

Introduction

Ex situ and *in situ* MAS NMR-UV/Vis Spectroscopic Study of Hydrocarbon Pool Compounds and Coke Deposits Formed by Methanol Conversion on H-SAPO-34

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The process of converting methanol to olefins on solid acid catalysts was developed as a route to produce light olefins from natural gas [1]. During the last decades, increasing efforts were made to clarify the mechanism of the methanol-to-olefin (MTO) conversion on acidic zeolite catalysts under industrial conditions by modern NMR spectroscopic techniques [2, 3]. In the MTO process, the conversion of methanol is dominated by the hydrocarbon pool route in which methanol is added to reactive organic compounds formed in the pores of acidic zeolite catalysts [1]. These compounds are mainly polyalkylaromatics, various carbenium ions, and polycyclic aromatics. Light olefins are formed via an elimination of alkyl groups from these hydrocarbon pool compounds [1]. To gain more insight into the formation of organic deposits on MTO catalysts, the novel *in situ* MAS NMR-UV/Vis technique [4] combined with on-line gas chromatography was applied in the present work. The organic deposits formed at 523-673 K on H-SAPO-34 inside a standard fixed-bed reactor (*ex situ*) and an MAS NMR rotor reactor (*in situ*) were investigated.

Experimental Section

Results and Discussion

As shown in Fig. 1a, for *the in situ* experiments, about 100 mg of dehydrated H-SAPO-34 were filled into a 7 mm MAS NMR rotor reactor under dry nitrogen in a glove box and pressed to a cylindrical catalyst bed. After transferring the rotor into the MAS NMR probe, a secondary dehydration of the catalyst was performed at 673 K for 1 h under flowing dry nitrogen (30 ml/min) and then kept at the respective reaction temperature. Then a continuous flow of ¹³C-enriched methanol with a modified residence time of W_{cat} /*F*me= 25 gh/mol was injected into the MAS NMR rotor reactor (Fig. 1a). For comparison, the catalytic studies were performed under the same conditions in a standard fixed-bed reactor (*ex situ*) as depicted in Fig. 1b, in which the glass fiber optics of a UV/Vis spectrometer was installed on top of this reactor. The same fiber optics was installed at the bottom of the MAS NMR rotor reactor equipped with a quartz window (Fig. 1a).



Fig. 2 shows the in situ ¹³C MAS NMR and UV/Vis spectra simultaneously recorded during the conversion of ¹³C-enriched methanol on H-SAPO-34 at 623 and 673 K under continuous-flow conditions in the MAS NMR rotor reactor. The in situ ¹³C MAS NMR spectra are dominated by signals at 18 to 29 ppm due to ¹³C atoms of alkyl groups, most of them methyl groups, and at 125 to 135 ppm due to aromatic compounds. These signals indicate the formation of polyalkylaromatics on the working H-SAPO-34 catalyst [2b]. The simultaneously recorded UV/Vis spectra consist of bands at 245, 280, 345, 400, and 430 nm. The bands at 245 and 280 nm indicate the presence of non-protonated dienes or aromatics and polyalkylaromatics, respectively. Broad bands at 345 and 430 nm can be explained by dienylic and trienylic carbenium ions, respectively. The strong band occurring at 400 nm is a hint for the formation of nonprotonated polycyclic aromatics. In addition, it was evidenced that the formation of polycyclic aromatics, which are typical for coke deposits, already starts at the reaction temperature of 673 K. Fig. 3 shows stack plots of UV/Vis spectra recorded at 673 K during the methanol conversion in the MAS NMR rotor reactor (a) and the fixed-bed reactor (b) as a function of time on stream. For both these reactors, a systematic increase of the UV/Vis bands at 385 to 425 nm occurs during the first 165 minutes. While the UV/Vis spectra recorded for methanol conversion in the MAS NMR rotor reactor is dominated by a broad band at ca. 400 nm, the spectra recorded for methanol conversion in the standard fixed-bed reactor show slightly separated bands in the above-mentioned range. This finding indicates that a more detailed assignment of the bands at 385 to 425 nm is possible.

Fig. 3 Stack plot of UV/Vis spectra recorded during the methanol-to-olefin conversion on H-SAPO-34



Fig. 2 *In situ* ¹³C CF MAS NMR (a, b) and UV/Vis spectra (c, d) recorded upon conversion of ¹³CH₃OH on H-SAPO-34 at 623 K (a, c) and 673 K (b, d) for 3 h in the MAS NMR rotor reactor.

Conclusion

at 673 K in the MAS NMR rotor reactor (a) and the standard fixed-bed reactor (b).

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References

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In the present work, *in situ* ¹³C CF MAS NMR-UV/Vis spectroscopy was applied for the investigation of organic deposits formed during the conversion of methanol on H-SAPO-34 under continuous-flow conditions at 623 and 673 K. The catalytic studies were performed using a standard fixed-bed reactor equipped with a UV/Vis glass fiber optics and the MAS NMR rotor reactor of an *in situ* MAS NMR-UV/Vis probe. While solid-state NMR spectroscopy allows quantitative studies of the ¹³C carbon atoms in different chemical environments, such as alkyl groups and aromatic rings, UV/Vis spectroscopy is sensitive for different aromatic compounds, such as polyalkyl-aromatics and polycyclic aromatics. The most important coke deposits observed by UV/Vis spectroscopy are polycyclic aromatics with chain-like topology, such as polymethylanthracenes. The detailed position and shape of the UV/Vis bands of these compounds were found to depend on the amount of coke deposits.