CATALYTIC REFORMING OF ALL HYDROCARBONS IN NATURAL GAS WITH CARBON DIOXIDE TO PRODUCE SYNTHESIS GAS OVER RHODIUM-ALUMINA CATALYST

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ABSTRACT

Reforming of natural gas with carbon dioxide to produce synthesis gas (H_2 + CO) has been investigated over rhodium (0.5 wt. %) supported on γ- alumina catalyst. The detection of both major and minor components in the natural gas before and after reforming, in addition to the produced synthesis gas, requires a high sensitive gas chromatograph.

This research aims to study the effect of the space velocity and temperature on the conversion of carbon dioxide and all the components of the natural gas. The space velocity 18000 mL g^{-1} h^{-1} and the temperature 800°C are the optimum operating conditions giving the highest conversion of both the natural gas and carbon dioxide, but the space velocity 36000 mL g^{-1} h^{-1} and the temperature at 700°C are the preferred conditions for production of the synthesis gas (H_2 + CO).

Key words: Reforming, Natural gas, Synthesis gas, γ-Alumina and gas chromatograph.

INTRODUCTION

Natural gas plays nowadays an important role in human life. A principle reason is the abundant supply of natural gas as a clean source of energy and for the production of high value chemicals. The estimate of proven natural gas reserves in the world is about 158 trillion cubic meters in recent years[1-3]. The production of natural gases from Egypt is in continuous increase. This attracts our attention to study the reforming of natural gas with carbon dioxide to form synthesis gas.

Conversion of methane and carbon dioxide, which are two of the most abundant carbon containing materials, into useful products is an important area of current catalytic

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research. The reforming reaction of methane with carbon dioxide to synthesis gas is a very attractive route for the production of energy and chemicals as methanol or oxo-alcohol synthesis[4,5]. Carbon dioxide is an important topic of the current catalytic reforming of methane to synthesis gas

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad (\Delta H = 247 \text{ KJ/mol})$$

This reaction is of interest because it generates low H_2/CO ratio (≤ 1), which is suitable for the Fischer and Tropsch synthesis[4] of higher hydrocarbons and oxygenated derivatives. Environmentally, this reaction is appealing due to the reaction of CO_2, as this gas is a contributor to the green house effect. Also, it has been studied for viability in chemical energy transmission systems[6,7]. Dry reforming requires the use of stable and effective catalysts, resistant to coking; hence investigations should be focused on the metal activity, the resistance to coke formation and the type of the support that improves the catalyst efficiency[8].

Recently, several studies on the dry reforming of methane focused on the noble metal catalysts, which exhibit better activity and very high stability due to the less sensitivity to carbon deposition. Rostrup-Rostrup-Nielsen and Hansen[9] compared the catalysts based on nickel, ruthenium, rhodium, palladium, iridium and latinum and found that rhodium provided high selectivities with carbon-free operations and high activities.

Erdohelyi et al.[10,11] reported that the support has no effect on the activity of Rh catalysts. In contrast, Nakamura et al.[12] and Zhang et al.[13] observed that the specific activity of Rh crystallities is significantly affected by the nature of the support.

Hou et al.[14] concluded that Rh dispersed highly on meso-porous Al_2O_3 (with high surface area) and exhibited higher coke resistance ability and higher reforming activity. At the same time, small amount of Rh enhanced obviously both the reforming activity and coke resistance ability of Ni.

Conversion of CH_4 and CO_2 to synthesis gas approaching those defined by the thermodynamic equilibrium can be obtained over most of the aforementioned catalysts as long as contact times are kept high enough[14]. Other workers studied the conversions of CH_4 arid CO_2 over the noble metal-alumina stabilized magnesia (Spinel) catalysts at different reaction temperatures. They showed an increase in CH_4 and CO_2 conversion with increasing reaction temperature[15].

The present work reports results of the investigation of the effects of the support alumina and the metal Rh on the reforming activity of not only methane but also all other components in natural gas[16]. Also, the study includes the effect of different gas velocities and different temperatures on the reforming process of natural gas and CO_2 in order to obtain the optimum conditions preferred for high conversion. Rh-based catalysts exhibit good stability for the whole temperature range, and resistance to sintering and to carbon deposition[17].

EXPERIMENTAL

Catalysts

The Rh catalyst was prepared using incipient wetness impregnation techniques[17]. γ-alumina (Puralox, Condea) was used as a support. Impregnation was carried out with aqueous solution of $RhCl_3.3H_2O$ (Merck) with 0.5% wt. metal loading. Then, the catalyst was dried overnight at 110ºC and calcined with air in a muffle furnace at 500ºC for 3 h. Details about the preparation and characterization of this catalyst wrer given elsewhere[18]. Before reaction and characterization tests, the catalyst was submitted to a standard reduction pretreatment by heating in pure hydrogen at a rate of 20 mL/min at 500ºC for 7 h.

Reaction apparatus

A quartz tube flow reactor (800 mm overall length, 13 mm in diameter) filled with 20 mg of catalyst between two layers of ceramic fibers was placed in a ventilated oven. A K-type thermocouple located inside the catalytic bed to control the reaction temperature was used. The reaction mixture of N.G. : CO_2 : N_2 in proportions 1 : 1 : 4 regulated by mass flow controllers was adjusted to give flow rates corresponding to gas hourly space velocities: 18000, 36000, 45000, 60000 mL g^{-1} h^{-1}, respectively. The mixture of reactants was introduced by switching a four-way valve located at the reactor inlet. Reaction temperatures from 600 to 800ºC were examined at atmospheric pressure. An ice-cold trap was set between the reactor exit and gas sampling to remove the water and condensables formed during reaction. After shifting from one temperature to another and the latter was reached, the catalyst bed was left for at least 15 min to be sure that the temperature was almost constant through the catalyst bed. After another 30 min products were received in gas samplers.

Gas chromatographic analysis

The used natural gas components (N_2, CO_2 and $C_1 - C_7$) and the produced gases (H_2 and CO) were analyzed using an Agilent 6890 plus, HP, gas chromatograph, equipped with thermal conductivity (TCD) and flame ionization (FID) detectors, and a fused silica plot Q capillary column (15 meter in length and 0.35 mm internal diameter). A packed column DC

200 of stainless steel in type (10 feet in length and 1/8 inch in diameter) was attached to the TCD and the capillary column plot Q (30 meter in length and 0.35 mm in diameter) was attached to the FID, The injector and detector temperatures were 200 and 250°C, respectively. The elution of the studied gas mixtures was achieved with temperature programming from 60 to 200°C at a rate 10°C min^{-1}. Nitrogen (oxygen-free) was used as a carrier gas for the analysis of the natural gas, while helium for the detection of CO and H$_2$. Flow rates were measured from the end of the column with a soap bubble flowmeter. Methane as an unretained marker was used to correct the dead volume in the column in the case of FID, and the air in the case of TCD.

The quantitative analysis of the liberated gas mixture was achieved using standard natural gas sample of known composition and according to the standard ASTM method[19].

The areas under the resolved chromatographic profiles were estimated by integration using a connected Epson data station unit.

RESULTS AND DISCUSSION

The distribution of the hydrocarbons and the inorganic gases of the used natural gas determined by gas chromatography were given in Table 1.

Table 1: Composition of the used natural gas

Component	Mol. %	Wt. %
N$_2$	0.368	0.582
CO$_2$	0.448	1.113
C$_1$	93.041	84.254
C$_2$	3.513	5.965
C$_3$	1.469	3.656
i-C$_4$	0.324	1.064
n-C$_4$	0.366	1.202
i-C$_5$	0.137	0.559
n-C$_5$	0.105	0.428
C$_6$	0.146	0.711
C$_7$	0.083	0.468
Total	100.000	100.000

It has been found that the studied natural gas contains mainly methane (93 mol %), the remaining paraffins represents about 6 mol %. The inorganic gases (nitrogen and carbon dioxide) represent 0.82 mol %, which carbon dioxide is about 0.45 mol %, it has a negligible effect compared with the used carbon dioxide as the oxidizing agent.

The studied catalyst Rh/ γ-Al$_2$O$_3$ was tested under atmospheric pressure, the feed gases (N.G. : CO$_2$: N$_2$ = 1 : 1 : 4) were introduced into the catalyst bed at the prescribed space velocities and temperatures in order to determine the optimizing conditions required for the N.G. reforming with CO$_2$ reaction, which give the best H$_2$-selectivity, CO-selectivity, as will as, CH$_4$ and CO$_2$ conversions. Also, the behavior of heavy hydrocarbons present in the natural gas towards CO$_2$ reforming reaction was studied. This represents a gap of study in the literature.

Methane conversion over the Rh / γ-Al$_2$O$_3$ catalyst

The interaction of methane with carbon dioxide by a ratio of 1 : 1 over 0.5% Rh/γ-Al$_2$O$_3$ catalyst was investigated at temperatures: 600, 700 and 800°C. Fig. 1 shows the variation of methane conversion with the studied temperatures at various space velocities (18000, 36000, 45000, 60000 mL g^{-1} h^{-1}). Generally, for each studied space velocity, the conversion of methane is increased with increasing temperature. It reaches a maximum conversion of 95 mol % at space velocity 18000 mL g^{-1} h^{-1} and temperature 800°C these results were matched with. Rezaei et al.[15] who observed the same results when carried out the activity tests at different temperatures ranging from 500 to 700°C in steps of 50°C over Rh/Spinel catalyst.

For each studied space velocity, the activity of catalyst is increased as temperature increases. This occurs because CO$_2$ reforming reaction is a highly endothermic reaction:-

$$CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2 \qquad \Delta H = 247\ KJ/mol$$

So, the CH$_4$ conversion increases from 600°C to 800°C as shown in Fig. 2.

It has been found that methane conversion is increased with the decrease of space velocity. This is due to the increase of contact reaction time. The CH$_4$ conversion increases in the order of 18000 > 36000 > 45000 > 60000 mL g^{-1} h^{-1}, where the contact time is: 55 x 10^{-6}, 27 x 10^{-6}, 22 x 10^{-6} and 17 x 10^{-6} h), respectively. However; increasing the GHSV leads to a decrease in CH$_4$ and CO$_2$ conversions which followed by a decrease in CO and H$_2$ yields[15].
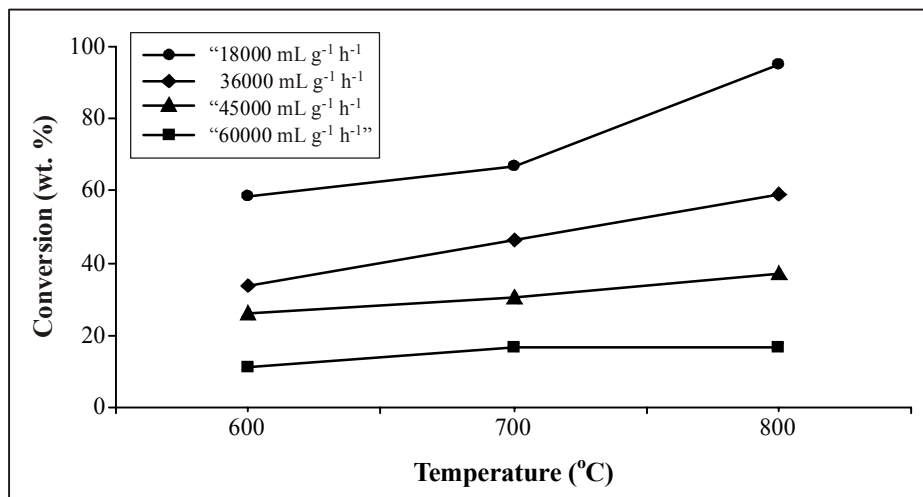
Fig. 1: Conversion of CH$_4$ with the temperature at four different space velocities on the Rh / γ-Al$_2$O$_3$ catalyst
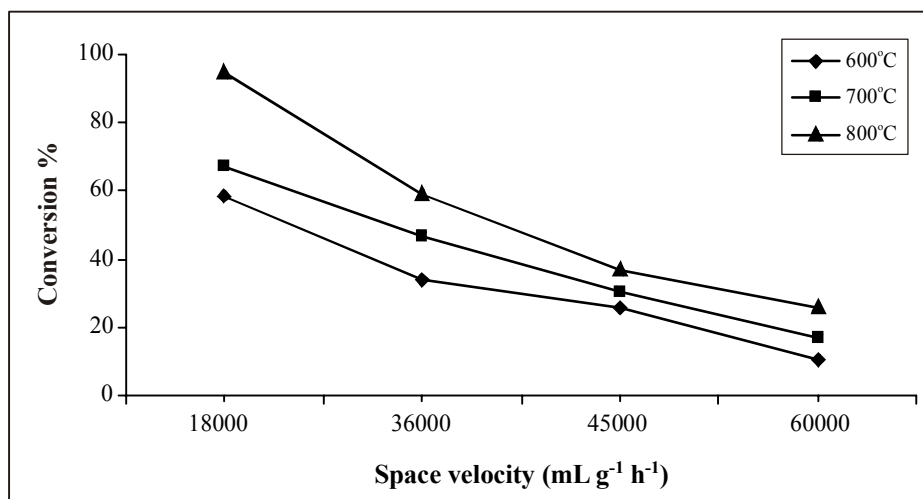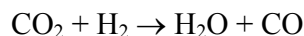

Fig. 2: Conversion of CH$_4$ with the space velocity at three different temperatures on the Rh / γ-Al$_2$O$_3$ catalyst

When Rh is supported on Al$_2$O$_3$ there is some direct or indirect interaction of the support with the Rh crystallites. The higher the dispersion, the higher the metal-support interfacial area, which results in metal-support interactions of higher intensity[13,20]. This result could be related to the amount of active carbon species which participate in the sequence of steps to form CO.

Over the Rh/Al_2O_3 catalyst, the amount of carbonaceous species C_XH_Y formed on the Rh surface during the CO/H_2 reaction increases with increasing Rh particle size, the dissociation of CO is responsible for the formation of these C_xH_y species[13]. While the significant quantities of (carbon deposited during the reaction do not seem to influence significantly the reaction rate accumulation of total carbon species on the catalyst surface is very rapid and does not change with time of exposure to reaction conditions). It is speculated that some of this carbon might be located on the Al_2O_3 carrier; however, other hydrogenation experiments of carbon over the Rh/γ- Al_2O_3 catalyst indicate that some transformation of active carbon to a less active form occurs; a result which explains the role of carbon on catalyst deactivation. This result could be understood by comparing the surface coverage of active carbon, which is in the sequence of steps to form CO. It is found that the active carbon over Rh/γ- Al_2O_3 is one order of magnitude higher than 0.02 of a mono-layer[20]. Sintering can account for the deactivation pattern for the Rh/γ- Al_2O_3 catalyst.

CO_2 Conversion

The conversion of CO_2 is always higher than at of CH_4 at the same conditions, although a feed ratio of unity was used. The difference is more pronounced at low temperature as shown in Table 2, for example for the Rh/γ-Al_2O_3 catalyst at space velocity of 18000 mL $g^{-1}\,h^{-1}$ and temperature of $600^{\circ}C$, the CH_4 conversion is about 58 %, while, that of CO_2 71 %. This occurs due to the reverse water gas shift reaction which takes place at lower temperatures i.e.

$$CO_2 + H_2 \rightarrow H_2O + CO$$

CO_2 has different pathways to be consumed so its conversion is usually higher than CH_4 conversion.

Table 2: Conversion of CH_4 and CO_2 and H_2/CO of synthesis gas at the studied conditions of temperature and space velocity

Temp. (^{o}C)	600			700			800		
Space velocity mL $g^{-1}\,h^{-1}$,	CH_4	CO_2	H_2/CO	CH_4	CO_2	H_2/CO	CH_4	CO_2	H_2/CO
18000	58.47	71.62	0.51	67.03	77.63	0.59	93.44	94.83	0.62
36000	33.96	41.97	0.60	46.62	59.49	0.65	58.94	66.01	0.64
45000	26.01	43.41	0.27	30.41	51.05	0.39	36.98	56.80	0.40
60000	10.79	5.15	0.19	16.71	25.06	0.33	25.56	37.74	0.27

In this study, the 0.5% Rh/Al_2O_3 catalyst exhibits good reactivity at the whole temperature range studied. At constant flow rate, the activity of catalyst is increased as the temperature increases. The CO_2 conversion at a constant space velocity increases as the temperature increases from 600°C to 800°C, as shown in Fig. 3. The temperature 800°C is the preferred degree giving the highest conversions of CO_2. At the same reaction temperature, the conversion of CO_2 increases ad as the space velocity decreases, i.e the CO_2 conversion order as follows: $18000 > 36000 > 45000 > 60000$ mL $g^{-1} h^{-1}$.
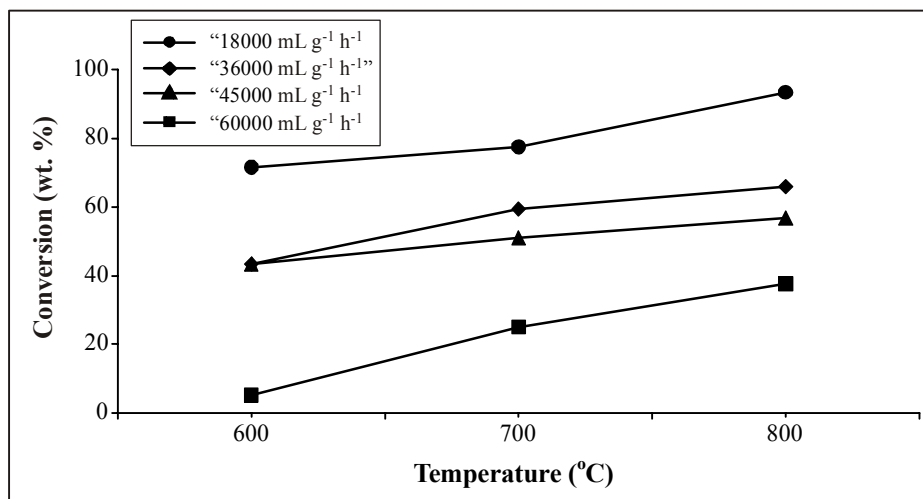

Fig. 3: Conversion of CO_2 with the temperatures at different space velocity on the Rh / γ-Al_2O_3 catalyst

Conversion of heavy hydrocarbons

Ethane and propane conversion

Over the Rh/γ-Al_2O_3 catalyst, the conversion of both ethane and propane increases with the decrease of space velocity which is the order of increasing contact time. The highest conversion occurs at the lowest space velocity (18000 mL $g^{-1} h^{-1}$), at all the three studied temperatures (Fig. 4). This may be due to the longest contact time which is suitable enough to complete the reaction. Also, the conversion of both ethane and propane increases with increasing the temperature, and the temperature 800°C is the most efficient degree giving the highest conversion percentage. Generally, the space velocity of 18000 mL $g^{-1} h^{-1}$ and the temperature of 800°C are the optimum conditions for obtaining the highest conversion percentage of both ethane and propane.

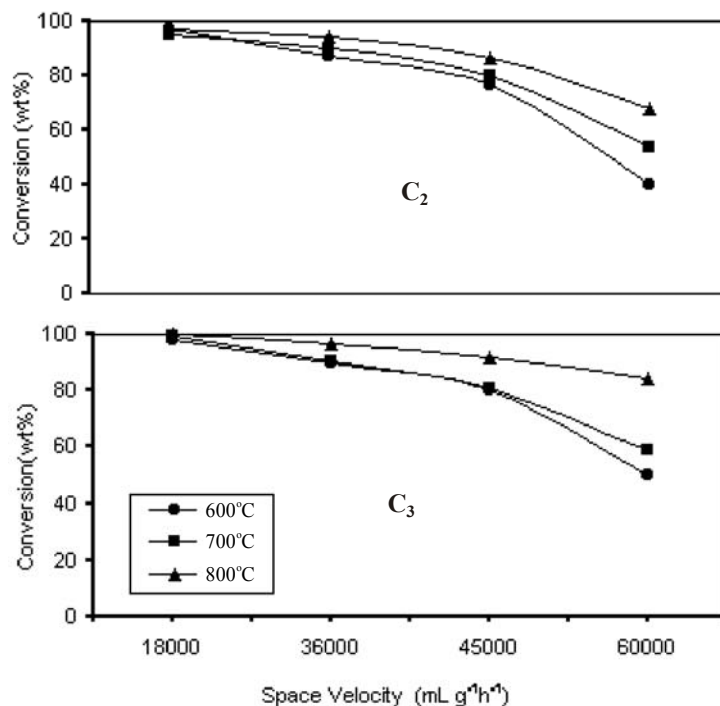**Fig. 4: Conversion of C_2 and C_3 with the space velocity at different temperatures on the Rh/ γ-Al$_2$O$_3$ catalyst**

Conversion of butanes and pentanes

Butanes (*n*- and *i*- C_4) and pentanes (*n*- and *i*- C_5) represent nearly 0.69 mol % and 0.34 mol %, respectively, of the composition of studied natural gas. However, their conversions are different depending on the working temperature. The conversions of both isomers of butanes and pentanes increase with decreasing the space velocity at the all studied temperatures. The space velocity of 18000 mL g^{-1} h^{-1} exhibits the most efficient velocity for the hieghest conversions, because this velocity offers the suitable enough time to complete the reaction. The temperature 800°C is the preferred one at all the studied space velocities used, as shown in Figs. 5 and 6.

At all the space velocities the *i*- C_4 conversion is higher than that of *n*- C_4 at temperature 800°C; this may occur because the *i*- C_4 is more active due to the branching in the chain. But the opposite occurs at the other two temperatures (600 and 700°C). It is clear that the temperature 800°C for *n*-C_5 and *i*-C_5 exhibit nearly complete conversion at all the studied space velocities (Fig. 6). In general, the conversion of both isomers of butane and

pentane decrease in the sequence of increasing of the space velocity, i.e. from 18000 to 60000 mL g^{-1} h^{-1}, which is the order of decreasing the contact time at constant temperature.
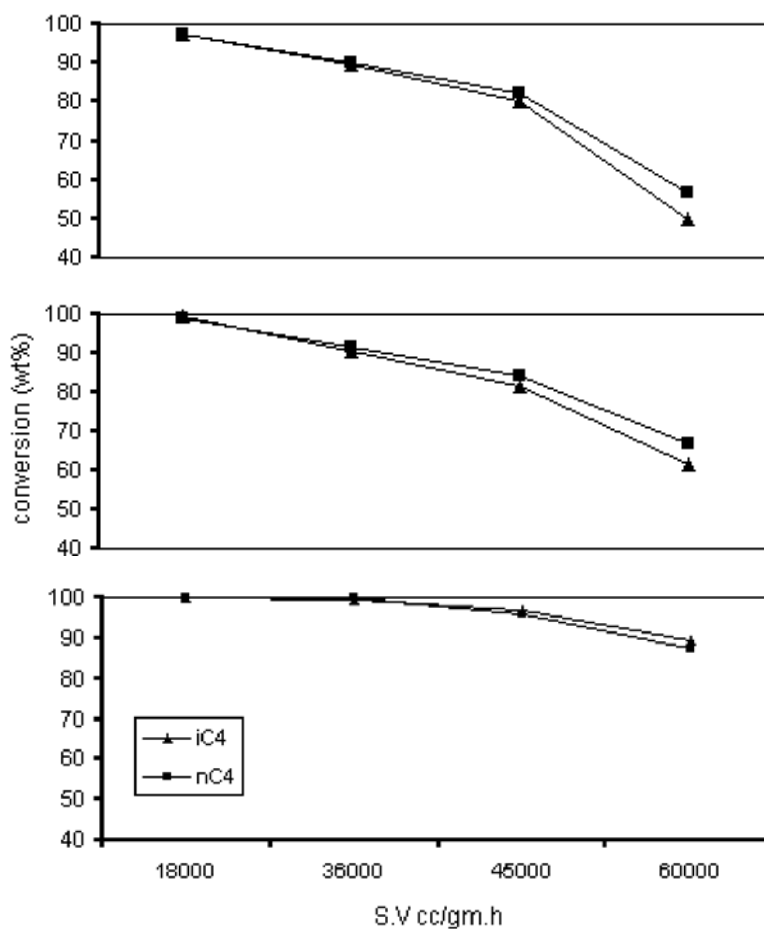

Fig. 5: Conversion of butanes with the space velocityat different temperatures on the Rh/γ-Al₂O₃ catalyst

Conversion of hexanes and heptanes

Over Rh/γ-Al$_2$O$_3$ catalyst, the hexane and heptane isomers exhibit conversions under the all working conditions of the space velocity and temperature, but with different percentages. Generally, the best conversions of hexanes and heptanes are obtained at the optimum conditions of space velocity 18000 mL g^{-1} h^{-1} and temperature 800°C, as shown in Fig. 7. However, at higher space velocities, the highest conversions are obtained at the temperature 700°C.

Formation of the synthesis gas (H$_2$ + CO)

Over the Rh/γ-Al$_2$O$_3$ catalyst and under all the experimental conditions of the space velocity and temperature, the CO$_2$ conversion is higher than that of CH$_4$ and the produced CO yield is higher than that of H$_2$, with a ratio of H$_2$/CO below unity.
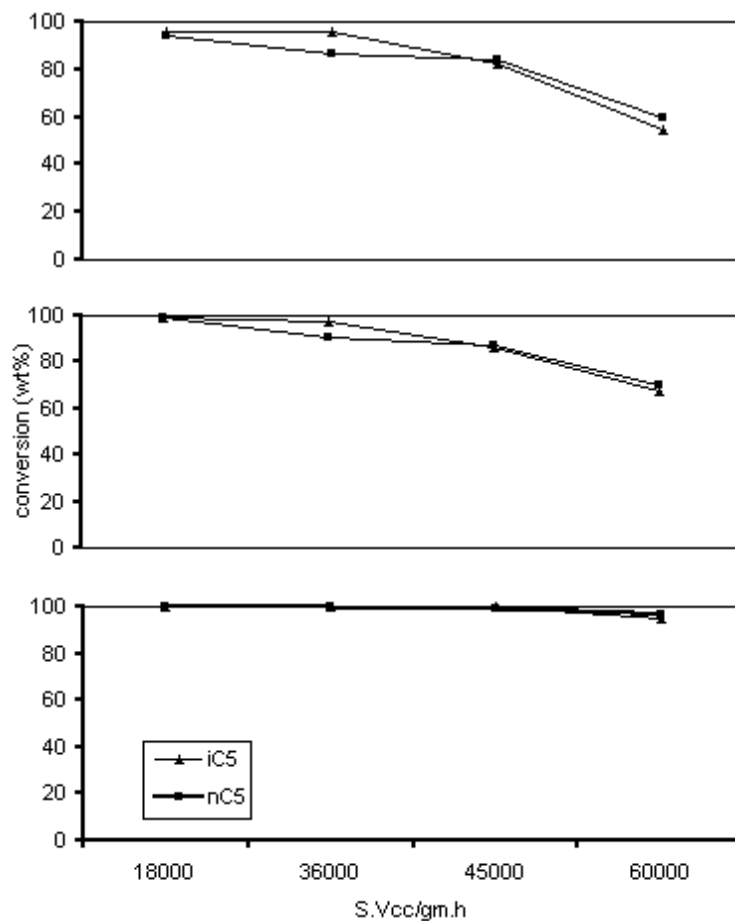

Fig. 6: Pentanes conversion with space velocity at different Temperatures on the Rh/γ-Al$_2$O$_3$ catalyst

According to the stoichiometry of: CH$_4$ + CO$_2$ → 2CO + 2H$_2$ equal conversions of both CH$_4$ and CO$_2$ should be expected in the reforming reaction, but this is not so. However, the CO$_2$ conversion is actually higher than that of CH$_4$ as given in Table 2. It has been found that H$_2$O is formed and the H$_2$/CO ratio is always lower than one in the CO$_2$-reforming of CH$_4$.

To explain the higher conversion of CO_2 than CH_4, the reverse water gas shift reaction must be considered:

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad \qquad …(1)$$

The hydrogen can be supplied by the dry reforming reaction:

$$CO_2 + CH_4 \rightarrow 2\ CO + 2\ H_2 \qquad \qquad …(2)$$

Or by the methane cracking:

$$CH_4 \rightarrow C + 2\ H_2 \qquad \qquad …(3)$$

Over the Rh/γ-Al$_2$O$_3$ catalyst and under the all-working conditions, there is a production of the synthesis gas (H_2/CO) as given in Table 2, but with different ratios. The space velocity 36000 mL g^{-1} h^{-1} and the temperature 700°C are the optimum conditions for producing the highest synthesis gas having H_2/CO ratio of 0.65 as given in Table 2 and shown in Fig. 8. It is clear that at constant temperature, the synthesis gas ratio (H_2/CO) is increased in the order of 36000 > 18000 > 45000 > 60000 mL g^{-1}.h^{-1}. All H_2/CO ratio are below unity in all cases; this may indicate that a reverse water gas shift reaction takes place as a side reaction.
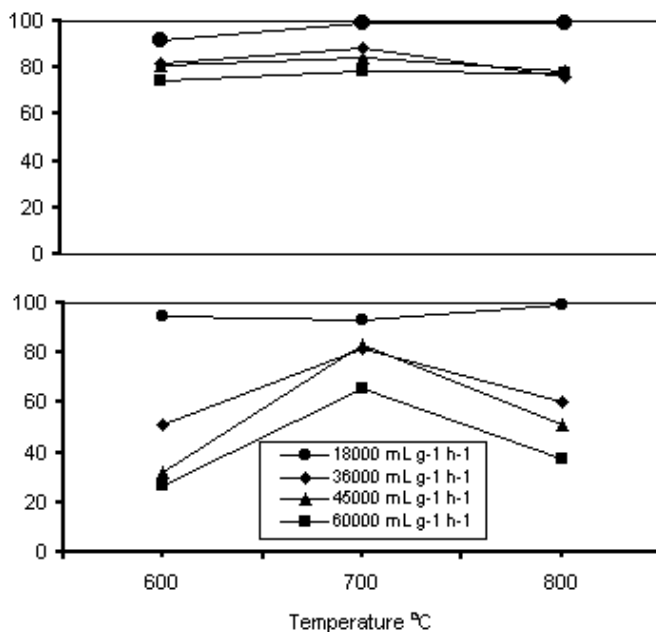

Fig. 7: Conversion of hexanes and heptanes with the temperature at different space velocities on the Rh/ϒ-Al$_2$O$_3$ catalyst

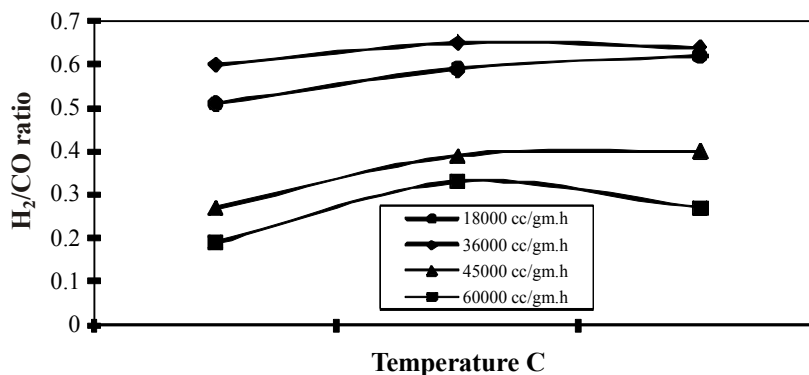**Fig. 8: H₂/CO ratio with the temperature at different space velocities over the Rh/ γ-Al₂O₃ catalyst**

$$\text{Fig. 8: } H_2/CO \text{ ratio with the temperature at different space velocities over the } Rh/ \gamma\text{-}Al_2O_3 \text{ catalyst}$$

CONCLUSION

(i)   The $Rh/\gamma\text{-}Al_2O_3$ catalyst exhibits good reactivity at the studied conditions of temperature and space velocity but with different degrees.

(ii)   The space velocity 18000 mL $g^{-1} h^{-1}$ and temperature $800^{o}C$ are the optimum conditions resulting in the highest conversion of not only methane but also other heavy hydrocarbons present in the natural gas (i.e. ethane, propane, butanes, pentanes, hexanes and heptanes).

(iii)   The $Rh/\gamma\text{-}Al_2O_3$ catalyst exhibits good selectivity toward the production of the synthesis gas ($H_2 + CO$) at the optimum conditions of the space velocity 36000 mL $g^{-1} h^{-1}$ and the temperature $700^{o}C$.

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