Combined Theoretical and Experimental Study on the Influence of Zeolitic Acid Strength on the Methanol Conversion Process

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This contribution encompasses a theoretical and experimental assessment of how zeolitic acid strength affects acid catalyzed methylation reactions. We show that molecular dynamics and metadynamics simulations provide insights into the adsorption and reactivity of methanol and benzene or propene in large pore AFI materials that correlate well with experimental measurements.

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 AFI catalysts with different acid strength, H-SSZ-24 and H-SAPO-5, for methanol to hydrocarbons (MTH) catalysis. The MTH reaction is a flexible reaction route to produce light alkenes or gasoline from an alternative hydrocarbon feedstock [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, this contribution encompasses a combined experimental and theoretical assessment of how zeolitic acid strength and composition affects methylation reactions

Experimental

Ab initio calculations in a 1x1x2 AFI super cell were carried out with the CP2K simulation package, using a DFT-D3 level of theory, at realistic reaction temperatures (350 ºC) and 1 bar. To enhance rare event sampling, a metadynamics approach is applied [3,4]. Catalytic tests were performed at atmospheric pressure in fixed bed glass reactors at temperatures between 250 and 400 °C and with a range of partial pressures and space velocities. The conditions were chosen to obtain low conversion of either reactant.

Results and Discussion

In this study, a thorough assessment of the influence of zeolitic acid strength on zeolite-catalyzed 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 earlier results, H-SAPO-5 clearly favours reactions involving alkenes, whereas reactions involving arenes are favoured in the more acidic H-SSZ-24 (Figure 1a). 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 at 350 °C. Hereby two indices were defined: the probability of forming co-adsorbed complexes exhibiting a proper orientation for methylation and the probability

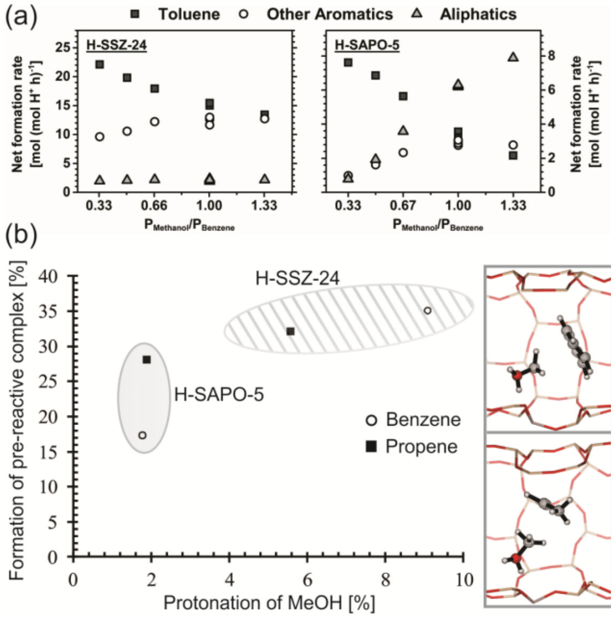

Figure 1: (a) Product formation rates during co-reactions of benzene and methanol as a function of the methanol to benzene molar feed ratio at 250 °C in H-SSZ-24 and H-SAPO-5.(b) Probability of methanol protonation and formation of a pre-reactive complex at 350 ºC for benzene and propene in H-SSZ-24 and H-SAPO-5. Snapshots of pre-reactive complexes are displayed in the inset.

of forming a protonated methanol molecule (Figure 1b). The probability to form protonated methanol was, as expected, higher in the more acidic H-SSZ-24. Furthermore, it was found that benzene and methanol are more likely to form a reactive co-adsorbed complex in H-SSZ-24 compared to propene and methanol, while the opposite was observed for H-SAPO-5.

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.[3,5] Some snapsnots of the high temperature metadynamics simulations are displayed in Figure 1. 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.

Conclusion

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. Detailed analysis of ab initio molecular dynamics simulations show that some well-chosen geometrical parameters correlate with the reactivity of alkenes versus aromatics towards methanol. The probability that methanol gets protonated and forms a pre-reactive complex with benzene or propene were found to indicate the reactivity of benzene and propene towards methylation.

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