Combined theoretical and experimental study on the influence of catalyst acid strength on the zeolite-catalyzed methanol conversion process

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Introduction

Acid catalysis is highly relevant in many chemical reactions. Fundamental understanding of the effect of Brønsted acid strength on key reactions is thus a topic of major interest. Therefore, we compare two isostructural catalysts with different acid strength, H-SSZ-24 and H-SAPO-5 (AFI), for methanol to hydrocarbons (MTH) catalysis. The MTH reaction is a flexible reaction route to produce light alkenes or gasoline from alternative hydrocarbon feed-stocks. [1] Under steady-state MTH conditions, product formation proceeds via continuous methylation of an adsorbed hydrocarbon pool, which subsequently eliminates alkenes. When comparing the product selectivity in the MTH reaction in the AFI materials, it was found that the strongly acidic H-SSZ-24 is more selective towards aromatic products and light alkenes than the moderately acidic H-SAPO-5.[2] Furthermore, it was found that while aromatic hydrocarbon pool species appear to play an important role in H-SSZ-24, these are of less importance in the weaker acid H-SAPO-5.[2] To elucidate the reasons for this change in the major reaction intermediates, an understanding of the key reaction steps involved in the MTH reaction and their individual sensitivity to changes in acid strength is necessary.

Results and Discussion

In this study, a thorough assessment of the influence of zeolitic acid strength on zeolite-catalysed reactions was made by co-reaction experiments and molecular simulations of methanol and benzene and methanol and propene in the isostructural AFI materials H-SSZ-24 and H-SAPO-5. In line with what was earlier found for the MTH reaction in both catalysts, H-SAPO-5 clearly favours reactions involving alkenes, whereas reactions involving arenes are favoured in the more acidic H-SSZ-24. A direct comparison of benzene and propene methylation at 350-400 °C further revealed that benzene methylation was significantly faster than propene methylation in H-SSZ-24, whereas the two reactions occur at similar rates in H-SAPO-5. A molecular level understanding of this observation was provided by performing DFT molecular dynamics simulations. It could be concluded that benzene and methanol are likely to form a highly favourable co-adsorbed complex in H-SSZ-24. The trends in reactivity could be predicted from the geometries of the co-adsorbed methanol – hydrocarbon complexes in the two catalysts, combined with the degree of methanol protonation at 350 ºC. The latter was found to depend both on the zeolitic acidity and the characteristics of the co-adsorbed hydrocarbon. In particular, for co-adsorbed benzene in the more acidic H-SSZ-24, a highly favourable adsorption complex combined with a low free energy for methanol protonation predicts a significantly higher reactivity than for any of the other investigated situations. These theoretical findings confirm the observed experimental methylation rates and provide insight into why the MTO product formation is governed by different catalytic cycles in both AFI

materials. Additionally, the key methylation reactions are also studied by means of a metadynamics approach, which provides additional insights into the mechanism of the methylation reaction and the reactivity of the different adsorption complexes [3].

Conclusions

Co-reactions and kinetic investigations strongly suggest that the methylation of alkenes is strongly favoured relative to methylation of aromatics in H-SAPO-5, while methylation of aromatics is facile over H-SSZ-24. Concurrently with the reactor studies, detailed analysis of ab initio molecular dynamics simulations show that some well chosen geometrical parameters can predict the reactivity of alkenes versus aromatics towards methanol. Both the probability that methanol and benzene or propene form a pre-reactive co-adsorption complex and the probability that methanol gets protonated straightforwardly indicate the reactivity of benzene and propene towards methylation.

References

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