

Experiment and model study for methane to benzene reaction on 5% Mo/HZSM5 catalyst: Insight into mechanistic pathway

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Highlights

- MTB reaction kinetic study was performed on 5%Mo /HZSM5 in packed bed reactor
- Spent catalyst characterized for understanding the coke formation by TGA studies
- A mechanistic model was developed using Langmuir-Hinshelwood-Hougen-Watson kinetic approach for predicting reaction and coke formation behavior.

1. Introduction

As an alternative approach to deriving petrochemicals, the methane to benzene (MTB) reaction has been studied extensively¹. Prior investigation suggests coke formation during reaction, with implication on catalyst activity². The mechanisms involved and forms of coke have been debated with validation by experiments being scarce. The present study is a part of our efforts to develop the mechanism for methane conversion to benzene, hydrogen, alongside coke species. The Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic modeling approach is applied to build an understanding of the reaction behavior. The proposed model considers several plausible steps, viz. adsorption, dehydrogenation, oligomerization, cyclisation and desorption³⁻⁵. Kinetic data generated from packed bed experiments coupled with ex-situ thermogravimetric analyzer studies have been used to develop and model the elementary mechanism.

2. Methods

5% Mo/HZSM5 with Si/Al=11.5 was prepared by the wet impregnation method⁶. The activity study was carried out in a fixed bed down flow quartz tubular reactor (8 mm diameter), and the catalyst was placed in the middle (isothermal) zone of the furnace. The MTB reaction studies were carried at 725, 750 and 775 °C at 9000 GHSV (300 mL/min @STP for 2gm catalyst) under atmospheric pressure. The reactor bed was heated to 725 °C by passing N₂ at 10 °C/min. The flow was then switched to 1:9 CH₄: H₂ mixture for carburization⁷, followed by 100% CH₄ for the reaction at respective temperature. A mass flowmeter (Agilent technologies) was used to monitor the gas flow at the outlet. The products were analyzed by online gas chromatography with TCD and FID (Bruker 450-GC, Petrocol DH50 fused silica capillary column and Carboxen 1010 PLOT fused silica capillary column). The catalyst was recovered after different reaction times (15, 25, 45 and 65 min) by cooling in the N₂ atmosphere.

The recovered spent catalyst was analyzed ex-situ by a thermogravimetric analyzer (NETZSCH 1000) using air as the medium. While heating to 700 °C, isothermal at 120 °C for 10 min was done to facilitate moisture removal. The heating was carried with a temperature ramp of 10 °C/min with a hold at 400, 450, 500, 550 and 600 °C to stabilize the temperature and capture minor weight losses with improved accuracy.

The LHHW kinetics was applied for predicting the reaction and coke formation kinetics. The coke species are considered as non-desorbing surface species, while C₆H₆ and H₂ were desorbed into the gas phase. Initial values for rate parameters were taken from literature, and optimized by non-linear optimization.

3. Results and discussion

The 5% Mo/ HZSM5 prepared was able to achieve the reported conversion⁸. The rate of CH₄ consumption during the reaction is shown in Figure 1. A. with an experimental error of ±0.02 mole/gm.cat/hr. The CH₄ conversion was observed to be below thermodynamic equilibrium conversion, and the data are thus useful

for kinetic estimations. The TGA studies performed on this catalyst are reported in Figure 1. B, C and D. TGA studies reported in earlier studies² have highlighted the formation of soft coke (Poly aromatic hydrocarbon or PAH) below 600°C, and we observed hints of 4 type of PAH species within the range of 400-600°C. We also believe there is a possibility of interconversion of these PAH, as can be seen in Figure 1. B, C and D a different reaction time. The rate equations were solved for a packed bed reactor model using LHHW kinetics.

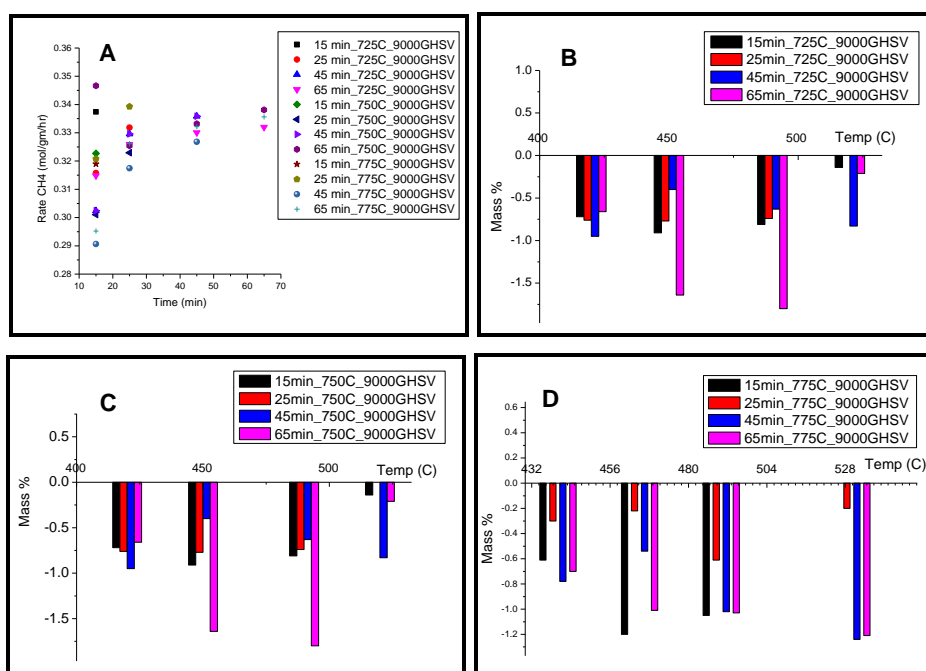


Figure 1. A) Kinetic study performed on 5% Mo/HZSM5 catalyst. B) Change in weight recorded during TGA studies performed on spent 5% Mo/ HZSM5 catalyst after MTB reaction at 725°C and 9000 GHSV. C) Change in weight recorded during TGA studies performed on spent 5% Mo/ HZSM5 catalyst after MTB reaction at 750°C and 9000 GHSV. D) Change in weight recorded during TGA studies performed on spent 5% Mo/ HZSM5 catalyst after MTB reaction at 775°C and 9000 GHSV

4. Conclusions

Packed bed reactor study has been performed on 5% Mo/HZSM5, and the recovered catalyst after reaction studied using thermogravimetric analyzer. Our studies suggest that methane undergoes a series of elementary reaction steps to form benzene, of which some desorbs into the gas phase forming part of the products and remaining reacts to form 4 type of PAH species. The LHHW model provides a further understanding in the scheme of simultaneous reaction and coke species formation.

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Keywords

MTB reaction, Coke formation, Poly aromatic hydrocarbon, LHHW kinetics.