SUMMARY AND CONCLUSIONS
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Natural gas (which comprises mainly of methane with smaller amounts of ethane, propane and butanes and traces of higher hydrocarbons) is an abundant resource in various parts of the world. As compared to oil, world reserves of natural gas have been growing continuously more and more over the past two decades. Because of the predicted short supply of petroleum oil in future, natural gas is being considered seriously as an alternative source of petrochemicals and petroleum products. Methane being the most inert among the hydrocarbons, its direct conversion to useful/value added products is very difficult. Therefore, economic conversion of methane to value added products is one of the most technologically important and challenging problem to the scientists and engineers. However, during the last decade considerable worldwide efforts have been devoted to the effective utilization of natural gas, particularly by its conversion to easily transportable and/or value added products (viz. methanol, liquid hydrocarbons, ethylene, syngas, etc) over a wide range of catalysts in the presence of free oxygen and over 'redox' catalysts in the absence of free oxygen.

The present work for the Ph.D. thesis was undertaken as a part of the comprehensive programme in our laboratory for the development of the catalysts and catalytic processes for the conversion of natural gas to value added products in an energy efficient and safe manner, with the following objectives.

1. To develop highly active/selective, productive and stable catalysts for the oxidative coupling of methane to C₂-hydrocarbons.
2. To study the homogeneous (non-catalytic) oxidative conversion of natural gas to ethylene and other lower olefins.
3. To study the homogeneous (non-catalytic) oxidative dehydrogenation of ethane to ethylene.
4. To study the catalytic partial oxidation of methane/natural gas to synthesis gas (i.e., CO and H₂) over composite catalysts containing Ni or Co and alkaline earth or rare earth metal oxides.
5. To study the following reactions for the catalytic conversion of methane to synthesis gas over NiO-CaO catalyst:
   - CO₂ reforming of methane
   - Steam reforming of methane
   - Simultaneous CO₂ and steam reforming of methane
   - Simultaneous oxidative methane-to-syngas conversion and steam reforming of methane
Simultaneous oxidative methane-to-syngas conversion and steam reforming of methane
Simultaneous oxidative methane-to-syngas conversion and \( \text{CO}_2 \) reforming of methane
Simultaneous oxidative methane-to-syngas conversion and steam and \( \text{CO}_2 \) reforming of methane

for developing the most energy efficient process operating in a safe manner by the conversion of methane to syngas with high conversion, selectivity, productivity and also with reduced coke formation, while requiring little or no external energy (i.e. for eliminating most of the limitations of the conventional steam reforming process for syngas production).

The thesis has been divided into following six chapters.

CHAPTER - 1: INTRODUCTION - OBJECTIVES AND SCOPE

In this chapter, the objectives and scope of the present work has been discussed.

CHAPTER - 2: OXIDATIVE COUPLING OF METHANE (OCM) TO \( \text{C}_2 \)-HYDROCARBONS

Oxidative coupling of methane to ethane and ethylene has been studied at atmospheric pressure over La-promoted MgO and CaO (with different La/Mg and La/Ca ratios) and \( \text{La}_2\text{O}_3-\text{BaO}-\text{MgO} \) catalysts in presence of free oxygen at different process conditions.

Lanthanum oxide-promoted MgO and CaO catalysts show a very high activity, \( \text{C}_2 \)-selectivity, \( \text{C}_2 \)-STY (space-time yield) with no deactivation (i.e. long catalyst life) in the oxidative coupling of methane to \( \text{C}_2 \)-hydrocarbons (at 800°C). Doping of MgO and CaO with lanthanum causes dramatic increase in both the catalytic activity and selectivity in the OCM to \( \text{C}_2 \)-hydrocarbons.

Studies on the beneficial effects of oxygen distribution on methane conversion and \( \text{C}_2 \)-selectivity in oxidative coupling of methane over La-promoted MgO catalyst have been carried out. Distribution of oxygen feed throughout the catalyst causes a significant increase in both the conversion and selectivity for \( \text{C}_2 \)-hydrocarbons in oxidative coupling of methane over La-promoted MgO.

Periodic fluctuations in reaction temperature indicating nearly symmetrical oscillations in the partial oxidation of methane by oxygen to ethane and ethylene in high yields over an \( \text{La}_2\text{O}_3-\text{BaO}-\text{MgO} \) (La/Mg = 0.1, Ba/Mg = 0.05) catalyst at reactor temperature above 550°C but below 700°C have been observed.
CHAPTER - 3: OXIDATIVE CONVERSION OF NATURAL GAS AND ETHANE TO ETHYLENE

Oxypyrolysis of Natural Gas

Non-catalytic oxypyrolysis of natural gas at 700-850°C in the presence of steam and limited oxygen (NG/O₂ = 6.0-18.5, NG/H₂O = 1.0, and GHSV = 1000-3000 h⁻¹) has been studied. By the non-catalytic oxypyrolysis of natural gas in the presence of steam and limited oxygen, ethylene and propylene, with high selectivity at carbon (in NG) conversion of practical interest and also with almost no coke or tar-like product formation can be produced in a most energy efficient and safe manner, requiring little or no external energy. This process involves a direct coupling of the exothermic oxidative conversion and endothermic thermal cracking reactions (of hydrocarbon in NG) due to their simultaneous occurrence, thus making the oxypyrolysis process almost thermoneutral, or mildly exothermic/endothermic, depending upon the process conditions and also avoiding the hot spot formation and reaction run-away conditions. Hence, the operation of this process is very simple, although it involves a complex network of a large number of hydrocarbon conversion reactions.

Homogeneous Oxidative Dehydrogenation of Ethane

Non-catalytic homogeneous dehydrogenation of ethane to ethylene under unsteady state showing sustained oscillations in the reaction temperature and product composition has been investigated in a flow reaction system at different process conditions. Unsteady reaction behavior involving periodic fluctuations in the reaction temperature and concentration of reaction species showing sustained oscillations in the homogeneous oxidative dehydrogenation of ethane is observed only in a narrow temperature range (610-650°C) for C₂H₆/O₂ feed ratio of < 8.0. The period and amplitude of the oscillations are strongly influenced by the temperature, space velocity, C₂H₆/O₂ ratio and feed dilution with N₂ or water vapours. The oscillations are thermokinetic ones and resulted due to poor heat transfer from the reactor, accompanied by the competing free radical reactions such as exothermic oxidative conversion of ethyl radicals to ethylene (which is favored at low temperature and/or high concentration of oxygen) and endothermic unimolecular cracking of ethyl radical to ethylene (which is favored at high temperature and/or low concentration of oxygen).

CHAPTER - 4: CATALYTIC OXIDATIVE CONVERSION OF METHANE TO SYNGAS

In this chapter, the results of comprehensive studies on the partial oxidation of methane to syngas (i.e. CO and H₂) at atmospheric pressure over a number of composite catalysts (containing Ni
or Co), given below, at extremely low contact time (i.e., at extremely high space velocity), at different temperatures (300-800°C) have been discussed.

- NiO-CaO (with Ni/Ca = 0, 0.1, 0.5, 1.0, 3.0, 10, ∞)
  - NiO-CaO calcined at 600-1200°C
  - NiO-CaO prepared using different catalyst precursors

- NiO-Yb₂O₃ (Ni/Yb = 1.0)

- CoO-LnOₓ (Co/Ln = 1.0, Ln = Ce, Nd, Sm, Eu, and Yb)

- NiO-LnOₓ (Co/Ln = 1.0, Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Er, and Yb)

- Ni/Al₂O₃ (18.7 wt % Ni)

- Pt-or Pd-or Ru-Ni/Al₂O₃ (18.7 wt % Ni, 0.1-2.5 wt % noble metals)

Catalytic partial oxidation of methane over NiO-CaO (with or without its prereduction by H₂) at low temperatures (≤ 700°C) yields syngas (H₂/CO ratio = 2.0) with high conversion/selectivity and extremely high productivity. If required, the H₂/CO ratio can be increased by adding water vapours in the feed.

Ni/Yb₂O₃ catalyst showed high activity/selectivity in catalytic oxidative conversion of methane to CO and H₂ at 700-800°C and extremely high space velocity (5 x 10⁵ cm³ g⁻¹ h⁻¹) at atmospheric pressure.

CoO-rare earth catalysts (particularly CoO-Yb₂O₃) show high activity and good selectivity with very high productivity in oxidative conversion of methane to CO and H₂ at low temperatures (≤ 700°C, as low as 300°C).

NiO-LnOₓ and (Ln = lanthanide, Ni/Ln ratio = 1.0) catalysts which show high activity/selectivity and very high productivity (without prereduction) in the oxidative conversion of methane to CO and H₂ have been studied. The catalysts are first activated in the initial reaction, which starts at 535-560°C, by the reduction of NiO and creation of active sites. The carbon deposition on the catalyst in the reaction, particularly for the NiO-Gd₂O₃, NiO-Tb₂O₇, and NiO-Dy₂O₃ catalysts, is quite fast but it has caused a little or no influence on the catalytic activity/selectivity. Pulse reaction of pure methane on NiO-Nd₂O₃ catalyst (at 600°C) shows involvement of lattice oxygen in the initial reaction and also reveals formation of carbon from CO on the reduced catalyst.

Partial oxidation of methane over Ni/Al₂O₃ catalyst at low temperatures (≤ 700°C) and extremely low contact time (space velocity = 5 x 10⁵ cm³ g⁻¹ min⁻¹) results in much higher selectivity
and productivity for CO and H₂ than that obtained at high contact time used earlier. An addition of noble metal (Pt, Pd or Ru) to the Ni/Al₂O₃ catalyst results in a large decrease in the reaction start temperature (from about 790°C to as low as 400°C) in the oxidative conversion of methane to syngas over the unreduced catalyst and also causes an improvement in the catalytic activity/selectivity, depending upon the noble metal and its concentration in the catalyst.

CHAPTER - 5: COUPLING OF EXOTHERMIC OXIDATIVE CONVERSION AND ENDOOTHERMIC STEAM AND/OR CO₂ REFORMING OF METHANE TO SYNGAS OVER NiO-CaO CATALYST

Under the present energy crisis, the conversion of methane to syngas with H₂/CO ratio close to 2.0 (which is desirable for methanol and Fischer-Tropsch synthesis) with high conversion, selectivity and productivity in a most energy efficient and safe manner, requiring little or no external energy, is of great practical importance for the effective utilization of natural gas by its conversion to value added and easily transportable products via syngas routes. This chapter focuses on the importance of the coupling of exothermic partial oxidation and highly endothermic steam and/or CO₂ reforming reactions of methane over the same catalyst. The coupling of these exothermic and endothermic methane conversion reactions has been done by carrying out

• Partial oxidation of methane simultaneously with the steam reforming
• Partial oxidation of methane simultaneously with the CO₂ reforming
• Partial oxidation of methane simultaneously with both the steam and CO₂ reforming over NiO-CaO catalyst at different process conditions (viz. temperature, CH₄/O₂, CH₄/H₂O and CH₄/CO₂ feed ratios and space velocities) to produce syngas with a desirable H₂/CO ratio (1.5-2.5).

By coupling the exothermic and endothermic reactions of methane over the same catalyst and manipulating the process conditions, the coupled process can be made mildly exothermic, nearly thermoneutral, or mildly endothermic and the limitations of the individual steam reforming, CO₂ reforming and partial oxidation processes are eliminated. The coupled process operates in a most energy efficient and safe manner with a requirement of little or no external energy. Also, there is a high possibility of developing a coupled process operating adiabatically in a very simple reactor with much favorable process economics. In these coupled processes, methane can be converted almost completely with very high selectivity (95-100 %) for both CO and H₂ and also with high CO
productivity. The H₂/CO ratio in product can be varied between 1.5-2.5 quite conveniently by manipulating the relative concentrations of O₂, steam and/or CO₂ in the feed.

CHAPTER - 6: SIMULTANEOUS STEAM AND CO₂ REFORMING OF METHANE TO SYNTHESIS GAS OVER NiO-CaO CATALYST

This chapter deals with the study of steam reforming, CO₂ reforming and simultaneous steam and CO₂ reforming of methane to CO and H₂ over NiO-CaO catalyst (without any prereduction treatment) at different temperatures (700° - 850°C) and space velocities (5,000-70,000 cm³ g⁻¹ h⁻¹). The catalyst has been characterized by XRD, XPS and temperature programmed reduction (TPR). In the CO₂ reforming, the coke deposition on the catalyst is found to be very fast. NiO-CaO (containing two distinct phases, NiO and CaO) shows high catalytic activity and selectivity in both the CO₂ and steam reforming reactions at ≥ 800°C for the conversion of methane to syngas. The nickel oxide from the catalyst is reduced to metallic nickel during the short initial period of the reforming reactions; the catalyst in its operating state is Ni⁰ dispersed on CaO. When CO₂ reforming reaction is carried out simultaneously with the steam reforming reaction (at ≥ 800°C and space velocity of about 20,000-30,000 cm³ g⁻¹ h⁻¹), over the NiO-CaO catalyst,

- methane can be converted almost completely to syngas with 100% selectivity for both CO and H₂,
- the carbon deposition on the catalyst (which is rapid in case of the CO₂ reforming alone) is drastically reduced,
- there is no net formation of CO₂ and H₂O and hence the selectivity for both H₂ and CO is 100%, and
- a desirable H₂/CO ratio (about 2.0 or between 1.5 and 2.5) can be obtained conveniently by manipulating the CO₂/H₂O ratio in the feed.