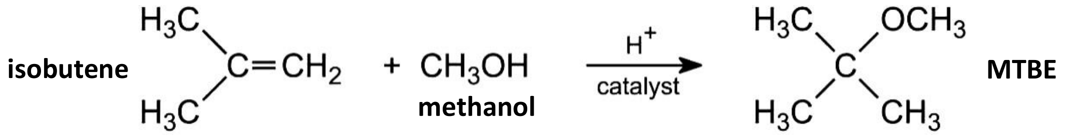
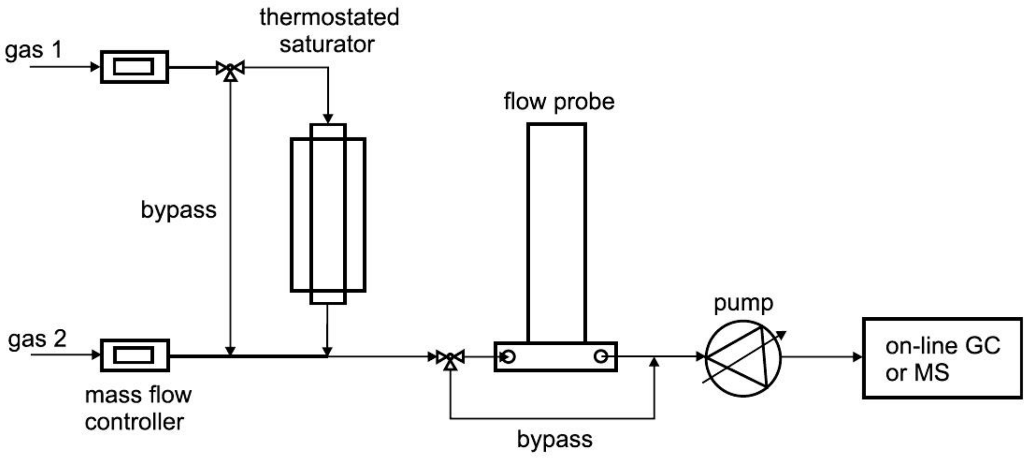
Combined *in situ* solid-state NMR and on-line GC studies of heterogeneously catalyzed reactions under continuous flow conditions

Spectroscopic background: For demonstrating *in situ* flow solid-state NMR spectroscopy (see Topic “3” of link “*In Situ* Solid-State NMR Techniques”) combined with on-line GC analysis of volatile reaction products (see Section “equipment 1” via the above-mentioned link), the **synthesis of methyl tert-butyl ether (MTBE) on zeolite H-Beta** has been investigated [1]. MTBE is used as a component in the fuel for gasoline engines, replacing tetraethyllead (TEL) as an antiknock (octane rating) additive to prevent engine knocking. It is one of a group of chemicals commonly known as oxygenates because they raise the oxygen content of gasoline. Furthermore, it is used in organic chemistry as a relatively inexpensive solvent with properties comparable to diethyl ether, but with a higher boiling point and less solubility in water. MTBE is manufactured via the chemical reaction of methanol and isobutene at temperatures of T = 313 to 363 K at Broensted acidic catalysts [2]:



Utilizing the **combined *in situ* solid-state NMR and on-line GC technique under continuous flow conditions**, the influence of the reaction temperature on the **reaction intermediates and/or deposites** on zeolite H-Beta, observed by *in situ* ^{13}C flow MAS NMR, and the **yield of MTBE** has been studied [1]. For this purpose, the equipment shown in Scheme 1 was utilized (see also Section “equipment 1” via link “*In Situ* Solid-State NMR Techniques” and Fig. 6 in Ref. [3]).



Scheme 1

At first, the **methanol up-take on dehydrated zeolite H-Beta** was determined simultaneously by *in situ* ^{1}H flow MAS NMR and by on-line GC analysis at the rotor outlet via the break-through curve. Nitrogen gas, connected at "gas 1" in Scheme 1, was loaded with methanol in the thermostated saturator. Subsequently, the methanol-loaded nitrogen gas was continuously injected into the spinning MAS rotor containing the dehydrated zeolite H-Beta during ^{1}H MAS NMR spectra were recorded. This quantitative adsorption experiment was carried out with a methanol pressure of p_{me} = 50.8 mbar and a carrier gas flow rate of 4.7 ml/min.

Fig. 1, left, shows the ^{1}H MAS NMR spectra of dehydrated zeolite H-Beta recorded before (t_{ad} = 0) and after (t_{ad} > 0) starting the methanol adsorption [1]. The spectrum of the unloaded zeolite H-Beta (t_{ad} = 0) consists of weak signals at δ_{1H} = 2.0 ppm and δ_{1H} = 4 to 5 ppm due to silanol groups and bridging OH groups (Si(OH)Al) [4, 5], respectively. With increasing methanol coverage, signals of methyl groups and hydroxyl protons contributing to adsorbate complexes occur at δ_{1H} = 3.6 ppm and δ_{1H} = 7 to 8 ppm [4], respectively. These signals increase until saturation is reached after an adsorption time of about 2 h.

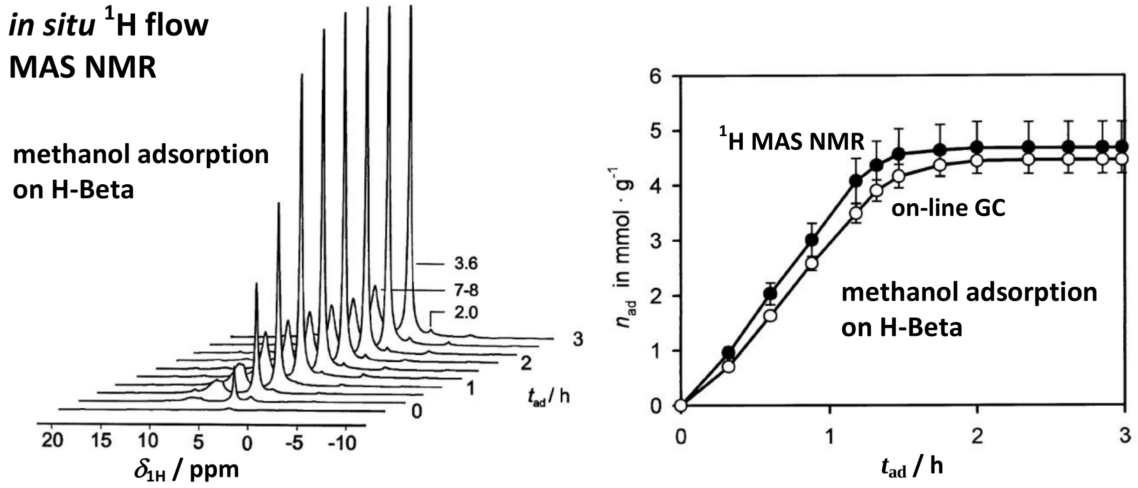


Fig. 1

The difference of the break-through curves of methanol molecules, determined by on-line GC analysis (see also Fig. 4a of Ref. [1]), for the empty MAS NMR rotor and the rotor filled with dehydrated zeolite H-Beta, led to the amounts of adsorbed methanol molecules plotted as the curve consisting of the open circles as function of adsorption time in Fig. 1, right. The curve described by the filled circles in Fig. 1, right, corresponds to the amounts of adsorbed methanol molecules, determined by quantitative evaluation of the *in situ* ^{1}H flow MAS NMR spectra in Fig. 1, left. Considering the experimental accuracies of *in situ* ^{1}H flow MAS NMR spectroscopy under flow conditions (±10%) and on-line gas chromatography, the **amounts of adsorbed methanol molecules determined by both methods agree well**.

The results of the **combined *in situ* ^{13}C flow MAS NMR and on-line GC studies of the MTBE synthesis** on zeolite H-Beta are shown in Fig. 2 [1]. For these experiments, a bottle with the reactant isobutene was connected at the gas inlet "gas 2" in Scheme 1, left. In Fig. 2, top, the isobutene conversion X_{ib}, the MTBE yield Y_{mtbe}, and the isobutene oligomer yield Y_{io}, determined by on-line GC analysis, are plotted as a function of time on stream. At the reaction temperature of T_{r} = 333 K, an isobutene conversion of X_{ib} = 29% and a MTBE yield of Y_{mtbe} = 27% were obtained in steady state. The decrease of X_{ib} and Y_{mtbe} after raising the reaction temperature to T_{r} = 353 K hints to a temperature-dependent limitation of the MTBE synthesis on zeolite H-Beta by the chemical equilibrium and a progressive catalyst deactivation by deposits.

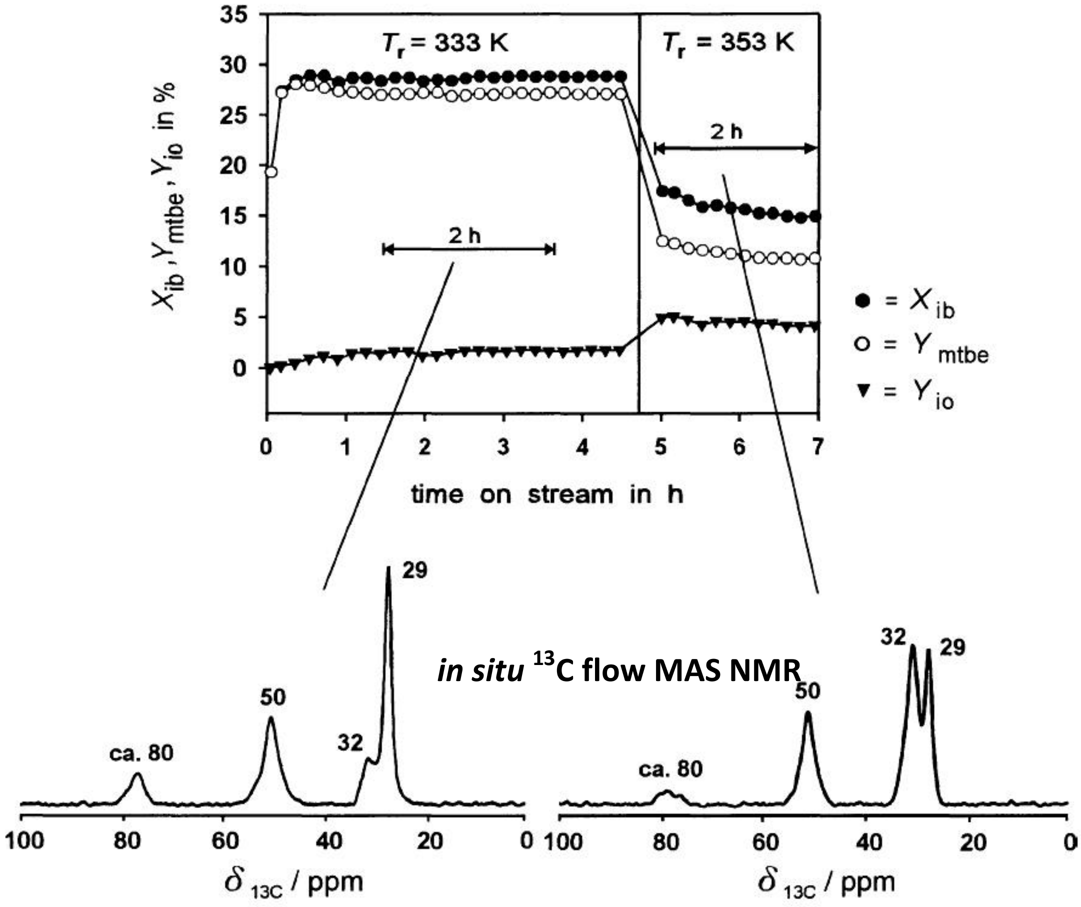


Fig. 2

The *in situ* ^{13}C flow MAS NMR spectra in Fig. 2, bottom, were recorded after reaching the steady state at T_r = 333 K (left) and 353 K (right), each in a time window of 2 h. Both spectra consist of signals at δ_{13C} = 29 ppm, 32 ppm, 50 ppm, and ca. 80 ppm. The signals at δ_{13C} = 32 ppm and 50 ppm are caused by methyl groups of isobutene oligomers and physisorbed methanol [6], respectively. The signal at δ_{13C} = 80 ppm is due to tertiary carbon atoms of isobutoxy species formed at the zeolite frame work [7, 8]. The methyl groups of these alkoxy species are responsible for the signal at δ_{13C} = 29 ppm [7, 8]. Since neither signals of isobutene (δ_{13C} = 22 ppm, 109 ppm, and 145 ppm [6, 9]) nor of MTBE (δ_{13C} = 26 ppm, 46 ppm, and 73 ppm [6, 9]) were observed in the *in situ* ^{13}C flow MAS NMR spectra in Fig. 2, bottom, the residence time of these molecules inside the MAS NMR rotor reactor must be short in comparison with their ^{13}C NMR spin-lattice relaxation times.

The ^{13}C MAS NMR spectrum recorded at T_r = 333 K (Fig. 2, bottom, left) shows a weak signal of methyl groups of isobutene oligomers at δ_{13C} = 32 ppm and a strong signal of methyl groups of isobutoxy species at δ_{13C} = 29 ppm, accompanied by the signal of tertiary carbon atoms of these species at δ_{13C} = 80 ppm. After raising the reaction temperature from T_r = 333 to 353 K (Fig. 2, bottom, right), the signal at δ_{13C} = 32 ppm increased significantly, which indicates a higher formation of isobutene oligomers at T_r = 353 K. This finding agrees well with the higher yield of isobutene oligomers found by on-line gas chromatography (Fig. 2, top, right). In addition, a significant decrease of the signals of isobutoxy species at δ_{13C} = 29 ppm and 80 ppm occurred. These observations indicate that **isobutoxy species play the role of intermediates on zeolite H-Beta, while isobutene oligomers could be the origin of permanent deposits** blocking micropores of this catalyst. Simultaneously with the increased reaction temperature from T_r = 333 to 353 K, the MTBE yield decreased from Y_{mtbe} = 27 to 11%.

Catalyst preparation: The zeolite H-Beta was synthesis and ion exchanged as described in Refs. [10] and [1], respectively. Before the use of this zeolite for *in situ* flow experiments, a dehydration was performed with the sample material in a glass tube connected with a vacuum line (see “sample tube system 1” and “vacuum line 1” via link “*In Situ* Solid-State NMR Techniques”). This treatment starts with an evacuation at room temperature for ca. 10 minutes followed by a temperature ramp from room temperature to T = 393 K within 2 hours. At this temperature, the sample is dehydrated for 2 hours. Subsequently, the temperature is increased up to T = 723 K within 3 hours and evacuated at this temperature for 12 hours. Finally, the sample tube system is closed via the vacuum valve and disconnected from „vacuum line 1“ after this line is ventilated with air. The transfer of the dehydrated sample into the MAS NMR rotor is performed without air contact, e.g., in a glove box purged with dry nitrogen gas (see Section “mini glove box” via link “*In Situ* Solid-State NMR Techniques”).

In situ studies: The *in situ* ^{1}H and ^{13}C flow MAS NMR experiments were performed utilizing a 7 mm Bruker MAS NMR probe modified as described in Section "flow probe 2”, accessible via link “*In Situ* Solid-State NMR Techniques”.

After purging the MAS NMR turbine with dry nitrogen, the hole in the rotor cap was opened and the injection and exhaust tubes are inserted into the MAS NMR rotor filled with the dehydrated zeolite H-Beta. The NMR investigations were performed at resonance frequencies of ν_0 = 400.1 MHz and 100.6 MHz for ^{1}H and ^{13}C nuclei, respectively, and with a sample spinning rate of ν_{rot} = 2.8 kHz. The *in situ* ^{13}C flow MAS NMR spectra were recorded after direct excitation with ^{1}H decoupling and with reactant molecules having natural ^{13}C-abundance. For each *in situ* ^{1}H and ^{13}C flow MAS NMR spectrum, 25 and 720 free induction decays, respectively, were accumulated with a repetition time of 10 s. The amounts of adsorbed molecules were determined by comparing their ^{1}H MAS NMR signal intensities with that of an external intensity standard (dehydrated zeolite H,Na-Y with an ion exchange degree of 35%).

The reaction products were on-line analysed by a gas chromatograph HP 5890 (Hewlett Packard) equipped with a DBWAX column (J&W Scientific), with a length of 30 m, and an inner diameter of 0.25 mm. The exhaust flow of the MAS NMR rotor reactor was sampled and analysed in steps of 4 min in the adsorption experiment and of 10 min during the catalytic experiments.

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