The effects of methanol or dimethyl ether as methylating agent during zeolite catalysed benzene methylation

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Keywords: zeolites, methylation, dimethyl ether, methanol, MD simulations, methanol-to-hydrocarbons

1 Introduction

Methylation of benzene and other aromatics are key reactions in several important industrial processes such as methanol conversion to gasoline or olefins (MTG/MTO) [1] and xylene production from toluene [2]. Microporous acid materials such as zeolites are commonly used as catalysts in these processes. This work combines experiments and theory to investigate the behaviour of methanol and dimethyl ether (DME) during benzene methylation over catalysts with different structures (MFI and AFI) and acid strength (AFI). Previous studies have revealed higher methylation rates for DME than methanol over H-ZSM-5 [3], but the methylation mechanisms are usually assumed to be similar. This study not only confirms a difference in methylation rates, but also reveals large differences in selectivity towards secondary products for methanol and DME.

2 Experimental/methodology

Catalytic experiments were performed in a fixed bed quartz reactor with 5 mg catalyst powder diluted in 40 mg quartz (particle size 250-420µm). Typically, 60 mbar of benzene was co-reacted with 60 mbar of either methanol or DME at differential conversion (WHSV = 205-375 h^{-1}, conversion < 2%) at 250-300 °C. The effluent was monitored continuously by on-line MS and a detailed analysis was performed by on-line GC-FID/MS after 10 minutes of reaction.

Ab initio molecular dynamics calculations were carried out with the CP2K simulation package to sample all relevant configurations of the guest molecules in the pores. The periodic DFT-D3 calculations were performed in a 1x1x2 H-SSZ-24 and H-SAPO-5 super cell and H-ZSM-5 unit cell, at 350 ºC and 1 bar. Rare event sampling was enhanced with a metadynamics approach [4].

3 Results and discussion

Net product formation rates obtained during benzene methylation at 250°C are shown in Figure 1. In agreement with previous studies on H-ZSM-5 [3], the use of DME led to higher total product formation rates than methanol. Furthermore, Figure 1 shows that the product distribution varied significantly based on the choice of methylating reactant. While DME predominantly yielded (sequential) methylation and dealkylation products (toluene, polymethylbenzenes and alkenes), the use of methanol led to a high selectivity towards diphenylmethane (DPM) and its methylated analogue. Similar trends were observed at 300°C for H-ZSM-5 and H-SSZ-24. DPM has previously been suggested as an intermediate during methylbenzene transmethylation reactions [5]. Preliminary results indicate a larger release of H_2

during the reaction when using methanol, indicating that DPM may be formed by phenylation of toluene accompanied by loss of H_2.

Figure 2 illustrates the proposed reaction scheme, where formed toluene is either methylated further or phenylated to form DPM. The reaction mechanisms and kinetics of toluene phenylation are currently under investigation. In addition, ab initio molecular dynamics simulations of co-adsorption and reaction of methanol and DME with benzene, toluene and xylene have been performed in order to obtain a deeper understanding of the experimental observations. Important differences in the stability and reactivity of different co-adsorption complexes formed between methanol or DME and aromatics with an increasing degree of substitution were observed may be possible linked with the observed selectivity and reactivity differences.

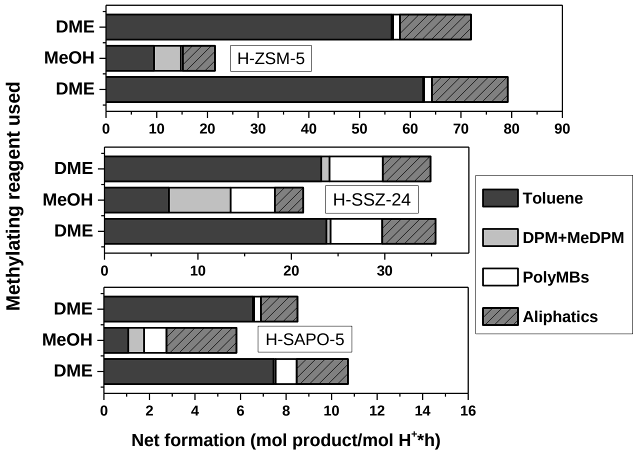

Fig. 1. Net product formation rates during benzene methylation over H-ZSM-5 (top), H-SSZ-24 (middle) and H-SAPO-5 (bottom) at 250°C. Experiments were run sequentially (e.g. DME-MeOH-DME).

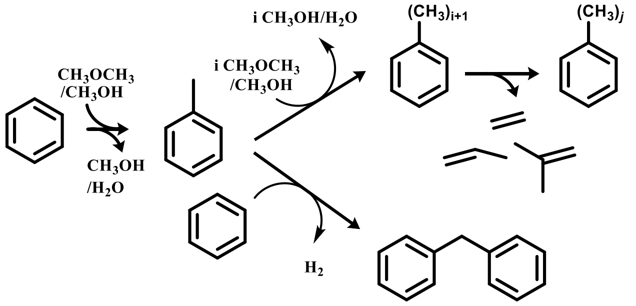

Fig. 2. Proposed reaction scheme for benzene methylation and successive reactions.

4 Conclusions

This study shows that use of methanol or DME in benzene methylation led to different reaction rates and product distributions. Similar behaviour was observed irrespectively of catalyst topology or acid strength. Compared to DME, the use of methanol led to lower rates of methylation and significantly higher yields of diphenylmethane. In depth experimental and theoretical studies are in progress to elucidate the reason for the observed selectivity differences and will be presented.

Acknowledgements

Financial support is received via the European Industrial Doctorates project “ZeoMorph” (FP7 ITN-EID), part of the Marie Curie actions. We thank the Foundation of Scientific Research - Flanders (FWO) and the European Research Council. Computational resources and services used in this work were provided by the Stevin Supercomputer Infrastructure of Ghent University and by the Flemish Supercomputer Center (VSC), funded by the Hercules Foundation and the Flemish Government – department EWI.

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