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Oxidative Coupling of Methane over Aerogel Catalysts

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Abstract: The oxidative coupling of methane to C₂ hydrocarbons was studied over La₂O₃/MgO, La₂O₃/MgO-CaO and La₂O₃/MgO/NiO/Al₂O₃ catalysts. Catalysts were prepared by aerogel method using organo metallic precursors. These were calcined at 950°C and characterized by surface area measurement, particle size analysis, basicity and XRD. The performance of these catalysts was evaluated for oxidative coupling of methane in the presence of molecular oxygen at temperature in the range of 650-800°C at atmospheric pressure in a continuous flow fixed bed SS reactor. La₂O₃/MgO-CaO has been found to be better catalyst for this reaction exhibiting high selectivity for C₂-hydrocarbons. Attempt has been made to correlate the physico-chemical properties of the catalysts with their activity towards formation of C₂-hydrocarbons.

Keywords: oxidative coupling; methane; aerogel method; catalyst

I. Introduction

The abundance of natural gas and availability of coal bed methane together with steadily depleting oil reserves highlights methane conversion to value added chemicals. It is well known that oxidative conversion of methane proceeds through three pathways with formation of different chemicals – products of deep oxidation (CO₂ and H₂O), oxygen containing products of partial oxidation (methanol, formaldehyde, syn gas), products of the oxidative coupling of methane (ethylene and ethane). In recent year attention has been focused on partial oxidation as a means of converting methane into higher valued materials such as oxygenates e.g. methanol and formaldehyde and C₂₊ hydrocarbons. A number of critical reviews are available in the literature on oxidative coupling of methane [1-6].

Oxidative coupling of methane(OCM) takes place at high temperatures (>600°C) and may be performed by two modes: Cyclic mode with alternate feeding of reactants (methane and oxidants) and cofeed mode with the simultaneous feeding of reactants. The first step in the catalytic partial oxidation of methane must involve the breaking of C-H bond on the catalyst surface. The free radical species thereby formed undergo reaction with the oxidant. Keller and Bhasin [7] were the first to report significant production of C₂ hydrocarbons by direct partial oxidation of methane over several metal oxide catalysts. They used cyclic feeding of methane and oxygen with developments of catalysts which give moderately high selectivities to C₂ hydrocarbons together with high conversion of methane. Ito and Lunsford [8] reported useful yields of C₂₊ hydrocarbons from the partial oxidation of methane over lithium doped MgO catalysts and after that there has been intense activity in developing both alkaline earth and rare earth oxides maximizing methane conversion and C₂ selectivities.

Lanthanum promoted MgO catalysts have been reported [9, 10] with high activity and selectivity in OCM reaction. Most of the catalysts used have been prepared either by wet impregnation method co-precipitation or by solid-solid mixing technique. Transition metal oxides have also been used as promoters for alkali/alkaline earth oxide catalysts for OCM reaction [11-13]. Recently nanocatalysts have got prominence in catalysis because of their higher catalytic activity over traditional catalysts [14-15]. Nano particles can be synthesized by several methods such as gas evaporation, laser vaporization, gel processing, homogeneous precipitation and freeze drying etc.

The present paper deals with the studies of rare earth/alkaline earth and rare earth/alkaline earth/transition metal oxide system as catalysts for oxidative coupling of methane. The catalysts have been prepared by aerogel technique and comparative studies have been made with respect to conversion, selectivity and C_2H_4/C_2H_6 ratio for OCM.

II. Experimental

Catalyst preparation: La_2O_3/MgO , $La_2O_3/MgO-CaO$ and $La_2O_3/MgO/NiO/Al_2O_3$ catalysts (abbreviated as cat 1, cat 2 and cat 3) were prepared by aerogel processing method. Cat 3 was prepared as follows. Solution (A) was prepared by dissolving the appropriate amount of precursors of catalytic components containing magnesium acetate, lanthanum acetate, nickel acetate in methanol and further a mixture of water and methanol (1:1) was added to it. Another solution/slurry (B) was prepared by dissolving aluminium tri sec-butoxide in sec-butanol. Solution (A) was added to solution (B) with stirring and heated at $50^\circ C \pm 10^\circ C$ for 2 hours at atmospheric pressure. Cat 1 and cat 2 were prepared by dissolving the acetates of the catalytic components in methanol and further a mixture of methanol and water was added and pH of the solution was raised to 9 by adding the appropriate amount of ammonia solution. The mass was heated over a hot plate ($40-55^\circ C$) for 2 hours. The gel formed was then transformed to a SS liner of 1 litre autoclave. The autoclave was made leak proof and the inner system was purged twice with nitrogen gas. It was then heated to $290-300^\circ C$ with stirring raising the temperature $3^\circ C/min$ with rise of auto gaseous pressure upto 110-130 bar and it was kept at this condition for half an hour. The solvent was then removed by venting out the vapour above the critical temperature of the solvent. The system was further purged twice with nitrogen gas and cooled. The product obtained was heated at $120^\circ C$ for 24 hours in an air oven. The powder catalyst was then calcined at $700-950^\circ C$ for about 10 hours and then it was pellitized and sized (-6+14 mesh) before packing in the reactor.

Catalyst characterization: The surface area was measured by Quantasorb (Quantachrome Corporation, USA) using nitrogen as the adsorbate. Particle size distribution of the power catalyst was determined by Laser Based Particle Analyzer (Fritsch GmbH) to measure the particle size distribution characteristics of various particles in the range 0.1 to $1250\mu m$. Basicity of the catalysts was determined by benzoic acid titration method. XRD patterns of the catalysts are collected on a D-8 ADVANCE (Bruker, Germany) X-ray diffractometer with Bragg-Brentano Geometry using parallel beam $CuK\alpha$ radiation. Different phases in the catalyst were identified with the help of search match procedure of Diffrac plus Software with reference to JCPDS powder diffraction File.

Activity Test: Oxidative coupling of methane was carried out in a continuous flow tubular SS reactor (ID 12 mm, length 30 cm) packed with 2 g of the catalyst between quartz wool plugs. The reaction temperature was measured by digital temperature controller. The feed gas consists of methane, oxygen and inert gas (N_2 or He). The gases were fed into the reactor through mass flow controller. The reaction was carried out at the temperature in the range of $650-800^\circ C$, CH_4/O_2 ratio 4.0 and 8.0, Space velocity 5000 and 10000 h^{-1} at atmospheric pressure. The feed and product gases were analyzed by an on-line gas chromatograph having Iris-32 software with a thermal conductivity detector and flame ionization detector using Porapak and Spherocarb columns.

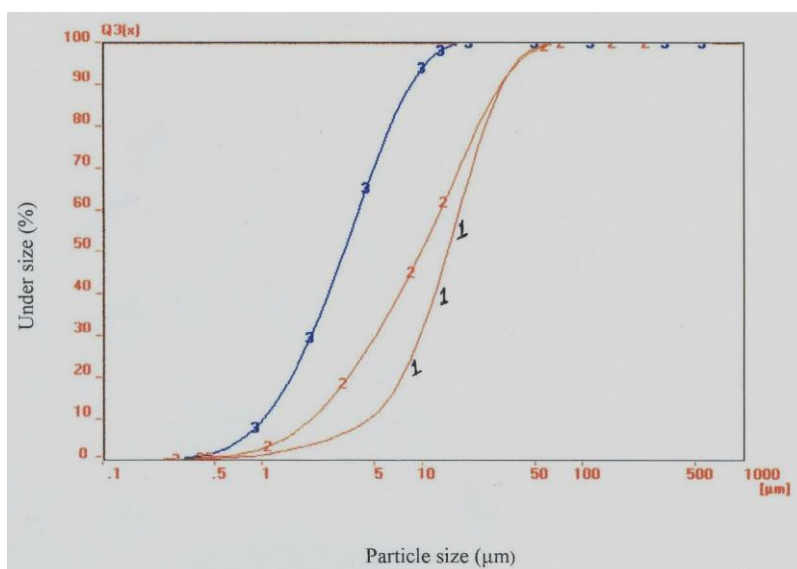
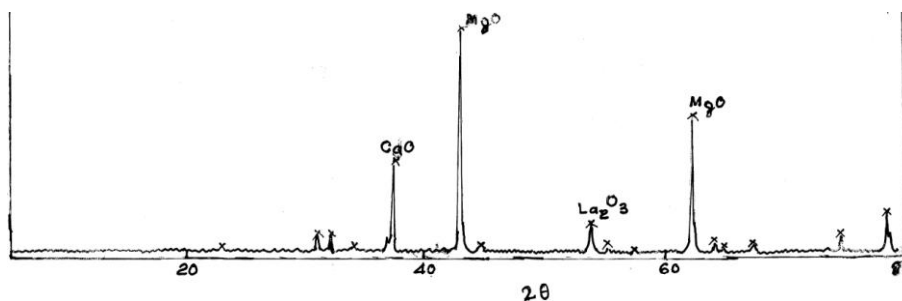
III. Results & Discussion

Oxides of rare earth and alkaline earth La_2O_3/MgO , $La_2O_3/MgO-CaO$ and another reforming catalyst $La_2O_3/MgO/NiO/Al_2O_3$ were prepared by aerogel processing method. These were calcined upto $950^\circ C$ and then activities were evaluated for oxidative coupling of methane. The results of the activity tests of these catalysts are given in Table 1. The catalysts were characterized by surface area measurement, particle size analysis, basicity and XRD. Surface area of cat 1, cat 2 and cat 3 were found to be 55.5, 78.5 and $173.0\text{ m}^2/g$ respectively. Particle size distributions of these catalysts are shown in Figure 1. From the particle size analysis it is observed that nickel containing catalyst(cat 3) has very narrow range of particles size ($1-9\mu m$). Other two catalysts showed particle sizes in the range of ($2-31\mu m$). The comparative particle size of the catalysts has been show in Figure 1. X-ray diffractogram of the cat 2 and cat 3 are depicted in Figure 2 and Figure 3 respectively. Basicity of cat 1, cat 2 and cat 3 were found to be 2.04, 2.41 and 1.82 mmol/g respectively. X-ray diffractograms of catalysts were recorded to know the different phases present in the catalyst system. Cat 2 comprises MgO , CaO , La_2O_3 phases and cat 3 comprises Ni and Ni_2O_3 and $NiAl_2O_4$ phases. Thus, it is evident that the precursors of the catalyst component decomposed completely changing into different oxide forms and particularly in the nickel containing catalyst as spinal forms.

Table 1: Activity and selectivity of different catalysts for OCM Reaction

Catalyst	CH ₄ / O ₂	Temp	GHSV	Conve rsion	Selectivity %						C ₂ + Selectivit y	C ₂ H ₄ / C ₂ H ₆
					CO	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃	C ₄		
		^o C	h ⁻¹	%								Ratio
cat 1	8	750	5000	22.1	58.9	28.2	2.9	9.7	0.4	0.0	13.0	0.30
cat 1	8	800	5000	28.7	70.2	18.2	2.5	8.8	0.3	0.0	11.6	0.30
cat 1	4	800	10000	30.3	27.7	56.8	4.7	10.5	0.3	0.0	15.5	0.45
cat 2	8	750	5000	7.1	4.8	21.6	21.4	50.0	1.9	0.3	73.6	0.43
cat 2	4	800	10000	15.6	4.8	21.5	38.0	33.6	1.1	1.0	73.7	1.13
cat 2*	8	800	5000	16.7	15.5	20.5	33.6	28.7	1.7	0.0	64.0	1.17
cat 2*	8	850	5000	22.4	23.5	18.3	35.1	20.9	1.0	1.2	58.2	1.70
cat 2*	4	800	5000	19.4	7.4	30.0	36.5	26.5	0.7	0.0	63.7	1.38
cat 2*	4	850	5000	27.7	14.8	31.0	37.3	16.0	0.9	0.1	54.2	2.33
cat 3	4	800	10000	25.2	14.0	60.3	6.6	19.2	0.0	0.0	25.8	0.34

*Pretreatment with O₂ in 50% H₂ (total flow rate = 50 ml/min) at 700°C for 1 hr

Figure 1: Particle size distribution of catalysts (1: cat 1; 2: cat 2; 3: cat 3)**Figure 2: X-ray diffractogram of cat 2****Figure 3: X-ray diffractogram of cat 3**

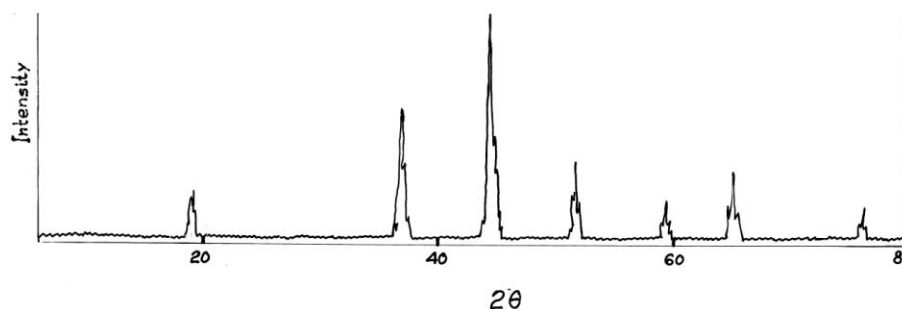
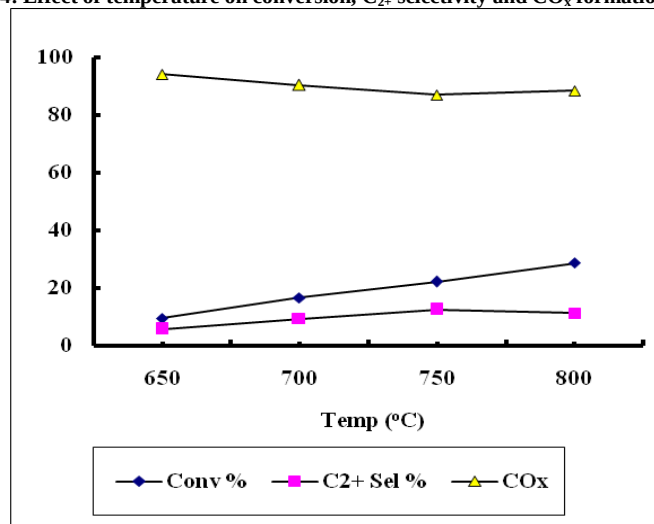


Table 1 summarizes the results of reaction of methane and oxygen over three sets of catalysts at atmospheric pressure. Catalysts have been evaluated at different temperatures in the range of 650-850°C, GHSV 5000 and 10,000 h⁻¹ and CH₄/O₂ ratio 4 and 8. La₂O₃/MgO catalyst gave maximum conversion of methane (28.7%) and the selectivity to C₂₊ hydrocarbons is low (15.5%). When CaO is loaded with La₂O₃/MgO, the selectivity increases (73.7%) but the methane conversion remained 15.6%. In case of Nickel containing catalyst, the conversion of methane was 25.2% and the selectivity to C₂₊ hydrocarbons 25.8%. Formation of oxides of carbon (CO+CO₂) was observed very high in case of both catalysts, La₂O₃/MgO and La₂O₃/MgO/NiO/Al₂O₃ whereas the catalyst loaded with CaO showed low formation of oxides of carbon (26%). It is interesting to note that ethylene formation was higher in case of CaO loaded catalyst specially at higher temperature. Temperature verses methane conversion, C₂₊ selectivity and formation of carbon oxides on cat 1 & cat 2 are shown in Figure 4 and Figure 5 respectively. The effect of reaction temperature C₂H₄/C₂H₆ ratio has been studied in the range of 650-850°C. Temperature verses C₂H₄/C₂H₆ ratio on cat 1 and cat 2 is shown in Figure 6.

Figure 4: Effect of temperature on conversion, C₂₊ selectivity and CO_x formation on cat 1



When cat 2 was pretreated with O₂ in 50% H₂ at 700°C, its activity towards conversion of methane increased up to 27.7% at 800°C and also the formation of ethylene among the hydrocarbons was higher (C₂H₄/C₂H₆ = 2.33) i.e. ratio of ethylene to ethane increased substantially around double the ratio obtained in the case of without pretreatment cat2. Cat 1 showed better conversion of methane which increased on increasing the reaction temperature up to 800°C but selectivity towards formation of C₂₊ hydrocarbons was poor and formation of carbon oxides was also very high. When the catalyst was loaded with CaO its performance changed towards better selectivity of C₂₊ hydrocarbons and conversion of methane was not substantial and carbon oxide formation was also very low as compared to unloaded catalyst. The conversion and selectivity both increased on increasing the temperature up to 800°C and ethylene formation also increased simultaneously. Thus, it has been observed that on incorporation of CaO with La₂O₃/MgO catalyst system, there is enormous increase in the selectivity towards formation of C₂₊ hydrocarbons and maximizing ethylene formation among the hydrocarbons. The increase of activity may probably be explained on the basis of basicity and oxygen-ion-conductivity, which are reported[16-19] to be the most important characteristics of the OCM catalysts to obtain high C₂-selectivities. It has been reported that doping of MgO with rare earth oxide causes an increase in the total number of strong basic sites [20] due to lattice distortion. The fact that the maximum C₂-selectivities obtained over La₂O₃/MgO-CaO catalyst is much larger than that for the La₂O₃/MgO catalyst, suggests

that though basicity is of fundamental importance, it alone is not responsible for controlling the activity/selectivity in the OCM reaction. Even a high basic catalyst requires a suitable oxygen-ion-conductivity in order to prevent reactive surface oxygen species (O^- , O_2^- and O_2^{2-}) from participation in deep oxidation of methyl species and C_2 -hydrocarbons formed by coupling. The basicity on the other hand also influences the formation of surface oxygen species, which are capable of activating methane [21]. Thus, it appears probable that $La_2O_3/MgO-CaO$ catalyst with high oxygen ion mobility favourably form surfaces with a relatively small amount of weakly adsorbed oxygen species and thereby reducing the non-selective surface reactions of methyl species and C_2 -hydrocarbons resulting marked increase in C_2 -selectivity.

So far as the nano-particle catalyst formed by aerogel processing is concerned, it has no remarkable effect on the selectivity but activity towards methane conversion is higher in case of both La_2O_3/MgO and $La_2O_3/MgO/NiO/Al_2O_3$ catalysts. In case of $La_2O_3/MgO-CaO$ catalyst, the selectivity for C_2 -hydrocarbon formation is very large.

Figure 5: Effect of temperature on conversion, C_2 -selectivity and CO_x formation on cat 2

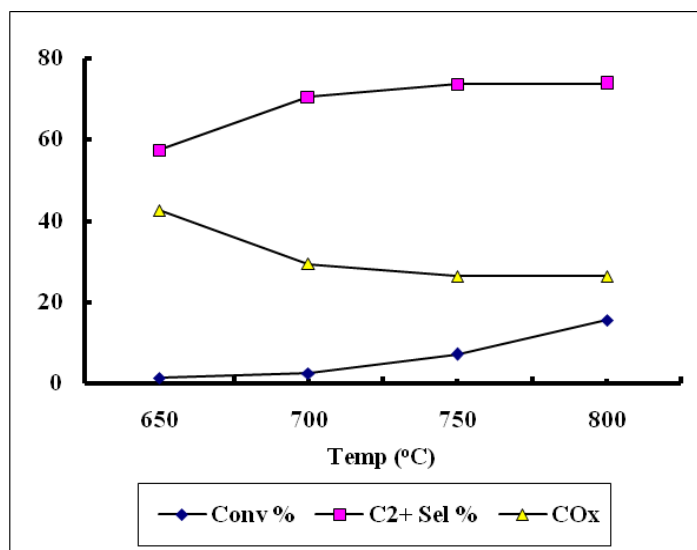
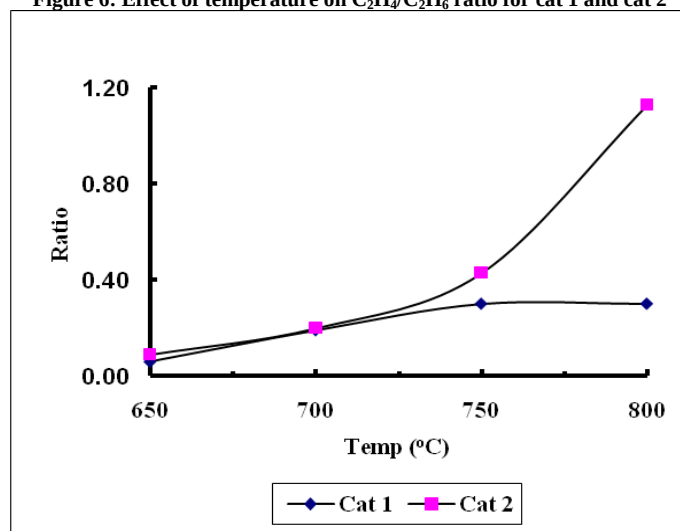


Figure 6: Effect of temperature on C_2H_4/C_2H_6 ratio for cat 1 and cat 2



IV. Conclusions

Incorporation of CaO over La₂O₃/MgO system increased the selectivity of C₂- hydrocarbons to a great extent in the oxidative coupling of methane. This may be attributed to the nano-particle size of the catalyst prepared by aerogel processing method and higher basicity. Transition metal (Ni) oxide containing catalyst did not show better activity and selectivity for C₂-hydrocarbons by oxidative coupling of methane.

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