

Oxidative Coupling of Methane over Heterogeneous Catalysts

Submitted as a part of the requirement for the partial fulfillment of the course work of CSIR-Harnessing Appropriate Rural Interventions and Technologies (CSIR-HARIT) for the award of Degree of PhD.



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Declaration – I **Rohan Singh Pal**, hereby certify that the work presented in this Report entitled “**Oxidative Coupling of Methane over Heterogeneous Catalyst**” in partial fulfillment of the course requirement for award of the Degree of PhD, being submitted to CSIR-HARIT Unit, CSIR-Indian Institute of Petroleum, Dehradun, is an authentic record of Project Research work carried out by me at CSIR-IIP Dehradun during the period **January 2019 to September 2020** and under the supervision of **Dr. Rajaram Bal**.

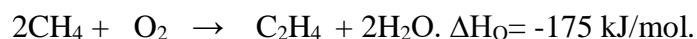
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1. Introduction

The oxidative coupling of methane is promising process to convert methane into value added chemicals like ethane and ethylene . when the oxidant is added to prevail over thermodynamic limitation and make the reaction exothermic. The general reaction is expressed as-:



However, higher temperatures are required to activate the C-H bond in CH₄. Typically , 700 - 850 °C is required for OCM, while no C₂ hydrocarbon have been detected below 550-600 °C.¹⁴ Except that, the separation of by-products is done at low temperature (< 100 °C). Thus, energy consumption for the process of collection of value-added C₂ hydrocarbon must be minimized. Catalysts becomes the primary factors in this process of producing C₂ hydrocarbons that influence conversion of methane and selectivity of C₂. Overall yield of C₂ hydrocarbons to the tune of greater than 30% will be essential criteria for its industrial application .

Table 1. Catalysts studied by other researchers

S.No.	Catalyst used	Temp. (°C)	Methane Conversion (%)	C ₂ Selectivity (%)	C ₂ Yield (%)	Reference
1	Ce/Na/CaO	750	9.7	80.8		1
2	SrO/La ₂ O ₃ /SA-5205	800	30.9	-	19.9	2
3	Alkali Chloride-Mn-Na ₂ WO ₄ /SiO ₂	750	55	33.6	26	3
4	Mn-Na ₂ WO ₄ /SiO ₂	800	32.7	58.6	19.2	4
5	3%Ce/5%Na ₂ WO ₄ /TiO ₂	800	49	56.4	27.6	5
6	Sr-Li/MgO	750	22.8	50-55	-	6
7	Li-MgO	780	25.4	41.2	-	7
8	Mn-Na-WO _x /SiO ₂	800	15.2	86	-	8
9	TiO ₂ -doped Mn ₂ O ₃ -Na ₂ WO ₄ /SiO ₂	720	26	76		9
10	Mn-Na ₂ WO ₄ /SiO ₂	800-875	20-30	70-80		10
11	15%Ba/Y ₂ O ₃	750	25	53-54	14	11
12	SrTiO ₄	800	20.8	56.3	11.7	12
13	La ₂ Ce _{1.5} Ca _{0.5} O ₇	750	32	76	22.5	13

The study of OCM into ethane and ethylene can be found in the literature since 1980s .^{15,16} After that, a lot of efforts have been made in this area, as a result number of catalysts for OCM has been developed, including Li/MgO, Mn-Na₂WO₄/SiO₂, ABO₃ type perovskite MO_x (M: rare earth Metal). Out of which, Mn-Na₂WO₄/SiO₂ catalyst exhibit a total C₂ yield 18 to 25% in ambient reaction conditions and excellent stability for time on stream (TOS) of more than 450 hrs .¹⁷ On the other hand Li/MgO catalyst gives C₂-selectivity \approx 20% and C₂-yield reached at its highest at high temp. (780°C) ¹⁸. However, at higher temperatures, the active sites are unstable and becomes inactive due to the loss of lithium.

Some other encouraging catalysts for oxidative coupling of methane are rare-earth metal oxides. It has been observed that MO_x performed significantly better reaction at low-temperature (<750 °C) and a yield of C₂ is about 15%. Recently, several MO_x catalysts (M= Ce, Pr, Tb, Sm) modified by doping of Na, Ca, Li and Mg metals are studied for OCM. ¹⁹ The doping of group I and group II metals in periodic table changes the basicity of catalysts and this can surely affect the stability of the catalysts at the reaction condition and C₂ selectivity. It has been noted that catalysts with greater number of basic sites are more selective towards the formation of C₂.²⁰ It's also reported that Li-TbOx/MgO is better from all others in activity and selectivity of C₂ at temp. greater than 600°C. In spite of that, low reaction performance of Li-TbOx/n-MgO catalyst under 600°C may be deligated through problems related with regeneration of active sites on MgO at lower temperatures.¹⁹ However, at lower temperatures, undoped Sm₂O₃/MgO, Ca-Sm₂O₃/MgO and Ca-CeO₂/MgO catalysts yielded greater yields of C₂ than the catalysts modified by Na and Li metals, because active sites are not fully activated at lower temperatures .¹⁹ Recently, it has been shown that MnTiO₃ gives superior activity at lower temperature , resulting in a CH₄ conversion \approx 20% and a C₂ selectivity \approx 70%.²¹ Based on some in-situ studies , it has been seen that at high temp. during reaction, Mn₂O₃ and TiO₂ is

transformed into manganese titanate (MnTiO_3), which resulted in an increased OCM performance i.e methane conversion $\approx 22\%$, C_2 selectivity $\approx 62\%$ at 650°C .²²

In short, in order to develop a encouraging process to convert methane into ethane and ethylene, OCM still faced with the challenge of low C_2 selectivity i.e $<50\%$, which brings to low process economics and hence its application at industrial level is obstructed.²³ Thus, the development of novel catalyst/processes is highly needed to give high carbon selectivity and high conversion from CH_4 for C_2 products simultaneously in non-oxidative reaction conditions.

2. Experimental Work

2.1 Catalyst Synthesis

The catalyst was synthesized via a two step method. First, support MgAl_2O_4 was synthesized, then Li was doped on the support MgAl_2O_4 by impregnation method.

2.1.1 Synthesis of support

MgAl_2O_4 spinel supports is synthesized by hydrolysis of magnesium nitrate hexahydrate with aluminium isopropoxide in ethanol. Stoichiometric quantities of aluminium isopropoxide and magnesium salt are mixed in ethanol in a round bottom flask. The flask was then heated at 60°C with stirring. After stirring for some time , flask was heated to 150°C and held at this temp. for 12 h. Then, the solvent was evaporated and the gel was dried at 100°C for 12hr. Finally, the dried powders grinded by using a mortar-pestle and calcined in air at 800°C for 12 h and this results in the formation of pure spinel MgAl_2O_4 support .

2.1.2. Synthesis of Li/ MgAl_2O_4 Catalyst

First, Li-salt solution was prepared by dissolving 0.31 g LiCl , 2.64 g cetyltrimethylammonium bromide (CTAB) in 10 ml water and 90 ml ethanol mixture. Prepared Li-salt solution was added drop-wise to the support MgO dispersed in 100 ml ethanol. The whole mixture solution

was stirred for 1h and then the temperature of the mixture was raised to 60 °C and continued stirring for 15h. The dried material was then calcined at 700 °C for 6h in air.

2.2. Catalytic Activity Measurements

Initially, the catalyst was preheated in the flow of N₂ gas to reaction temperature and hold at this temperature for 30 min then feed gases are co-feed in a ratio of N₂:CH₄:O₂: = 7:2:1. Generally, 20 mg catalyst is placed between two quartz wool bed at the centre of the 6 mm quartz tube reactor. OCM reaction is performed at temperature range 600-800 °C. The reaction products are analyzed by using an online gas chromatography (SCION 456 GC) equipped with a TCD detector using Carboxen 1010 column. Carbon and mass balance was calculated to be within ± 5%.

3.Result and Discussion

3.1. Catalyst Characterizations

3.1.1. BET-Measurement

Support MgAl₂O₄ showed a surface area of 51.9 m²/g but after Li-loading surface area of the catalyst decreased, should be due to corrosive nature of Li, which have affected the morphology of MgAl₂O₄. The surface area of fresh 5%Li-MgAl₂O₄ was found to be 40.2 m²/g. After catalysis surface area of the catalyst was further decreased due to heat treatment and may be due to further agglomeration.^{24,25} Surface area of spent 5%Li-MgAl₂O₄ was 18.3 m²/g. The loss of Li after catalysis was also supported by the previous reports.

Table 2 Physicochemical Properties of prepared catalysts

Catalyst	Surface Area (m ² /g)
MgAl ₂ O ₄	51.89
5%Li / MgAl ₂ O ₄	40.17
10%Li / MgAl ₂ O ₄	29.24
15%Li / MgAl ₂ O ₄	21.46

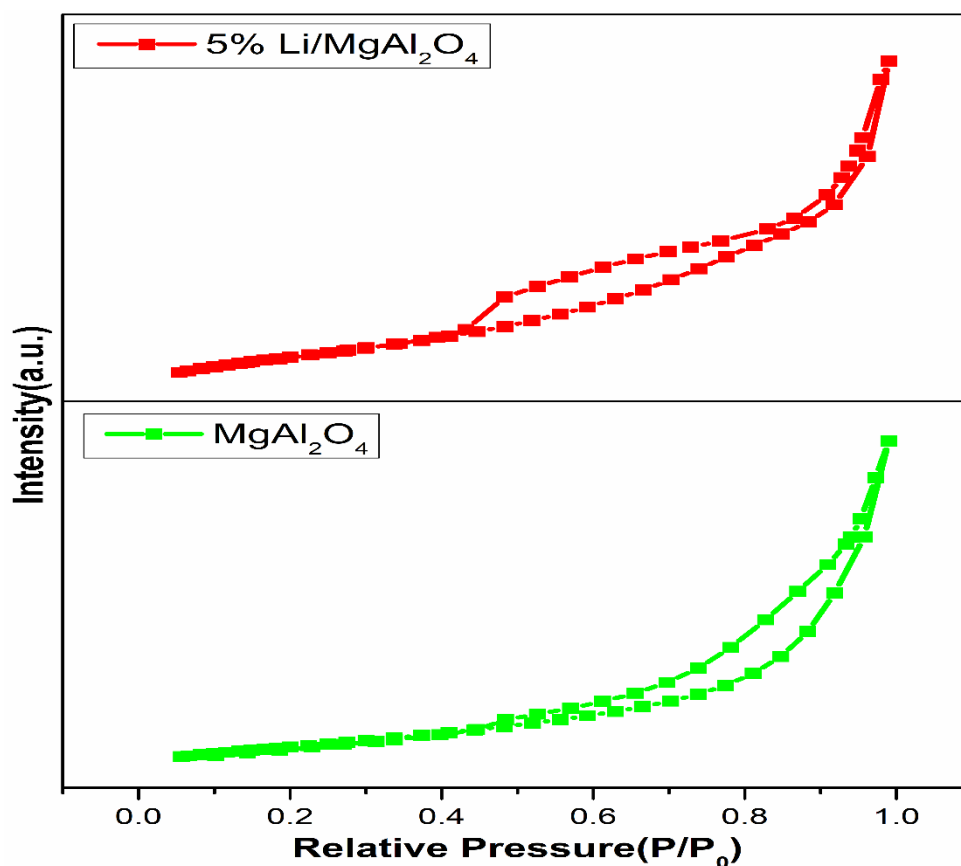


Figure 1 Isotherm plot of MgAl₂O₄ support and 5% Li/MgAl₂O₄

3.1.2. XRD analysis

XRD patterns of synthesized MgAl₂O₄ support showed sharp XRD peaks, which indicates the high crystallinity of the material (Figure). The XRD pattern of synthesized MgAl₂O₄ is exactly

matches with the JCPDS Card 822424 which is for pure MgAl_2O_4 spinel. XRD pattern of 5%Li- MgAl_2O_4 catalyst showed no difference from the support MgAl_2O_4 (Figure), but on increasing the Li amount from 5 wt.% to 10wt.% a peak at 2θ value 43.03° was observed due to formation of $\text{Mg}(\text{OH})_2$ (JCPDS Card 86-0441) and a small peak at 22.0° was observed, and it could be due to the formation of Li_2CO_3 or Li_2O . Absence of any Li-species peaks in 5%Li/ MgAl_2O_4 could be assigned to the fact that Li-loading was quite low or the formed species was very small (below 5 nm).^{26,27} Previous studies also revealed that even at 20wt% Li-loading, there was no peak for any Li-species noticed.²⁸

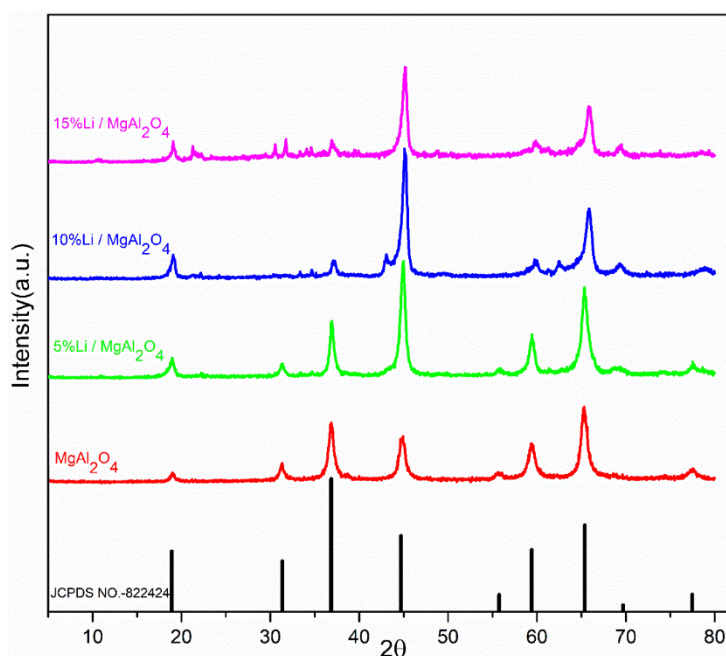


Figure 2 XRD Pattern of support MgAl_2O_4 and 5wt.% , 10wt.% , 15wt.% Li / MgAl_2O_4

3.2. Catalytic Activity

Oxidative coupling of methane reaction is carried out between the temp. $600\text{-}800^\circ\text{C}$, and it is reported that minimum reaction temperature required for reaction is about 600°C .²⁹ Our reaction results also revealed the same. 5%Li- MgAl_2O_4 catalyst was found active for methane coupling reaction at and above 600°C . Our reaction was carried out between $600\text{-}800^\circ\text{C}$ where strong basic sites are the effective sites for the conversion of CH_4 to C_2 products. The increased

activity of Li- MgAl_2O_4 catalyst is due to the fact that Li doping led to the substitution of Mg^{2+} by Li^+ , creating a negatively charged centre and defect by dissolving into the matrix.²⁹ Methane activation at the negatively charged O-atom centre forms $\text{CH}_3\cdot$ radicals and it couples in the gas phase to produce ethane.^{30,31} Activity of this prepared 5%Li- MgAl_2O_4 catalyst is showed in the following figures-:

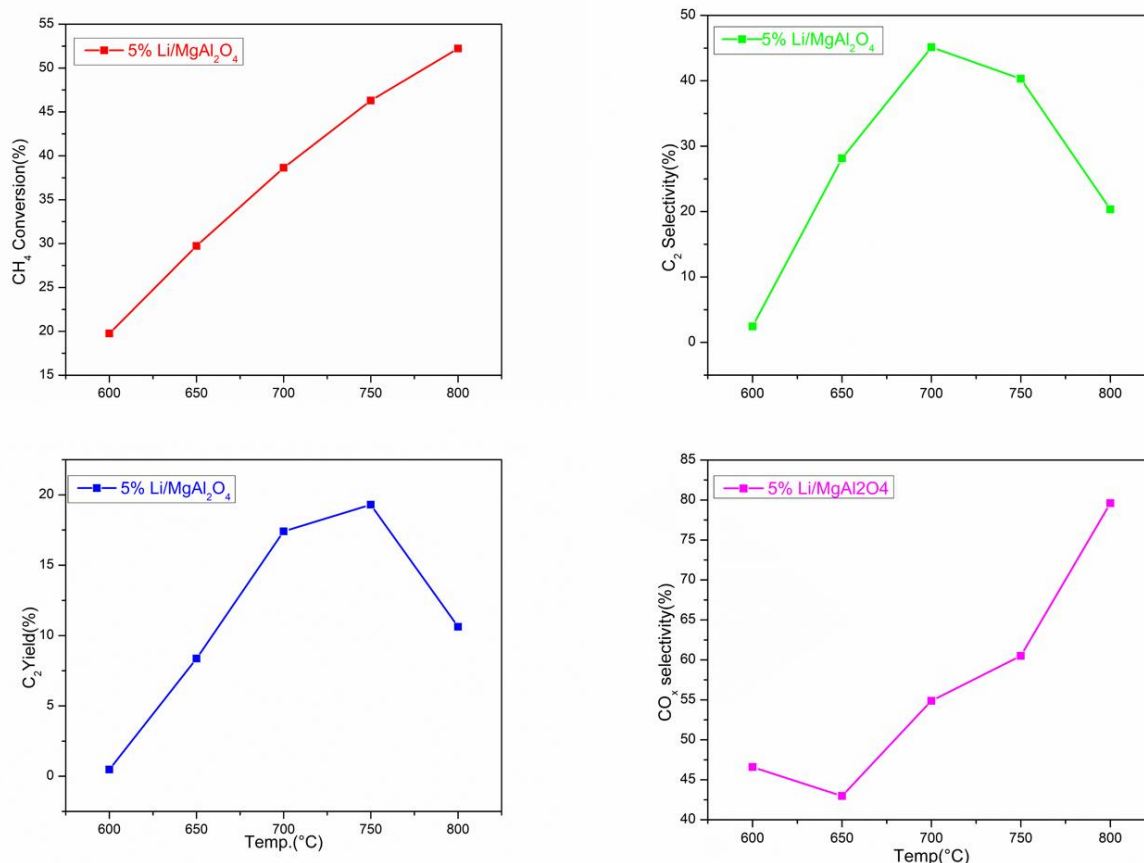


Figure 3 CH₄ conversion, C₂-Selectivity, C₂-Yield, CO_x Selectivity Graph of Prepared Catalyst

4. Conclusions

Li- MgAl_2O_4 catalyst was synthesized by a two-step method and found to be very active for OCM reaction. Catalyst synthesis process played a significant role for the formation of a larger number of defect sites by incorporation of Li^+ into MgAl_2O_4 crystal lattice by replacing Mg^{2+} and Al^{2+} and creating active O^- centre for methane activation. Surface Li species were

responsible for higher methane conversion whereas the Li defects sites were responsible for higher C₂ selectivity. 5 wt.% Li was found to be optimum loading to obtain the maximum C₂ yield. Above 5wt% Li-loading, although the C₂ selectivity was increased due to increase in defect sites but methane conversion was decreased due to loss of active surface area of the material. The Li-loading highly affected surface area of Li-MgAl₂O₄ catalyst, which affected methane conversion during OCM. Activity loss of the catalyst was also found to be due to loss of Li as volatile LiOH during OCM. The activity of the catalyst was observed to be decreasing above 750 °C due to the loss of Li from the catalyst surface.

As the prepared catalyst is giving very good activity for C₂ products, so the development of our catalyst which can give a commercial standard as our results are comparable with siluria process (Methane conversion 38%, C₂ Selectivity 61 %)

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