

Catalyst composition effect and mechanistic study on non-oxidative methane conversion into olefin and aromatic hydrocarbons

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Highlights

- Mo_xC_y type carbide cluster is the effective phase for C-H activation and C₂ coupling
- C-H activation barriers decreases on more reduced Mo₄C₂ carbide cluster
- 5 wt% Mo loading over support is effective for conversion and aromatic selectivity
- Lower SAR (SiO₂/Al₂O₃) of zeolite support results high aromatic selectivity

1. Introduction

Methane, the major component of natural gas (>85%) is widely exploited as raw material for the production of higher hydrocarbons and value added chemicals. In this regard, direct non-oxidative methane conversion into valuable chemicals can be an effective technology for natural gas utilization. Zeolite supported molybdenum (Mo) is the well-known catalyst for this process¹. Porosity, framework structure and acidity of the said catalyst plays a crucial role in the catalytic performance. Metal (Mo) loading to these zeolite supports tunes the acidity of the support and its dispersion which significantly affect the reaction. Thus the catalyst preparation and its characterization study is the key factor for the process to achieve effective conversion with high product yield. In the present investigation, different factors, such as effect of metal (Mo) loading over zeolite (HMCM-22), effect of SAR (SiO₂/Al₂O₃) of zeolite, effect of reaction parameters such as space velocity (GHSV) have been studied for the direct non-oxidative methane conversion process. Selection of molybdenum (Mo) as the base metal for the process was investigated by density functional theory. Molybdenum carbide formed during the reaction has been proposed to be the active phase for C-H activation of methane, C₂ coupling and aromatic formation reactions.² Mo_xC_y³ type cluster were supposed to be suitable form of molybdenum carbide species for methane activation and C₂ coupling. In this reference, Mo₄C₂ nanocluster grafted over Al and Si site of zeolite channel was reported for C-H bond activation and a 112 kJ/mol energy barrier was observed when grafted over Al site.³ In the analysis we have investigated the C-H bond activation and ethylene (primary intermediate of benzene) formation via C₂ coupling over Mo₄C₂ nanocluster with varying charge on the cluster, the active phase for initial methane activation and C₂ coupling.

2. Methods

DFT calculations were studied based on DNP basis set using DMol³ module in Material Studio 8 (Biovia, San Diego, USA) along with GGA corrected with exchange-correlation functional by PW91 for the calculation of activation and reaction energies. Zeolite supported Mo catalyst was synthesized by wet impregnation method using ammoniumheptamolybdate as Mo precursor and characterized by XRD, BET, NH₃-TPD, TEM & FT-IR analytical techniques. Catalytic evaluation was carried out in a continuous tubular fixed bed reactor (15 mm ID) packed with 2.5 g of catalyst at 973 K under atmospheric pressure.

3. Results and discussion

DFT Result: DFT calculation have been employed to study the CH₄ activation and C-C coupling for ethylene formation on Mo₄C₂ cluster. Methane is activated on the Mo₄C₂ cluster with an intrinsic activation barrier ~ 116 kJ/mol, related to the second methane activation. The highest intrinsic barrier was obtained for the C-C coupling step forming C₂H₆ (~ 151 kJ/mol). The activation of C₂H₆ (~70 & 95 kJ/mol) was relatively easy and C₂H₄ will be formed easily on the catalyst surface. All the energy barriers observed for these elementary steps have been shown in Figure 1. Also C-H bond activation barrier decreases as the Mo₄C₂ cluster is more reduced in nature (less positive) as confirmed by Table 1.

Experimental Result: Different loadings of Mo (2, 5 & 10 wt %) over zeolite support (HMCM-22) were analyzed for the catalytic performance. 5 wt% Mo loading was most efficient for methane conversion reaction with 20% benzene selectivity compared to 2 & 10 wt% loading as shown in Figure 2 (a). Silica alumina ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) of zeolite (HMCM-22) was also tested for the reaction by varying the acidity, and it was observed that lower SAR (30) is effective for aromatic selectivity compared to higher SAR (55) as shown in Figure 2 (b).

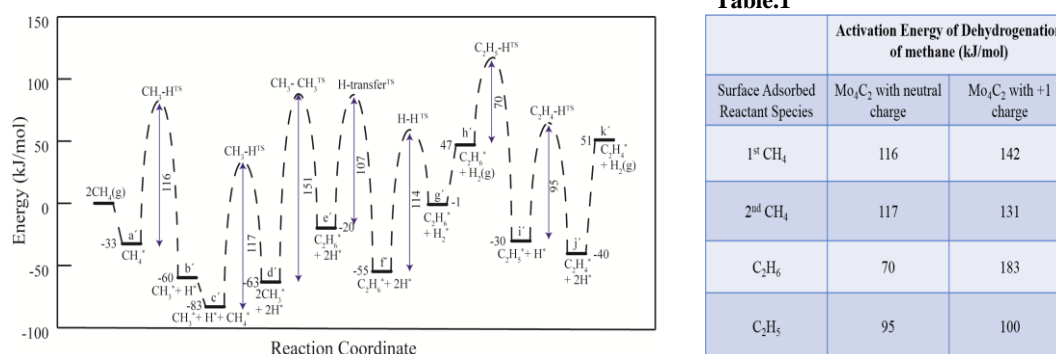


Figure 1. Reaction diagram for methane dehydrogenation and C-C coupling to form ethylene on Mo₄C₂ cluster

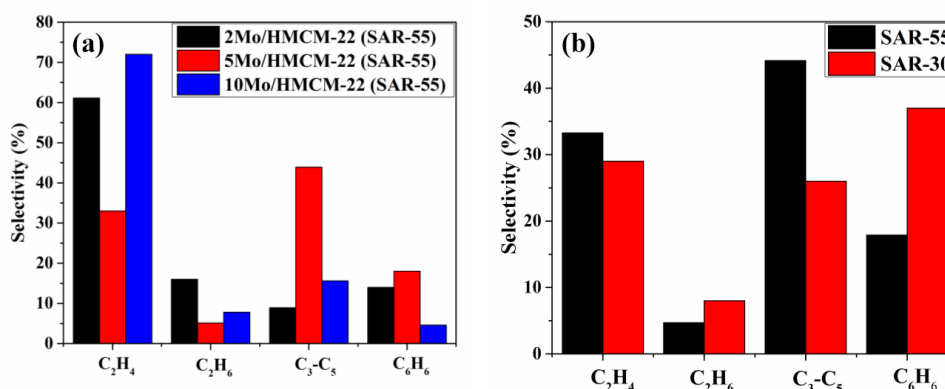


Figure 2. Product selectivity for (a) 2, 5, and 10 wt% Mo loaded MCM-22 (SAR-55) catalyst and (b) for two different SAR of 5Mo/HMCM-22 (30 & 55) catalyst

4. Conclusion

Mo₄C₂ type carbide cluster (formed in situ the reaction) with less positive charge was observed an effective phase for C-H activation and C-C coupling to form ethylene by DFT calculations. In the experimental section, the catalyst parameter such as 5 wt% Mo loading over MCM-22 support is effective for aromatic selectivity (20% benzene) and the lower SAR (30) of the zeolite support gives higher aromatic selectivity (35% benzene) compared to higher SAR (55).

References

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Keywords

Carbide cluster, zeolite, SAR ($\text{SiO}_2/\text{Al}_2\text{O}_3$), aromatics