

Formation of cyclic compounds and carbenium ions by conversion of methanol on weakly dealuminated zeolite H-ZSM-5 investigated *via* a novel *in situ* CF MAS NMR/UV-Vis technique

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In studying the conversion of methanol on weakly dealuminated zeolite H-ZSM-5, simultaneously by *in situ* MAS NMR and *in situ* UV-Vis spectroscopy under continuous-flow conditions, the formation of cyclic compounds and carbenium ions were found to be formed already at 413 K.

The *in situ* investigation of working solid catalysts is an important approach to improve our knowledge about the mechanisms of heterogeneously catalyzed reactions.¹ MAS NMR spectroscopy provides both structural and dynamic information about heterogeneous reaction systems and is, therefore, a very suitable method for this purpose. Since 1995,² various *in situ* MAS NMR techniques for the study of heterogeneously catalyzed reactions under continuous-flow (CF) conditions have been developed which allow a direct investigation of the formation and transformation of surface compounds in the steady state and a simultaneous gas chromatographic analysis of the reaction products. In the present work, the *in situ* CF MAS NMR technique was combined with *in situ* UV-Vis spectroscopy in a single probe. With this novel *in situ* CF MAS NMR/UV-Vis technique, the advantages of two spectroscopic methods are combined: (i) the more detailed separation and assignment of signals of adsorbates on the surface of solid catalysts by MAS NMR spectroscopy, and (ii) the high sensitivity for all compounds absorbing radiation in the UV-Vis region, such as allylic compounds, aromatics, and carbenium ions, by UV-Vis spectroscopy.

During the last decade, increasing efforts were made to clarify the mechanism of the conversion of methanol-to-olefins (MTO) on acidic zeolites. The most favoured reaction mechanism for the MTO process is the 'hydrocarbon pool' mechanism.^{3–9} According to this mechanism, large carbonaceous compounds are formed in the pores of acidic zeolite catalysts, which add methanol and split off light olefins, such as ethene, propene, and butenes. *In situ* ¹³C MAS NMR investigations of the methanol conversion on zeolite H-ZSM-5 and silicoaluminophosphates H-SAPO-18 and H-SAPO-34 under continuous-flow conditions showed that the hydrocarbon pool formed in the steady state consists of a mixture of aliphatic and cyclic olefins and of polyalkylated aromatics.^{6,7} *Via in situ* ¹³C CF MAS NMR spectroscopy of zeolite H-ZSM-5 performed during an alternating conversion of ¹³CH₃OH and ¹²CH₃OH, it could be evidenced that the hydrocarbon pool plays a catalytically active role in the MTO process.⁹ By application of a pulse-quench reaction technique and studying the organic compounds formed on the catalyst material by solid-state ¹³C MAS NMR spectroscopy, Haw and co-workers could show that polymethylbenzenes are the most active compounds occurring in the hydrocarbon pool formed on acidic zeolites.⁸ Very recently, it could be shown that on Brønsted acidic zeolites H-Y, H-ZSM-5, and H-SAPO-34, surface methoxy groups contribute to the formation of the hydrocarbons in the induction period of the methanol conversion at 433 to 523 K.¹⁰ On the other hand, UV-Vis investigations of the methanol conversion on dealuminated zeolites H-ZSM-5 indicated that cyclohexenylic, polyenylic, and diphenylic carbenium ions as well as condensed aromatics are formed already at 400 K.¹¹

In the present work, the novel *in situ* CF MAS NMR/UV-Vis technique was applied to study the formation of hydrocarbons by the conversion of methanol on a weakly dealuminated zeolite H-

ZSM-5 at low reaction temperatures.[†] A commercial, variable-temperature 7 mm MAS NMR probe of Bruker BioSpin was modified with an injection system as described elsewhere.² In addition, a glass fiber was attached to the bottom of the stator as shown in Fig. 1. The 7 mm MAS NMR rotor was equipped at the bottom with a quartz glass window. *Via* this quartz glass window and using the glass fiber, the catalyst sample inside the rotor could be investigated by a fiber-optic UV-Vis spectrometer.

The weakly dealuminated zeolite H-ZSM-5 was dehydrated at 673 K under vacuum for 12 h before it was filled into the MAS NMR rotor under dry nitrogen inside a glove box. The methanol (¹³CH₃OH) flow (*W/F* = 25 gh mol⁻¹) was started after reaching the temperature of 413 K. The ¹³C MAS NMR spectrum recorded at 413 K during the continuous conversion of methanol (Fig. 2a, left) shows signals at 51 and 61 ppm caused by methanol and dimethyl ether (DME), respectively, and a very weak signal at *ca.* 23 ppm, probably due to alkanes or alkylated cyclic compounds. The occurrence of the signals at 23 and 61 ppm indicates that the conversion of methanol on weakly dealuminated zeolites H-ZSM-5 starts already at 413 K. The simultaneously recorded UV-Vis spectrum (Fig. 2a, right) consists of bands at *ca.* 275, 315, and 375 nm. The narrow peaks at *ca.* 500 nm are due to the equipment. According to the literature, the band at 275 nm indicates the formation of neutral aromatic compounds,^{13,14} while the bands at 315 and 375 nm may be due to mono- and di-enylic carbenium ions,¹³ respectively. According to Bjørger *et al.*,¹⁴ adsorption of hexamethylbenzene on zeolite H-Beta leads to the formation of hexamethylbenzenium ions causing a band at 390 nm. It is important to note that the UV-Vis spectrum of the non-dealuminated zeolite H-ZSM-5, *i.e.* of the parent zeolite H-ZSM-5, recorded under the same reaction conditions, consists only of a very weak band at *ca.* 300 nm (not shown). This indicates that the formation of first hydrocarbons and carbenium ions, already at 413 K, is influenced by the presence of extra-framework aluminium species acting as Lewis acid sites. In addition, it can be concluded that the compounds responsible for the bands occurring in Fig. 2a, right, are mainly formed by the conversion of methanol and not by impurities in the methanol feed.

As the first reaction product of the methanol-to-olefin conversion on acidic zeolites, the formation of ethene is often discussed.¹⁵ In

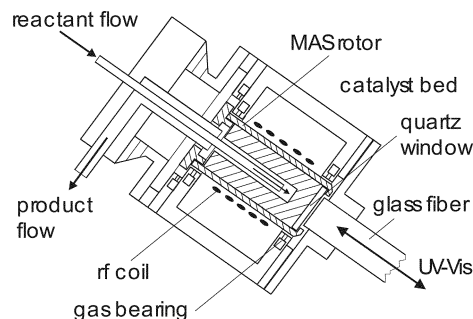


Fig. 1 Scheme of the *in situ* CF MAS NMR/UV-Vis probe consisting of an MAS NMR turbine equipped with an injection system for solid-state NMR studies under continuous-flow (CF) conditions and a quartz fiber-optic for simultaneous UV-Vis investigations.

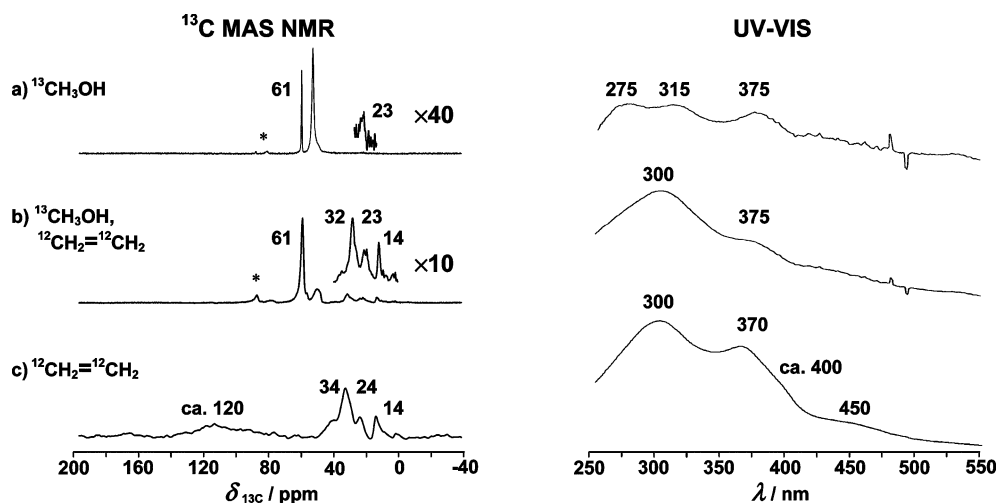


Fig. 2 ^{13}C CF MAS NMR (left) and UV-Vis (right) spectra of a dealuminated zeolite H-ZSM-5 recorded (a) during conversion of $^{13}\text{CH}_3\text{OH}$ under continuous flow conditions ($W/F = 25 \text{ gh mol}^{-1}$) at 413 K for 2 h, (b) during a subsequent conversion of $^{12}\text{CH}_2=^{12}\text{CH}_2$ ($W/F = 10 \text{ gh mol}^{-1}$) at 413 K for 1 h, and (c) during conversion of $^{12}\text{CH}_2=^{12}\text{CH}_2$ ($W/F = 10 \text{ gh mol}^{-1}$) at 413 K on a non-used catalyst for 2 h. Asterisks denote spinning sidebands.

the present case, therefore, the organic compounds responsible for the ^{13}C MAS NMR signals at 23 ppm and the UV-Vis bands at 275, 315, and 375 nm may be formed also by ethene. To verify this assumption, the weakly dealuminated zeolite H-ZSM-5, used to convert methanol, was subsequently applied to study the conversion of ethene (Fig. 2b). ^{13}C MAS NMR signals appearing at 14, 23, and 32 ppm, during conversion of ethene at 413 K for 1 h, are due to alkyl groups of small amounts of alkylated cyclic compounds, such as cyclopentene, cyclohexene, cyclohexadiene, and benzene. The simultaneously recorded UV-Vis spectrum shows bands at 300 and 375 nm. Again, these bands are a hint for the formation of neutral cyclic compounds and dienyl carbenium ions, respectively.¹³

The conversion of ethene on a non-used dealuminated zeolite H-ZSM-5 led to the spectra shown in Fig. 2c. The ^{13}C MAS NMR spectrum consists of signals at 14, 24, and 34 ppm caused by alkyl groups of cyclic compounds. In addition, a broad signal in the chemical shift range of olefinic and aromatic compounds occurred at ca. 120 ppm. The UV-Vis spectrum consists of bands similar to those in the former experiment and an additional weak band at ca. 450 nm which may be due to condensed aromatics¹⁶ or trienyl carbenium ions.¹³ A weak shoulder at ca. 400 nm could be an indication for the formation of hexamethyl-benzenium ions.¹⁴

In conclusion, the simultaneous investigation of methanol conversion on weakly dealuminated zeolite H-ZSM-5 by ^{13}C CF MAS NMR and UV-Vis spectroscopy has shown that first cyclic compounds and carbenium ions are formed already at 413 K. Probably, extra-framework aluminium species acting as Lewis acid sites are responsible for the formation of hydrocarbons and carbenium ions at low reaction temperatures. While NMR spectroscopy allows identification of the signals of the main reactants in more detail, UV-Vis spectroscopy gives hints as to the formation of low amounts of cyclic compounds and carbenium ions.

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Notes and references

† Experimental section. Zeolite H-ZSM-5 ($n_{\text{Si}}/n_{\text{Al}} = 22$) was prepared according to ref. 12 and was weakly dealuminated by calcination at 923 K under flowing nitrogen (60 l h^{-1}). Before the catalytic application, the zeolite was characterized by AES/ICP, X-ray diffraction, ^1H , ^{27}Al , and ^{29}Si

MAS NMR spectroscopy. A small ^{27}Al MAS NMR signal occurring at ca. 0 ppm after calcination at 923 K indicated the presence of extra-framework aluminium species. Methanol- ^{13}C (^{13}C -enrichment of 99%) was purchased from Euriso-Top. Ethene with a natural abundance of ^{13}C -isotopes ($^{12}\text{CH}_2=^{12}\text{CH}_2$) was obtained from Fluka (99.95%). ^{13}C high-power proton decoupling (HPDEC) MAS NMR investigations were performed on a Bruker MSL 400 NMR spectrometer at a resonance frequency of 100.6 MHz using a modified 7 mm Bruker MAS NMR probe. The sample spinning rate was 2.5 kHz. A repetition time of 10 s and up to 1000 scans were used to record the spectra. UV-Vis spectra were recorded applying an AvaSpec-2048 Fiber Optic spectrometer, an AvaLight-DH-S deuterium light source, and a glass fiber reflection probe FCR-7UV20-3-SR-S1 by Avantes.

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