CHAPTER 1
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Natural gas plays nowadays an important role in human life . A principal 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 2002.

In recent years much research has been devoted to the chemical transformations of methane, in particular its conversion into synthesis gas, or " Syngas ". Syngas is the starting material for the manufacture of liquid energy carriers by the Fischer- Tropsch reaction known as gas – to – liquids or GTL process and the production of base chemicals, such as methanol, and dimethyl ether (DME) " the fuel of the 21st century " by catalytic processes . Synthesis gas forms the feed stock for hydroformylation, hydrogenation, or reduction processes .

During the last decade there has been increasing interest in the reforming of natural gas by carbon dioxid , not only as an alternative route for syngas production , but also as a method for the recycling or reusing of carbon dioxide in chemical energy transmission systems .

Recent energy forecasts prepared by the International Energy Agency show that fossil fuels will predominate as an energy source during the 21st century , so that world emissions of CO_2 will increase by 50 % in 2010 when compared to 1990 levels .The limitation of world carbon dioxide emissions, which constitute the main contribution to the green house effect, is currently one of the most ambitious challenges in the field of catalysis .

It is expected that over the medium to longer term future there will be a move towards the development of CO_2 recovery technologies .

The high reaction enthalpies associated with methane reforming by carbon dioxide and its reverse reaction make this process one of the most suitable for applications in the storage of renewable energy sources .

The production of natural gases in Egypt is in continuous increase . This attracts our attention to study the reforming of natural gas with carbon dioxide to form synthesis gas .

There are three routes using methane as the starting material to give syngas:-

(1) Steam reforming , leading , ideally , to $H_2 / CO = 3$

$$CH_4 + H_2O = CO + 3H_2 \qquad , \Delta H^\circ_{298} = 206 \text{ k J [1]}$$

(2) CO_2 reforming , leading to $H_2 / CO = 1$

$$CH_4 + CO_2 = 2CO + 2H_2 \qquad , \Delta H^\circ_{298} = 247 \text{ k J [2]}$$

(3) partial oxidation , leading to $H_2 / CO = 2$

$$CH_4 + \tfrac{1}{2} O_2 = CO + 2H_2 \qquad , \Delta H^\circ_{298} = -38 \text{ k J [3]}$$

Reforming of methane by carbon dioxide offers important advantages over steam reforming of methane, mainly due to the formation of a suitable H_2 /CO ratio for use in Fischer – Tropsch synthesis.

Among these routes, steam reforming is by far the most mature and widely applied Process . Supported nickel catalysts, e.g ., Ni /Al_2O_3 , are used for this purpose . If a H_2 / CO ratio > 3 is required , steam reforming can be combined with the water gas shift reaction ;-

$$H_2O + CO = CO_2 + H_2 \qquad , \Delta H^\circ_{298} = -41.16 \text{ k J [4]}$$

Nickel based catalysts require a high partial pressure of steam . When used for route (2) without steam in the feed , carbon deposits are formed which deactivate the catalysts. It has been suggested that noble metal catalysts for example. , Rh , Ru , or even sulfur passivated nickel catalysts will not suffer from the carbon deposition problem typical for nickel in the absence of steam addition to the feed.