

**A Fundamental Study on Non-Oxidative Methane Activation and Oligomerization Reactions Using Bi-Metallic Catalysts to Form Higher Hydrocarbons and Graphene.**

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This last part of the report investigates the effect on adding promoters like Fe, Rh and K on the Mo/HZSM-5 catalyst before methane dehydrogenation reactions are performed. The following results have been obtained after these catalysts have been used for MDA reactions and a manuscript is currently being prepared based on these results. Figure 1 shows the XRD analysis of fresh and spent catalysts. The molybdenum species are in the form of  $\text{MoO}_3$  and  $\text{Mo}_2\text{C}$  in the fresh and spent catalysts respectively. Thus, it was evident that  $\text{Mo}_2\text{C}$  species acts as the active site in methane dehydroaromatization.

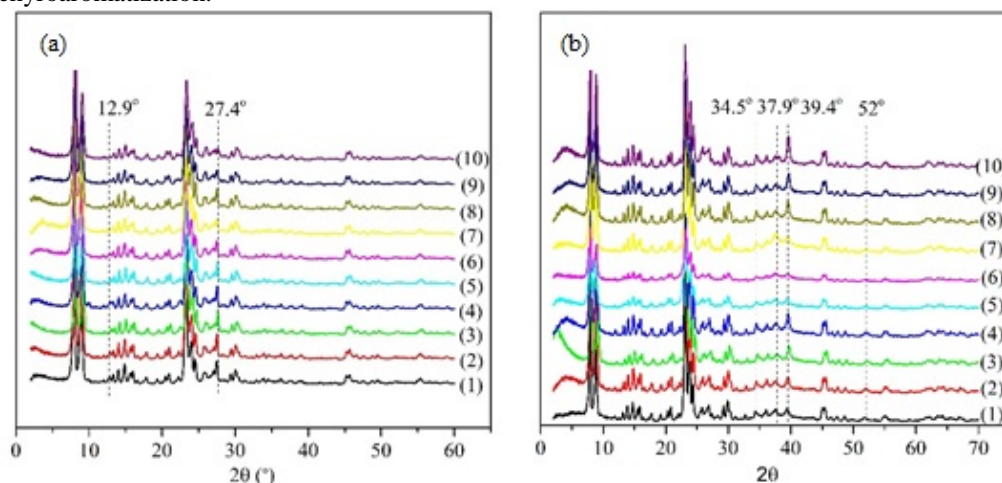


Figure 1 –(a) XRD patterns of fresh and (b) spent catalysts. (1) 10 wt% Mo/HZMS-5, (2) 0.5 K-10 Mo/HZSM-5, (3) 1 K-10 Mo/HZSM-5, (4) 1.5 K-10 Mo/HZSM-5, (5) 0.5 Rh-10 Mo/HZSM-5, (6) 1 Rh-10 Mo/HZSM-5, (7) 1.5 Rh-10 Mo/HZSM-5, (8) 0.5 Fe-10 Mo/HZSM-5, (9) 1 Fe-10 Mo/HZSM-5, (10) 1.5 Fe-10 Mo/HZSM-5.

Figure 2 shows the SEM images of spent catalysts consisting of 1.5 wt% promotor metal and 10 wt% Mo. The surface morphology of unmodified Mo/HZSM-5 and K-Mo/HZSM-5 were almost similar. At 1.5 wt% of Rh loading larger aggregates of metal species were found on the Rh modified Mo/HZSM-5. In case of Fe-Mo/HZSM-5 carbon nanotubes were found on the surface of the catalyst. These nanotubes were not found on unmodified or K, Rh modified Mo/HZSM-5. Thus, the presence of Fe promotes the formation of these nanotubes during the MDA reaction. Figure 3 shows the conversion of methane and selectivity of benzene over unmodified and promoted 10 wt% Mo/HZSM-5. The unmodified and Fe-Mo/HZSM-5 catalysts showed better activity for methane conversion, but the selectivity of benzene dropped below ~45% within 100 mins of reaction. Adding smaller quantity of Rhodium (0.5 wt%) and potassium (1 wt%) enhanced the benzene selectivity. It was noted that the benzene selectivity was stable around 50-65% even after 255 mins of

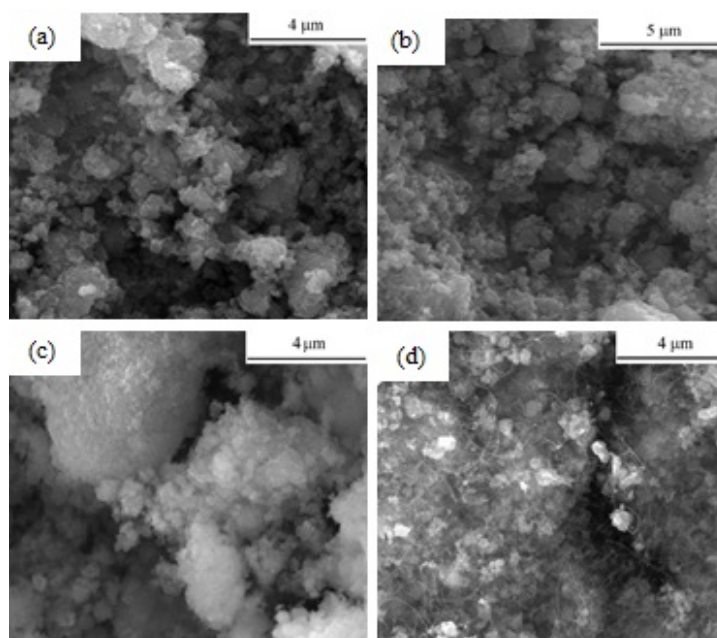


Figure 2 - SEM images of spent catalysts of (a) 10 wt% Mo/HZMS-5 (b) 1.5 K-10 Mo/HZSM-5 (c) 1.5 Rh-10 Mo/HZSM-5 (d) 1.5 Fe-10 Mo/HZSM-5.

reaction. Though the addition of Rh and K did not significantly improve the conversion of methane, they improved the benzene selectivity. In the presence of these promoters, the conversion of benzene to other heavier hydrocarbons (which are generally considered as coke) was hindered.

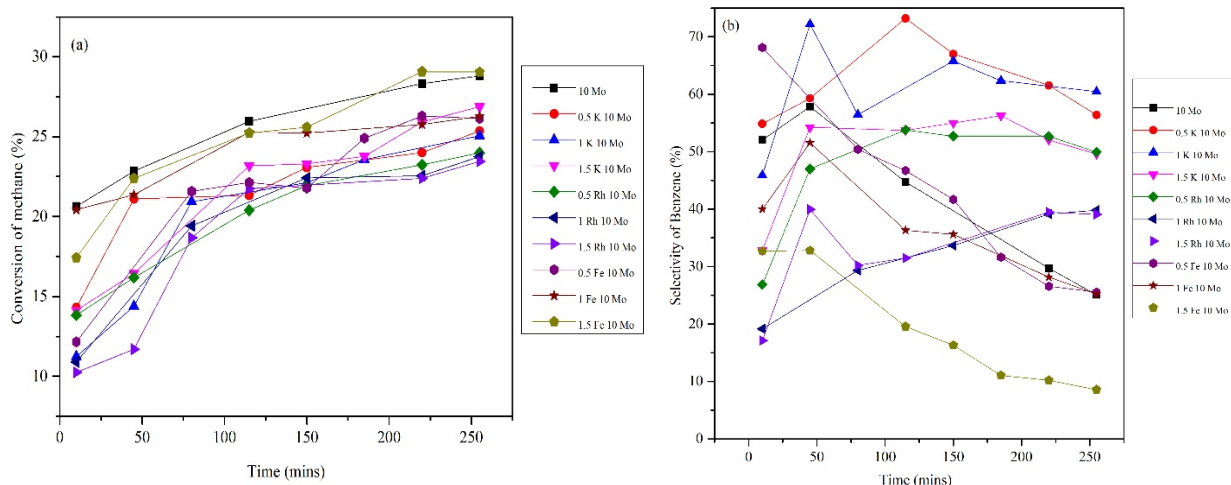


Figure 3 - (a) Conversion of methane and (b) Selectivity of benzene on unmodified and promoted 10 wt% Mo/HZSM-5.

Figure 4 shows the TPO studies of spent catalysts. It is evident that the weight loss due to carbon removal was significantly high in case of Fe-Mo/HZSM-5 when compared to other catalysts. The K-Mo/HZSM-5 and Rh-Mo/HZSM-5 catalysts formed less carbon when compared to unmodified 10 wt% Mo/HZSM-5. The significant weight loss in Fe-Mo/HZSM-5 corresponds to the burning of carbon nanotubes. The less carbon content in K and Rh promoted catalysts shows that addition of these promoters significantly decreased the formation of heavier hydrocarbons and helped in better stability of benzene.

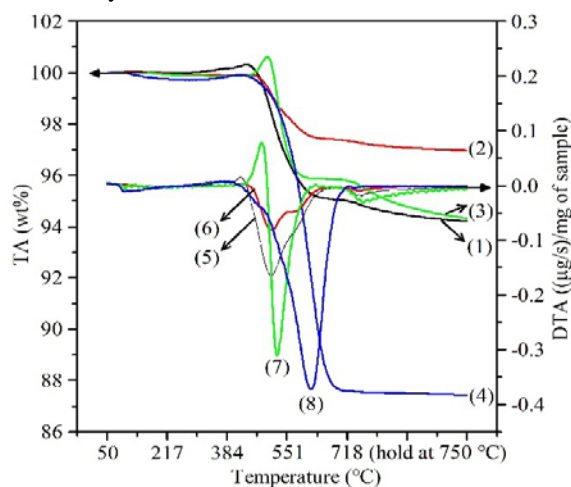


Figure 4 - TPO profiles of 10 wt% Mo/HZSM-5 [(1) TA, (5) DTA], 1.5 K-10 Mo/HZSM-5 [(2) TA, (6) DTA], 1.5 Rh-10 Mo/HZSM-5 [(3) TA, (7) DTA] and 1.5Fe-10 Mo/HZSM-5 [(4) TA, (8) DTA].

Impact on the student: This funding has helped support a doctoral student for 2 years. During that time, one manuscript has been published (Ramasubramanian V, Ramsurn Hema and Price Geoffrey Methane dehydroaromatization – A study on hydrogen use for catalyst reduction, role of molybdenum, the nature of catalyst support and significance of Bronsted acid sites, Journal of Energy Chemistry, DOI: 10.1016/j.jechem.2018.09.018). We are also in the process of finishing the second manuscript which will be submitted by the end of this year. Furthermore, the student has had the chance to use the travelling funds to present the findings of this research at conferences and symposia (AIChE 2017, Great Plains Catalysis Society 2018, Pentasectional Meeting of ACS 2018).