Development of Indigenous Coal Fly Ash Derived Co Based Catalyst for Partial Oxidation of Methane

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DEDICATION

“This thesis is dedicated to My supervisor Dr. Muhammad Taqi Mehran and especially to my brother Asif Zaffar and his wife Cecily Chantel Zaffar for their endless motivation, support and encouragement throughout my studies and the research”

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Abstract

Catalytic partial oxidation of Methane was executed over various fly ash derived zeolite-4A supported cobalt catalyst. The zeolitic support was prepared by two step hydrothermal treatment of fly ash from local coal fire plant. After the Zeolite 4A synthesis, cobalt content of 2.5, 5 ,7.5 and 10 weight percent was impregnated on Zeolite 4A through wet impregnation method. Characterization of the prepared samples were done by SEM, XRD, FTIR, TGA and BET. The prepared catalysts sample were tested and operated at 800 °C, atmospheric pressure with feed gas mixture containing CH_4 and O in molecular ratio $CH_4 /O_2 = 2$ in thermcraft vertical fixed bed reactor. The calculations carried out showed, that the best sample was with 10% weight loading of cobalt and it showed the methane conversion of 65% with Co selectivity above 50% and hydrogen yield near 50% .The sample with 10% weight loading run smoothly on stream for 10 hours. It can be inferred that the use of cobalt based catalyst for Partial Oxidation of Methane in comparison to other metals (especially nickel and Iron) is advantageous due to less deposition of carbon on the catalytic surface and hence less deactivation problems and produce clean hydrogen in comparison to SMR other than as an economical process due to efficient heat management . Finally, characterization of the spent catalyst was a carried out and results showed that catalyst retain its structure and most of its properties.

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List of Abbreviations

Z-4A	Zeolite 4A
POM	Partial oxidation Of Methane
SMR	Steam Methane Reforming
OCM	Oxidative coupling of Methane
ATR	Autothermal Reforming
FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-ray powder diffraction
BET	Brunauer–Emmett–Teller
CMR	Catalytic membrane reactor
FTs	Fischer Tropsch synthesis

Chapter 1

Introduction

1.1 Background of the research

Methane is the basic hydrocarbon almost above 90% fundamental component of the natural gas however it is also considered as greenhouse gas, so methane conversion is getting more and more attention. The recent development of shale oil industry and hydraulic fracking had made the conversion of methane much more important. Shale gas mainly consist of methane that is found stuck within shale formations. In contrast to only 1% of US natural gas production by shale in 2000 it has reached 50% in 2014. Most of the reserves of natural gas are in distant and unreachable locations, so the industry is presently facing the odd of reducing the geographical imbalance by creating such technologies and processes to market distant natural gas reserves. Keeping in view climate change and climate mitigation moreover, any process for the conversion of methane into syngas (followed by conversion to useful chemicals) at far flung area is economical in comparison to transfer of methane from far flung areas and resources by pipes. In Conventional SMR (steam methane reforming) we face hard and expensive problems like the disposition of carbon and coking of the catalyst along with maintaining the stability of catalyst due to excessive heat generation because of the exothermicity of combustion reaction however, in POM such problems are avoided. Catalytic POM is a very advantageous process for having hydrogen and oxygen comprising compounds like methanol, formaldehyde, synthesis gas, further we can also use the oxidative coupling of CH_3OH to convert it into ethane, ethylene and many other useful hydrocarbons. POM is among the most important and swiftly evolving field of the catalysis. POM can be divided into two types, one without the presence of catalyst and the other with catalyst. Extensive research of the catalytic POM to synthesis gas which provide a multipurpose feedstock for FTs, as well as CH_3OH and NH_3 formation [1]. The preparation technique and the route for the formation of syngas is very important and these techniques usage are very much related with products obtained and their utilization in the downstream processes. Catalytic POM gives a substantial remedies to solve heat management and huge amount of exterior energy requirements related difficulties faced in convention steam reforming of methane technologies [2]. The final properties and usage of the syngas produced can be associated with the quantity and the ratio of carbon monoxide and Hydrogen present in the syngas formed. The efficiency of POM is analysed in the terms of carbon conversion and economical comparison with well-developed processes like steam methane reforming (SMR). The general POM reaction can be depicted by the following equation.

$$\mathbf{CH_4 + ½\ O_2 \rightarrow CO + 2H_2} \quad \left(\mathbf{\Delta H = -36\ kJ/mol}\right) \tag{1}$$

The new instalment of the coal fired power plants in the country had although subsided the energy crisis but the production of fly ash which is hazardous material as the by product from the burning of coal had forced to think and to take substantial steps to convert fly ash to some useful products. The environmental and health related concerns also forced us to search for cleaner methods and cheaper raw materials so to convert fly ash to some useful product is not only beneficial for us but is also in our best of the interest. Zeolite preparation from the fly ash is quite easy as fly ash consists of the ingredients which are mainly present in Zeolite. Hydrothermal 2 Step treatment method is used for converting coal fly ash into zeolite. The chemical and industrial applications of zeolites are very well established. Zeolite is used in number of reforming processes in refineries. And can be used easily incorporated for methane reforming. Moreover, the hydrogen obtained from Partial oxidation of methane is among the purest hydrogen derived and can be used directly in number of processes where high purity hydrogen is required such as Fuel cells. Hydrogen obtained from syngas cab be used for reforming steps in refineries as the environmental concerns are growing and to meet mounting global demand for H_2 in refineries because of the need to process heavier and dirtier feedstocks. However, it should be clearly kept in mind that POM is not a problem free process the use of oxygen is expensive for which a separation plant and the POM problem Approximately for hundred years the methane reforming processes are commonly using a nickel catalyst. The current industrial processes are mostly based on Nickel catalyst, however nickel also promotes carbon formation, which cause catalyst deactivation and reactor plugging to overcome this problem and make the carbon formation thermodynamically unfavourable industrial steam reformers add excess steam which in turns create the formation of carbon dioxides/carbon monoxide formation and also leads to higher H_2/C0 ratio which very unfavourable for downstream processes . After nearly 100 years of development, we can summarize that the important catalysts can be categorized into three classes which had been generally investigated for the POM to synthesis gas. These catalysts include Ni, Co and Fe supported catalysts, supported nobel metal catalysts and transition metal carbide catalysts. In our study we have used supported cobalt catalyst and we will discuss it further in coming sections.

1.2 Problem Statement

The deterioration of the catalyst because of various factors including carbon deposition on the catalyst surface as shown by equation (2) and (3), economic considerations and environmental concerns related to greenhouse gas emissions are the main problems faced by the today industrial world. CH_4 combustion is well known strong exothermic reaction, on the other hand CH_4 reforming reactions are endothermic in nature. The exothermicity of combustion reaction leads to extreme difficulties related to heat administration, stability and safety in commonly used reactors. By using direct reaction mechanism syngas is formed, without the formation of CO_2 and H_2O intermediates. The direct reaction system has the benefit of being only slightly exothermic, thus lessening the problems mentioned above. However, the indirect scheme (included the formation of intermediates)is thermodynamically ideal and the application of the catalysts in the indirect process seem to encourage the formation of intermediates , with some few exceptions , as some catalyst favour both systems concurrently [3].

$$CH_4 \rightarrow C + 2H_2 \qquad (2)$$

$$2CO \rightleftharpoons CO_2 + C \qquad (3)$$

The products formed by the conversion of synthesis gas have very low yields in comparison to the common fuels used. The main reason for these low yields of products is that they are more reactive than the methane itself., as in the case of OCM of CH_4 to ethane, there is an inherent to maximum achievable yield of 30-40%. So, the analysis of these problem will be very beneficial to catalyst related people at national and international level.

1.3 Research Hypothesis

It is well established fact that transition metals, especially nickel, cobalt and Iron are very suitable catalysts for Methane reforming reactions. Coke deposition is the main problem associated with nickel catalysts and high heat management is on the other hand a big problem in SMR, so we selected a well-developed alternative process that is POM in the presence of cobalt catalyst with Zeolite 4A support. It was inferred that the main constituents of the prepared zeolite, such as SiO_2 Al_2O_3 other than acting as a support will also help increasing the conversion of CH_4, selectivity of H_2 and CO in POM reaction along with cobalt metal.

1.4 Research Objectives

The research presented in this thesis deals with the performance and activity of catalytic POM. The main objective of this work is the formation and study the performance of the developed catalyst, its activity, conversion of methane, H_2 and C0 yield. The experimental work carried out in this research is very well according to the literature data. The specific objectives of this research are:

- To prepare zeolite as a catalyst's support material and to synthesis catalyst samples
- To Characterize the prepared sample samples.
- To run the process of POM.
- To study and understand the effects of catalyst on the chemical processes involved in the process.

1.5 Scope of the Study

Catalyst preparation and testing is one of the main field of chemical engineering. The first step of the study was the collection of fly ash from local coal power plant which have to be converted into zeolite. After collecting fly ash from coal power plant first it was refined through the mechanism of screening and drying of up to 400°C. Then the fly ash was converted to Zeolite. Through wet impregnation method cobalt was impregnated on Zeolite is studied and analysed in variety of Ways. Looking into the process, it can be said that this process depend upon variety of approaches such as reaction mechanism, catalyst used, support applies, operating conditions (like temperature, pressure and reactant ratios etc.) kinds of support, different metals as a catalyst, promoters and differences of the raw material from which we obtained methane.

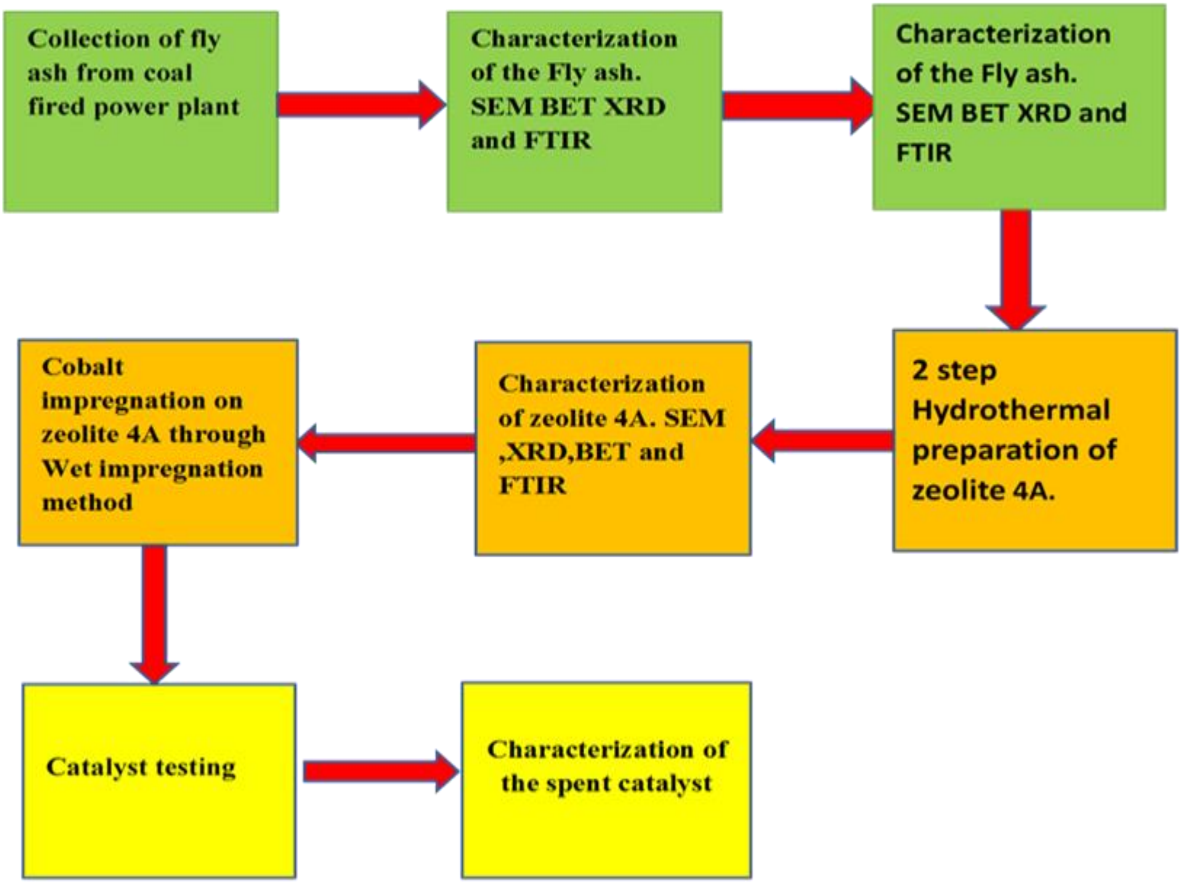


Figure 1.1 Research flow and scope of the thesis

Chapter 2

Literature Review

2.1. Partial oxidation of Methane for Fuel Grade Chemicals

The direct alteration of CH_4 to CH_3OH is termed as holy grail, it will bring the paradigm shift and revolutionized nearly all the fuel and chemical industry [4]. Methanol is very significant fuel for transportation, heating and also used instead of MTBE (methyl tert-butyl ether) as to improve octane number of petrol [5] but it should be noted that till now the direct conversion is in the beginning level and very low reaction yields are achieved through direct conversion.[6] Although the syngas route is expensive one but currently it is the most established method. Maximum yield is impossible along with soot and carbon deposition problem in this syngas route. Among the most industrially established process is steam methane reforming, the autothermal process which is hybrid of POM and SMR had got well deserved attention but however POM processes do not have an industrial application yet.

Methane is the second most wearisome greenhouse gas and considered as chemical for the atmospheric degradation, first is the carbon dioxide. The conventional reforming techniques do not require further discussion as these are the basic methods of numerous pertinent technologies for the conversion of methane to methanol and other fuels. There are many well-established processes for conversion of CH_4 to methanol among these some important ones are reforming processes, photocatalyst processes, plasma technology processes, biological and supercritical water processes. These mentioned technologies are well developed for the conversion of CH_4 to CH_3OH [7].

Intense research is going on for the methods for the conversion of CH_4 to the chemicals and fuel grade chemicals without the passing of synthesis gas step. though, the relevant chemical processes (methane dehydro-aromatization (MDA) and oxidative coupling of methane (OCM)) currently lack the required efficiency for commercialization [8]. Figure 2.1 explains the feasible methods of conversion of methane to fuel grade chemicals.

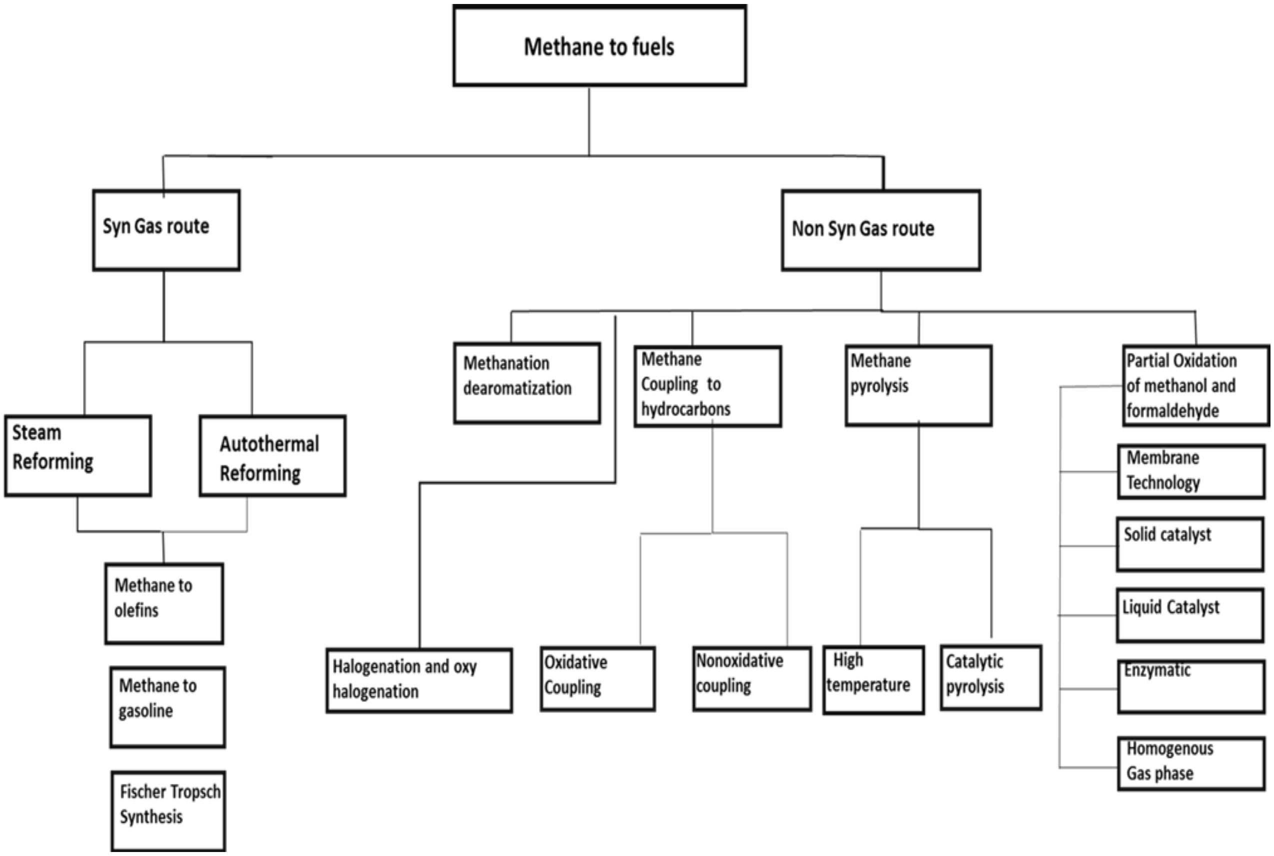


Figure 2.1 Utilization of CH_4 to fuels via various routes

Thorough examination of heterogeneous catalysis established the fact that wide variety of catalysts can be used for catalytic processes ranging from only metals, metallic oxides, manifold metal oxides, zeolitic frameworks and homogeneous catalysis complex catalysts.

One other important of the methane conversion along with heterogenous catalytic reaction is the homogenous gas phase reactions. The main homogenous gas phase reactions that is utilized is OCM. This OCM comprises the reaction of methane and oxygen on the catalyst surface at high temperature to form C_2H_6 as a main product and C_2H_4 as a secondary product. Homogenous based reaction used chemicals like H_2SO_4 etc to produce methanol. The yield of the methanol produced by homogeneous catalytic system is much higher than that of heterogenous catalyst produces.

However, due to irreversible reduction and bulk metal development, nearly all these catalysts displayed deprived selectivity and the maximum methanol production were up to 6% in the process. In order to increase the CH_3OH production, and by the virtue of the development in engineering and technology a lot of scientists are concentrating keenly in the homogeneous gas phase oxidation reactions of CH_4 without the presence of heterogenous catalytic systems.

Economic analysis established that the development of direct route technology can substitute the well-established techniques even when a lowest conversion of 6.9%–11% and selectivity to CH_3OH of over 65% achieved.

By the experimentation it has been proved that degenerate chain branching reaction can be performed on the gas phase reaction for the conversion of CH_4 to CH_3OH in the absence of metallic or heterogenous catalysts [5].

2.2 Catalyst for Partial oxidation of methane

In general, any metal can be used and almost all metals have been tested for catalytic activity for POM, but most commercially used catalysts are nickel and nickel-based oxides. The problems associated with nickel are degeneration because of sintering and carbon build up while in a process. Carbon deposition in nickel is related with its particle size of 5-12nm [9]. The Group VIII metals has shown the following activity order for hydrogen production from SRM Ruthenium ≈ Rhodium > Nickel > Iridium > Palladium ≈ Platinum >> Cobalt ≈ Iron, (Ru) and (Rh) have improved stability on stream, for extended periods as compared to Ni [10].. Economics should be kept in check while selecting catalyst for POM. Presently mixed catalysts (combining two or more than two) are used, which are termed as catalytic system. Reduced metal site has been reported as the active site in most of these catalytic systems. In majority of the latest researches, well established, sophisticated preparations using metal inserted on well-defined frameworks had replaced the conventional metal combining with supports catalyst. In numerous recent works, iridium and ruthenium derived complex combinations like pyrochlores, such as $Pr_2Ru_2O_7$, $Gd_2Ru_2O_7$ or $Eu_2Ir_2O_7$ have depicted fascinating properties in comparison to mostly used ruthenium on aluminium oxide support. The similar phenomenon was observed for $RhVO_4$ supported on SiO_2 in comparison to RH/SiO_2. Other Mixed arrangements such as perovskite: $LaCrO_3$, $LaNiO_3$, $LaRhO_3$, $LaCoO_3$ or spinel show excellent capacities. Rhodium and other noble metals are also commonly used [11]. Following is the table for the most used catalysts for POM along with CH4 conversion and hydrogen and carbon monoxide selectivity.

Table 2.1 Various Catalysts and their Conversion and selectivities. For POM

Support	Metal loading	Operating Temp(°C)	X_{CH4} (%)	S_{H2} (%)	S_{CO} (%)	Ref
Al_2O_3	Co	800 °C	74	90	86	[12]
Al_2O_3	Ni/Co	800 °C	73	89	85	[12]
Al_2O_3	Fe/Co	800°C	57	80	71	[12]
Zeolite	Ni/Co	800 °C	93	89	82	[13]
Zeolite	Ni	800 °C	95	92	80	[13]
Zeolite	Co	800 °C	28	4	24	[13]
Pt/Al_2O_3	Pt	900 °C	49.93	43.62	40.33	[14]
MgO-1	Rh	500	59.6	90.1	76.9	[15]
MgO-5	Rh	500 °C	60.7	87.5	77.6	[16]
Ni0/MgO	Ni	800 °C	40	51	60	[17]
Al_2O_3	Rh	776 °C	94	99	97	[18]
$Eu_2Ir_20_7$		776 °C	94	98	96	[18]

Al_2O_3	Ca and Co	700 °C	88	95	94	[19]
SiO_2	Zr and Ni	800 °C	92	88	90	[20]
CeO2	Ni	800 °C	90	84	88	[21]
Zeolite	Co and Rh	650°C	92	95	88	[22]
Mg-Al oxide	Co	750 °C	83	87	79	[23]
Al_2O_3	Pt	777 °C	87	91	94.3	[24]
aluminate spinals	15.0Ni,5.0Co)	800 °C	23	30	36	[25]
aluminate spinals	10.2Ni,3.4Co	800 °C	42.5	33	39	[25]
aluminate spinals	25.9Ni	800 °C	80	56	42	[25]
neodymium-calcium	Cobalt	800 °C	85	96	92	[26]
ceria-alumina supports	Cobalt	800 °C	83	75	71	[27]

2.3 Cobalt as a catalyst for POM

From the literature we can summarized that the conversion of methane in the presence of oxygen or air into syngas production is studied or tested in number of different catalysts, different catalytic quantities and preparation techniques. Advantages of Cobalt are mentioned in the previous chapter very well, here further studies of cobalt as catalyst for POM will be elaborated. Many studies establish the fact that commonly the two following crystallography phases of cobalt are involved in POM reaction.

1. hcp-Co
2. FCC-Co

Heterogenous catalysts are extensively used in number of the formation of industrial products, especially the chemicals, refinery products, fertilizers and pharmacological products. Though, for their effective use, heterogenous catalyst must resist tough conditions in the reactors without degradation and wear and tear. Cobalt has been very scarcely used as a catalyst for the POM, mostly single metal, combined metals, single oxide, multiple oxides and complex of various metals have been tested for POM.

There have been some studies on supported Co or Fe catalysts for the partial oxidation of methane to synthesis gas. But it is thought that Co and Fe catalysts have a much lower performance for POM reaction, because these metals leads to the formation of CoO and Fe_2O_3 which have higher activity for complete oxidation of methane [31,44,53]. The order for POM activity of the supported catalysts is Nickel > Cobalt > Iron: It is pointed out that cobalt catalysts are active for POM to synthesis gas only when promoted with elements, which favoured Co reducibility [54]. Therefore, cobalt catalysts with high Co content often show high performance for the POM reaction [28,55]. As it is proposed that the active component of cobalt catalysts for POM is metallic Co, and cobalt metal is much easier to oxidize. However, the stability of the cobalt catalyst depends on preparation technique by which catalyst is prepared [56,57]. The choice of support has a significant effect on the performance of the cobalt catalyst for POM. The deactivation of an alumina supported cobalt catalyst may be due to the sintering of the active component and the formation of Co/Al_2O_4: High methane conversion to synthesis gas has been achieved over Co/ZrO_2; while conversion decreased dramatically when Co/La_2O_3 was used [58]. To summary, it can be concluded that Ni and Co supported on various frameworks can be considered for POM to syngas formation. In comparison to cobalt and nickel, Iron based catalysts have been focused very rarely due to instant formation of Fe_2O_3. Mostly the inactivity of the Ni catalyst for POM is associated with cocking, and the harm to nickel because of the damaging flow rates. Cobalt and Iron have greater melting and vaporizing points as compared nickel, so these metals can act as replacements for Ni catalysts if a higher result of catalytic performances are required. Moreover, hints for the methods of modifying Ni catalytic system to overwhelm coke deposition are found in the most works on SMR, where approaches for monitoring crystallite size or the adding of the promoters are finely recognised [15] same can be true for cobalt based Catalysts. It can be summarized the main disadvantage with cobalt catalysts is its low activities and stabilities as compared to other metals used as catalyst loading.

2.4 Zeolite as catalyst support and its Significance

Number of justifications can be given why support is vital, among them the most important one is the ability to stabilize the phase of catalyst which in turn is associated with preservation of small metal particles as well as price i.e. lessening of expensive catalyst constituent’s cost. The working mechanism of support provides robust foundation for the dispersion of the dynamic component of catalyst. The most Important property of supports, that form the basis of their selection for the process is indispensable porosity. If the requirement is to obtain thermodynamically stable product as in the water gas shift reaction then high surface area supports are used [28] on the other hand if the preference is for kinetic controlled products then low surface area supports are commonly utilized e.g. the partial oxidation of C_2H_4 to the epoxide using Ag loaded on α-Al_2O_3 [29]

Zeolites consist of 3D crystalline framework that favourably adsorb small molecules and eliminate bigger molecules. Every nano porous substance has the great ability to provide exceptional chemical and structural characteristics that are valuable for an engineering and industrial uses. The ability and tendency to swap a positively charged ion (cations) is one of the important characteristics of zeolites for the usage in catalysis. Higher density of active sites is present in the zeolite due to their high surface areas, so these nano porous catalysts significantly participate in the reaction at a molecular level. The consequence of this is increased performance, and in turn robust catalytic structure. Characteristics dependence of zeolite on Angstrom level (10^{-10} m) along with other nano-porous substances provides noteworthy potential for future usage in many innovative fields , like biotechnology and nanotechnology [30]. Zeolites due to their high stability, high surface area and most importantly due to the regularity of their pore structure are the excellent choice for catalyst supports [31]. The other main benefit of the usage of zeolite as the other supports is the tendency of Zeolite to separate metal atoms in the pores and so avoid sintering of metal atoms, which would significantly decrease the functional surface of the catalyst. Zeolite 4A supports with numerous particles morphology caused in gaining discrete size of cobalt nano particles. The main disadvantage associated with zeolite is as numerous studies established that the greater amount of silica in the support causes the greater formation of nano-carbon material.

9% of total electricity is being produced is by coal powered power plants in Pakistan currently, whereas other developed countries are producing roundabout 20 to 50 % of electricity from coal fired power plants. number of coal fire plants had been installed recently to meet the energy demand of the country. Experimental work conducted to synthesize uncontaminated Zeolite-4A derived by fly ash for partial oxidation of methane had obtained from the local coal Power Plant. The mentioned industry uses bituminous grade coal imported from Indonesia.

There are many disadvantages associated with coal fire plants and main of that is contribution to increase in greenhouse gas effect and the production of the coal fly ash and so keeping this paradox in mind we have to come to middle way to utilize coal in a maximum protective and less harmful way..

The present utilization of coal power plant’s fly ash in Pakistan does not exist. Although many of the countries used their fly ash from coal fired power plants for number of useful products such as construction industry due to pozzolanic nature of fly ash etc. Fly ash comprises of well, powdered particles mostly spherical in shape, either solid or hollow, and generally amorphous in nature. Mostly, the specific gravity of coal ashes lies in the range of 2.0 but differs to a great degree, from 1.5-3.0. This difference is because of a number of various factors like the structure of particle , progression, and chemical alignment [32]. There are plenty of fly ashes, classification of fly ashes is carried out based on the calcium (Ca) present in them. As shown in Fig. 2.2 below, Class C is the one with hydraulic nature with high Calcium (CaO) whereas Type F is pozzolanic in nature with low calcium (CaO).

Figure 2.2 Classification of fly ash

The fly ashes are categorized into different classes based on their chemical present in them, and this classification will greatly vary due to various coal types and their origination. Based on the ASTM standards, fly ash is classified on the basis of its main elements Silicon, Aluminium, Iron and Calcium as these elements exists in the form of oxides so usually in terms of their percentages the Fly ash can be classified. C and F types of fly ash are classified in the following table. Fly Ash Classification (ASTM C 618-95).

Table 2.2 Classification of Fly ash from coal power plant

Chemical Composition	**Fly Ash**	
	Class C	**Class F**
(SiO_2) + (Al_2O_3) + (Fe_2O_3), min %	50	70
SiO_3), max.%	5	5
Moisture content, max, %	3	3
Loss of ignition, max, %	6	6
Available alkali (as Na_2O), max%	1.5	1.5

Zeolites commercially used as adsorbents and catalysts are microporous, aluminosilicate minerals. Several cations such as Na+, K+, Ca^{2+}, Mg^{2+} and others can be accommodated by porous structure of zeolite. These positive ions are loosely attached and can easily be exchanged for others which are in a contact in a solution. Classification of zeolite is based on Preparation technique used for the making of Zeolite. Based on crystallographic structure, the structure commission (SC) of international zeolite Association give a unique three letter code[33].

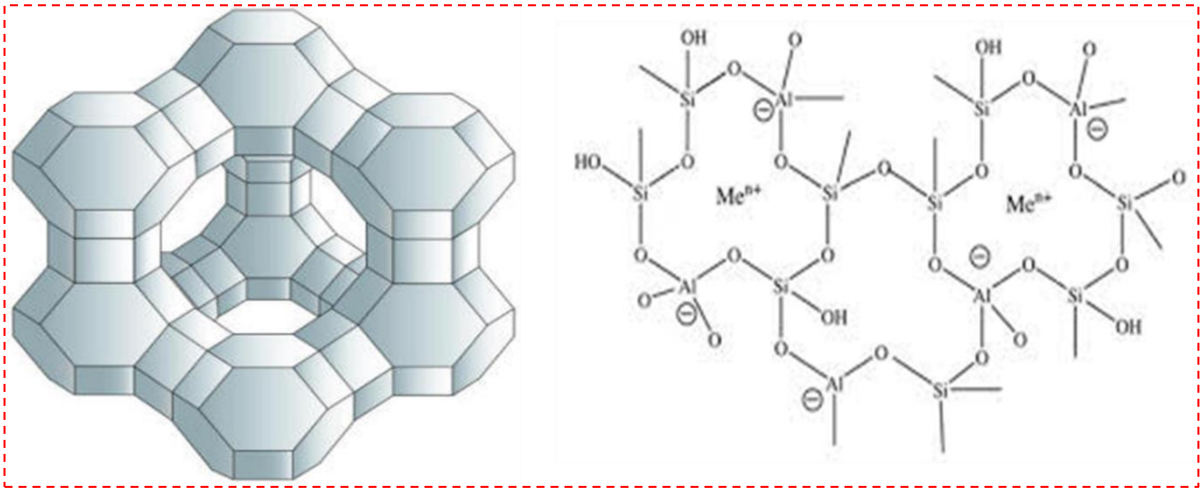


Figure 2.3 (a) zeolite structure (b) Chemical orientation of Zeolite

Classification of zeolite is depicted in Table 2.3

Table 2.3 Classification of Zeolite

Nomenclature	**Formula**
Zeolite A	$Na_2O.Al_2O_3.2SiO_2.4,5H_2O$
Zeolite H	$K_2O.Al_2O_3.2SiO_2.4H_2O$
Zeolite P	$Na_2O.Al_2O_3.2 - 5SiO_2.5H_2O$
Zeolite X	$Na_2O.Al_2O_3.2,5SiO_2.6H_2O$
Zeolite Y	$Na_2O.Al_2O_3. 4.8SiO_2.8,9H_2O$
ZSM-5	$Na_nAl_nSi_{96-n}O_{192}\cdot16H_2O$ (0<n<27)

2.5 Important process parameters

At the different temperatures and its consequence on the product distribution on the process of POM can be analysed from thermodynamic equilibrium designs. For most of the range of temperature used shown in Figure 2.5(a) no conversion of CH_4 is observed at lower temperature (less than 200°C) as the kinetic barrier to the reaction is not attained. Thermodynamic analysis can predict product formation between the temperature of 600°C and 1100°C. While on the other hand by increasing the temperature the selectivity to Carbon monoxides and Hydrogen increases and conversion of methane also increases. This result in high production of synthesis gas at temperature around 1000°C as shown in the figure

The consequence of pressure on POM reaction is depicted in Figure 2.5(b). Increasing the pressure in the system leads to a decrease in both the CH_4 conversion, and the selectivities to CO and $H_,$ as predicted by the thermodynamics. Entropically, at higher pressure, the reforming reactions are less favourable, since this result in gas expansion and are driven away from syngas creation, whilst the total combustion reaction is less affected, so that CO_2 and H_2O becomes increasing favourable with increasing pressure.

The result of the Methane/oxygen ratio on the product distribution from the partial oxidation reaction is shown in Figure 2.5(c). At a CH_4 / O_2 ratio of 2 the stoichiometry is ideal for the partial oxidation reaction, and high yields of synthesis gas are produced. However, if this ratio is decreased, the stoichiometry becomes closer to that needed for the total combustion reaction. So, the development of carbon dioxide and water becomes more favourable, at the expense of synthesis gas selectivity, while the methane conversion increases. If the methane/oxygen ratio is increased, an excess of methane is present which will result in the lowering of he methane conversion. However, the stoichiometry is now further from that required by the total combustion reaction, and so the synthesis gas selectivity increases.

We can have a desired product distribution by varying the space velocities of reactants shown in Figure 2.5(d) .The higher space velocities are mostly not favourable as the reaction become limiting and some of the reaction that may contribute to reach the POM reaction to completion might not attain equilibrium [34].Literature studies had shown that at low space velocities are suitable and values less than 4×10^4 h^{-1} the thermodynamic equilibrium is achieved. Hot spot formation also come into play at higher space velocities

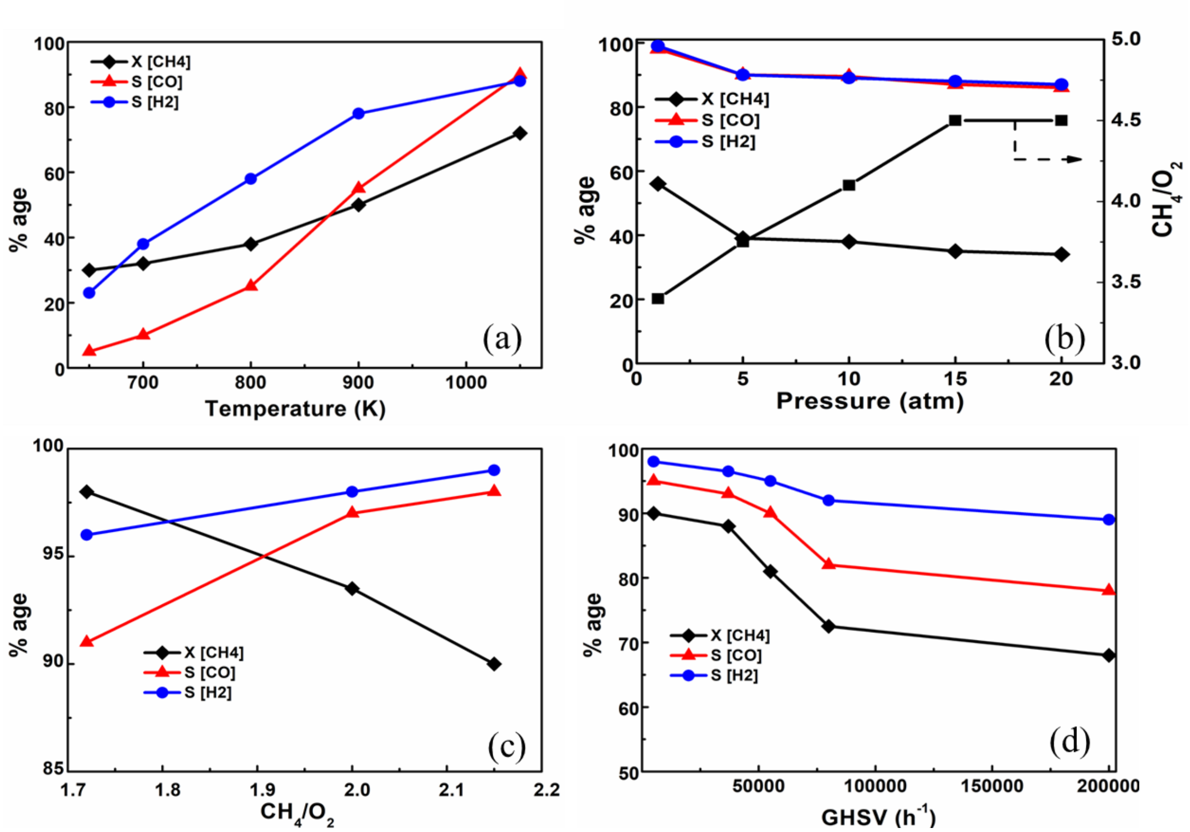


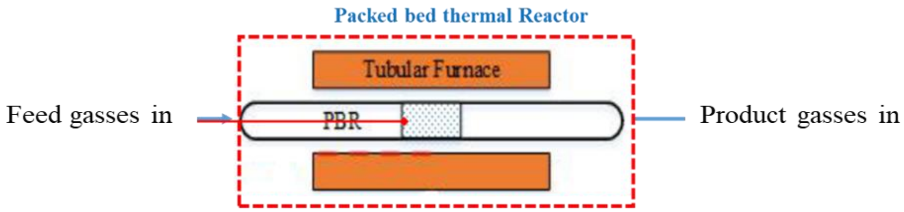
Figure 2.4 Process parametric effect of POM catalytic activity on Co/Al$_2$O$_3$ (a)Effect of temperature (b) effect of pressure (c) effect of CH$_4$/O$_2$ ratio (d) effect of flow rate correspond to GHSV^{-1}. Adopted from Andrew and York

2.6 Reactor Configurations for POM

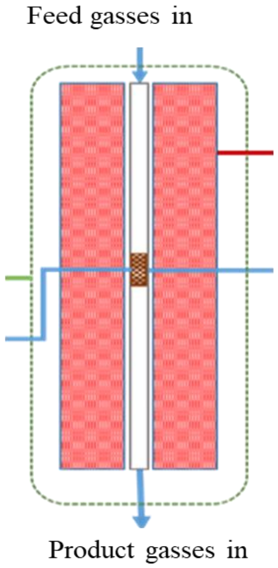
Numerous kinds of catalytic reactors have been used for the study of POM reaction, ranging from fixed bed reactors, fluidized-bed reactors and dual-bed or mixed-catalyst bed reactors. Dual bed reactors are used in ATR, basically they consist of two beds placed in a such manner that have a common centre (concentrically) moreover the feed is introduced in point injection manner at the midpoint of the reactor. Monolith reactors and membrane reactors are also used for POM as they provide additional benefit of separation of produced hydrogen which can be easily used further. Dense perovskite membrane reactors had been tested for POM to produce syngas at commercial scale. [3].

The analysis has shown that for POM by Rh supported on Al_2O_3 the reactor is divided into 2-3 regions, mostly these regions are related with combustion zone and reforming zone. Mostly the high oxidation states exists at the inlet of the reactor resulting in great chances for complete oxidation reactions ,whereas at the outlet of the reactor with novel or zero valent oxidation states resulting in greater chances for the reactions of reforming nature [12]. Over the last several decades many researches had focused upon evaluating the connection between thermodynamic properties and crystallographic properties of metal oxides in solid phase and their how behaviour of immediately attaining high ionic and electronic conductivity. Many works provide a novel kind of anion of oxygen and electron steering brownmillerite resulting membrane constituents these constituents unified into (CMRs) catalytic membrane reactors for accomplishing the spontaneous conversion of natural gas to syngas at easily achieved rates with complete constituents steadiness and performance for prolonged operations [35]**.**

We can generalize reactor configuration into two kinds for POM reaction as shown by the figure 2.5. One is horizontal configuration and the other one is vertical configuration. Both configurations have particular benefits and shortcomings. The property and advantageous of the reactor depend upon the way feed and products interact inside the reactors, residence time allowed by the configuration etc.



(a) Horizontal Configuration



(b) Vertical Configuration

Figure 2.5 Thermal reactor configuration for POM (a) horizontal configuration (b) vertical configuration

2.7 Summary

Partial oxidation of methane is among the important methane reforming processes along with SMR and ATR. POM required less energy as heat from the reaction can be used in reforming process. Moreover, syngas produced by this process has favourable Hydrogen and Co ratio which can be readily used in Fischer Tropsch products synthesis. Hydrogen obtained from this process can also be easily used in processes where high purity hydrogen is required such as fuel cells. It can be summarized that a large number of catalysts for POM has been synthesized and tested along with various operating parameters and rector configurations. The important operating parameters are temperature, pressure, GHSV and the ratio of $CH_4/0_2$.Nickel based Catalyst are most commonly used for POM along with alumina-based supports, but number of other modified catalyst and supports are extensively in use. Cobalt based catalyst in the presence of Zeolite-4A provides a promising advantage for POM reaction as it avoids sintering and carbon deposition problem as faced by the conventional catalysts.

Chapter 3

Materials and Methodology

3.1. Materials

Raw material used in this research for material preparation are listed below Table 3.1

Table 3.1 Materials used in the methodology

Name	**Purity**	**Made /Source**
Flay ash	NA	Local power plants
NaOH	99.9 %	Sigma -Aldrich
Distilled water	99.99	Sigma-Aldrich
Al_2O_3 powder	99.99%	Sigma-Aldrich
Ethyl Alcohol	99.5	Sigma-Aldrich
Acetone	99.5	Sigma-Aldrich
Cobalt nitrate hexahydrate	99.9%	Sigma-Aldrich

3.2. Zeolite Preparation from Fly Ash

Zeolite 4A can be classified as type of zeolite with chemical formula $Na_2.Al_2O_3.2SiO_2.4,5H_2O$ [36]. Z-4A was prepared by modified two step hydrothermal treatment method adopted from [37] presented in Figure 3.1. First the collected fly ash was dried in an oven at 110 °C for overnight, crushed, and after sieving it from a screen of 0.2 mm. The 30 g of fly ash was introduced into 5N NaOH solution in 700 mL beaker reactor. The temperature for the dissolution was kept at 100 °C for two hours without the stoppage of the stirring at approximately at 400 Revolution Per Minute with the help of magnetic stirrer. Filtration process was then carried out to obtain a clear solution. The molar ratio of the synthesized mixture was adjusted as

$SiO_2/Al_2O_3 \approx 1$, Na_2O/SiO_2 1-2, and $H_2O/Na_2O \approx 40$ for the preparation of sole and pure Zeolite-4A phase.

A mixed solution was prepared to attain this ratio, so 200 milli litter of aluminate solution (5 N NaOH solution and 3 gram of Al powder) was added to pure filtrate fly ash solution. Then this solution was stirred for 30 minutes at room temperature with 500 RPM. Primary Gel was prepared by aging solution for 12 hours for overnight. After this the solution was filtered and filtrate were kept in Teflon autoclaves (heat resistant templates) and placed in oven for 1.5 hour for 90 °C and then for 2 hours at 95 °C after that solution was kept for cooling for 12 hours it was again filtered and sample was washed filtered, dried for 12 hours again and calcined at 650 °C for 4 hours.

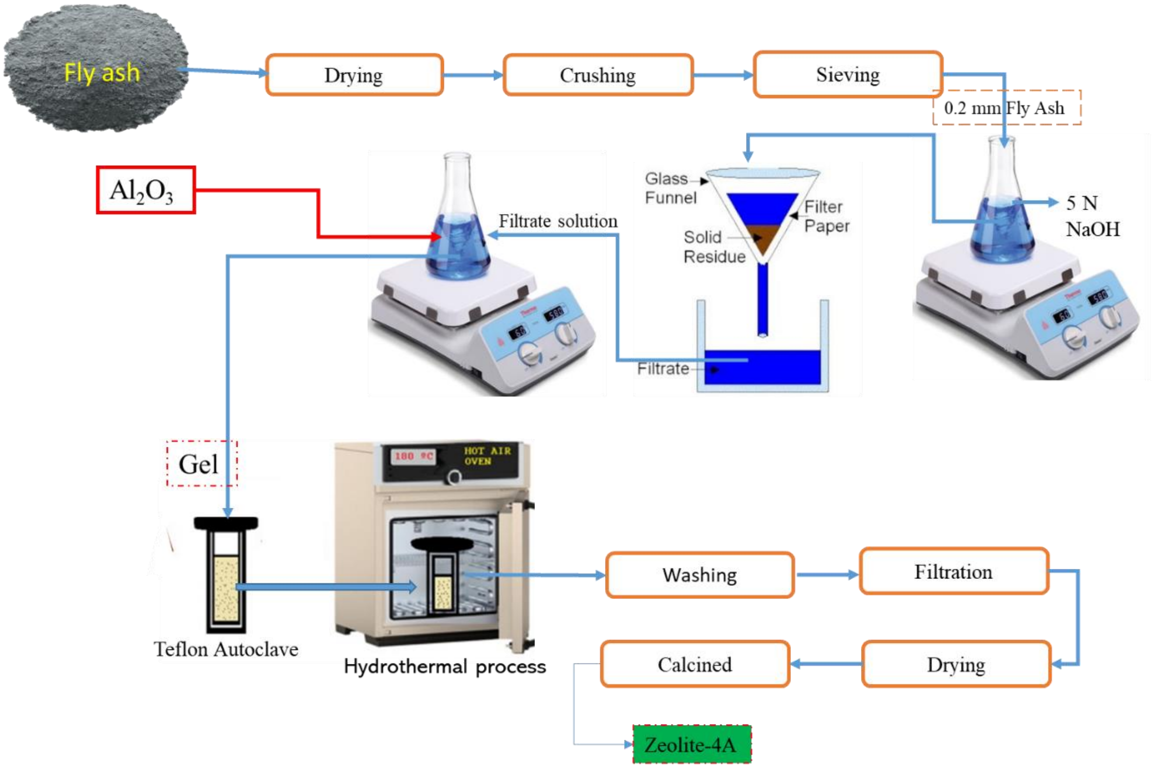


Figure 3.1 Schematic of the Zeolite-4A preparation

The reaction mechanism of the zeolite 4A formation is presented below step by step in Figure 3.2. Maintaining the temperature of 90–95 °C the nucleation stage of the input mixture was achieved at hydrothermal treatment and autogenous (arising from within or from a thing itself.

pressure. The zeolitization process is affected by the temperature due to the high precision of possible reactions according to steps (2,3) shown below. Reorganization of the aluminosilicate gel took place by the virtue condensation reactions which might include polymerization and de-polymerization among the pair of various newly ions formation and a more ordered framework at pseudo-equilibrium after supersaturation phase[38].

$$NaOH + NaAl(OH)_{4\ Aq} + Na_2SiO_{3\ Aq} \xrightarrow{25°c} \underbrace{Na_x(AlO_2)_y\ Si(O_2)_c.NaOH.H_2O}_{\text{Amorphous gel phase}} \qquad \text{(Step 1)}$$

$$[Zeolite = Al - OH]^- Na^+ + = Si - O^- \xrightarrow{25°c} [Zeolite = Al - O - Si =]^- Na^+ + OH^- \quad \text{(Step 2)}$$

$$[Zeolite = SiO^-\ Na^+ + Al(OH)^{-4} \xrightarrow{25°c} [Zeolite = Si - O - Al(OH^-)_3] \quad \text{(Step 3)}$$

$$\underbrace{Na_x(AlO_2)_y(SiO_2)_c\ .NaOH}_{\text{Gel phase}} \xrightarrow{25-95°c(Crystallization\ temperature\ )} \underbrace{Na_x(AlO_2)\ _a(SiO_2)_b.2H_2O}_{\text{Zeolite phase}}$$

Figure 3.2 Reaction Mechanism of Zeolite-4A formation

This freshly created solution is termed as secondary gel and function as the zeolite forerunner where nucleation and crystal growth can happen on already established sites afterward the induction period Ts. Relaxation time for the system is represented by “Tp” this is the time in which primary gel formation is achieved. “Ts” represent the time needed for nuclei development and “Tc” represent period needed for the development of crystal

$$Induction\ time\ (T_1) = T_P + T_S + T_C$$

Z-4A nuclei by consuming aluminosilicate species on its surface develop into a bigger one after the hydrothermal treatment by the using the solution phase that can be preferred by incorporating of ageing time at 25°C to fully develop the formation mechanism and to advance additional agglomeration of crystal nuclei to give the final desired material.

The most important factors to keep in mind is timing for the crystallization etc.The developed Zeolite 4A showed extremely zeolite phase and an active surface area of 306 m^2/g. The this provides the basis for the design of scale-up reactor at capacity of 50 kg/day and perform further experimentation on the pilot scale facility.

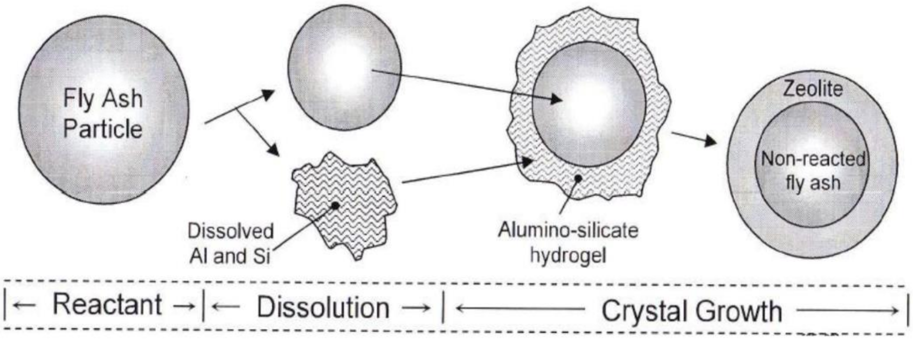


Figure 3.3 Schematic showing the proposed process for fly ash zeolitization. Adopted from Fansuri et al., 2008

3.3. Preparation of Co/Zeolite-4A

The wet incipient impregnation technique was applied to load the Co. The 0.1 M solution of cobalt nitrate was prepared using Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$ Sigma Aldrich) precursor and DI water to load 2.5%, 5%, 7.5% and 10%. Then Zeolite was introduced to the solution and further stirred for 20 minutes at 60 °C. After stirring, the washing of the prepared samples was carried out with DI water and were dried overnight at 120 °C in oven. Before usage of prepared catalyst for POM, were calcined at temperature of 800°C for 4 hrs.

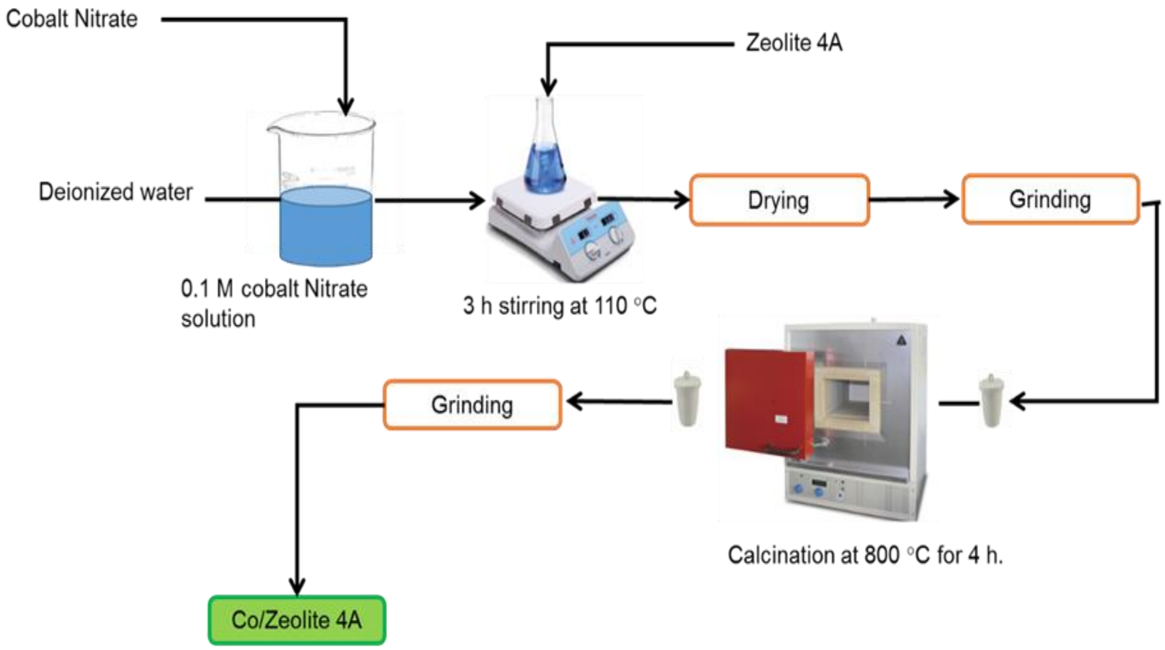


Figure 3.4 Schematic of the preparation of Co/Zeolite-4A

3.4 Material Characterization

To determine physicochemical properties, XRD was done by using D8 Advance (Bruker Advanced, Germany) furnish with Bragg-Brentano configuration and scintillation detector with a radiation wavelength of 1.5418 Å was used to examine crystal phases. The samples were scanned ranging from $2\theta=10°$ to 80° and with a step size of 0.05° per 5 s. DIFFRAC Plus EVA Version 5.0 software was used to examine the XRD analysis.

The morphology of the ash samples was analysed by SEM using JEOL JSM-6490A (Japan) to check the suitability as a support material for Co impregnation and as catalyst formation.

Thermal stability of the ash samples was performed on TGA 5500 (TA Instruments, USA). Before starting the analysis, N_2 was used for purging at a flow rate of 35 mL min-1 for 30 minutes. The 10 mg of the sample was taken for the analysis. Each sample was heated up to 900 ℃ from ambient temperature with N_2 gas flow of 35 mL min-1 with 10 ℃ min-1 of heating rate.

FTIR was carried out to analyse the functional groups in the ash samples using Cary 630 (Agilent Technologies, USA). The absorption of infrared spectra ranges from 4500 to 7500 cm^{-1} with a resolution of 2 cm^{-1} was scanned.

3.5. Experimental Setup for POM and calculations

Schematic diagram of POM experimental setup is shown in Figure 3.5. Feed gas, CH_4 and O_2 were regulated with a mass flow controller (MF4603-n1-1-bv-a, Servoflo Corporation, USA). The reactor consists of cylindrical stainless steel (SS-316) tube with dimension 40 cm in length having 12 mm inner and 14 mm outer diameter. The catalyst was loaded in the central of the reactor tube hold by quartz wool. The thermocouple was placed near a catalyst bed to measure the reactor temperature. Feed and product gases were directly introduced into Gas Chromatograph (GC-2010 Pro, SHIMADZU Japan) equipped with TCD column (RT-MS5A, 30 m x 0.32 mm ID, 30 µm) used to detect H_2, CO_2, CH_4, and CO.

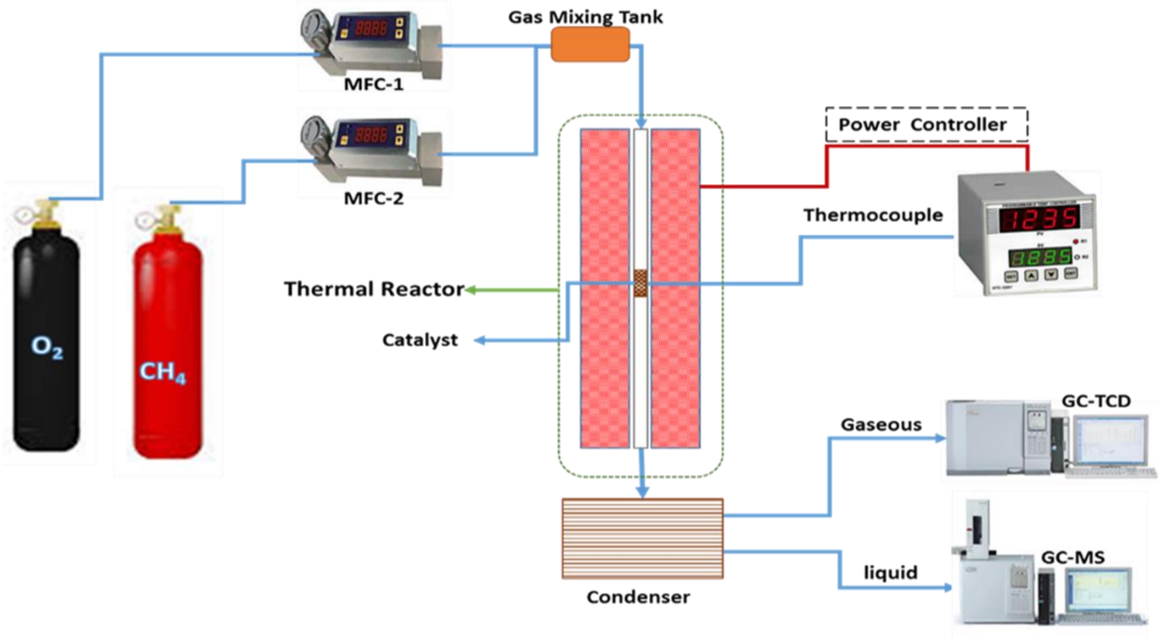


Figure 3.5 Schematic of experimental setup for POM in laboratory

The catalytic activity was analysed using the following equation for CH_4 conversion, CO andH_2, selectivity and yield, where n represent no of moles.

$$\mathrm{CH_4\,conversion}\left(\mathrm{X_{CH_4}}\right)\% = \left[\frac{(\mathrm{n\ CH_4})_{\mathrm{converted}}}{(\mathrm{n\ CH_4}\ )_{\mathrm{feed}}} \times 100\right]$$

$$\mathrm{H_2\ selectivity}\left(\mathrm{S_{H_2}}\right)\% = \left[\frac{(\mathrm{nH_2}\ )_{\mathrm{produced}}}{(2\times \mathrm{nCH_4})_{\mathrm{converted}}}\times 100\right]$$

$$\mathrm{CO\ selectivity}\left(\mathrm{S_{CO}}\right)\% = \left[\frac{(\mathrm{nCO})_{\mathrm{produced}}}{(\mathrm{nCH_4})_{\mathrm{converted}}}\times 100\right]$$

Chapter 4

Results and discussion

4.1. Characterization of prepared samples

Recognition of zeolite 4A framework structure can be supported on the basis of X-ray diffraction (XRD) which is the ordinary method to determine identity and crystallinity of zeolites and gives a exclusive impression of each phase. XRD results for fly ash and Co/Zeolite-4A are shown in Figure 4.1 and 4.2 respectively. The analysis of the XRD pattern of the fly ash showed that the major phase was quartz **(SiO_2)** with main peak at 26.9 θ and less powerful peaks of mullite ($3Al_2O_3.SiO_2$) and finally major peaks at 26.4θ is related to magnetite and hematite. The occurrence of amorphous phases is recognized as a broad diffraction 'hump' in the region between 18 to 32 θ.

A quantifiable quantity of crystallinity of Zeolite-4A is created by adding the heights of around eight peaks in the XRD diffraction pattern. Percentage crystallinity is obtained by the addition of the height of the peaks of the unidentified material divided by the addition of peak heights of a standardized zeolitic material that has been chosen to be purely crystalline (or 100%). The Evaluation of the percentage of crystallinity is the addition of comparative intensities of the maximum powerful peaks of the fly ash derived zeolite and commercial Zeolite-4A. Main peaks were chosen particularly due their least tendency towards changing because of the influences such as cation compensation and to the factor to which the sample is hydrated.

$$\%\, Crystallinity = \frac{\sum_{i=1}^{9} PIPi}{\sum_{i=1}^{9} PIRZi}\ x$$

Where $PIPi$ = i^{th} number of higher peak intensity of the products , $PIRZi$ = i^{th} number of higher peak intensity of the standard. Addition of nine individual intensities was nominated for the percentage crystallinity and was enumerated by the application of above equation.

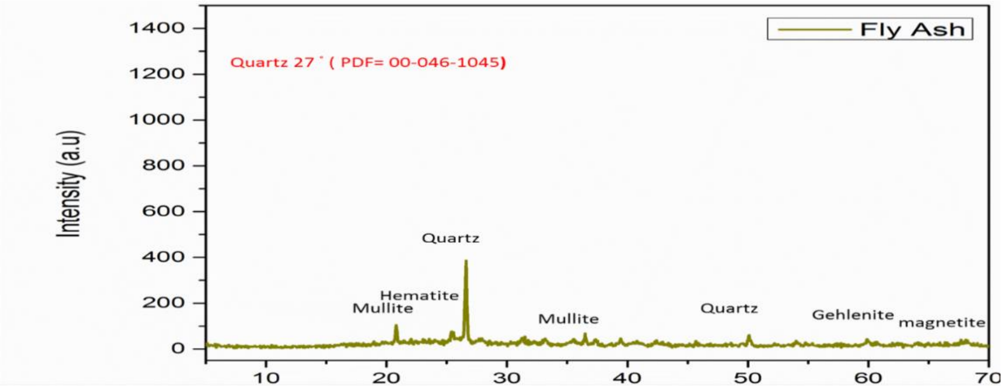
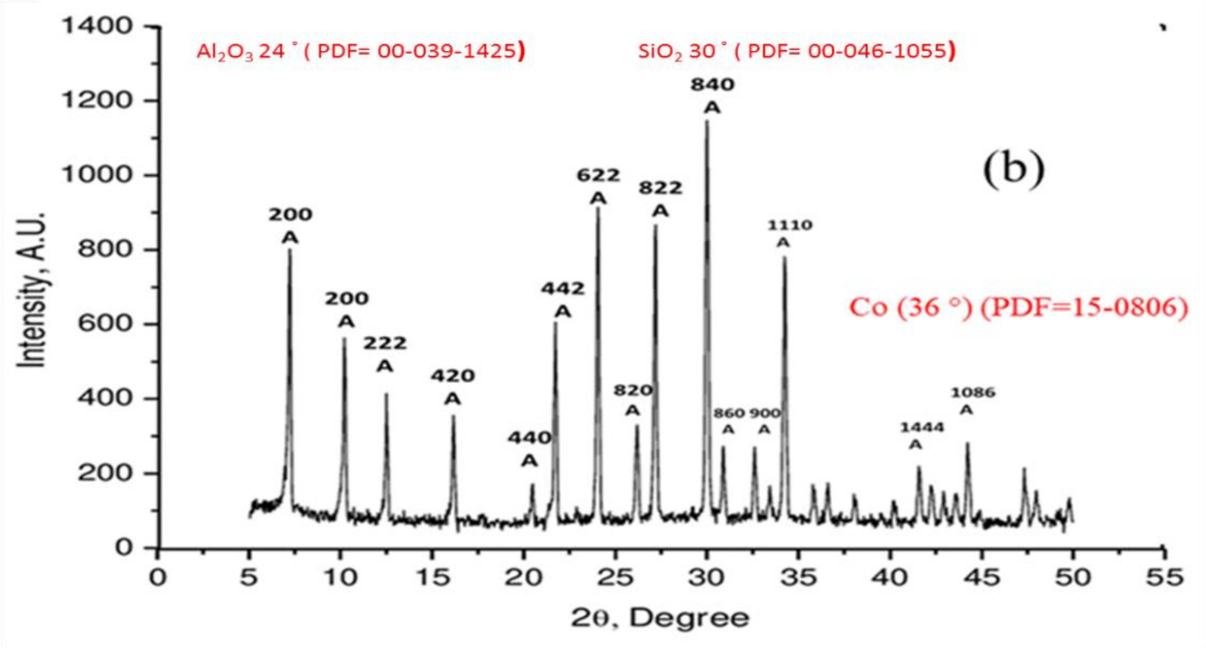


Figure 4.1 XRD pattern of (a) Fly ash (b) Co/Zeolite-4A.

Characterization of fresh Co/Zeolite-4A was presented in figure (number).The zeolite loaded cobalt showed the metallic form at 2θ=44.2° with hlk (111) pdf #15-0806 with d-spacing of 0.204.The oxide ($Co_3 O_4$) form was also detected at 2θ= 36.8° with hlk (311), space group fd3m(227) with d spacing of 0.24. In the X-ray diffractograms of Co*/HYand

From the XRD of Co/zeolite 4A it could also be observed that the number of diffract peaks did not change with respect to fly ash zeolite, indicating that no crystalline transformation occurred during metal impregnation. Thus, the FAU structure still prevailed for Co/Zeolite-4A sample. Cobalt species were present in the cavities and/or surface of HY(catalyst supported).



The uniformity of the number of diffraction peaks with regard to metal impregnation on zeolite confirms that no crystalline transformation occurred during the metal loading via wet impregnation method

Fly ash, zeolite, zeolite after cobalt impregnation and spent catalyst were all analysed by SEM. Surface morphology of the prepared catalyst Type A zeolite comprises of spherical voids of 11.38, diameter approximately at the centre of each unit cell. Surface morphology of the prepared Zeolite-4A. it is well known that surface of zeolite is tetrahedron in shape. The surface of the prepared samples was analysed with a secondary electron detector using the accelerating voltage of 20 kV. On the comparison of the fly ash SEM images with that of prepared Zeolite, it can easily deduce that the textural transformation took place due to change of irregular formed particles of fly ash into uniformed cubic crystal of zeolite

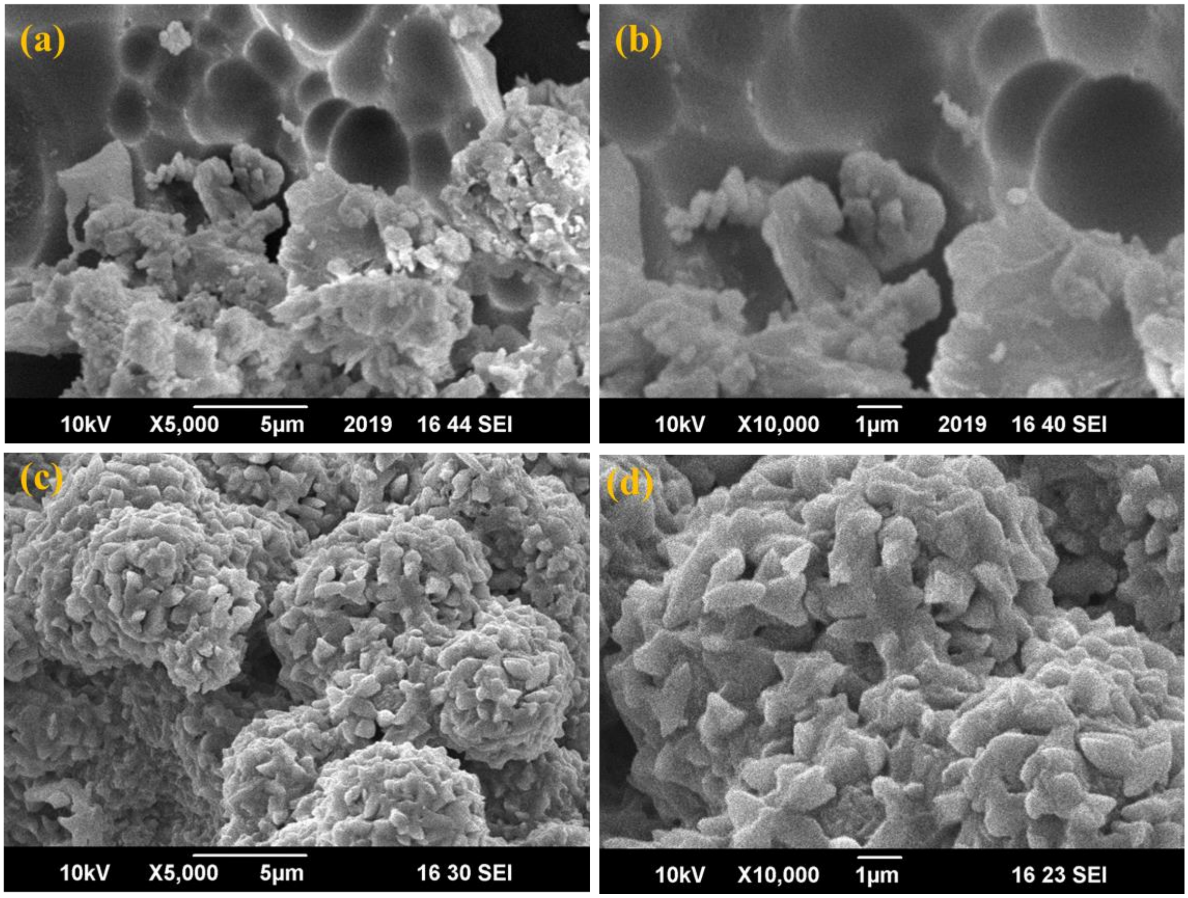


Figure 4.2 SEM micrograph (a) fly ash 5 μm (b) fly ash 1 μm (c) Co/Zeolite-4A 5 μm (d) Co/Zeolite-4A 1 μm

The Figure 4.3 shows the SEM micrograph of new Co/Zeolite-4A catalyst with two different magnifications. The irregular structure in form of pellets was presented in SEM image (Figure 4.3(a)). Properly the Co can be seen in fresh catalyst sample which is further confirmed in XRD. Co had been properly fused into the zeolite-4a support and after modifying, the agglomerated sample structure was transformed into crystalline structure. However, in Figure 4.3(b) with magnification at 5 μm gravestone type structure was also observed. Co was intermixing with Zeolite-4A and non-uniform particles were obtained.

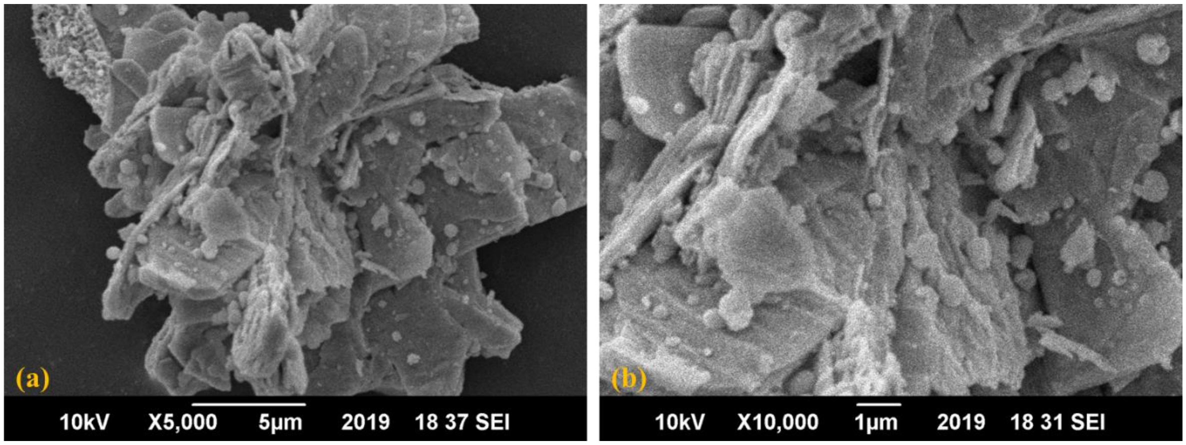


Figure 4.3 SEM micrograph of Co/Zeolite-4A with magnification (a) 5 μm (b) 1 μm

The TGA profile of the prepared sample Co/Zeolite-4A is shown in Figure 4.4. Analysing the Figures, it can be seen that loss of the weight from the sample presented a substantial variation with detected loss of 10.33% of lab synthesis zeolite 4A in comparison to 13.15% of market Z4A.

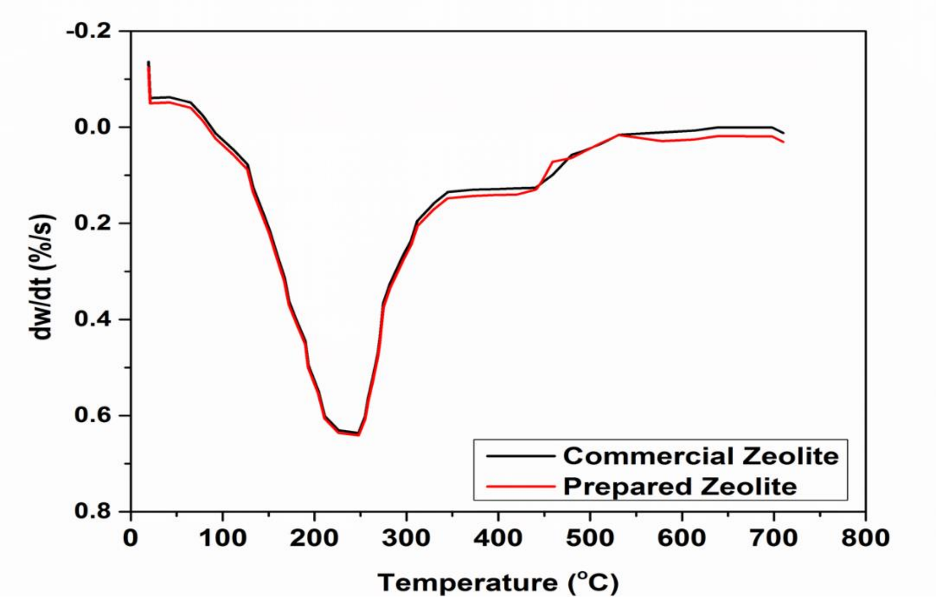


Figure 4.4 TGA of Prepared and Commercial Zeolite -4A

A comparatively big change of water among Fly Ash and market zeolites 4A could be accredited to the surface of Fly ash derived zeolite that has better porosity because of great surface area [39] these results are also defensible by BET results (Table 5).

It is presumed that H_2O is restricted into groups of H_2O molecules at various energy stages based on its place in the lattice of prepared zeolite-4A and kind of its corresponding cations [40]. A visible weight loss happened in the temperature range of 210 °C for the testing sample proving that desorption of the H_2O along with volatiles has happened and inside their pores[41] .

The characteristic H_2O in zeolite is linked to the water that can easily move into and out of zeolite lattice without unsettling it. It is supposed that, the weight loss above 210 °C is related with the water losing ability, that originates from the splintering of hydration complexes with transferable cations of zeolitic structure [42, 43]. From Figs 4.4 and 4.5, it has been observed that both specimens lose weight continuously till the reaching 410 °C, however afterwards the weight loss becomes constant. The previous studies very well established that observation of dehydration of the zeolite till 410 °C. Insignificant weight loss happening above 410 °C can be associated to the hydroxylation method that progressed by the demolition of hydroxyl bonds with cations leading to the exclusion of more water from zeolitic voids [44]. The Silicon/Aluminium ratio has also been described to have a directly proportion related consequence on the high temperature stability of Zeolite-4A. Si/Al ratio is also related to the differences of lattice constant associated to bond lengths of Aluminium-Oxygen (1.528 Å) and Silicon-Oxygen (1.598 Å) is ascribed to this direct effect [45].The TGA Data of our research was in consistence with results stated by various studies in the literature [41, 46]. First and foremost, it has been observed the zeolite samples hold their structural stability and solidity even at greater temperatures of approximately 850 °C, due to which these category of zeolite 4A is beneficial in procedures involving greater temperature steadiness. Hence it is proved the Zeolite-4A derived from coal-based ash will resist severe environments and the structure will remain intact.

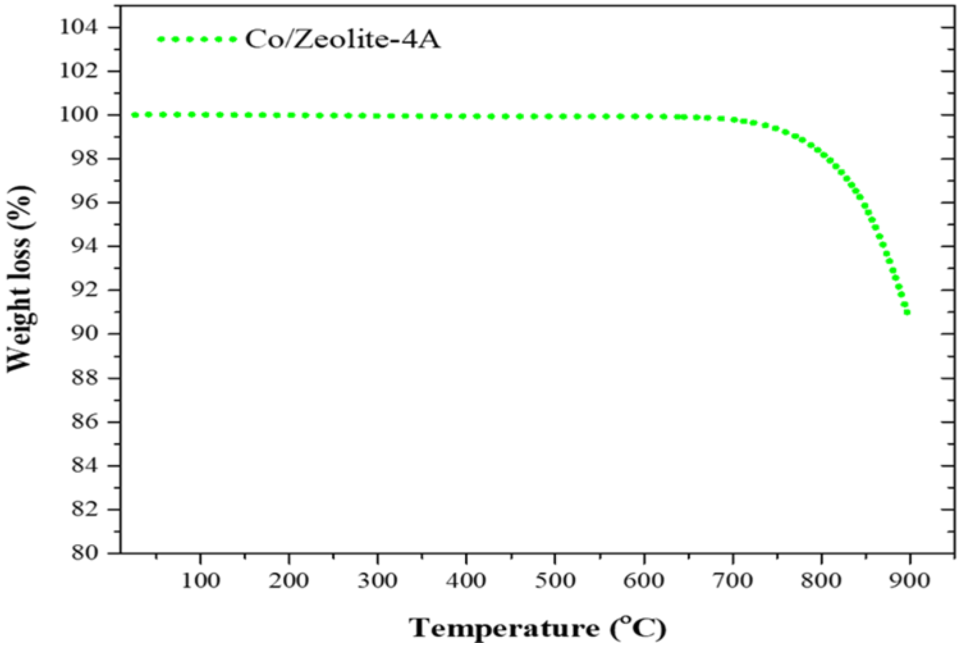


Figure 4.5 TGA profile of prepared catalyst 5%Co/Zeolite-4A

FTIR technique was applied for the monitoring of the structural features of Fly ash and Zeolite-4A the result is depicted in Figure 4.5. The three prominent bands shown in the figure (Number) defines the features of aluminosilicate related compounds. The band emerged at 650 cm^{-1} is related to R-O (R is either Silicon or Aluminium) symmetric stretching vibrations that is due to quartz presence in the fly ash and the band present at 1046.25 cm^{-1} is related with asymmetric stretching vibrations of Aluminium and silicon [41, 47].Very dull band shown at 763 cm^{-1} is most probably due to existence of mullite (Figure 4.5) . After Zeolite Formation, the conversion of fly ash to Zeolite-4A is evidently seen with the help of bands. These vibrations are shared by all Z-4A significantly revealed in the section of 940-1240 cm^{-1} with asymmetric stretching mode. The uniform widening of R-O tetrahedral in coal fly ash at 103.24 cm^{-1} had moved to

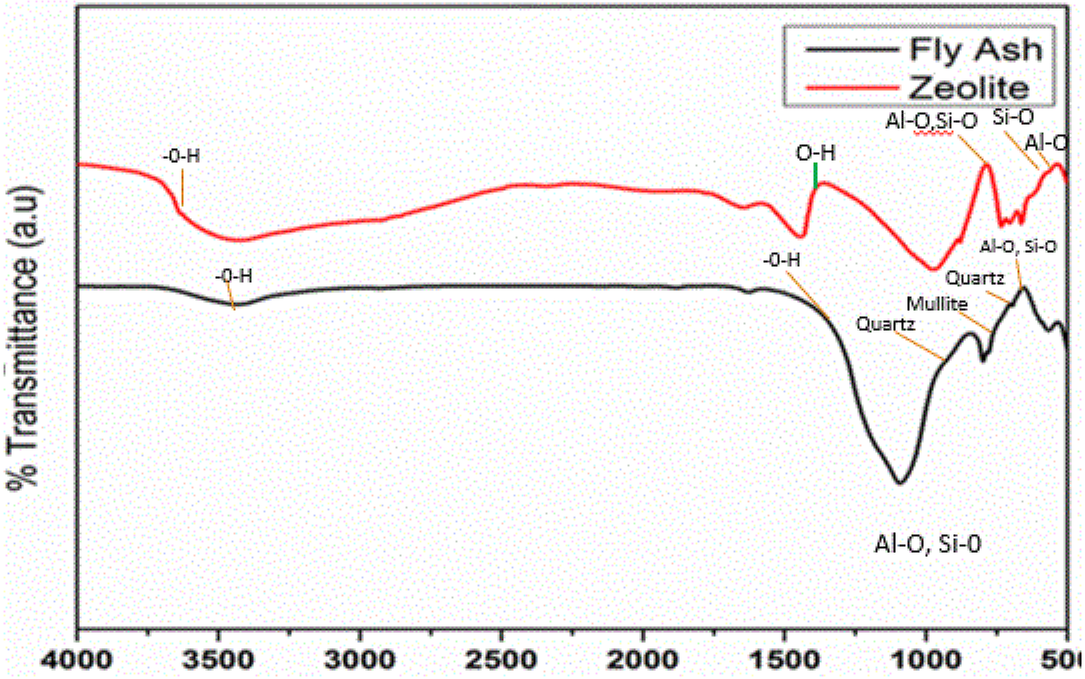


Figure 4.6 FTIR of fly ash and zeolite

lesser magnitude of 957.37 cm^{-1} with a loud and greater intensity that is a chief property in the structure of Z-4A [41, 48, 49]. This is the proof that few of the Silicon of Si-O-Si bond has been substituted by Aluminium for Si-O-Al bond that proposes that structure of Z-4A produced may have smaller Silicon/Aluminium ratio (≈1) than initial material [48]. SEM results too established its definite cubic morphology resulted due to ≈1 Silicon/Aluminium ratio used in raw material mixture. It is well testified that the spectrum seemed in the section of 940-1240 cm^{-1} are delicate to silicon to aluminium ratio of Zeolit-4A [47]. The shift of unique Fly ash spectrum 1037.17 cm^{-1} to lesser amplitudes of dominant peak at 952.48 cm^{-1} also established that glassier constituent of the fly ash might have come in reaction with NaOH the alkaline activator and lead to the formation of Z-4A framework. The not clear band at 65.05 cm^{-1} could related to uniformed stretching of Silicon and aluminium bond [50]. These results validate the results of XRD that have been stated before which is, that the transformation of aluminosilicate minerals in fly ash to particular mineral phases of Zeolite-4A. As showing by the spectra of Zeolite-4A, strong group observed at 1640.81 cm^{-1} is the typical bending method in H_2O molecule [51] . The strong band at 3284.16 cm^{-1} is related to hydroxyl group attached with oxygen ions of the structure [50, 51].The spectral assessment of both samples prepared zeolite and data from literature Z-4A are quite similar and found to validate the assertion, height and width of each peaks showing the occurrence of similar operational units.

Table 4.1 Characterization of the Zeolite determined by N_2 adsorption desorption

Name	BET Surface Area m^2/g	Pore Volume cm^3/g	Average diameter
Fly ash	34.5	0.186	1.9
Prepared zeolite-4A	308	0.789	3.0

The graphical represenatation of the BET measurements is presented in the figure 4.6

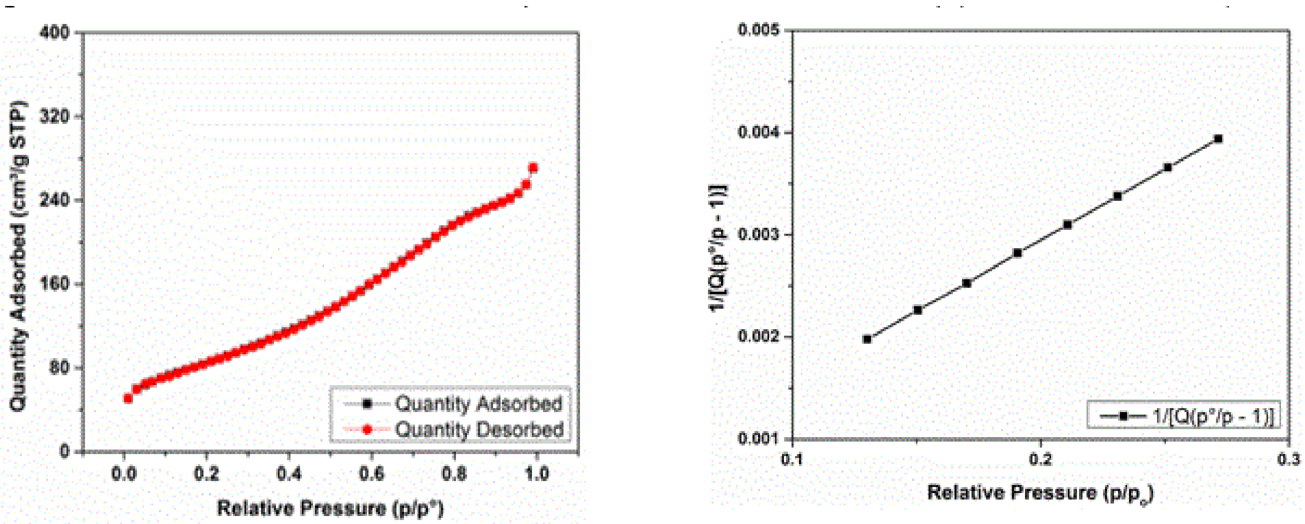


Figure (a) Type II Isotherm

Figure (b) linearized Graph For Specific Volume Determination

Figure 4.7 N_2 Adsorption desorption of fly ash and Zeolite-4A

4.2. Catalyst Screening for POM

The partial oxidation process is very much temperature dependent and it is very well-established fact that product selectivity and catalyst performance of POM are very much temperature dependent Fig. 4.6 (a) illustrates the CH_4 conversion over different Co loadings on Zeolite. The increasing trend in conversion of CH_4 (X_{CH4}) with experimental conditions; reaction temperature 800 and flow rate 30 mL min^{-1}. Various Co loading such as 2.5%, 5%, 7.5% and 10% and its effect on the CH4 conversion. As the Co loading increases, the conversion of CH_4 increased. While using zeolite, the CH_4 conversion was approximately 30%. While addition of Co increased the methane conversion as shown by the graph the 2.5% Co/Zeolite depicts 43 % CH_4 conversion. Similarly, with the introduction of 5 and 7.5% Co/Zeolite the methane conversion reached the value of 55 and 64 % respectively. However, in 10% Co/Zeolite-4A the methane conversion reached the value of 67%. Fig. 4.6 (b) showed the selectivity of hydrogen production. There was not too much variation in graph of hydrogen selectivity. When simple Zeolite was used as catalyst the selectivity was 29%. When 2.5% Co/Zeolite was used as catalyst the selectivity increased to 45%. Increase in hydrogen selectivity can be observed by increasing the cobalt content as shown by the graph of 5 and 7 % weight loadings. Maximum selectivity was achieved to 53% for 10% Co/Zeolite-4A. Similarly, Fig.4.6 (c) displays the graph for yield Y_{CO} (%) of CO production. In case of simple zeolite, the Y_{CO} (%) was round about 24%. As the percentage of Co increases in zeolite, the yield increases. In other words, percentage of carbon monoxide is directly proportional to Cobalt weight loading which can also be seen in Fig. 4.6 (c). By addition of 2.5% Co in 0.2 gram of cobalt the yield has been increase from 24% to 35%. Increasing yield of CO has been shown in figure at 5 and 7% cobalt weight loading. While in case of 10% Co addition, the Y_{CO} (%) is 50 % approximately.

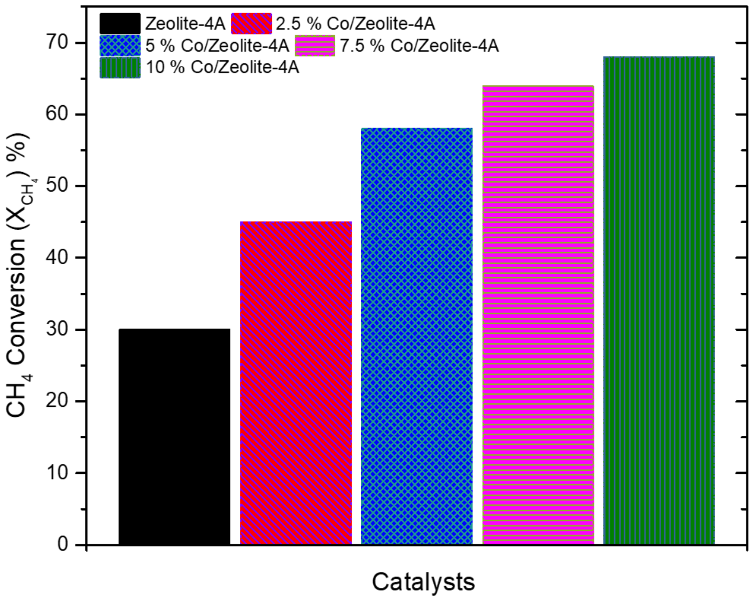


Figure 4.8 Catalyst screening for CH_4 conversion in POM reaction: flow rate =30 ml min^{-1}, catalyst loading =0.3 g reaction temperature =800 °C

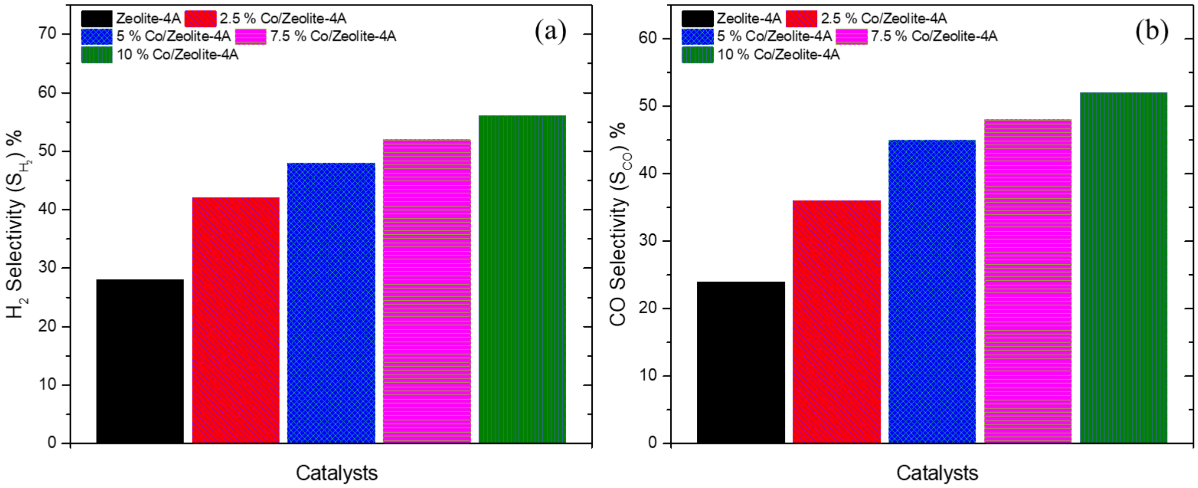


Figure 4.9 Catalyst screening for POM (a) H_2 selectivity (b) CO selectivity: reaction: flow rate =30 ml min^{-1}, catalyst loading =0.3 g, reaction temperature =800 °C

4.3 Stability analysis of Co/Zeolite-4A

Now the effect of the 10% Co/Zeolite 4A time on stream (TOS) on CH_4 conversion, H_2 selectivity and H_2 yield with catalyst loading 0.2 g, reaction temperature was 800 °C, feed flow rate of 20 ml min-1 is shown in Fig. 4.7.The support formation and surface properties also influenced the CH_4 conversion, H_2 selectivity and H_2 yield. It was expected that as the catalyst was being used for methane decomposition will ultimately be deactivated as carbon was deposited. It was observed that methane conversion was found increased for first 3 hrs after that it was gradually increased. Approximately after 5 and half hrs the catalyst was fully deactivated. Round about 0.6 g was accumulated on 0.2 g of Co/Zeolite-4A catalyst sample. The obtained amount was in good form against the calculated one. Life of catalyst and catalytic activity mainly depends upon the pore structure of catalyst [52]. It may also affect the morphology of deposited carbon and exhaust gas composition. Moreover, with slight decrement in selectivity after 1 hrs is starts increasing throughout the time. Similarly, the Y_{H2} was increasing from the starting to end.

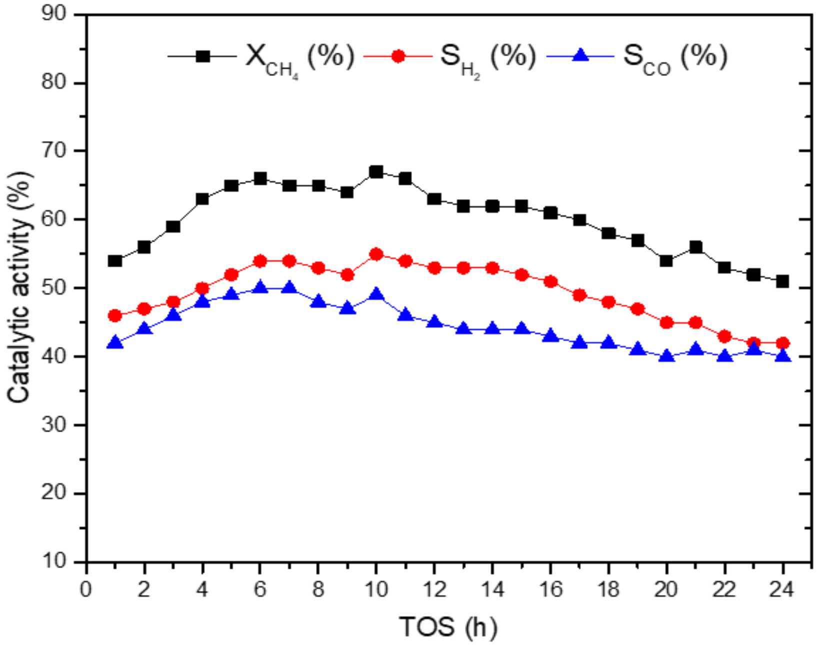


Figure 4.10 Catalyst stability for POM using 10%Co/Zeolite-4A (a) H_2 selectivity (b) CO selectivity: reaction: flow rate =30 ml min^{-1}, catalyst loading =0.3 g, reaction temperature 800 °C.

4.4 Characterization of the Spent Catalyst

TGA of the spent catalyst was carried out and it can be clearly seen that contrary to the TGA of fresh prepared catalyst the spent catalyst shows weight loss around 800 °C

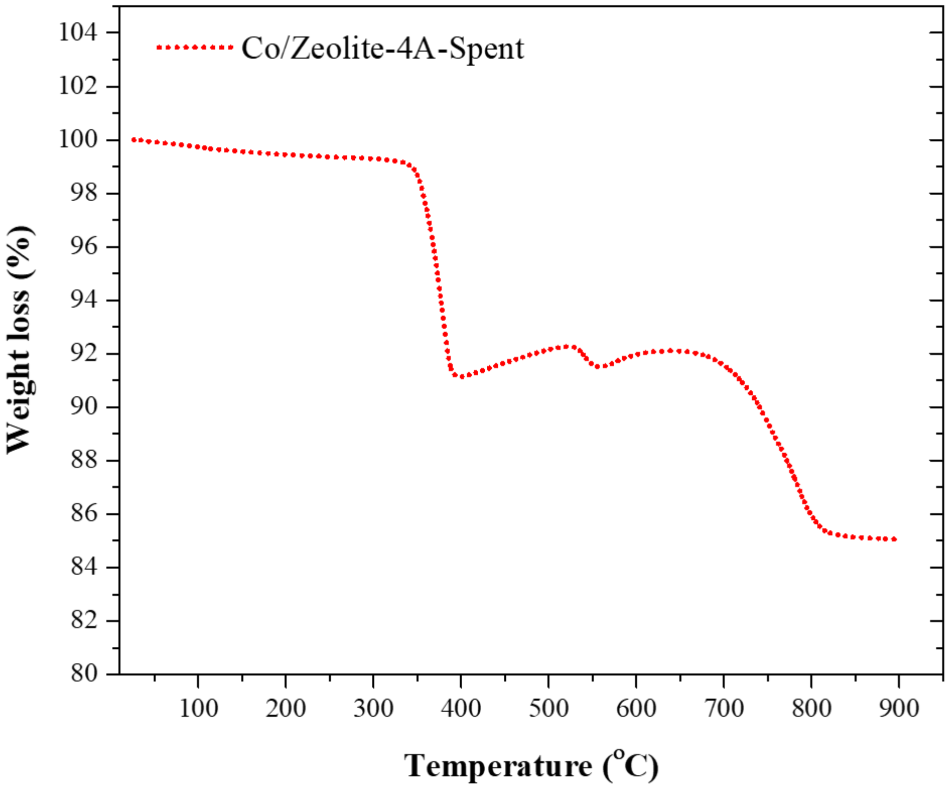


Figure 4.11 TGA profile of spent 10% Co/Zeolite-4A after 24 hours of TOS

4.5 Future Prospect

The need for the energy has increased drastically and in turn methane reforming has been emphasized to this meet energy need. One of the vast filed been studied and need focus for methane reforming is by the application of plasma. Various kinds of electrical discharges can be used such as dielectric barrier discharges, corona gliding and microwave plasma. In plasma reforming the electrical energy is used to generate free radicals to achieve oxidation reaction. The advantage of plasma reforming is that it can even occur without the application of catalyst with high methane conversion and higher Hydrogen and CO selectivities. With the application high voltage, the gas can be ionized to electric energy discharge due to the interaction of gas atoms or gas molecules with electrons. These highly excited species due to functional electric field, results in the creation of plasma which is also known as fourth state of the matter. Due to very short start up, large operating power of the fuel and its compactness and robustness as shown by literature studies, the significant benefits of this technique can be applied for the automotive industry. The process with best conditions and mechanism showed 95% of conversion of methane with very minimal use of the energy.

Other area of interest for POM is development of membranes. The kind of membranes used in reforming process is known as transport membranes development. By using Membranes hydrogen can be generated on site although it is cost effective technology but with the time improvement of technology is leading for economical membranes. By using reactors that have membranes the oxygen needed to achieve the Catalytic POM reaction is divided from air introduction to one side of the membrane at temperatures around 25 °C and reasonable pressure (0.04-0.25 bar) and reaction happen on the other side with CH_4 and steam at higher pressure (2-25 bar) to form synthesis gas. As indicated by the latest developments like of, li et al.[53] they used a novel catalytic system which consist of perovskite system ($BaCe_{0.1} Co_{0.4} Fe_{0.5} O_{3-\delta}$) fixed with lithium Lanthanide Nickel and aluminium oxide catalytic system . It is well known that the unaccompanied membrane is very little active in the Catalytic Partial Oxidation of Methane reaction but along with catalyst it increases both CH_4 conversion and carbon monoxide selectivity up to about 96%. On the other hand, the O_2 infiltration improved by approximately eight times higher; this performance was maintained for more than 1000 hours. A changed composition of the membrane ($Ba_{0.5} Sr_{0.5} Fe_{0.8} Zn_{0.2} O_3$) sintered at approximately 1200 °C was introduced by Luo et al. [54] to test the catalytic POM reaction. Running this catalytic system approximately for the duration of 110 h on stream showed the conversion of methane to approximately 70%, Carbon monoxide selectivity was above 95% and a H_2/CO ratio approximately 2. The most common difficulty faced in the application of such membranes is the absolute pressure difference across the membrane. It may tend the procedure to become highly expensive and air must be compressed to confirm same pressures on both sides of the membrane. Such catalytic membrane is required which ensure high mechanical strength if suitable pressure of the air is applied. In any circumstance, the operation may be excellent right for minor or middle scale operations. However, at the present period of application of catalytic membrane systems, it is not feasible to envisage when they will be ready for application for the industrial scale. Important problems are to be resolved, and this technique is not yet to level where it can contest for industrial scale manufacture of syngas within the reasonable upcoming time. The application of total pressure difference across the membrane is the most important difficulty in the making CMR for POM. This problem of pressure application on the membrane may make this technique expensive and economical non-feasible. In most of the cases air have to treated by the mechanism of compression to guarantee same pressures on both sides of the membrane. When we applied high optimal pressure high strength membrane will be required. It can be concluded that this process, could only beneficial for minor and medium scale operations. Presently, progress in membrane technology, does not give information that when they can be applied for industrial scale.

Conclusion and recommendation

Experimentation of the prepared catalysts and evaluation of the performances of the prepared samples for the catalytic POM showed marked differences in the results. The main difference was observed in our studies can be associated to different weight loadings. The availability of greater metal surface for reforming might lead to modifications that continue dominate are CH_4 detachment, affinity of the sites which will bind, the firmness of OH surface species, active specie's surface residence time and participation of the lattice oxygen atoms which help the surface species. This research establishes the fact that a novel mechanism for the syngas cannot be anticipated. The splitting of the methane molecule can occur either on the catalytic surface which is reduced though detachment of the CH_4, this can happen either due to the presence of oxides of the active species at higher temperatures which are reduced due to direct contact with CH_4 or from the reaction with Hydrogen, Carbon and Carbon dioxide. Metal cobalt catalysts along with Zeolite-4A establish that the basic reactions that are involved tends to establish the fact that the formation of H_2 as a basic product depends on the greater activation energy barrier to the creation of OH. Consequently, zeolite-4A support system that is used in the study should not help in the stabilization of hydroxyl group. The other important characteristic of the catalyst system used should be to preferably tends toward the creation of Hydrogen and Carbon monoxide as priority products in comparison to secondary products like carbon dioxide and water molecule. For this it must have a decrease capacity towards a low surface coverage of secondary products, such that the chances of O-H, O-CO and OH–H connections are reduced. Making the energy barriers such that H_2 and CO desorption is helpful, as it would prevent their reintroduction into a particular area of the catalytic bed. Furthermore, the catalyst must be highly unreactive for the coke deposition and carbon development at these little surface exposures. This work can greatly contribute to discipline of catalytic POM as this study is carried out at the well-established standards of catalyst development and conditions for the carrying out the reactions are recognised. Especially many possible avenues for continuous research like detailed strategy for making catalytic system which increase the catalytic performance and steadiness. The foremost problem faced could be the initiation of nano or micro sized entrenched particles of the metal that can be fix easily in the main catalytic framework, these entrenched particles are very smaller than the particles which produce catalytic effect and characteristically favour the carbon deposition and progress of it. In addition, the other significant field to be researched thoroughly is the introduction and consequence of the introduction of promoters. Many promoters have been anticipated and tested to increase the distribution and efficiency of cobalt based catalysts, best percentage loadings of catalytic metal and the promoter is still depended on extensive testing and experimentation. The progress of hypothetical models that can forecast the consequence of various promoters on catalytic metal distribution and performance would be very helpful. There is also a lot of space for examining the outcome of combined metal construction (such as alloy) in multifaceted and sophisticated catalytic frameworks (such as perovskites) by the stabilization and changed metal particle geometry. Introduction of cobalt catalysts and its functioning cannot be restricted only to metal oxide starters but also on the supports of metal catalytic frameworks which have very optimized surface residence time and concentration of oxygen is very well suited for the formation of syngas. At the last hypothetical understandings and modelling like TGA evaluation for great collections with twists and phases are undoubtedly value for the examining on all related transition metals.

It can be concluded that from the above study that catalytic POM is a process of important significance along with other reforming processes, for the methane conversion which is increasing with the increase of intensive environmental regulation and measurement. An extensive research van be carried out for catalytic metals and support formation. Especially keeping in view, the national need of the development of biodegradable materials and industrial waste usage for the useful purposes, zeolite development is very important, and this work can lay the foundation of Zeolite development at the national level.

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