CHAPTER 2
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The reforming of methane with carbon dioxide was first studied by Fischer and Tropsch using nickel - and Cobalt – based catalysts (Fischer et al ; 1928) . This reaction was later commercialized as the Calcor process (Tenner ; 1985) . It is well known that supported group VIII metals are good catalysts for CH_4 reforming reaction . Ni - alumina catalysts have been reported to be the most effective catalysts for this reaction . However , they suffer a serious problem of deactivation due to carbon deposition nickel sintering and phase transformation (Wang et al ; 1996) , (Gadalla et al ; 1988) and (Xu et al ; 1992) . Therefore , development of new stable Ni - catalysts is of great interest to the practical application of this reaction . Supported rhodium is one of the most effective catalysts (Richardson et al ; 1990) . Based on the present knowledge , carbon formation during CO_2 – reforming appears to be far less on noble metals than on nickel (Rostrup-Nielsen ; 1974) . Whereas rhodium and ruthenium are far more active than nickel (Rostrup- Nielsen ; 1973) , platinum and palladium may be considered having activity comparable to that of nickel (Erdöhelyi et al ; 1994) and (Rostrup - Nielsen ; 1974) . Catalytic activity of a catalyst is influenced by several factors such as the nature of support , active phase precursor employed and pre – treatment , type of metal , metal Loading , and conditions of reaction .

2. 1. The Effect of Types of Metal and Support :-

The catalysts based on noble metals are reported to be less sensitive to coking compared to Ni - based catalysts (Rostrup – Nielsen et al ; 1993).

Gronchi et al (1997) investigated the catalytic activities of Rh and Ni metals on SiO_2 or La_2O_3 for $CH_4 + CO_2$ reforming at controlled .The gas flow rate was100 ml min^{-1} , CH_4 / CO_2 feed ratio was 1or 2 and diluted with N_2 , the catalyst weight was 200 – 500 mg . They have found that the amount of deposited carbon on the Rh catalysts at the same temperatures , was less than on Ni catalysts . The comparison between the Rh and Ni catalysts by the area specific deposition rates of carbon showed a less activity of the Rh ones at 823 K . The difference between the Rh and Ni catalysts was tentatively explained considering the activity of the metal in the CO dissociation .

Ferreira-Aparicio et al (1998) prepared two series of transition metals (Co,Ni , Ru , Rh , Ir , Pt) based catalysts have been prepared using silica and γ -alumina supports. Their activity and stability for the dry reforming of methane in the temperature interval from 673 up to1023K have been examined 10 – 50 mg of catalyst were charged between two quartz wool plugs into a tubular " U " – shaped quartz reactor . A reaction mixture of CH_4 , CO_2 and He in proportions (10:10:80) at a flow rate of 100 ml / min was used for reaction tests . Comparison of the behavior of silica and alumina supported catalysts indicated that the support has a great influence not only on the specific activity but also , on the reaction mechanism and in some cases , in the catalyst stability under reaction conditions . The order of catalytic activity for the dry methane reforming at 723K on a TOF basis was found to be :-

$$Rh > Ni > Ir > Ru \sim (Pt > Co$$
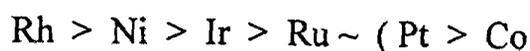
Over the alumina supported catalysts which partially agrees with that given by Rostrup – Nielsen et al (1991) and by Mark et al (1996) for the reforming of methane with carbon dioxide over magnesia supported catalysts at a reaction temperature of 823 K , with the only exception of Ru.

Solymosi et al (1991) have also reported at 773 K for alumina dispersed metals a some what different order :-

$$Ru > Pd > Rh > Pt > Ir .$$

This sequence differs from that observed for silica supportrd metals :-

$$Ni > Ru > Rh \sim (Ir > Co \sim (Pt$$

Richardson et al (1990) studied the ruthenium and rhodium metals (0.5wt%) supported on γ - $Al_2 O_3$ for reforming of methane with carbon dioxide at low ratios of CO_2 / CH_4 in the temperature range $600 - 800^{\circ}C$ and GHSV 51.1×10^{-3} h^{-1} .They confirmed that Rh and Ru have comparable activities but that Rh was much more stable .

Rostrup – Nielsen (1994) compared catalysts based on Ni , Ru , Rh , Pd , Ir and Pt , he found that Ru and Rh showed high selectivity for carbon - free operation . These controversial findings indicate that several factors contribute to changes of specific activity for a given catalyst . Not only the nature of the metal but also the carrier , the metal - support interactions and the reaction conditions , as the temperature range or the pressure , result in different performance and distinct kinetics for each one of them .

There seems to be a general agreement related to the participation of the carrier in the enhancement of the catalytic performance of a certain metal , in some cases has been associated to the acidic characteristics of the support or even to different reaction pathways . On the other hand , deactivation of catalysts during the dry reforming reaction depends mainly on the nature of the active phase (Ferreira- Aparicio et al ; 1998).

The effect of catalyst structure on CO_2 reforming of methane has been studied by Mark e al (1996) in the temperature range $550 - 850$ $^{\circ}C$ the gas flow was 1:1 (CH_4 / CO_2) gas mixture (35ml min^{-1}) and 30 mg of catalyst

oxide supported Rh , Ir , Pd , Ru , Pt , over γ- Al_2O_3 support and (0.5 wt % of metal) the observed activity sequence is

Rh > Ru > Ir >> Pd , Pt .
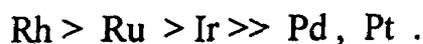
The activity of these catalysts could be correlated with the accessible surface area .Over a wide range of catalysts and supports studied , the rate per unit surface area (TOF) did not depend significantly on metal dispersion , indicating that CO_2 reforming at high temperature is structure insensitive .

Wang et al (2003) studied the catalytic activity of Re based catalyst and Rh based catalyst for CO_2 reforming reaction of methane at 973K . The conversions of methane and CO_2 and the formation rates of CO and H_2 are listed in the Table (2.1) .

Table (2 .1) . Activity comparison of Re based catalysts and Rh catalysts for CO_2 reforming of methane T = 973 K ; SV of METHANE = 5000 ml /h /g ; feed ratio of CH_4 / CO_2 = 1 / 1.1 .

Catalyst	Conversion (%)		Formation rates(mol/s/g)	
	CH_4	CO_2	H_2	CO
Re/HZSM-5	79	78	75.2	94.6
Rh/ HZSM-5	77	71	73.8	93.0
Rh/ KZSM-5	78	78	75.2	93.5
Rh/Al$_2$O$_3$	76	68	66.3	87.4
Re/ Al$_2$O$_3$	78	68	62.6	83.4
Re/ KZSM-5	74	66	63.9	85.1

It was indicated in Table (2 .1) that both Rh and Re based catalysts exhibit promising high activity for the reforming reaction at the temperature 973 K although HZSM-5 supported Re catalyst exhibits a little higher activity than Rh based catalyst.HZSM-5 supported Re catalyst exhibited better activity than Al_2O_3 and KZSM-5 supported Re catalyst .

Group V and VI transition metal carbides have been prepared by Brungs et al (1999) and tested for the dry reforming of methane with carbon dioxide , at elevated pressure . Mo_2C and WC were the most stable catalysts while the group V metal carbides showed the stability order :

Vanadium > niobium > tantalum catalyst .

Erdöhelyi et al (1994) have investigated the reforming of methane with carbon dioxide in the temperature range of 400 - 500°C over Rh and Pd supported on TiO_2 , Al_2O_3 , SiO_2 and MgO .

For Pd , TiO_2 appeared to be the best support in terms of specific activity , among those investigated so the activity decreased in the order of

TiO_2 > Al_2O_3 > SiO_2 > MgO .

The authors have also reported that only very little amount of carbon was formed during reaction under the experimental conditions examined (PCH_4 = 0.25 bar, CH_4 / CO_2 = 1.0 , T = 400 – 500°C) concerning Rh they have stated that the CH_4 reforming reaction at high temperatures on supported Rh catalysts depends hardly at all on the nature of the support .

Reforming of methane with carbon dioxide to syngas (CO / H_2) has been investigated by Tsipouriari et al (1994) over Rh (rhodium) supported on SiO_2 , TiO_2 , γ - Al_2O_3 , MgO , CeO_2 and YSZ (ZrO_2 (8mol % ($Y_2 O_3$))) catalysts in the temperature range of 650° – 750°C at 1 bar total pressure , PCH_4 = 0.2 bar and (0.5 wt % Rh) metal CH_4 / CO_2 = 1.

A strong carrier effect on the initial specific activity , deactivation rate , and carbon accumulation was found to exist . In certain cases , the reaction also appears to be structure sensitive , structure sensitivity is also affected by the carrier , since the higher dispersion the higher the metal carrier gas interfacial area . The activity decreasing in the order of

YSZ (Yttria – stabilized zirconia) > $Al_2 O_3$ > TiO_2 > SiO_2 > MgO .

The effect of carrier and metal particle size on the catalytic performance of Rh in the reaction of reforming of methane with carbon dioxide were investigated by Zhang et al (1996) . The results of the catalytic activity were obtained under 1 atm   Pressure , total flow rate between 50 and 400 ml / min , and the catalyst bed hight was between 3 and 5 mm , the catalyst particle diameter was less than 0.02 mm , CH_4 / CO_2 ratio is 1 and in the temperature range 600 - 800°C . The specific activity of Rh catalyst was found to strongly depend on the carrier employed to disperse the metal . The activity decreasing in the order of

$$(YSZ) > Al_2O_3 > TiO_2 > La_2O_3 > MgO$$

a result which correlates directly with the acidity characteristics of the carrier where the higher the acidity the higher the initial reaction rate .

Brodford et al (1999) was in agreement with Zhang et al (1994) where the metal support interaction of CO_2 reforming of methane was investigated over series of SiO_2 – and TiO_2 – supported transition metals .

The amount of catalyst used during experiments was varied between 4 and 50 mg to probe the influence of the reverse reaction and to maintain differential conditions.
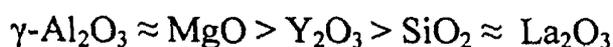
Typical activity tests were carried out under ca. 740 Torr absolute pressure, with a feed composition of CO_2 / CH_4 / He = 1 / 1 / 1 .8 and a total feed flow rate of 20 ml min^{-1} (WHSV = 24000 - 300 000 cm^3 h^{-1} g^{-1}) over a temperature range of 673 – 723 K (Brodford et al ; 1999) . Catalyst activity was found to depend on both the support and the dispersion character of the metal ; however, different trends were observed for metals on SiO_2 and on TiO_2 , with the former , a maximum in activity was observed with Pt whereas with the later , optimum performance was obtained with Rh . Nagaoka et al (2001) results demonstrate that Ru / TiO_2 is one of the promising catalysts for industrial use . Since strong resistance to coke deposition of Ru / TiO_2 was not associated with particle size of Ru or

basicity of support , it may be attributed to characteristics of metal catalysts supported on TiO_2 , so called SMSI .

Rhodium supported on various metal oxides was studied in the dry reforming reaction using methane and carbon dioxide by Yokota et al (2002) . A reaction mixture consisting of CO_2 / CH_4 / Ar = 25: 25 :50 was fed to the reaction with a flow rate of 100 mℓ min^{-1}. The catalytic activities were measured in the temperature range between 773 and 973K , the catalytic performance of Rh for CO_2 - CH_4 reaction was significantly affected by the kind of support . The TOF for methane conversion decreased in the following order :-

TiO_2 > La_2O_3 ~ CeO_2 > ZrO_2 ~ MgO ~ SiO_2 $\approx$ MCM $-$ 41 > $\gamma - Al_2O_3$. The highest TOF of Rh was observed on TiO_2 .

The carbon dioxide reforming of methane over the reduced supported Rh (0.5 wt %) catalysts were investigated by Wang et al (2000) ; Two kinds of oxides , reducible (CeO_2 , Nb_2O_5, Ta_2O_5, TiO_2, and ZrO_2) and irreducible (γ-Al_2O_3 , La_2O_3 , MgO , SiO_2 and Y_2O_3) were used as supports . After reduction, the feed gases (CH_4 / CO_2 = 1 / 1) were introduced into the catalyst bed at a flow rate of 20 ml min^{-1} , which for a 20.0 mg catalyst corresponds to a space velocity of 6.0 x 10. ml h^{-1} g^{-1} temperature of reaction was 800°C . For the irreducible oxides , after 50 h on stream the sequence became :-

γ-Al_2O_3 $\approx$ MgO > Y_2O_3 > SiO_2 $\approx$ La_2O_3

For the reducible oxides , after 50h on stream the sequence became :-

ZrO_2 > Ta_2O_5 > CeO_2 >> TiO_2 >> Nb_2O_5

The TPR indicated that there are much stronger interactions between rhodium oxide and La_2O_3 or MgO . While no compounds between rhodium oxide and support were formed over the calcined SiO_2 , γ-Al_2O_3 , Ta_2O_5 , Y_2O_3 supported catalysts .

With the exception of γ - Al_2O_3 supported catalyst , all the catalysts for which no compounds were identified after calcinations exhibited decay in activity during reaction . Though no compound was formed between rhodium oxide and alumina the interaction was sufficiently strong to ensure the stability of the catalyst .

Carbon dioxide reforming of methane has been studied over two ruthenium catalysts supported on silica and on γ - alumaina by Ferreira - Aparicio et al (2000) . For catalytic testing , 10 - 50mg were placed in a tubular reactor with 1 wt % metal loading , reaction mixture of CH_4 : CO_2 : He in proportions 10 :10 : 80 and regulated by mass at a flow rate of 100 cm^3 / min . The reaction of CH_4 and CO_2 was tested over Ru / SiO_2 and Ru / γ - Al_2O_3 at 823 and 1023K results indicated that , despite similar initial conversion values , the evolution of the behaviors of both catalysts as a function of time in reaction is quite different .

The Ru / SiO_2 catalyst suffered deactivation especially during the first 3 h this deactivation was the result of carbon deposition on its surface .The rate of loss of catalytic activity for Ru /Al_2O_3 sample was slower ; this suggests that the loss of activity is probably the result of a slow and continuous sintering of the metallic phase which is not complete even after 3 h in reaction .

Nakamura et al (1994) observed widely different turnover frequencies Rh which decreased in the order :-

$$Rh / TiO_2 > Rh / Al_2 O_3 > Rh / SiO_2 ,$$

Both supported on silica and on alumina , show excellent stability though Rh / Al_2O_3 exhibits a much higher specific activity as compared with Rh / SiO_2.

Nakamuraet al (1994) have reported that the activity of Rh / SiO$_2$ catalyst which does not form carbonate is enhanced by adding MgO , Al$_2$O$_3$ or TiO$_2$, i .e ., compounds which facilitate carbonate formation .

On the contrary to above results :-

To examine the influence of the support on the activity , Michael et al (1996) prepared various Rh (1%) catalysts . Besides commercial Al$_2$O$_3$ and TiO$_2$ supports , highly porous SiO$_2$, Al$_2$O$_3$, ZrO$_2$ and binary mixed oxides were prepared by the sol - gel method. All the catalysts showed stable activity over the usual reaction time of 6 − 8 h CH$_4$ conversion increased with increasing metal surface area , while the rate per unit surface area (TOF) calculated for the various catalysts remained constant .

On the other hand , no correlation of catalyst activity with any physical properties of the supports could be detected .The influence of the support on the reactions therefore was limited to affecting the metal dispersion during the course of the catalyst preparation and stabilizing the dispersion during catalyst use . These results underline the structure insensitivity of the CO$_2$ reforming even with different catalyst supports .

Both γ -Al$_2$O$_3$ and the binary oxide ZrO$_2$ (5%) / SiO$_2$ are especially good catalyst supports . Rh catalysts based on there supports not only showed high activity but also promise to be thermally stable even after long reaction times .

Also ; It was shown by Lercher (1996) that ZrO$_2$ was crucial for Pt and Ni catalysts to minimize coke deposition under the CO$_2$ / CH$_4$ reforming conditions . A well - dispersed nickel catalyst on ZrO$_2$ seemed to be a viable alternative to the noble- based catalyst .

The CO$_2$ reforming of CH$_4$ over Co supported on an alkaline earth metal oxide (MgO , CaO , SrO or BaO) as well as on γ - Al$_2$O$_3$ and SiO$_2$ was investigated by Ruckenstein et al (2000) . Among these supports , only

MgO exhibited a high and stable activity at the high space velocity of 60000 ml g^{-1} h^{-1}, which remained unchanged during the Period of study of 50 h.

Gronchi et al (1997) investigated the catalytic activities of Rh and Ni metals on SiO_2 or La_2O_3 at $CH_4 + CO_2$ reforming conditions. The flow rates of gases is100 ml / min, CH_4 / CO_2 feed ratio is 1or 2 and diluted with N_2, the catalyst weight was 200 - 500 mg. The CO_2 was consumed at a higher rate than CH_4 with every catalyst. For Rh – catalysts, the apparent rate of disappearance of both reagents positively depended on the La_2O_3 content .The Rh (0.2 %) / La_2O_3 catalyst had the greatest activity, probably due to the high dispersion of the metal. Testes have been performed on Ni / SiO_2 and Ni / La_2O_3 catalysts with a different metal content (30 % and 4 %) at temperatures of 823 - 923K using a CO_2 / CH_4 = 1 feed ratio.

pessi et al (1994) reported that the CO_2 and CH_4 conversions were similar at low temperature but, when the temperature was increased, the conversions with the SiO_2 support become greater than the La_2O_3 one. CO_2 consumptions were higher than CH_4 ones on both catalysts. However, CH_4 was more preferentially consumed on silica than on lanthana support, as the ratio of CH_4 converted to CO_2 indicated.

The catalytic production of hydrogen through the carbon dioxide reforming of methane was carried out both in a plug – flow reactor and in a dense Pd/Ag membrane reactor. In the former device, the activity and stability of Pt / La_2O_3 were investigated and compared to the Rh / La_2O_3 solids (Múnera et al ; 2003) .The best Pt and Rh catalysts were used in the membrane reactor and in both cases significant increases in CH_4 and in both CH_4 and CO_2 conversion were recorded. Despite their similar activities, the Rh (0.2 %) La_2O_3 was much more stable than that

Pt / La_2O_3 formulations . The origin of the deactivation was found to be the partial sintering of the platinum after 100 h on stream at 823K .

Zhang et al (1995) reported that the Ni / La_2O_3 catalysts exhibit high activity and excellent long term stability for carbon dioxide reforming of methane to syngas .

Ni / La_2O_3 catalysts exhibit significant enhancement of activity with time on stream during the initial 2 - 5h of reacting , which then tends to be essentially invariable with time on stream for at least 100 h of reaction (Zhang et al ; 1996) . It is proposed that the interaction between nickel and lanthanum species creates a new type of synergetic sites at the Ni - La_2O_3 interfacial area , which offer active and stable performing of carbon dioxide reforming of methane to syngas over the stated catalyst .

Bhat et al (1997) studied Rh supported on crystalline oxide . NaY , HY zeolites , the obtained catalysts combined extraordinary stability with high activity and selectivity and turnover frequency than the other amorphous oxide supports .

One cause of the extraordinary stability of zeolite supported rhodium is the absence of coke formation . The second cause for the unusual stability is the lack of metal agglomeration beyond the stage of 40^oA Rh particles .

Considerable research over the past decade has indicated that supported rhodium is best overall catalyst , in terms of activity and stability , for dry reforming of methane with carbon dioxide .

Ru / NaY and Ru / HY catalysts prepared by ion - exchange from aqueous solution of [Ru $(NH_3)_6$]Cl_3 were potential catalysts for CO_2 reforming of the CH_4 (Portugal et al ; 2000) . The catalysts' activity were investigated under 1atm pressure with a CH_4 / CO_2 / N_2 feed of compositions varying between 10-20 / 20-30 / 30-60 or CH_4 / CO_2 of 50 / 50 at total flow rate

between 100 and 400 ml / min with 0.05 - 0.29 gm of catalyst with metal weight loading between 0.5 - 3.0 wt % and temperature range of 723 - 973 K Ru / NaY showed high stability and did not deactivate during a period of 300 h on stream .

There is another way to improve the ability of the support :-
The effect of support phase and catalyst preparation methods on catalytic activity and carbon deposition were systematically investigated over nickel catalysts supported on Al_2O_3 , SiO_2 and MgO for the reforming reaction of methane with carbon dioxide byWang e t al (1998) catalyst with well – developed porosity exhibited higher catalytic activity . Strong interaction between metal and the support made the catalyst more resistant to sintering and coking , thus resulting in a longer time of catalyst stability .The high activity and stability of Ni / CaO - Al_2O_3 in the CO_2 reforming of CH_4 was also confirmed by Gadalla et al (1988) .

Goula et al (1996) claimed a 5 wt % Ni on calcium aluminate catalyst is for the reforming of methane and that the support composition (CaO / Al_2O_3 ratio) affects the catalyst stability , the amount and the reactivity of the carbon species formed during reaction and the relative proportion of reaction routes leading to carbon formation . It was suggested that the catalyst with support molar composition CaO / Al_2O_3 = ½ exhibits superior activity and lower coke deposition than the one supported on CaO / Al_2O_3 with 12 / 7 molar ratio .

Also , CeO_2 is an effective promoter and / or support for Ni catalysts , It has been reported that the addition of ceria (or other rare - earth metal oxides) generally improves the behavior of alumina – based catalysts used for automotive emission control . Its presence has other beneficial effects on the catalyst performance , such as improving the dispersion of the active phase , or shifting the transition of the γ - Al_2O_3 used as support to the low

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surface area phase α - $Al_2 O_3$ (soria et al ; 1996) and (Morterra et al ; 1996) to higher temperatures .

Wang et al (1998) also found that CeO_2 as a promoter can enhance the activity , stability , and carbon resistance . And reported that the weight loading of 1-5 wt % CeO_2 was the optimum . Xu et al (1999) found that the promoter MgO is the most effective one the suppression of CH_4 dehydrogenation . The CeO_2 promoted catalysts can lower the temperature of reforming reaction of CH_4 with CO_2 and improve the resistance to carbon deposition . Also the activity promoted by CeO_2 and MgO keeps well over 900 h . This indicates that the catalysts has not only high activity and selectivity , but also high stability and good resistance to carbon deposition .

2 . 1 .1 . Effect of Additive on Metal Performance :-

As was recently reported by various investigators Yamazaki et al (1992) , Cheng et al (1996) , Horiuchi et al (1996) , Zhang et al (1994) and Choudhary et al (1995) that , the addition of alkali or alkaline earth oxides to Ni - based catalysts is effective in preventing coke formation .

Calcium aluminate mixed oxides proved to be very stable and active catalysts for hydrocarbon cracking . Lemonidou et al (1989) studied the influence of Ca on the activity of supported Ni catalyst . The catalyst activity depended on the properties of the supports (SiO_2 , $\alpha - Al_2 O_3$, $\gamma - Al_2O_3$) and / or the amount of Ca added . Small amount of Ca increased the activity and stability of Ni / α - Al_2O_3 where Ca improved the dispersion of Ni , strengthened the interaction between Ni and Al_2O_3, and retarded the sintering . A higher amount of Ca covered the surface of α - Al_2O_3 and enhanced the decomposition of CH_4 .

Juan - Juan et al (2004) studied the effect of potassium on the catalytic activity and structural properties of a Ni / Al$_2$O$_3$ catalyst used for the CO$_2$ reforming of methane . Ni / Al$_2$O$_3$ and Nik /Al$_2$O$_3$ catalysts showed very similar CH$_4$ and CO$_2$ conversion at 973 K (under TPR and isothermal conditions) and the XAFS analysis of the used samples reveals a similar nickel structure . However , the whole process was different because in Ni / Al$_2$ O$_3$ catalysts the formation of coke was much higher.

Jae - Hee et al (2004) prepared CuNi / Al$_2$O$_3$ catalysts to investigate the effects of the Cu addition to Ni /Al$_2$O$_3$ catalyst in CO$_2$ reforming of methane . The 1 wt % Cu addition to the Ni /Al$_2$O$_3$ catalyst enhanced the stability and the activity of the Ni /Al$_2$O$_3$ catalyst , but CuNi /Al$_2$O$_3$ catalyst with over 5 % Cu were deactivated more rapidly than the Ni /Al$_2$O$_3$ catalyst without Cu component . A long – term stable Cu / Ni / SiO$_2$ catalyst for CO$_2$ – reforming of methane to produce syngas at 800°C was developed . The stability of the Cu / Ni catalysts depended on the reaction temperature and Cu / Ni ratio .

Crisafulli et al (2002) reported a study on the effect of addition of various amounts of Ru to supported catalysts towards the CO$_2$ reforming of methane , in the case of silica supported samples addition of Ru strongly enhanced the catalytic performance of Ni sample , the influence of Ru addition was instead much less remarkable on H - ZSM5 Zeolite supported sample .

The CO$_2$ reforming of CH$_4$ was investigated over V - promoted Ni / Al$_2$O$_3$ catalysts by Valentini et al (2003) Low V wt % addition suppressed the NiAl$_2$O$_4$ formation , the carbon deposition low and the surface area increases , the sample with high V wt % presented the highest carbon

deposition, which was attributed to the increase in CH_4 decomposition promoted by the V.

Hou et al (2003) found that the small amounts of Rh - promoted Ni / α - Al_2O_3 catalysts possessed higher activity than pure Ni /α -Al_2O_3 catalysts and exhibited excellent coke resistance ability in methane reforming with CO_2 .The Rh improved the dispersion of Ni , retarded the sintering of Ni and increased the activation of CO_2 and CH_4 on the surface of catalyst .

On the other hand , reforming of CH_4 with CO_2 proceeded at 400°C over a catalyst consisting of ruthenium metal and CeO_2 highly dispersed on mordenite by Hashimoto et al (2002) the catalyst , Ru - CeO_2 / MZ , was highly active for the reforming of CH_4 under the conditions at which a carbon formation reaction is thermodynamically about to take place .

2. 2. Factors Affecting the Reforming Reaction :-

2 .2. 1. Temperature :-

Mark et al (1996) examined CO_2 – reforming reaction in the temperature range 50 - 850°C; using Rh and Ir supported on alumina catalyst . From kinetic study they reported that at 600°C the water - gas shift reaction was about 50 % and at 850°C about 10 % away from equilibrium .

Zhang et al (1996) studied CO_2 reforming of methane in the temperature range 600 – 800°C ; using rhodium supported on Al_2O_3 , TiO_2 , L_2O_3 , MgO and YSZ and they reported that the degree of deactivation is reduced when the reaction takes place at higher temperature . Also , the significant quantities of water were observed when the reaction was carried out at low temperatures , while only trace amounts were detected at high reaction temperatures .

Tsipouriari et al (1994) studied the reaction under integral reactor conditions in the temperature range 650 –750 °C ; using rhodium supported on SiO_2 , γ- Al_2O_3 , TiO_2 , CeO_2 , MgO and YSZ . For an extended period of time 50 h . The rate of deactivation was found to be lower at higher conversion and to decrease with increasing temperature .

The catalytic activities of Rh / NaY were tested by Bhat et al (1997) at temperature ranging from 723 – 973 K with a constant feed composition of 20:20:60 ml / min of CH_4 : CO_2 : Ar , respectively .
The data show that equilibrium is reached near 850 K . As expected , the conversion of CH_4 increases with temperature and so does the H_2 / CO ratio This reflects the interference of the water - gas shift reaction (WGSR) .

At lower temperature in the presence of CO and H_2 the reverse WGSR is favored leading to the formation of more CO .

Wang et al (1997) using Rh / SiO_2 catalyst noted that , at 800°C , methane conversion was higher than CO_2 conversion , whereas , CO_2 conversion was higher than methane conversion at 700°C . It was assumed that the extent of deep dissociation reaction would be much larger at 800°C than that at 700°C and the surface oxygen formed through the dissociation of CO_2 would penetrate into the bulk much faster at 800°C than that at 700 °C .

Gronchi et al (1997) reported that the activity of Rh / La_2O_3 , Rh / SiO_2 , Rh/ LO_2O_3 (5 %) - SiO_2 catalysts increased with the temperature .
At low temperature (723 – 823 K) , the ratio of CO / CO_2 advances towards 2 for the silica supported catalyst , but sets towards 1 with Lantana supported catalyst .
At temperature higher than 823K the CO/CO_2 ratios come closer in the range between 1.6 – 2 , depending on the feed ratio and independent of the support .

Where the CO obtained / CO_2 converted ratio rage from 2 (i..e. the stoichiometric value of DR reaction) and 1 (i.e the stoichiometric value of RWGS) . The low stoichiometric ratios can be explained by also considering coke formation from CO dissociation

$$COs + * \rightarrow Cs + Os$$

Gronchi et al (1997) further studied the catalysts , Ni (30 %) / SiO_2 and Ni (4%) / La_2O_3 with a CO_2 / CH_4 = 1 feed ratio at temperatures of 823 – 923 K , The CO_2 and CH_4 conversions were similar at low temperature but , when the temperature was increased , the conversion with the SiO_2 support become greater than the La_2O_3 one .

Yokota et al (2002) carried out the catalytic reaction in a fixed – bed continuous flow reactor at atmospheric pressure and temperature range between 773 – 973K . The TOF for CH_4 conversion of 0.5 wt % Rh – supported catalysts increased as temperature increased , and TOF was maximum at 973K .

Verykios (2003) reported a significant decrease of carbon accumulation by increasing temperature of reforming from 650 to 750°C over Rh / Al_2O_3 . This result is suggested to be largely due to removal of carbon by steam, according to the following reaction :-

$$C + H_2O = CO + H_2$$
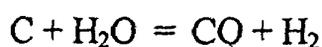
This reaction is expected to become more significant with increasing reaction temperature .

The CO_2 - reforming reaction of methane studied over Iridium based catalysts were stable at high temperature 1023K several papers concerning the dry methane reforming over Ir-catalysts at high temperature agree in remarking their high resistance towards carbon formation under reaction conditions (Ashcroft et al ; 1991) and (Mark et al ; 1996).

Wang et al (2003) reported that the reforming reaction becomes much more difficult at lower temperatures because of the coke deposition on catalyst at lower reaction temperatures . The catalytic performance of Re/ HZSM-5 catalyst and Rh / HZSM-5 catalyst for CO_2 reforming reaction of methane was compared in a lower temperature of 858 K . The formation rates of CO and H_2 on Re / HZSM-5 are evidently higher and more stable with time on stream even than that on Rh / HZSM-5 at the lower reaction temperature . Therefore , Re based catalyst exhibits much better catalytic performance for the reforming reaction at low temperature than the traditional Group VIII metal such as Rh based catalysts .
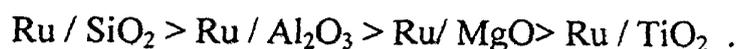
2 .2. 2 . Pressure :-

Supports (SiO_2 , Al_2O_3 , MgO and TiO_2) effects of Ru catalysts for the CH_4 / CO_2 reforming were studied under 2 Mpa (industrial condition) in order to develop catalysts which have strong resistance to coke deposition , and the results were compared with those under atmospheric pressure (Nagaoka et al ; 2001) .

At pressure 2 Mpa the reactant gas (CH_4 / CO_2 = 1 vol /vol) with the W/F of 4.6×10^{-3} – 6.7×10^{-2} ghl^{-1}, under 0.1 Mpa the W/F is 9.3×10^{-3} g h l^{-1} at 1023K . The order of the catalytic activity of the four catalysts investigated was dependent on the reaction pressure , where , the activity can be , correlated to the basicity of supports under 0.1 Mpa

$$Ru / MgO > Ru /Al_2O_3 > Ru / TiO_2 > Ru / SiO_2$$
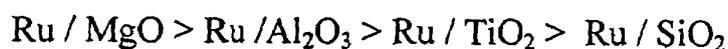
Which it is in agreement with the BET surface area of the catalysts . Under 2 Mpa the activity was according to the following order :-

$$Ru / SiO_2 > Ru / Al_2O_3 > Ru/ MgO > Ru / TiO_2 .$$

The results show the key role of the reaction pressure . Coke was not deposited on all supported Ru catalysts under 0.1 Mpa , while deposited on

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Ru / SiO_2 , Ru /Al_2O_3 and Ru / MgO , except for Ru/TiO_2 under 2 Mpa with the same W/ F of 9.3×10^{-3} g h l^{-1} .

2. 2 .3 .Effect of Space Velocity :-

Methane reforming by CO_2 over 0.5 wt % Co/ TiO_2 reduced at 1123 K (reaction condition : CH_4 / CO_2 = 1 , 1023 K ; 2.0 Mpa) studied by Nagaoka et al (2003) . CH_4 conversions at different SVs for the Co / TiO_2 was shown , where , the initial activity decreased with increasing the SV . However , the initial CH_4 conversion of the catalyst at the SV of 3000 $mlg^{1}h^{-1}$ was 23.0 % (34.6 % at equilibrium) and was not so much different from that of the catalyst at the SV of 6000 $mlg^{-1}h^{-1}$. On the other hand , as SV was increased , the deactivation of the catalyst was accelerated and the catalyst lost its activity completely after reaction for 20h at a SV of 12,000 $mlg^{-1}h^{-1}$ It was also found that the amounts of coke were insignificant regard less of the SV and were only 0.01 wt. % after the reaction for 24 h at the SV of 12 ,000 $mlg^{-1}h^{-1}$. Although equilibrium conversion was not obtained even with a low SV of 3000 $mlg^{-1}h^{-1}$, the catalyst kept stable activity for 50 h and did not show a significant amount of coke . SV caused slow deactivation for the catalyst and it would be attributed to the oxidation of metallic cobalt .

However , the slow deactivation was prevented by the addition of a small amount of ruthenium (Ru / Co = 0.05) and it was found that strong resistance to coking for the CO / TiO_2 reduced at 1123 K was also retained after the addition of ruthenium .

2. 2. 4. Time On Stream :-

The long term stability performance of 0.5 wt % Rh / SiO_2 , & Al_2O_3 , TiO_2 and YSZ catalysts was examined by (Zhang et al ; 1996) at 750 °C F_{tot} = 100 ml / min $m_{cat.}$= 200 mg with a feed containing 20 % CH_4 , 20 %

CO_2 , and 60 % He . It was apparent that the long - term stability of the Rh / SiO_2 and Rh / YSZ catalysts were the best among the four catalysts and exhibited essentially no deactivation under the conditions employed in this test . For the Rh / TiO_2 catalyst the deactivation rate was initially high but became less significant after about 100 h of reaction for the Rh / Al_2O_3 , the difference between the conversion over the fresh catalyst (after 10 min of reaction) and that obtained after 50 h on stream is only several percentage units .

Tsipouriari et al (1994) studied the variation of the average Rh crystallite size on Rh /Al_2O_3 , TiO_2 , YSZ and MgO catalyst with time on stream under integral reactor operation at $650^{\circ}C$. It was apparent that in the case of Rh / Al_2O_3 catalyst , a stabilization reduction of the dispersion of Rh (sintering) occurred under the stated reaction conditions . The degree of sintering of the Rh / TiO_2 , Rh / YSZ and Rh / MgO catalysts was significantly smaller .

For Rh / NaY Bhat et al (1997) reported the absence of any appreciable deactivation during 300 h of time on stream and after multiple thermal cycles due to the extraordinary stability of zeolite supported rhodium catalyst .

Rh / SiO_2 catalysts exhibit a very slight deactivation after 4 h of reaction with a CH_4 / CO_2 ratio of 1 (Gronchi et al ; 1997) which is in agreement with the values predicted by Erdohelyi et al (1993) and this deactivation was caused by carbon formation . 0.2 Rh / La_2O_3 quickly deactivated at 923 K and TG analyses performed in isothermal conditions indicated that at comparable metal dispersion the specific carbon deposition rate is 20 - 30 times greater in presence of lanthana than silica .

Over γ - Al_2O_3 and MgO supported Rh , the conversions of CH_4 and CO_2 remained unchanged during the period of study , 100h (Wang et al ; 2000) La_2O_3 also provided a stable activity during the period of study , 50 h . However ; deactivation was observed over SiO_2 and Y_2O_3 . Over SiO_2 , the conversions were high initially but decreased noticeably during the first 28 h , to become almost unchanged from 28 to 50 h .Compared with SiO_2 , the decay of the conversion over Y_2O_3 was relatively small . For reducible oxides supported catalysts ; No significant deactivation occurred over Nb_2O_5 , but the conversion of CH_4 and CO_2 were low . Ta_2O_5 and TiO_2 provided initially much higher conversion than the other reducible oxides , but they decayed with time on stream . Deactivation occurred mainly during the first 24 h of reaction . Over the CeO_2 and ZrO_2 , the conversions were initially low , but increased with time on stream . The strong variation of activity with time on stream is a typical feature of the reducible oxide supports . This studies were performed under flow rate of 20 ml / min (CH_4 / CO_2 = 1 / 1) space velocity , 60000 ml / h /g , temperature = 800 $^{\circ}$C , Rh % is 0.5 wt % and amount of catalyst is 20.0 mg .

2. 2. 5. CH_4/ CO_2 Ratio :-

Mark et al (1996) reported that with increasing CO_2 in the feed , a decreasing H_2 / CO ratio in the product is indicative of a decreasing contribution of the reforming reaction and an increasing contribution of the reverse water – gas shift (RWGS) reaction to the overall process .

Bhat. et al (1997) showed the effect of varying the (CH_4 / CO_2) ratio in the feed for the 3.2 % Rh / NaY catalyst . The H_2 / CO product ratio showed little dependence and was near unity , indicating the absence of major side reactions .

Gronchi et at (1997) , (1995) studied the reforming of methane by carbon dioxide over Rh / La_2O_3 , Rh /SiO_2 , Rh / La_2O_3 (5%) – SiO_2 catalysts at 813 K with two CH_4 / CO_2 feed ratio .

The results showed that the conversions of CH_4 and CO_2 do not significantly depend on feed ratio . At feed ratios < 1 , the conversions obtained with all the catalysts have similar values .

2. 2. 6. *Metal Loading (Metal Particle Size or Metal Dispersion) :-*

Mark et al (1996) examined the influence of the metal dispersion on the catalyst activity , by preparing differently dispersed Rh and Ir catalysts supported on commercial γ - Al_2O_3 . The catalysts were prepared with different total metal loadings in the range from 0.5 to 5 wt % .

The reaction rates (expressed per unit surface area) (TOF) showed that the reaction was independent of the metal dispersion , where the rarely identical CH_4 conversions were obtained with a highly dispersed Rh (0.5%) and a poorly dispersed Rh (5 %) catalyst (i.e) CO_2 - reforming reaction could be termed structure insensitive . This is in contrast with studies on single crystal surface , where methane activation has been found to be structure sensitive .

The activities of Rh for CH_4 - reforming with CO_2 was investigated over Rh/Al_2O_3 , Rh / SiO_2 , Rh / TiO_2 catalyst by Zhang et al (1996) .

Different dispersions were achieved by varying the metal loading between 0.2 and 10 wt % and the showed the TOF with the average Rh particle size, at $650^{o}C$ PCH_4 = 0.2 bar, CH_4 / CO_2 = 1.0 , they found that the structure sensitivity of this catalytic systems strongly depends on the carrier employed to disperse the metal . The Rh / TiO_2 catalyst exhibits strong structure sensitivity, the Rh / Al_2O_3 catalyst shows a moderate sensitivity , while the Rh / SiO_2 catalyst exhibits a facile behavior .

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The sensitivity of the intrinsic activity of Rh to particle size , or degree of dispersion under T = 650°C , PCH$_4$ = 0.2 par , CH$_4$ / CO$_2$ = 1 , was also investigated by Tsipourari et al (1994) employing the Rh/ γ-Al$_2$O$_3$, Rh / SiO$_2$ and Rh / TiO$_2$ catalyst . Where the metal loading was between 0.2 -10 wt % , the structure sensitivity of this catalytic system was a strong function of the carrier employed for the dispersion of Rh . The Rh / TiO$_2$ catalyst exhibits strong structure sensitivity with increasing Rh paretic size in the range of 1 to 4 nm the Rh /Al$_2$O$_3$ catalyst was a moderate one , while the Rh / SiO$_2$ catalyst exhibit a facile behavior .

Rh / NaY catalysts with varying rhodium contents namely 0.5 - 7.3 wt. % of rhodium over NaY , have been studied for the CO$_2$ reforming of CH$_4$ by Bhat et al (1997) . For all these catalysts thermodynamic equilibrium was reached at around 873K .Rhodium loading of 0.5 to 0.93 wt. % in NaY was found to suffice for obtaining the desired high activity and selectivity .

For Rh / SiO$_2$ catalyst with rhodium loadings from 0.05 % to 8 % , at 700°C , CO$_2$ conversion was higher than CH$_4$ conversion ; where as at 800°C , CH$_4$ conversion was higher than CO$_2$ conversion and the difference between the two conversion increased with the increase of rhodium loading . Thus , (Wang et al ; 1997) concluded that besides the direct dissociation of methane, oxygen - assisted dissociation could be another pathway for methane dissociation.

$$(CH_4,s + O_s \rightarrow CH_{3,s} + OH_s)$$
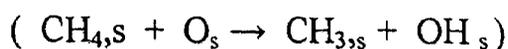
At T = 800°C , over the 0.5 wt % Rh / γ-Al$_2$O$_3$ catalyst the conversions of CH$_4$ and CO$_2$ to yield CO and H$_2$ increased with increasing amount of catalyst in the range investigated (2.5 – 20.0 mg) (Wang et al ; 2000) . Also , the turnover frequency (TOF) depended significantly on the particle diameter of Rh in the range of 1-7 nm . This strongly indicates that the reforming reaction is structure sensitive on γ - Al$_2$O$_3$ supported Rh catalyst .

YoKota et al (2002) showed the relationship between Rh dispersion and TOF for CH_4 conversion at 973 K , 0.5 wt % Rh / support , 0.05gm , feed gas Ar / CO_2 / CH_4 = 50 / 25 / 25 ml /min , atmospheric pressure . The TOF decreased with increasing dispersion of Rh . It was concluded that the Rh was structure sensitive in the CO_2 - CH_4 reaction .

2. 2. 7. Type of Reactor :-

The dry reforming reaction has been carried out in on Ru - based ceramic tubular membrane reactor , in which two Ru depositions have been performed using the Co -condensation technique . These experiments have also been carried out using a traditional reactor for comparison between membrane reactor and tubular reactor . (Paturzo, et al ; 2003) . It is observable in Table (2.2) that both CH_4 and CO_2 conversions decrease when changing from MR to TR (5% Ru) and then to TR (0.5 % Ru) . Considering the CH_4 conversion per unit of time factor , it is shown that MR gives the best performance while the TR (0.5 % Ru) is the lowest . These results confirm the good catalytic activity of the Ru deposited inside the ceramic membrane , since a fine dispersion of the metal acts in the sense of increasing the activity of the catalytic surface .

Considering again Table (2.2), it should be observed that the gap between CH_4 and CO_2 conversions in MR is 5.6% , while this difference is about 13.7 %for TR (5%Ru) and about 10.5 % for TR (0.5 % Ru) . This experimental evidence might be due to the different catalyst distributions present in MR and TRs.

These aspects can be viewed as an improvement of the catalyst activity in terms of reactants conversion due to the mentioned Ru dispersion technique over the ceramic support .

Table (2.2) . Comparison between MR and TR in terms of CO_2 and CH_4 conversion per unit of time factor, T= 400 $^\circ$C , $CH_4 / CO_{2, FEED}$ = 70 ml/min , P = 1.2 bar (abs) (the terms in the brackets refer to the Ru percentage in the catalyst pellets packed in the TR).

Type of reactor	MR	TR (5 % Ru)	TR (0.5 % Ru)
Ru wight (mg)	55	200	20
Time factor (g_{Ru} min/ml_{CO2})	7.86×10^{-4}	2.86×10^{-3}	2.86×10^{-4}
CH_4 conversion(%)	15.23	2.17	0.35
CH_4 conversion / time factor ((g_{Ru} min/ml_{CO2})$^{-1}$)	1.9×10^{-4}	7.6×10^2	1.2×10^3
CO_2 conversion(%)	20.8	15.9	10.8
CO_2 conversion / time factor ((g_{Ru} min/ml_{CO2})$^{-1}$)	2.6×10^{-4}	5.6×10^3	3.8×10^4

CO_2 – reforming of methane was conducted over 13 wt % NiO/ γ - Al_2O_3 in a *micro quartz* reactor in fixed - bed / fluidized - bed switching modes under the condition of 1atm , a fixed furnace temperature 800°C and a fixed CO_2 / CH_4 molar ratio of 1.5 , the amount of catalyst and the flow rate of a feed mixture of CO_2 and CH_4 were fixed to be 160 mg and 250 ml / min (STP , GHSV = 93 750 h^{-1}) , respectively by Effendi et al (2002) .

Similar mode switching experiments were also performed with the two commercial Ni-based catalysts , FCR- 4- 02 and N139 . The results are summarized in Table (2.3) As listed in the table , CH_4 and CO_2 conversions recorded in case of fixed – bed mode were 77 and 65 % for FCR – 4 - 02 and 59 and 52 % for N 139 , while under the fluidized - bed operation they increased , respectively , to 89 and 76 % for the former and 70 and 64 % for the latter .

These increased conversions in the fluidized - bed mode , plus or previous observations with other catalysts .

Table (2.3) .Results of CO_2 - CH_4 reforming over Ni-based catalysts in fixed - bed / fluidize bed switching mode .
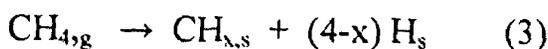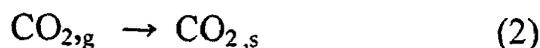
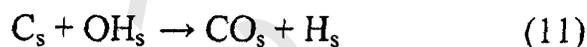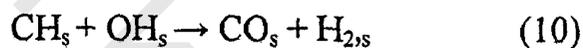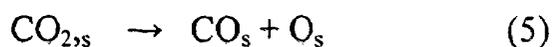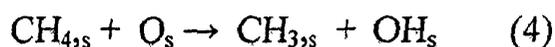| Catalyst	Mode	Bed temperature (^{o}C)	CH₄ conversion (%)	CO₂ conversion (%)	H₂ / CO
NiO / γ -Al₂O₃	Fixed	742	48	51	0.70
	Fixed -fluidized	736	92	80	0.82
FCR – 4 - 42	Fixed	749	77	65	0.76
	Fixed - fluidized	738	89	76	0.79
N139	Fixed	748	59	52	0.69
	Fixed - fluidized	741	70	64	0.71

2 . 3 . Reforming Reaction Mechanisms :-

The most general CO_2 / CH_4 reforming reaction mechanisms were proposed by Wang & Au (1977) using Rh / SiO_2 catalyst (Scheme 1) and of Verkios (2003) using Rh / γ – Al_2O_3 catalyst (Scheme 2) . The proposed mechanism has been confirmed by experimental results in each case . There are only slight differences between the two schemes ; while steps 4 , 6 , 8 and 10 of scheme (1) are not included in scheme (2) , steps 4 , 7 , 10 and 11 of scheme (2) are not included in scheme (1) . Steps 7 , 10 and 11 of scheme (2) represent the natural release of the adsorbed CO , H_2 and H_2O gases , being trivial , they may have been omitted from scheme (1) . Other differences seem unique for the type of support utilized in each case

<div align="center">
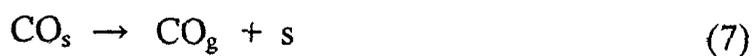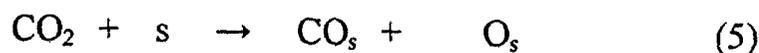
Scheme (1)

Rh / SiO_2 (Wang & Au ; 1977)

</div>

$$CH_{4,g} \rightarrow CH_{4,s} \qquad (1)$$

$$CO_{2,g} \rightarrow CO_{2,s} \qquad (2)$$

$$CH_{4,g} \rightarrow CH_{x,s} + (4-x) H_s \qquad (3)$$

<div align="center">28</div>

$$CH_{4,s} + O_s \rightarrow CH_{3,s} + OH_s \qquad (4)$$

$$CO_{2,s} \rightarrow CO_s + O_s \qquad (5)$$

$$CO_{2,s} + H_s \rightarrow CO_s + OH_s \qquad (6)$$

$$CO_s \rightarrow C_s + O_s \qquad (7)$$

$$CH_{x,s} + O_s \rightarrow CO_s + xH_s \qquad (8)$$

$$O_s + H_s \rightarrow OH_s \qquad (9)$$

$$CH_s + OH_s \rightarrow CO_s + H_{2,s} \qquad (10)$$

$$C_s + OH_s \rightarrow CO_s + H_s \qquad (11)$$

$$OH_s + H_s \rightarrow H_2O_s \qquad (12)$$

scheme (2)

$Rh / \gamma - Al_2O_3$ (Verkios ; 2003)

$$CH_{4,g} + s \rightarrow CH_{4,s} \qquad (1)$$

$$CO_{2,g} + s \rightarrow CO_{2,s} \qquad (2)$$

$$CH_{4,s} + (4-x)s \rightarrow CH_{x,s} + (4-x) H_s \qquad (3)$$

$$CH_{x,s} + x_s \rightarrow C_s + xH_s \qquad (4)$$

$$CO_2 + s \rightarrow CO_s + O_s \qquad (5)$$

$$CO_s + s \rightarrow C_s + O_s \qquad (6)$$

$$CO_s \rightarrow CO_g + s \qquad (7)$$

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$$O_s + H_s \rightarrow OH_s + s \qquad (8)$$

$$OH_s + H_s \rightarrow H_2O_s + s \qquad (9)$$

$$H_2O_s \rightarrow H_2O_g + s \qquad (10)$$

$$H_s + H_s \rightarrow H_{2,g} + 2s \qquad (11)$$

$$C_s + OH_s \rightarrow CO_s + H_s \qquad (12)$$
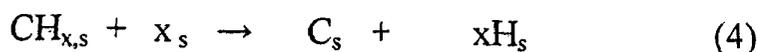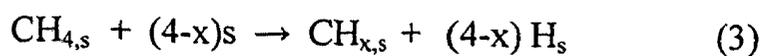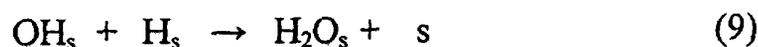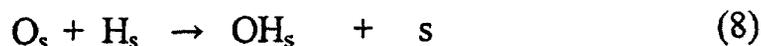
Most of the literature reported that the catalytic reaction of CH_4 with CO_2 requires the simultaneous adsorption and activation on the catalyst surface for both methane and carbon dioxide (Steps 1 & 2 in both schemes) Erdohelyi et al (1993) , Turlier et al (1993) , Solymosi et al (1991) , Csereny et al (1994) and Ferreiro – Aparicio et al (2000) .

In addition to the dissociation of CH_4 step (3) in both schemes , oxygen – assisted dissociation step (4) scheme (1) was suggested by Solymosi et al (1993) and Wang et al (1997) while oxygen – assisted dissociation step (8) scheme (1) was suggested by Bradford et al (1999), Cheng et al (2001), Rostrop – Nielsen et al (1993) , Turlier et al (1993) and Ferreiro - Aparicio et al (2000)

Step (11) scheme (1) and step (12) scheme (2) provide another way for the formation of CO over supported Rh catalyst (Verykios et al ; 1996) .

A number of researchers Kim et al (1994) , Nakamura et al (1994) , Wang et al (2000) , Gronchi et al (1997) and Erdohelyi et al (1993) have found that H_2O was formed and CO / H_2 ratio was always higher than one in the CO_2 – reforming of methane. These results imply that some CO_2 is hydrogenated to give CO and H_2O the so called reverse water gas shift reaction :

$$CO_2,s + H_s \rightarrow CO_s + OH_s \; ; [6] \; (\text{scheme} (1))$$

$$OH_s + H_s \rightarrow H_2O_s \text{ [12] (scheme (1))}$$
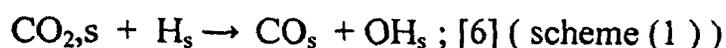
Kim et al (1994) and Gronchi et al (1995) have pointed out that the dissociation reduction of CO_2 could lead to CO step (5) schemes (1) & (2) or surface carbon step (7) schemes (1) & (2), together with oxide formation Au et al (1970) pointed out that carbon formed in the deep dissociation of CO_2 could react with O_s or OH_s to give CO .

$C_s + O_s \rightarrow CO_s$ [the backward reaction (7) in scheme (1) and (6) in scheme (2)] and ,

$C_s + OH_s \rightarrow CO_s + H_s$ [reaction (11) in scheme (1) and (12) in scheme (2)]
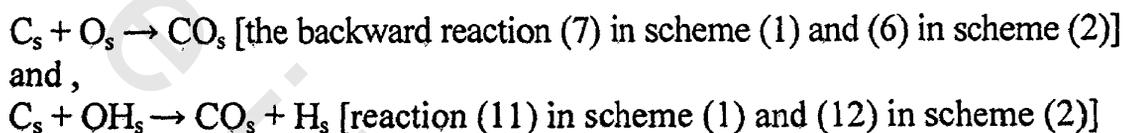
2. 4. Catalyst Deactivation :-

Among rhodium supported on SiO_2, TiO_2, γ- Al_2O_3, MgO CeO_2 and YSZ (ZrO_2 ($8mol\%Y_2O_3$)) catalysts , with the exception Rh / γ-Al_2O_3 catalyst, very small quantities of carbon accumulate on the catalyst surface (Gronchi et al ; 1997) and (Tsipouriari et al ; 1994) . Thus , the deactivation which is observed with time of exposure to the reaction mixture should be attributed mostly to sintering of the metal particles and to a smaller extent to carbon deposition .

Wang et al (1984) tracing experiments (using $^{13}CH_4$) coupled with temperature programmed oxidation (TPO) revealed that the carbon species accumulated on the surface of the Rh /Al_2O_3 catalyst during reforming reaction at $750^{\circ}C$ are primarily derived from the CO_2 molecular route . The amount of carbon present on the working catalyst surface which is derived from the molecular CH_4 is found to be very small .

Swaan et al (1994) also showed by ^{13}C labeling that the reactive surface carbon in CO_2 reforming originates from CH_4 , while the less reactive carbon accumulation follows the catalyst deactivation rate.

Similar findings were reported by Tsipouriari et al (1996) , Verykios (2003) and Efstathiou et al (1996) .

(Bhat et al ; 1996) noted that zeolite Y supported rhodium catalysts with rhodium contents as low as 0.5 - 0.93 wt % did not deactivate during 300h of time on stream and after multiple thermal cycles .

In contrast , rhodium supported on amorphous oxides deactivated significantly under the same conditions of reaction . One cause of extraordinary stability of zeolite supported rhodium is the absence of coke formation . The second cause for the unusual stability is the lack of metal agglomoration beyond the stage of $40A^o$ Rh particles . An obvious possibility is that the zeolite framework efficiently suppresses any particle mobility . It is easy to imagine that metal particles can slide more easily over the surface of an amorphous support than move through a three - dimensional framework with holes that are much smaller than the size of the particle .

The rates of deactivation observed over Rh crystallites supported on various carriers are found to be largely different , (Zhang et 1 ; 1996) . For the case of γ-Al_2O_3 , SiO_2 and TiO_2 there also exists a particle size effect on the rate of deactivation , which is larger in the case of Rh / TiO_2 catalyst. Higher deactivation rates are obtained over smaller Rh particles .

The carrier plays an important role on the rate of deactivation , while high deactivation rates are observed over Rh/TiO_2 and Rh/MgO catalyst , low deactivation rates are observed over the Rh/YSZ , γ-Al_2O_3 , La_2O_3 , and SiO_2 catalysts . At least three factors contribute to catalyst deactivation , namely , carbon deposition , sintering of metal crystallites , and blocking of the Rh surface sites by species originating from the carrier , the importance of each factor is largely determined by the nature of the carrier .

An accepted mechanism for carbon deposition based on the CO_2 molecule is via the following dissociation steps :-

$$CO_2 + 2s \rightarrow CO\text{-}_s + O\text{-}_s$$

$$CO\text{-}_s + s \leftrightarrow C\text{-}_s + O\text{-}_s$$
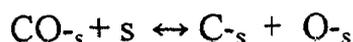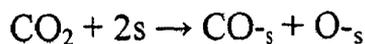
Here (s) is a site on the Rh surface or along the metal-support interface . According to these reaction steps the dependence of both CO_2 and CO dissociation steps on the nature of the site (s), i.e, a site on the Rh surface versus a site along the metal support interface, could explain the differences in carbon deposition among the present support Rh catalyst. On the other hand , other reaction steps of carbon removal may also be considered as sensitive to the nature of the site (s) , such as

$$H_2O + 2s \rightarrow OH\text{-}_s + H\text{-}_s$$

$$C\text{-}_s + OH\text{-}_s \rightarrow CO\text{-}_s + H\text{-}_s$$
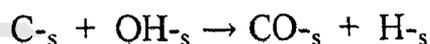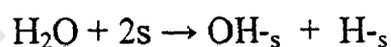
On the other hand , in the case of Ni – based reforming catalysts , accumulated carbon is derived mostly from the CH_4 molecule (Swaan et al ; 1994) and (Goula et al ; 1996) These results demonstrate the different chemistry and kinetics of carbon deposition and removal steps during reforming reaction of CH_4 with CO_2 over Rh versus Ni catalysts .

Rostrup - Nielsen et al (1993) suggested that partial sulphiding of the catalyst leads to a drastic decrease in the number of sites for carbon formation , while sufficient sites for the reforming reaction are maintained A new pretreatment of catalyst , deposition – removal (D - R) treatment , is proposed to suppress carbonaceous deposition on Ni / Al_2O_3 catalyst for CO_2 reforming of CH_4 .

This treatment is based on the hypothesis that active cores forming carbon whiskers are different from surface active coros for the main reaction. The increase in the activity was explained by the development of active sites on newly exposed nickel layers which strongly interact with the support (Ito et al ;1999) .

A new activation process was proposed for supported nickel catalysts in CO_2 reforming of methane by (Souza et al ; 2004) .The activation was performed by heating the catalyst up to 800°C under the a mixture of CH_4 / CO_2 = 2 . Before activation the nickel catalysts present were only nickel aluminate species ; these species are partially reduced to metallic nickel during activation . SEM pictures showed formation of carbon filaments embedded with dispersed nickel particles, which are the active sites for methane reforming with CO_2 .

The nickel loading and the support greatly influence the catalyst stability, and the conversion increased with Ni loading on alumina support .

(Erdohelyi et al ; 1994) noted that reproducible results were obtained only at stoichiometric composition or with excess of carbon dioxide.

(Bodrov et al ; 1967) noted that carbon lay-down is the dominating reaction under conditions of methane excess in the feed and they recommended a CO_2 / CH_4 ratio 1 for the investigation of the reforming reaction .

With regard to the alumina supported platinum Ferreira-Aparicio et al (1998) stated that the catalyst seems to suffer a strong deactivation at high temperature . Several authors agree in pointing that platinum catalyst is one of those in which deactivation takes place faster Mark et al (1996) and Bitter et al (1996) have found a very similar behavior for their alumina supported Pt-catalyst . They state that same carbon accumulation takes place over the alumina support, even in the absence of any metallic phase. So for the Pt- catalysts, after the elapse of a certain time, carbon reaches metallic particles and encapsulates them .

According to Aparicio et al (1998) results , this behavior cannot be only assigned to the carrier given that a catalyst as Rh /Al_2O_3 , even showing a higher activity, does not exhibit the same trend . So , the deactivation

behavior observed for the Pt / Al$_2$O$_3$ catalyst , which exhibits the highest initial metallic dispersion , is probably related to the sintering of the active phase . This explanation is supported by the hydrogen chemisorptions values obtained over the spent samples .
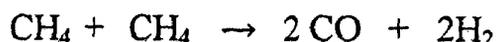
2. 5. Reforming Kinetics :-

Kinetic experiments were performed at pressure of 1 atm . (101.3 kpa) and 600 , 650 and 700°C , using 45 – 60 mesh particles of Rh / γ-Al$_2$O$_3$ catalyst to avoid internal diffusion limitations by Richardson et al (1990) . Carbon dioxide partial pressures varied from 0.085 to 0.550 atm . and methane from 0.250 to 0.550 atm . A range of CO$_2$ / CH$_4$ from 1 to 5 was covered with 38 runs . Conversions were usually below 0.10 , approaching differential conditions .

Rates , calculated from these conversions , were those of the forward part of the rate equations . The data were tested , using linear regression analysis , with rate equations suggested by Langmuir – Hinshelwood and redox mechanisms by Paripatyadar (1987) The recommended formula was :-

$$r_R = k_R \, K_{CH4} \, K_{CO2} \, P_{CO2} \, P_{CH4} \, / \, (1 + K_{CO2} \, P_{CO2} + K_{CH4} \, P_{CH4})^2$$

Where k_R is the rate constant for reaction :-

$$CH_4 + CH_4 \rightarrow 2\,CO + 2H_2$$

and the K's and P's the appropriate adsorption equilibrium constants and partial pressures (atm) respectively .

Mark et al (996) were studied the reforming kinetics in a temperature range 500 – 850°C of a 1 : 1 (CH$_4$ / CH$_4$) mixture on an Ir / Al$_2$O$_3$ catalyst Kinetics modeling was carried out by numerical integration of selected rate equations and direct fitting to the experimental data over the whole temperature range . It was found that the experimental data could be

represented by several kinetic models , but the best fit and the only one to provide meaningful parameters over the whole temperature range studied was obtained with the following rate equation ,

$$r_R = k_{ref} \, (PCH_4 - (P^2H_2 \, P_2CO \, / \, K_{ref} \, P_{CO2}))/1 + (P^2_{CO} \, K_{R,C-z} \, P_{CO2})$$

This kinetic study also confirmed that the chemical reaction was rate determining and was not affected by transport phenomena .

Dependencies of reaction rates on partial pressure of CH_4 and CO_2 were determined over a range of partial pressure for 3.2 % Rh / NaY catalyst by Bhat et al (1997) . The reaction orders for CH_4 (a) , and CO_2 (b) , were determined by fitting the data to a power rate law of the form :-

$$r_i = k \, P^a_{CH4} \, P^b_{CO2}$$

Experiments were done at a total pressure of 1 bar , keeping the partial pressure of one reactant constant and varying that of the other reactant using argon to make up the difference .

The rate was found to be first order w.r.t CH_4 and zero order w.r.t CO_2 , i.e. a = 1 & b = 0 .

Initial catalyst TOF_s at 723 K were also examined as a function of the weight hourly space velocity (WHSV) by varying the catalyst mass over Rh / SiO_2 and Ni / TiO_2 by Bradford et al (1999) .

The difference in observed trends between the two catalysts , which have a similar sieve fraction , indicated that the variation in TOF with WHSV was not due to external mass – transfer resistance , and Weisz et al (1957) calculations indicate that the observed variation in TOF with WHSV for Ni/ TiO_2 , and other catalysts , is not due to internal mass – transfer limitations.

Gesser et al (1994) have shown during their investigation of CH_4 - CO_2 reforming over a W wire that the influence of the reverse water – gas shift reaction diminishes with increasing space velocity .

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But , further analysis of (Bradford et al ; 1999) has indicated that the relationship with WHSV was almost certainly due to the influence of the reverse reaction , i.e., the hydrogenation of CO to CH_4 conversion approaches that expected at thermodynamic equilibrium .

The effect of CO_2 and CH_4 pressures on forward CH_4 turnover rate (r_f) at 873 K and 100 – 1500 kpa total pressures over Rh / Al_2O_3 catalyst were studied by Wei et al (2004) . These turnover rates were normalized by H_2 chemisorptions uptakes before catalytic measurements. Measured net rates were corrected for the approach to equilibrium for each CH_4 reaction in order to obtain rigorous forward reaction rates. Specifically, measured rates were corrected for approach to equilibrium (η) from thermodynamic data (Stull et al ; 1987) .

Forward CO_2 reforming reaction rates increased linearly with increasing CH_4 partial pressures (5 – 450 kpa) at temperatures between 823 and 1023 K ; these rates were not influenced , however , by CO_2 partial pressures (5– 450 kpa) .

Forward rates were not influenced by CO or H_2 concentrations , whether they were varied by external addition or by changes in residence time and CH_4 conversion .

Finally , CH_4 reforming rates using CO_2 as co – reactants become simply first – order in CH_4 and zero – order in CO_2 .

2. 6. Catalyst Preparation Methods :-

2 . 6 .1. Precipitation Method : - gel formation , as simple mixing of the components and Precipitation provides a method of obtaining the solid material in a porous form .

It consists of adding a precipitating agent to aqueous solutions of the desired components . Washing , drying , and some times calcinations and activation are subsequent steps in the process . Concentration of the aqueous solutions , temperature , and time of the drying and calcining steps may influence the surface area and pore structure of the final product . Of particular importance is the washing step to remove all traces of impurities, which may act as poisons .

A special case of the precipitation method is the formation of a colloidal precipitate which gels. Catalysts containing silica and alumina are especially suitable for preparation by gel formation , since their precipitates are of colloidal nature . Detailed techniques for producing catalysts through gel formation or ordinary precipitation are given by Ciapetta & Plank (1954) In some instances a porous material can be obtained by mixing the components with water , milling to the desired grain size , drying and calcining . Such materials must be ground and sieved to obtain the proper particle size .

2. 6. 2. Grafting Method :-

It is defined as the removal from solution of a compound containing metal through interaction with hydroxyl groups on the surface of an inorganic support .

Multiple grafting followed by calcinations will result in a mono layer of metal oxides on the surface of a support oxide . A related technique is chemical vapor deposition (C V D) , which makes use of a volatile

inorganic or organo – metallic compound that is deposited on the surface of a support oxide by reaction with the support hydroxyl groups .

2. 6. 3. Promoters and Inhibitor Method :-

Components of the catalyst must include the catalytically active substance itself and may also include a carrier , promoters , and inhibitors .

Innes (1954) has defined a promoter as a substance added during the preparation of a catalyst which improves activity , selectivity or stabilizes the catalytic agent so as to prolong its life . The promoter is present in a small amount and by itself has little activity . More details were published by Innes (1954) .

An inhibitor is the opposite of a promoter .

Inhibitors are useful for reducing the activity of a catalyst for an undesirable side reaction .

2. 6. 4. Ion Exchange Method :-

By the interaction of the slurry ((cation or anion complex (metal precursor)) with the support in a certain slurry / solid ratio . The slurry is stirred at room temperature for 48 h . Then the slurry is filtered and thoroughly washed with distilled water .

This mode of impregnation by exchange has advantages that it theoretically creates an atomic dispersion of metal on the surface of the support .

Solid state ion exchange : -

The mixture of support and the metal precursor in a given atomic ratio of metal to support is carefully ground in a mortar , calcined in an oven in static conditions at a heating rate of 10 $^{\circ}$C min^{-1} and at 350 $^{\circ}$C for 6 h , cooled , washed 5 times with deionized water , and finally dried at 120 $^{\circ}$C

2. 6. 5. Impregnation Method :-

As the most simple and widely used preparation technique for making supported metal oxide catalysts . The term impregnation denotes a procedure whereby a certain volume of an aqueous or non – aqueous solution containing a metal compound is adsorbed into the pores of an inorganic oxide .

Two impregnation procedures can be distinguished :-

If the support is dipped into an excess amount of solution , the process is called wet impregnation .

More precise control over the metal oxide loading is achieved with a technique called dry impregnation , pore volume impregnation or incipient wetness impregnation .The support is then contacted with a solution of appropriate concentration , corresponding in quantity to the total known pore volume of the support , or slightly less This allows precise control of concentration of the active metal oxide component on the support . In some cases multiple impregnation steps should be applied .

The steps in the preparation of catalyst impregnated on a carrier may include :-

1. evacuating the carrier .
2. contacting the carrier with the impregnating solution .
3. removing the excess solution .
4. drying .
5. calcinations and activation .

The final step , reduction of the oxide to the form , is best carried out with the particles in place in the reactor by passing hydrogen through the equipment . Activation in situ prevents contamination with air and other gases which might poison the reactive metal . In this case no precipitation was required . If the solution used to soak the carrier contains potential

poisons such as chlorides or sulfates , it may be necessary to precipitate the required constituent and wash out the possible poison .

The nature of the support can affect catalyst activity and selectivity . This effect presumably arises because the support can influence the surface structure of the atoms of dispersed catalytic agent . For example , changing from a silica to alumina carrier may change the electronic structure of deposited metal atoms . This question is related to the optimum amount of catalyst that should be deposited on a carrier . The dispersion of the catalyst on the carrier may also be an important factor .

It is interesting to note that a 5.0 wt % metal content catalyst prepared by 10 individual deposition of 0.5 wt % was much more active than the 5.0 wt % added in a single treatment .

This method gave a much larger active metal surface , presumably because of better dispersion of the metal atoms on the support surface .