6 is occurred due to the formation of carbon (C) on the surface and from step 7 to step 16 is occurred to form methane (CH_4).



$$\mathbf{CO_2 + * \rightarrow CO_2*}$$
$$CO_2* \rightarrow CO* + O*$$
$$CO* + O* + \mathrm{H2} \rightarrow CO* + O* + \mathrm{H2}*$$
$$CO* + O* + H_2* \rightarrow CO* + H_2O*$$
$$CO* + H_2O* \rightarrow CO* + H_2O\uparrow$$

$$\mathbf{CO* \rightarrow C* + O*}$$
$$C* + O* + H_2 \rightarrow C* + O* + H_2*$$
$$C* + O* + \mathrm{H2}* \rightarrow C* + OH* + H*$$
$$C* + OH* + H* \rightarrow C* + H_2O*$$
$$C* + H_2O* \rightarrow C* + H_2O\uparrow$$

$$\mathbf{C* + H_2 \rightarrow C* + H_2*}$$
$$C* + H_2* \rightarrow CH* + H*$$
$$CH* + H* \rightarrow CH_2*$$
$$CH_2* + H_2 \rightarrow CH_2* + H_2*$$
$$CH_2* + H_2* \rightarrow CH_3* + H*$$
$$\mathbf{CH_3* + H* \rightarrow CH_4*}$$

Figure 1: Reaction steps involved in CO_2 methanation

A second proposed mechanism for CO_2 methanation is the direct hydrogenation of CO_2 to CH_4 without the formation of CO intermediates. It is also called the formate pathway and Vensselli et al. support the hydrogenation mechanism by direct means. As CO_2 is negatively charged atom at low temperature and is primarily linked chemically via the carbon atom. In this case, the adsorption of H towards CO_2 causes the complex to flip, in which the two oxygen atoms bind to the surface and H binds to the carbon, forming a formate intermediate. By this way, presence of hydrogen prevents the formation of CO [25].

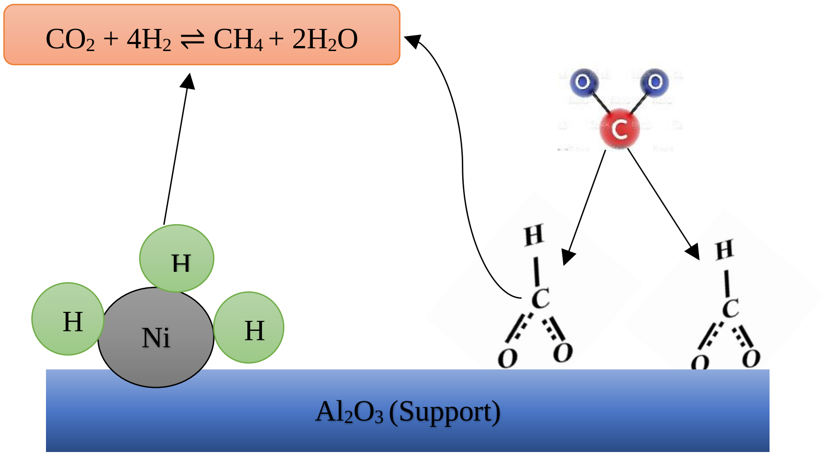


Figure 2: Schematic of reaction mechanism in CO_2 methanation

2.3. Transition metal catalysts

Transition metals are largely used as catalysts for CO_2 methanation and the discussion is made by classifying into two broad categories as mentioned below.

2.3.1. Non-Noble Transition Metal

Non-noble transition metals such as Ni, Co, Cu, Fe, etc. have been used as a catalyst for hydrogenation of CO_2. Among this Nickel is found to be the most active metal because of its easy availability, superior catalytic activity and cheap/acceptable price value. Therefore, to achieve the property like Nobel metals, a catalyst should ensure a good catalytic activity, selectivity and stability. Also, it should be capable of being recovered and regenerated after use by keeping its initial properties. Activity of Nickel catalyst depends on various parameters such as preparation method, presence of second metal, type of support and Ni loading. Here literature review of Ni and Ni-based catalysts is reported and we have again classified into two categories for clear understanding.

2.3.1.1. Monometallic Ni catalysts

From Table 1, it has been observed that, among the prepared catalysts, the catalyst with 30% Ni content is reported to possess the maximum CH4 selectivity. The catalytic performance improved as the nickel content increased from 15% to 30% due to the increased availability of active sites. Due to the formation of much larger Ni particles, which confined access to the internal area of the pore walls as a result of further agglomeration, BET results revealed that as nickel loading increased, the specific surface area increased and then decreased. During a 10-hour period on stream, the catalyst displayed great stability, indicating that it was resistant to sintering. 30wt.% Ni/Al_2O_3 catalyst has been tested by varying calcination temperature ranging from 500 to 800℃ and seen the effect with respect to specific surface area (m^2/g), pore volume (cc/g) and pore diameter (nm). Also, the study of the effects of reaction temperature, H_2/CO_2 molar ratio, GHSV, and calcination temperature has been done for 30 wt.% Ni/Al_2O_3 catalyst. And it was found, CO_2 conversions increased significantly when the reaction temperature was raised from 200 to 350°C. Because of the shorter residence time of the reactants on the catalyst surface and the lower quantities of adsorbed species on the catalyst surface, increasing GHSV to higher values had no effect on CH_4 selectivity. However, the conversions of carbon dioxide dropped. As the calcination temperature was raised, the BET area and reducibility fell, and the catalytic activity also decreased [11]. In terms of physiochemical properties, degree of reduction for Ni/Al_2O_3 catalysts has been estimated by using H_2-TPR characterization technique at 500℃. For 20wt.%Ni catalyst, it rises to 6.2%, then drops to 4.4% for 25wt.% Ni catalyst. This illustrates that the reducibility of Ni catalyst increases as Ni loading increases from 5wt.%Ni to 20wt.%Ni, but thereafter drops. The development of weakly linked NiO to the alumina support occurs when the NiO particle size increases between 5wt.%Ni and 20wt.%Ni and thus increasing the reducibility of the catalysts [12].

Table 1. Physiochemical and catalytic activity data of Ni/Al_2O_3 catalysts

	Al_2O_3	**10Ni**	**15Ni**	**20Ni**	**25Ni**	**30Ni**
BET surface Area (m^2/g)	301.6[11]	105.2[14]	297.3[11]	349.6[11]	292.6[11]	269.2[11]
Pore Volume (cc/g)	0.327[11]	0.17[14]	0.576[11]	0.583[11]	0.584[11]	0.557[11]
Pore Diameter (nm)	4.3[11]	8[10]	7.7[11]	6.6[11]	7.9[11]	8.2[11]
Crystallite Size (nm)	-	12.3[14]	17.2[10]	7.3[15]	24[10]	4.2[16]

CO$_2$ Conversion (%) at 523[14] K, 623 K [16] [18] [25] and 633 K [17]	-	53[14] ,72.1[17]	71[25]	80[12]	70[18]	72[16]
CH$_4$ Selectivity (%) at 633 K [17], 623 K [16] [18] [25]	-	92[25] ,96.1[17]	100[25]	100[25]	97[18]	98[16]
TOF × 10^{-2} (S^{-1}) at 523 K [14]	-	3.48[14]	13.1[24]	-	-	-

2.3.1.2. Bimetallic Ni-based catalysts

The introduction of second metal has a great impact on CO$_2$ methanation. As it leads to enhance the catalytic activity, great impact on reducibility, Ni particle size, specific surface area and conversion of CO$_2$. CO$_2$ methanation has been investigated on the use of various metals such as Pt, Ni, Fe, Co, Ir, Cu, Rh, Ru, Pd, etc., but Nickel metal is found to be the best active metals as far as non-noble transition metal is concerned for CO$_2$ methanation. Also, it is available at acceptable/lower price compared to other metals. The Ni based non-noble transition bimetallic catalysts such as Ni-M (M = Fe, Cu, Co, Cu), have been showed the good catalytic performance. Ni-based bimetallic catalysts with Ni as the primary metal have shown superior catalytic activity compared to monometallic Ni in the methanation of CO$_2$ [21]**.** The Ni-based bimetallic catalysts (Ni-Fe/γ-Al$_2$O$_3$) showed good catalytic performance for CO$_2$ methanation below 500°C. This catalyst with Ni/Fe > 1 achieved 100% conversion at 225°C whereas for the monometallic catalyst (Ni/γ-Al$_2$O$_3$) to achieve 100% conversion the temperature required was 275°C. In terms of CH4 selectivity at 350°C, monometallic catalyst (Ni/γ- Al$_2$O$_3$) achieved 90% whereas the Ni-Fe catalyst (Ni/Fe>1) achieved 100% selectivity at same temperature [13]. Table 2A shows the bimetallic catalytic properties with metal loading of 10wt.%. The CH$_4$ yield, CO$_2$ conversion, TOF and degree of reduction of 7.5Ni2.5Fe/Al$_2$O$_3$ catalyst shows the highest value as compared to other variant of loading in Ni-Fe as well as with the use of different support such as ZrO$_2$, TiO$_2$ and SiO$_2$, where the term called TOF is nothing but to calculate the number of converted CO$_2$ molecules over metallic active sites per second and the identification of the number of metal active sites performed by H$_2$-TPD data. The trend of CH$_4$ selectivity in terms of varying support is as follows 7.5Ni2.5Fe/Al$_2$O$_3$ > 7.5Ni2.5Fe/ZrO$_2$ > 7.5Ni2.5Fe/SiO$_2$ > 7.5Ni2.5Fe/TiO$_2$ [22].

Table 2A. Physiochemical and catalytic activity data of Bimetallic Ni-Fe/Al$_2$O$_3$ catalysts

	Ni	**Fe**	**Ni**	**Fe**	**Ni**	**Fe**	**Ni**	**Fe**
	10%	**0%**	**7.5%**	**2.5%**	**5%**	**5%**	**2.5%**	**7.5%**
BET surface Area (m^2/g)	105.2[14]		162[24]		-		-	
Degree of Reduction (%)	43.2[22]		45.2[22]		43.3[22]		45.1[22]	
CO_2 Conversion (%) at 523 K	11.4[22], 54[14]		22.1[14]		8.0[22]		1.9[22]	
TOF × 10^{-2} (S^{-1}) at 523 K	3.6[22], 3.48[14]		5.9[22]		1.9[22]		0.3[22]	

From Table 2B, it can be concluded that, Ni-Co bimetallic catalysts are very active for CO_2 and H_2 conversion even at low temperatures (300–350 °C). Ni metal content had a significant impact on conversion and CH_4 selectivity. The addition of Co improved the reducibility and metal dispersion of Ni species. The positive effect of Co addition was only seen with catalysts with low Ni loading of 10% by weight. But as the temperature vary from 350 to 400℃, there is a decrement in CO_2 conversion with decreased loading percentage of Co metal [12] [29].

Table 2B. Physiochemical and catalytic activity data of Bimetallic Ni-Co/Al_2O_3 catalysts

	Ni	**Co**	**Ni**	**Co**	**Ni**	**Co**	**Ni**	**Co**	**Ni**	**Co**
	10%	**10%**	**15%**	**5%**	**20%**	**10%**	**20%**	**5%**	**10%**	**3%**
BET surface Area (m^2/g)	141[12]		143[12]		132[12]		134[12]		142.4[29]	
Pore Volume (cc/g)	0.32[12]		0.32[12]		0.28[12]		0.30[12]		0.43[29]	
Reduced Ni/Co at 623 K	31[12]		-		28[12]		13[12]		-	
CO_2 Conversion (%) at 623 K [12] and 673 K [29]	85[12]		82[12]		80[12]		-		78[29]	

From Table 2C, data indicated that the prepared Ni-Cu/Al_2O_3 (5wt.%Ni-5wt.%Cu) catalyst was reduced at 390℃. During the TPR test, there are numerous types of metal interactions with the support (Al_2O_3). When Ni-Cu/Al_2O_3 catalysts were compared with commercial Ni/Al_2O_3 (17.9 nm) catalysts, Cu particles increased the active particle size of Ni (19.3 nm) as mentioned in Table 2C [30].

Table 2C. Physiochemical and catalytic activity data of Bimetallic Ni-Cu/Al_2O_3 catalysts

	Ni	Cu	Ref.
	5%	5%	
BET surface Area (m^2/g)	93		[30]
Pore Volume (cc/g)	0.45		[30]
Metal Surface Area (m^2/g)	11.38		[30]
Crystallite Size (nm)	19.3		[30]
Dispersion (%)	1.74		[30]
CO_2 Conversion (%) at 598 K	89		[30]

2.3.2. Noble Transition Metal

Noble metals such as Pt, Pd, Rh, Ru are found to be the best catalysts for CO_2 methanation as it has excellent activity and stability at low temperature. In terms of deactivation such as coking and metal sintering, it is showing more resistivity towards deactivation as compared to other transition metals. But it cannot be used in frequent way due to its low availability and high price value. That is why it is not preferable for industrial purpose. Which is why we need catalysts which is having cheap/acceptable rate and also easily available. Therefore, transition metals such as Ni, Co. Fe, Cu, etc. have been focused which shows and have the capability to achieve the nearby properties of Noble metals. Even though still it is a big challenge to find the best substitute for the noble metals in field of CO_2 methanation. The combination of Ni with noble metals attempts to transmit some of the advantages of Ni-based catalysts, such as outstanding low-temperature activity, stability, and high reducibility, without the need for large noble metal loading. It increases the number of methanation sites available as well as the amount of hydrogen spilled into neighboring Ni sites. [13].

Table 3A. Physiochemical and catalytic activity data of Ru/Al_2O_3 catalyst

	1%Ru	2%Ru	3%Ru	4%Ru	5%Ru	Ref.
BET surface Area (m^2/g)	198	193	185	172	179	[15]
Pore Volume (cm^3/g)	0.41	0.43	0.42	0.38	0.43	[15]
Pore diameter (nm)	8.0	8.4	8.5	8.5	9.1	[15]
Crystallite size (nm)	7.4	8.1	11.0	11.3	12.1	[15]

Metal Dispersion (%)	5.5	4.7	4.5	4.2	3.9	[15]
Metal Surface Area (m^2/g)	0.20	0.34	0.499	0.61	0.71	[15]
Reducibility (%) at 723 K	100	100	100	100	100	[15]
CO_2 Conversion (%) at 723 K	50	70	80	85	85	[15]
TOF (S^{-1}) at 523 K	0.03[31]	0.03[31]	-	0.81	0.02[31]	[15]

An alumina-supported Ni and Ru catalyst was prepared by wetness incipient impregnation method with varied metal loadings and characterized by multiple techniques (BET, XRD, H_2-TPR). According to the data obtained from Table 3A, increasing Ni and Ru loading results in the formation of additional basic sites, suggesting that both active phases can adsorb CO_2, an essential step in the CO_2 methanation mechanism. Also, it is observed that, as the loading of Ni & Ru increases, it leads to the formation of CO_2 adsorption & H_2 dissociation active sites. In terms of TOF, from, it is clearly indicated that, 4%Ru/Al_2O_3 catalyst was quite more efficient than 12%Ni/Al_2O_3. Also, increasing of Ni content from 4 to 20% leads to a gradual decrease of specific surface area and mesopore volume from 214 m^2g^{-1} to 131 m^2g^{-1} and from 0.563 cm^3g^{-1} to 0.326 cm^3g^{-1}, respectively. As the prepared catalysts contain different CO_2 adsorption sites with different strength. According to desorption temperature or chemical bond strength, basic sites can be classified into 3 categories i.e., Weak ($T < 150$ °C), Medium ($T = 150 – 350$ °C) and Strong ($T > 350$ °C). XRD peaks has been observed for γ-Al_2O_3 at 2θ of 37.7° (3 1 1), 45.8° (4 0 0) and 66.8° (4 4 0) planes. From XRD data it is concluded that, γ-Al_2O_3 is rather an amorphous than a crystalline solid, which makes the identification of crystalline nano-particles more difficult due to peaks overlapping. For Ni/Al_2O_3 catalysts, the presence of crystalline Ni phases was only identified for catalysts with Ni contents more than 8% and appearance of XRD peaks at 44.3, 51.7 and 76.1° 2θ revealed the formation of elemental Ni in reduced catalysts. In the case of Ru/Al_2O_3 catalysts, diffraction peaks at 28.0, 35.1 and 54.2° 2θ were observed in calcined catalysts. After reduction pretreatment at 300 °C, new XRD peaks were detected at 38.4, 42.2 and 44.0° 2θ confirming the presence of Ru in reduced state. The intensity of the peaks grows with the increase of Ru loading from 1 to 5%. XRD peaks of hexagonal Ru is more intense as compared to cubic Ni, because higher crystallinity and crystallite sizes, which have also been estimated by Scherrer equation. XRD result showed that, as the crystallite size increases from 7.4 nm to 12.1 nm, the active phase dispersion decreases comparatively. This trend is consistent with H_2 chemisorption results, which showed that Ru dispersion decreases slightly from 5.5 to 3.9%

as metallic content increases from 1 to 5%. The presence of larger Ru particles formed by agglomeration of several Ru nanocrystals may then be associated with the lowest dispersion of a 5% Ru/Al_2O_3 catalyst. In case of Ni catalyst, Ni dispersion decreases around 25% by increasing Ni content from 4 to 20% due to the formation of larger NiO particles [15].

Table 3B. Physiochemical and catalytic activity data of Rh/Al_2O_3 catalyst

	Rh (3 wt.%)	**Ref.**
BET surface Area (m^2/g)	180	[27]
Crystallite size (nm)	3	[31]
CH_4 Selectivity (%) at 723 K [26] and 823 K[27]	94.1[26], 100[27]	[26] [27]
CO_2 Conversion (%) at 723 K [26] and 623 K [27]	69.4[26], 40[27]	[26] [27]
Reaction rate (μmol s^{-1} g^{-1}) at 723 K	7.7	[26]

Table 3C. Physiochemical and catalytic activity data of Al_2O_3 supported 0.5% (wt.% loading) noble metal catalysts

	Ru	**Rh**	**Pt**	**Pd**	**Ref.**
Metal Crystallite Size (nm)	1.3	1.4	1.0	1.1	[28]
Metal Dispersion (%)	70	79	100	100	[28]
Reaction rate (μmol s^{-1} g^{-1}) at 603 K	20.353	12.79	10.355	0.973	[28]
CO_2 Conversion (%) at 673 K	25	15	10	-	[28]
CH_4 Selectivity (%) at 673 K	90	99	5	-	[28]
TOF × 10^{-2} (S^{-1}) at 673 K	0.595	0.348	0.416	0.021	[28]

Table 4 addressed the promotional effect of Ni (10%) and noble metals (0.5%) catalysts using alumina as support with pressure of 1 atm and the reaction temperature upto 300°C. It shows that reduction rate of NiO is enhanced by the introduction of noble metal and it is in the sequence of Ni-Rh > Ni-Pt > Ni-Pd > Ni. Presence of noble metal also improve the dispersion of metallic catalysts and H_2 chemisorption capacity (Ni-Pt > Ni-Rh > Ni-Pd > Ni). Promotion of noble metal in the form of bimetallic catalyst enhance the catalytic properties by using Ni (10 wt.%)-Pt (0.5 wt.%)/γ - Al_2O_3, Ni (10 wt.%)-Pd (0.5 wt.%)/γ - Al_2O_3, and Ni (10 wt.%)-Rh (0.5 wt.%)/γ -

Al_2O_3 at reaction temperature below 300°C (CO_2:H_2 = 1:4). Among these Ni-Pd/ γ - Al_2O_3 found to be the best performed catalyst for CO_2 methanation. In case of Ni-Pd/ γ - Al_2O_3, at 300°C the CH_4 selectivity and CO_2 conversion has been observed to be 98.7% and 90.5% respectively. Similarly at 250°C the CH_4 selectivity and CO_2 conversion has been observed to be 96.6% and 74.6% respectively. Also, it has been observed that maximum specific surface area has been detected for Ni-Pt/γ - Al_2O_3 and at the same time minimum metallic crystallite size is also obtained for Ni-Pt/γ - Al_2O_3 catalyst which means if we decrease the crystallite size the specific surface area will gradually increase. In terms of TOF, which indicate the enhancement of catalytic properties is found to be the highest for Ni-Pt/γ - Al_2O_3 and the sequence is in the form of Ni-Pt (3.90×10^{-2}/s) > Ni-Pd (3.73×10^{-2}/s) > Ni (3.48×10^{-2}/s) > Ni-Rh (1.85×10^{-2}/s). In terms of activity, Ni-Pt/γ - Al_2O_3 and Ni-Pd/γ - Al_2O_3 are found to be the most active catalyst in the temperature of 180-270°C and it decreases in the series of Ni-Pd/γ - Al_2O_3 ≥ Ni-Pt/γ - Al_2O_3 > Ni/γ - Al_2O_3 > Ni-Rh/γ - Al_2O_3. From characterization it is also concluded that, if small amount of noble metal is added with Ni catalyst, it helps in enhancement of dispersion of the metal on the support and also improve the reducibility of NiO [14] [22]. Table 3C shows the physiochemical and catalytic activity data of noble metal (Rh, Ru, Pt, Pd) catalysts at 0.5wt%. metal loading, which indicate the methanation activity of Ru and Rh catalysts is much higher than that of Pd or Pt catalysts, which tend to enhance the WGS reaction. As the temperature increases above 350°C the CH_4 selectivity and CO_2 conversion decreases simultaneously. In terms of reaction rate, Rh shows the higher reaction rate as compare to other noble metals [28].

Table 4. Physiochemical and catalytic activity data of Bimetallic Ni-M/Al_2O_3 (M = Rh, Pd, Pt) catalysts

	Ni	**Rh**	**Ni**	**Pd**	**Ni**	**Pt**
	10%	**0.5%**	**10%**	**0.5%**	**10%**	**0.5%**
BET surface Area (m^2/g)	107.2[11]		104.0[14]		107.3[14]	
Pore Diameter (nm)	4.8[14]		6.5[14]		4.4[14]	
Metal Dispersion (%)	7.4[14]		6.9[14]		10.4[14]	
CO_2 Conversion (%) at 523 K	33[22]		90.5[22]		69[22]	
CH_4 Selectivity (%) at 523 K	91[14]		98.7[14]		96[14]	
TOF × 10^{-2} (S^{-1}) at 523 K	1.85[22]		3.73[22]		3.90[22]	

2.4. Research Gap

Numerous CO_2 methanation difficulties and elements have been investigated and clarified in earlier review studies. Nonetheless, there remains a knowledge vacuum in the current state of the art devoted only to synergistic interactions between catalytic activity and catalytic features. To close this gap, new developments in CO_2 methanation catalytic systems are needed, as well as current evaluation and synergistic relationships between strong metal-support interaction, particle size, metal dispersion, chemical composition, acidity/basicity, reducibility, porosity, and surface area. Therefore, some of the research gaps has been noticed from the literature survey such as: Ni catalyst (Ni/Al_2O_3) suffers from low thermal stability, Carbon deposition issue at low temperature due to high CO formation, Serious thermal sintering at high temperature leads to low metal surface area, rate of reaction will affect badly at low temperature, efficiency of catalysts after using 10-12 cycle is decreased, catalyst suffers from deactivation at low temperature, still a big challenge to replace the use of noble metal in the field of CO_2 methanation in aspect of catalytic activity, etc.

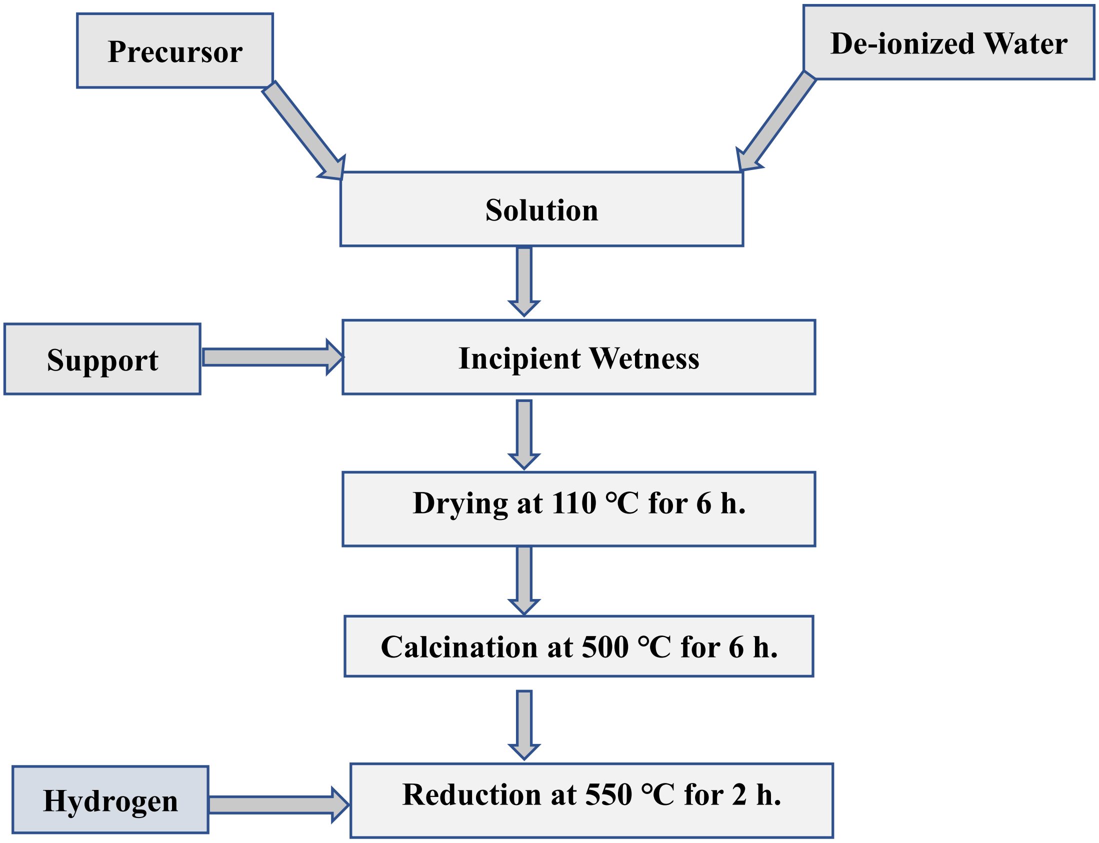
3. Current objectives

The main objectives of the present research work are:

- To develop effective method to synthesize low-cost catalysts
- Synthesis of Ni based ($Ni/\gamma\text{-}Al_2O_3$) and bimetallic non-noble based catalysts (Ni-Fe, Ni-Co and Ni-Cu) and compare with the noble metals (Pt, Pd, Rh and Ru) using Al_2O_3 as support in order to improve the catalytic properties of the samples.
- Structure sensitivity study of best non-noble (Ni_3M) and noble metal (Pt, Pd, Rh and Ru) catalysts.

4. Catalysis Synthesis

There are various methods for preparing catalyst such as Impregnation method, Incipient Wetness impregnation, Dry or capillary impregnation, Sol-gel method, Dip coating method, Co-precipitation method, Micro-emulsion method, etc. Amongst all these methods incipient wetness impregnation method is found to be the best suited method for the preparation of monometallic (Ni) and bimetallic (Ni-Pt, Ni-Pd, Ni-Rh, Ni-Ru, Ni-Fe, Ni-Co and Ni-Cu) Ni based catalyst because of less expensive as compared to other synthesis methods, no gel formation and also it gives high surface area and high dispersion of active metal but with long synthesis time duration. On the other hand, synthesis of the catalyst takes place by taking alumina as support. The metal precursor Ni $(NO_3)_2{\cdot}6H_2O$ (Sigma Aldrich, 99.99%) is required for Ni metal-based catalyst. At first Ni $(NO_3)_2{\cdot}6H_2O$ aqueous solution is to be impregnate dropwise over Al_2O_3 (support) (v_p= 0.6 cm^3g^{-1}). Secondly the impregnated sample will be drying at 110°C for 6 h, after that again drying will take place at 120°C for 6 h. Thereafter, calcination will be processing at 500°C for 6 h at heating rate of 5°C/min. After that reduction will processed at 550 °C for 2 h and finally catalysts will synthesize as mentioned in figure 3 with the help of schematic view. Preparation of a supported metal or metal alloy catalyst primarily requires the choice of a suitable support and total metal loading. At the beginning, γ-Al_2O_3 is chosen as catalyst support, total metal loading of 15 wt.% for Ni and Ni_3M (M = Fe/Co/Cu) catalysts and 3 wt.% for Rh, Ru, Pd, Pt are considered. The amount of different precursors (in g) and fresh water (in ml) required for corresponding catalyst synthesis are tabulated below for both non noble and noble based catalysts.



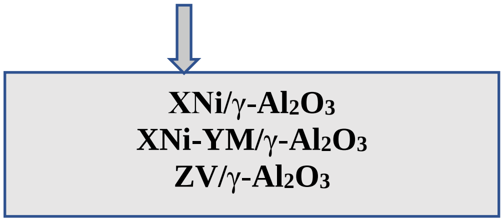


Figure 3: Schematic flow chart for the preparation of catalysts by Incipient Wetness impregnation method

X: % loading of Ni metal

Y: % loading of M (M = Fe/Co/Cu) metal

Z: % loading of V (V = Pt, Pd, Rh, Ru) metal

Table 5. Nomenclature of Al_2O_3 supported Ni, Ni-M (M = Fe, Co, Cu) and Noble metal catalysts

Sample Nomenclature	**Sample Description**	**% Metal loading (g metal/g catalyst)**		**Nominal Ratio Ni:M**	**Ref.**
		Ni / Ru / Rh / Pt / Pd	**Fe / Co /Cu**		
Al	Al_2O_3 support	-		-	Our work
15Ni/Al	Metallic Ni supported on Al_2O_3	15	-	-	-do-
11.25Ni3.75Fe/Al	Bimetallic Ni-Fe supported on Al_2O_3	11.25	3.75	3:1	-do-
11.25Ni3.75Co/Al	Bimetallic Ni-Co supported on Al_2O_3	11.25	3.75	3:1	-do-
11.25Ni3.75Cu/Al	Bimetallic Ni-Cu supported on Al_2O_3	11.25	3.75	3:1	-do-
3Ru/Al	Metallic Ru supported on Al_2O_3	3	-	-	-do-
3Rh/Al	Metallic Rh supported on Al_2O_3	3	-	-	-
3Pt/Al	Metallic Pt supported on Al_2O_3	3	-	-	-
3Pd/Al	Metallic Pd supported on Al_2O_3	3	-	-	-do-

Table 6A. Amount of precursor & fresh H_2O required for Ni/Al_2O_3 and $Ni-M/Al_2O_3$ (M = Fe, Co, Cu) catalysts

Catalyst	Amount of Al_2O_3 (g)	Name of precursor		Amount of precursor (g)		Amount of H_2O in precursor (ml)	Amount of fresh H_2O to be added
		Ni	M	Ni	M		
15Ni/Al	4.25	$Ni(NO_3)_3.6H_2O$	-	3.699	0	1.373	1.176
11.25Ni3.75Fe/Al	4.25	-do-	$Fe(NO_3)_3.9H_2O$	2.774	1.356	2.55	0.977
11.25Ni3.75 Co/Al	4.25	-do-	$Co(NO_3)_2.6H_2O$	2.774	0.926	2.55	1.863
11.25Ni3.75 Cu/Al	4.25	-do-	$Cu(NO_3)_2.3H_2O$	2.774	0.713	2.55	1.361

Table 6B. Amount of precursor & fresh H_2O required for M/Al_2O_3 (M = Rh, Ru, Pt, Pd) catalyst

Catalyst	Amount of Al_2O_3 (g)	Name of precursor	Amount of precursor (g)	Amount of H_2O in precursor (ml)	Amount of fresh H_2O to be added (ml)
3Rh/Al	4.25	$Rh(NO_3)_3.\ xH_2O$	0.4736	0	2.857
3Ru/Al	4.25	$Ru(NO)(NO_3)$	0.4721	0	2.91
3Pt/Al	4.25	$Pt(NH_3)_4(NO_3)_2$	0.2977	0	2.91
3Pd/Al	4.25	$Pd(NO_3)_2.\ 2H_2O$	0.3755	0.0507	2.859

1) **<u>Calculation for monometallic catalyst</u>:**

   - 15 wt.% Ni/Al_2O_3

BASIS: - 5 g.

Molecular weight of Ni = 58.69

Molecular weight of Ni $(NO_3)_3.6H_2O$ (precursor) = 290.8 g/mol

Let,

X = Amount of Nickel (Ni)

(Ni/Al_2O_3) = (X/5-X) = (0.15/0.85) = 3/17

X = 0.75

- 58.69 g of Ni corresponds to 290.8 g of Ni $(NO_3)_3.6H_2O$
- 1 g of Ni corresponds to 4.932 g of Ni $(NO_3)_3.6H_2O$
- 0.75 g of Ni corresponds to **3.699 g** of Ni $(NO_3)_3.6H_2O$

Amount of water associated with precursor solution taken: -

Amount of water present in precursor = 6 × H_2O

= 6 × 18 g

= 108 g

- Water pore volume of Al_2O_3 = 0.6 cm^3/g
- 4.25 g of Al_2O_3 corresponds to 4.25 g × 0.6 cm^3 = **2.55 ml or 2.55 cm^3 of water to saturate the pores**

- 290.8 g of Ni $(NO_3)_3.6H_2O$ (precursor) corresponds to 108 g water present
- 1 g of Ni $(NO_3)_3.6H_2O$ = (108/290.8) = **0.371 g**
- **3.699 g** of Ni $(NO_3)_3.6H_2O$ = 0.371 X 3.699 = **1.373 ml or 1.373 cm^3**

Amount of fresh water added = 2.55ml – 1.373ml = **1.176 ml**

2) Calculation for bimetallic catalyst:

- 15 wt.% Ni_3Co/Al_2O_3

BASIS: - 5 g.

Molecular weight of Ni = 58.69

Molecular weight of Ni $(NO_3)_3.6H_2O$ (precursor) = 290.8 g/mol

Let,

X = Amount of overall bimetal quantity required

(Ni/Al_2O_3) = (X/5-X) = (0.15/0.85) = 3/17

X = 0.75

- (3/4 of Ni) x (0.75) = 0.5625

- (1/4 of Co) x (0.75) = 0.1875

(1) For Nickel: -

- 58.69 g of Ni corresponds to 290.8 g of Ni $(NO_3)_3.6H_2O$
- 1 g of Ni corresponds to 4.932 g of Ni $(NO_3)_3.6H_2O$
- 0.5625 g of Ni corresponds to **2.77425 g** of Ni $(NO_3)_3.6H_2O$

Amount of water associated with precursor solution taken: -

Amount of water present in precursor = 6 × H_2O

= 6 × 18 g

= 108 g

- Water pore volume of Al_2O_3 = 0.6 cm^3/g
- 4.25 g of Al_2O_3 corresponds to 4.25 g × 0.6 cm^3 = **2.55 ml or 2.55 cm^3 of water to saturate the pores**

- 290.8 g of Ni $(NO_3)_3.6H_2O$ (precursor) corresponds to 108 g water present
- 1 g of Ni $(NO_3)_3.6H_2O$ = (108/290.8) = **0.371 g**
- **2.77425 g** of Ni $(NO_3)_3.6H_2O$ = 0.371 X 2.77425 = **1.029 ml or 1.029 cm^3**

Amount of fresh water added = 2.55 ml – 1.029 ml = **1.5207 ml**

(2) For Cobalt: -

- (1/4 of Co) x (0.75) = 0.1875
- 58.93 g of Co corresponds to 291.03 g of **Co $(NO_3)_2.6H_2O$**
- 1 g of Co corresponds to 4.938 g of Co $(NO_3)_2.6H_2O$
- 0.1875 g of Co corresponds to **0.926 g** of Co $(NO_3)_2.6H_2O$

Amount of water associated with precursor solution taken: -

Amount of water present in precursor = 6 × H_2O

= 6 × 18 g

= 108 g

- Water pore volume of Al_2O_3 = 0.6 cm^3/g
- 4.25 g of Al_2O_3 corresponds to 4.25 g × 0.6 cm^3 = **2.55 ml or 2.55 cm^3 of water to saturate the pores**

- 291.03 g of Co $(NO_3)_2.6H_2O$ (precursor) corresponds to 108 g water present
- 1 g of Ni $(NO_3)_3.6H_2O$ = (108/291.03) = **0. 371g**
- **0.926 g** of Co $(NO_3)_2.6H_2O$ = 0.371 X 0.926 = **0.343 ml or 0.343 cm^3**

Amount of fresh water added = (2.55-1.029-0.343) ml = **1.8633 ml**

5. Catalyst Characterization

After preparing the sample, catalysts will be characterized by various thermal and physic-chemical techniques such as Brunauer Emmett Teller Analysis (BET), X-Ray Fluorescence Spectroscopy (XRF), Hydrogen temperature-programmed reduction (H_2-TPR), X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Transmission Electron Microscope (TEM). A brief description of the procedure is mentioned in the below sub sections.

5.1. BET (Brunauer Emmett Teller)

The BET analysis of the catalysts will operate by N_2 adsorption–desorption isotherms at a liquid nitrogen temperature of 77K. The pore size distribution, pore volume, specific surface area and total surface area of the mesoporous alumina (γ-Al_2O_3) support is generally determined with help of this characterization technique. Using a 7-point linear plot, the BET surface area will estimate based on partial pressure ratios (measuring between 0.05 and 0.3). In all cases, at first, the samples will be degassed at 498K for 8 h before surface area measurements are performed.

5.2. XRF (X-Ray Fluorescence Spectroscopy)

Prior to reactions, the elemental composition of each fresh catalysts is used to characterized by X-Ray Fluorescence Spectroscopy (XRF). This analysis is utilized to determine the bulk metal composition of pellets of proposed Ni-M (M= Fe, Co, Cu) catalysts using a spectrophotometer with a Rhodium (Rh) tube operating at 30-60 kW as the source of radiation. The Boric powder will be used as a binder to make pellets of reduced catalysts diluted with support (Al_2O_3). With the help of this XRF analysis, it will confirm the reasonable agreement between the experimental and nominal loading of catalysts which validates the synthesis procedure.

5.3. Hydrogen- Temperature Programmed Reduction (H_2-TPR)

H_2-Temperature programmed reduction (H_2-TPR) experiment is used to measure the reducibility of calcined catalysts on a percentage basis. It is basically carried out in a quartz tube equipped with a thermal conductivity detector (TCD). In this characterization technique, NiO reduction will be focused to know the degree of reduction of metal oxide (%). To conduct the H_2-TPR, the samples will at first be pre-treated with 500℃ in air, followed by 10% H_2-Ar introducing at 900℃. Afterward, Ni surface area will be determined using pulsed H_2 adsorption analysis.

5.4. XRD (X-Ray Diffraction)

The crystalline phases of catalysts after calcination and reduction will determine with powder X-ray diffraction which uses Ni filtered Cu-Kα radiation which operates at 45 kV and 40 mA. Thereafter, the XRD patterns will record with 2θ ranging from 10° to 80° with a scanning speed of 4 or 3°/min. By using Pearson's Crystal Data library, the crystalline phases will be identified. The mean average crystallite size of metallic NiO will be determined using Scherrer’s equation. The required Scherrer’s equation for the calculation of average crystallite size from the XRD characterization technique is given below:

$$D = \frac{K\lambda}{\beta\ Cos\theta} \tag{4}$$

Where,

D = Crystallite size (nm)

k = 0.9 (Scherrer’s constant)

λ = 0.15406 nm (Wavelength of X-ray source)

β = FWHM (Radians) (Full width at half maximum)

θ = Peak position (radians) or angle of incident of X-ray radiations

5.5. Scanning Electron Microscopy (SEM)

By using SEM, one can examine the surface structure of the catalyst and support, as well as how different calcination techniques and catalyst preparation techniques affect it. SEM black and white images of the catalysts were gained and collected by scanning electron microscopy (SEM) analysis using a scanning electron microscope with an accelerating voltage of 10.0 kV and a spot size of 3.0.

5.6. Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) can be used to examine the morphology, particle size distribution, and average particle size of the synthesized catalysts. TEM imaging and high-resolution TEM (HRTEM) imaging is used to carry out with a microscope equipped with a field emission gun at 200 kV and a point-to-point resolution of 0.19 nm. With the help of these characterization techniques, we can determine the average particle size by taking several measurements in two orthogonal directions.

6. Catalytic Activity Tests

The catalytic activity tests for steady state CO_2 methanation will perform in a fixed bed reactor system and the required product (CH_4) is going to observe with the help of gas chromatography (GC) furnished with a 5A molecular sieve, a porapak T column, FID, TCD and a methanizer. The performance of catalytic reaction of CO_2 methanation will depend on various parameters such as temperature, pressure, types of method used for the synthesis of catalysts, the stoichiometric ratio of H_2/CO_2 and many more. Thermodynamically, CO_2 methanation reaction operates under a range of 250-400℃ and an atmospheric pressure of 1 atm. As CO_2 methanation is a two-step reaction process and if the temperature rises above 400℃, then the formation of CO intermediate dominates over CH_4, as CO is produced at the first step of CO_2 methanation process called reverse water gas shift reaction ($H_2 + CO_2 \rightleftharpoons CO + H_2O$). CO_2 methanation reaction is highly exothermic in nature along with certain enthalpy change (ΔH) of -165 kJ/mol, due to which at rising temperatures of methanation reaction, the catalytic activity property does not support. Before the reaction proceeds, a certain amount of catalyst (in mg) will be placed inside the reactor. After that the cylinder of CO_2 and H_2 reactant gas connects to the reactor through mass flow controllers which will control the gas flow rate will purge into the reactor. Then the reaction will start and after a certain period of time, the product will be collected to analyze through gas chromatography (GC) with a thermal conductivity detector (TCD). The schematic view of the CO_2 methanation reaction setup has been described below in figure-2.

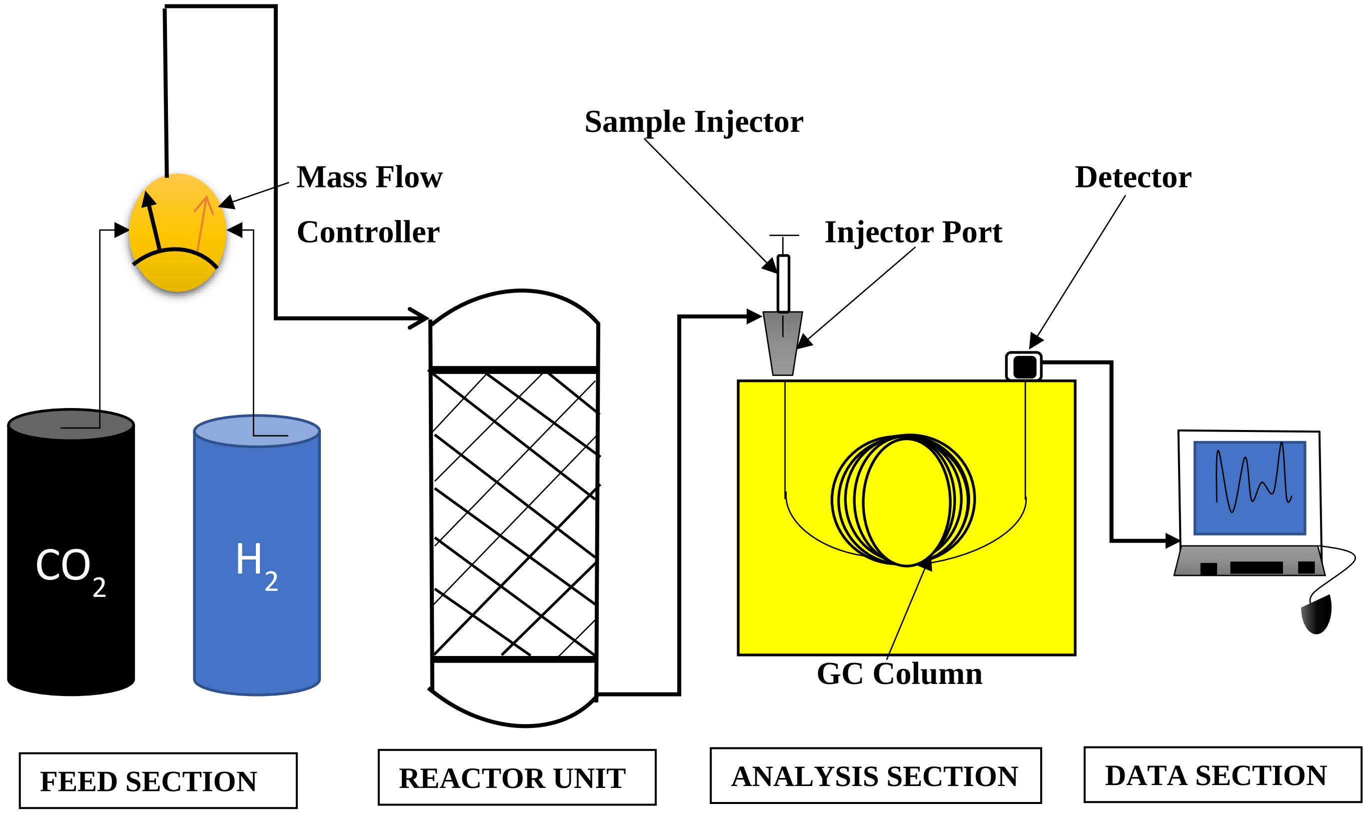


Figure 4: Schematic of experimental setup for CO_2 methanation

7. Summary

The need for developing a low-cost and active (comparable to noble metal) non-noble transition metal (Ni) based catalyst has been highlighted. Several catalysts have been proposed which includes four non-noble (Ni and three Ni_3M = Ni-Fe, Ni-Co, Ni-Cu) and four noble metals for consideration. All the catalysts will be first synthesized by impregnation method with a chosen metal loading. This would be the starting point for our next set of tasks which includes characterization, catalytic activity test in order to finally propose the most suitable catalyst with respect to noble metals (Rh, Ru, Pt, Pd).

Nomenclature

Symbol	**Description**	**Unit**
ΔH^0_R	Enthalpy change of reaction	kJ/mol
*	Active sites	—

S_{BET}	Specific surface area	m^2/g
X_{CO2}	CO_2 Conversion	%
S_{CH4}	CH_4 Selectivity	%
TOF	Turnover frequency	S^{-1}
M	Ru, Rh, Pd and Pt	-

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