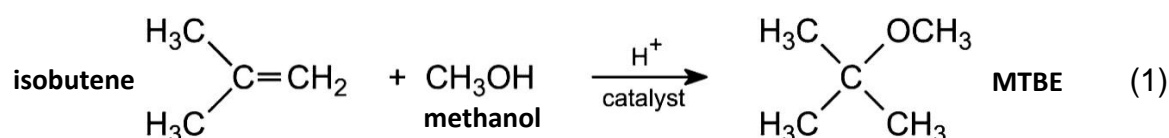
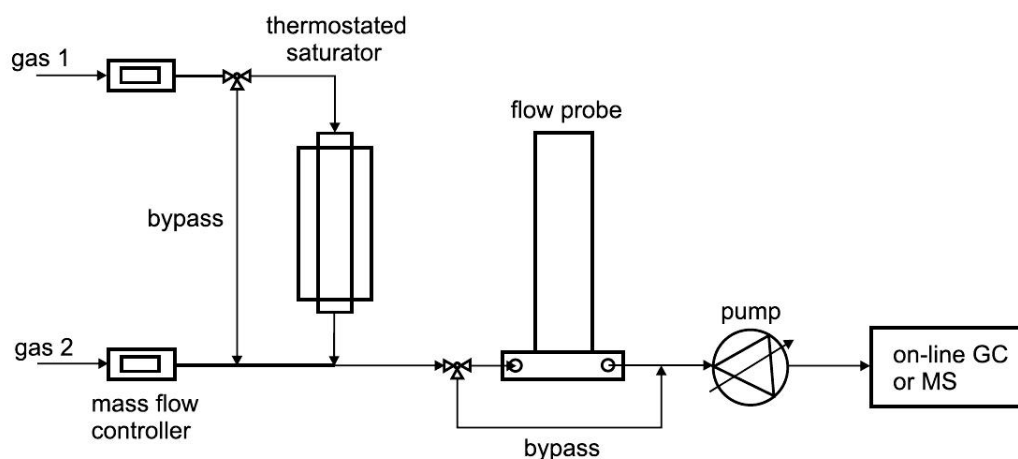


Combined *in situ* solid-state NMR and on-line GC studies of heterogeneously catalyzed reactions under continuous flow conditions

Spectroscopic background: For demonstrating *in situ* flow solid-state NMR spectroscopy (see Topic 5 of link “*In Situ* Solid-State NMR Techniques”) combined with on-line gas chromatographic (GC) analysis of volatile reaction products (see Section “equipment 1”, accessible 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 gasoline fuel of Otto engines, replacing tetraethyllead (TEL) as an additive to prevent engine knocking. It is one of the 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 Brønsted acidic catalysts [2]:



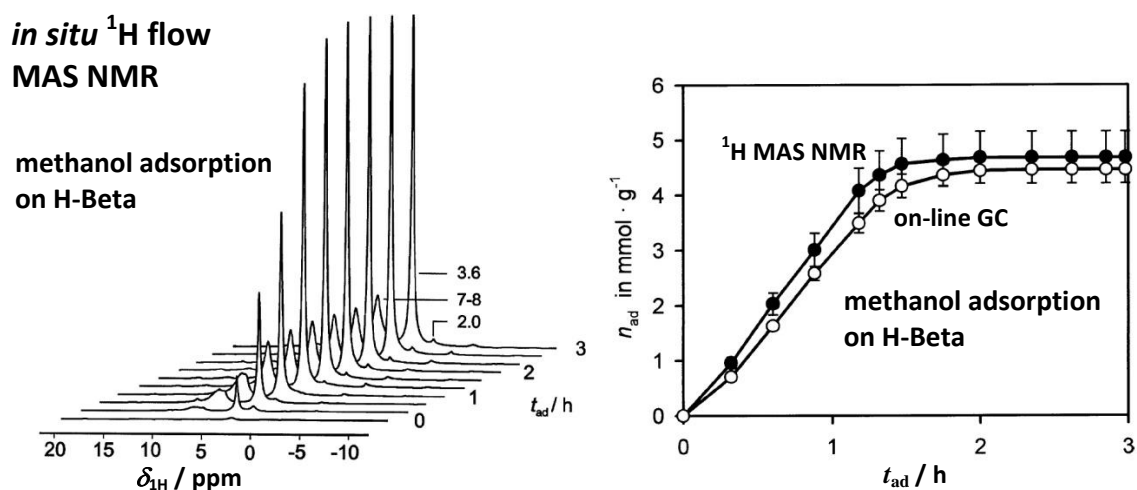
Utilizing the **combined *in situ* solid-state NMR and on-line GC technique under continuous flow conditions**, the influence of the reaction temperature on the **reaction intermediates and/or deposits** on zeolite H-Beta, observed by *in situ* ^{13}C flow MAS NMR, and the **yield of MTBE** has been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



Scheme 1

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

Fig. 1, left, shows the *in situ* ^1H MAS NMR spectra of dehydrated zeolite H-Beta, recorded before ($t_{\text{ad}} = 0$) and after ($t_{\text{ad}} > 0$) starting the methanol adsorption [1]. The spectrum of the unloaded zeolite H-Beta ($t_{\text{ad}} = 0$) consists of weak signals at $\delta_{1\text{H}} = 2.0$ ppm and $\delta_{1\text{H}} = 4$ 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 $\delta_{1\text{H}} = 3.6$ ppm and $\delta_{1\text{H}} = 7$ to 8 ppm [4], respectively. These signals increase until saturation is reached after an adsorption time of about 2 h.



The difference of the break-through curves of methanol molecules, determined by on-line GC analysis (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* ^1H flow MAS NMR spectra in **Fig. 1, left**. Considering the experimental accuracies of *in situ* ^1H flow MAS NMR spectroscopy under flow conditions ($\pm 10\%$) and on-line GC analysis, 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, additionally, an isobutene bottle was connected at the 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 $T_r = 333\text{ K}$, an isobutene conversion of $X_{\text{ib}} = 29\%$ and a MTBE yield of $Y_{\text{mtbe}} = 27\%$ were obtained in the steady state. The decrease of X_{ib} and Y_{mtbe} after raising the reaction temperature to $T_r = 353\text{ K}$ 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.

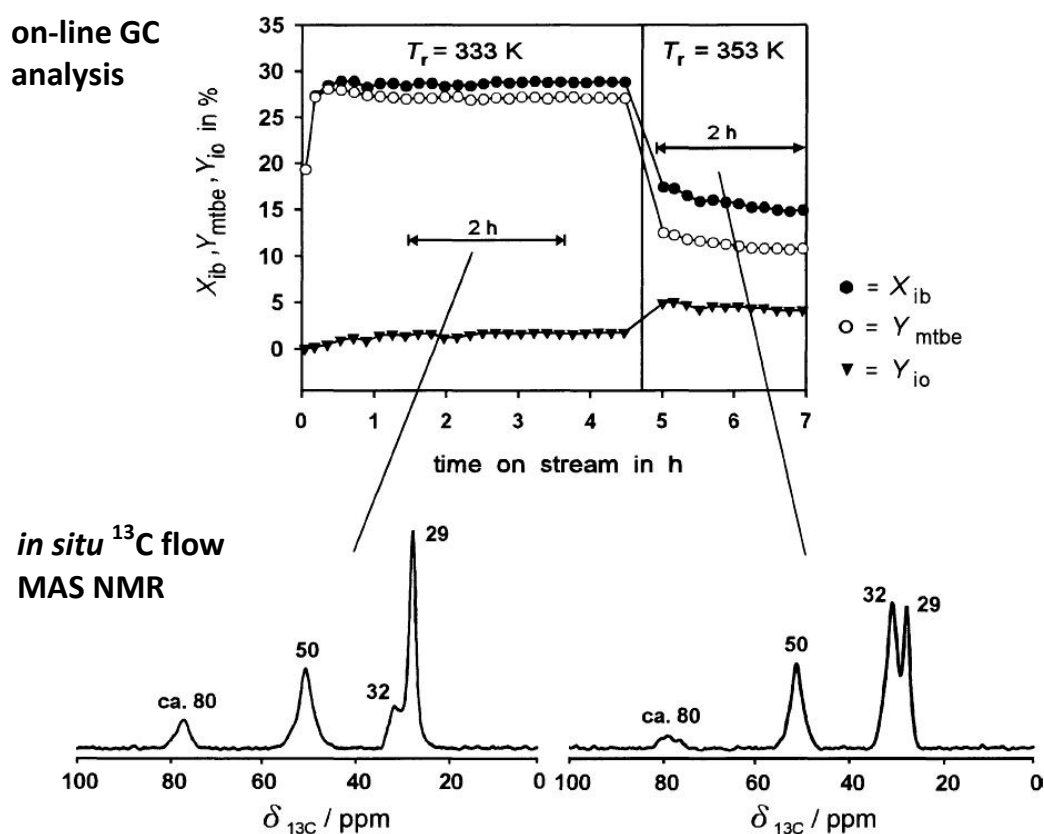


Fig. 2

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 $\delta_{13\text{C}} = 29$ ppm, 32 ppm, 50 ppm, and ca. 80 ppm. The signals at $\delta_{13\text{C}} = 32$ ppm and 50 ppm are caused by methyl groups of isobutene oligomers and physisorbed methanol [6], respectively. The signal at $\delta_{13\text{C}} = 80$ ppm is due to tertiary carbon atoms of isobutoxy species formed at Brønsted acid sites of the zeolite [7, 8]. The methyl groups of these alkoxy species are responsible for the signal at $\delta_{13\text{C}} = 29$ ppm [7, 8]. Since neither signals of isobutene ($\delta_{13\text{C}} = 22$ ppm, 109 ppm, and 145 ppm [6, 9]) nor of MTBE ($\delta_{13\text{C}} = 26$ 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 [1].

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 $\delta_{13\text{C}} = 32$ ppm and a strong signal of methyl groups of isobutoxy species at $\delta_{13\text{C}} = 29$ ppm, accompanied by the signal of tertiary carbon atoms of these species at $\delta_{13\text{C}} = 80$ ppm. After raising the reaction temperature from $T_r = 333$ to 353 K (**Fig. 2, bottom, right**), the signal at $\delta_{13\text{C}} = 32$ 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 GC analysis (**Fig. 2, top, right**). In addition, a significant decrease of the signals of isobutoxy species at $\delta_{13\text{C}} = 29$ ppm and 80 ppm occurred. These observations indicate that **isobutoxy species play the role of intermediates in the synthesis of MTBE on zeolite H-Beta, while isobutene oligomers are the origin of coke deposits** blocking micropores of this catalyst.

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 “sample tube system” at “vacuum line 1” (see Sections “sample tube system 1” and “vacuum line 1”, accessible 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 was dehydrated for 2 hours. Subsequently, the temperature

was increased up to $T = 723$ K within 3 hours and evacuated at this temperature for 12 hours. Finally, the sample tube system was 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 was performed without air contact in a mini glove box (see Section “mini glove box”, accessible via link “*In Situ* Solid-State NMR Techniques”), purged with dry nitrogen gas. Subsequently, the MAS rotor was closed with a rotor cap containing a hole in the center.

***In situ* studies:** The *in situ* ^1H 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”.

During purging the MAS NMR turbine with dry nitrogen, the hole in the rotor cap was opened and the injection and exhaust tubes were inserted into the MAS NMR rotor filled with the dehydrated zeolite H-Beta. The NMR investigations were performed at a Bruker MSL 400WB spectrometer with resonance frequencies of $\nu_0 = 400.1$ MHz and 100.6 MHz for ^1H and ^{13}C nuclei, respectively, and with a sample spinning rate of $\nu_{\text{rot}} = 2.8$ kHz. The *in situ* ^{13}C flow MAS NMR spectra were recorded after direct excitation, with ^1H decoupling, and with reactant molecules having natural ^{13}C -abundance. For each *in situ* ^1H 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 ^1H MAS NMR signal intensities with that of an external intensity standard (dehydrated zeolite H,Na-Y with an ion exchange degree of 35%) at the same temperature like used in the *in situ* MAS NMR experiments.

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.

References:

- [1] M. Hunger, M. Seiler, T. Horvath, *A technique for simultaneous in situ MAS NMR and on-line gas chromatographic studies of hydrocarbon conversions on solid catalysts under flow conditions*, Catal. Lett. 57 (1999) 199-204, DOI:

- [10.1023/A:1019064003201](https://doi.org/10.1023/A:1019064003201).
- [2] B. Schleppinghoff, M. Becker, [patent EP0082316B1](https://patent.google.com/patent/EP0082316B1), *Process for the production of methyl tert-butyl ether (MTBE) and of hydrocarbon raffinates extensively delivered from i-butene and methanol and apparatus thereto*, 03.07.1985, EC Erdoelchemie GmbH, Germany.
 - [3] M. Hunger, *In situ flow MAS NMR spectroscopy: State of the art and applications in heterogeneous catalysis*, Prog. Nucl. Magn. Reson. Spectrosc. 53 (2008) 105-127, DOI: [10.1016/j.pnmrs.2007.08.001](https://doi.org/10.1016/j.pnmrs.2007.08.001)
 - [4] M. Hunger, T. Horvath, *Sorption of methanol on zeolite HBeta investigated by in situ MAS NMR spectroscopy*, Catal. Lett. 49 (1997) 95-100, DOI: [10.1023/A:1019028532141](https://doi.org/10.1023/A:1019028532141).
 - [5] L.W. Beck, J.F. Haw, *Multinuclear NMR studies reveal a complex acid function for zeolite Beta*, J. Phys. Chem. 99 (1995) 1076-1079, DOI: [10.1021/j100004a004](https://doi.org/10.1021/j100004a004).
 - [6] M. Hunger, T. Horvath, J. Weitkamp, *Methyl tertiary-butyl ether synthesis on zeolite HBeta investigated by in situ MAS NMR spectroscopy under continuous-flow conditions*, Microporous Mesoporous Mater. 22 (1998) 357-367, DOI: [10.1016/S1387-1811\(98\)00078-X](https://doi.org/10.1016/S1387-1811(98)00078-X).
 - [7] M.T. Aronson, R.J. Gorte, W.E. Farneth, D. White, *Carbon-13 NMR identification of intermediates formed by 2-methyl-2-propanol adsorption in H-ZSM-5*, J. Am. Chem. Soc. 111 (1989) 840-846, DOI: [10.1021/ja00185a009](https://doi.org/10.1021/ja00185a009).
 - [8] A.G. Stepanov, K. Zamaraev, J.M. Thomas, *¹³C CP/MAS and ¹H NMR study of tert-butyl alcohol dehydration on H-ZSM-5 zeolite. Evidence for the formation of tert-butyl cation and tert-butyl silyl ether intermediates*, Catal. Lett. 13 (1992) 407-422, DOI: [10.1007/BF00765044](https://doi.org/10.1007/BF00765044).
 - [9] H.-O. Kalinowski, S. Berger, S. Braun, p. 115 and 164, *¹³C-NMR-Spektroskopie*, Georg Thieme Verlag, Stuttgart, 1984, ISBN: [3-13-632801-0](https://doi.org/3-13-632801-0).
 - [10] J. Perez-Pariente, J.A. Martens, P.A. Jacobs, *Crystallization mechanism of zeolite beta from (TEA)₂O, Na₂O and K₂O containing aluminosilicate gels*, Appl. Catal. 31 (1987) 35-64, DOI: [10.1016/S0166-9834\(00\)80665-X](https://doi.org/10.1016/S0166-9834(00)80665-X).