

Temperature-Jump Relaxation Magic-Angle Spinning NMR Study of the Methyl *tert*-Butyl Ether Reaction in a Boron Pentasil Zeolite

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Abstract: Temperature-jump relaxation magic-angle spinning NMR experiments are for the first time applied to study a heterogeneously catalyzed reaction. A temperature jump from 20 to 100–150 °C creates a nonequilibrium state of the system consisting of methyl *tert*-butyl ether (MTBE), methanol, and isobutene, which are adsorbed on a boron pentasil zeolite in a sealed glass tube. The rate constants of MTBE decomposition and formation were determined, and the corresponding apparent energies of activation are 51 and 32 kJ mol⁻¹, respectively. The NMR findings are in agreement with experimental results obtained in a fixed bed reactor or in an autoclave.

Introduction

In situ observation has become the most important method in spectroscopic studies of heterogeneously catalyzed reactions.¹ Also the equipment for the *in situ* magic-angle spinning nuclear magnetic resonance (MAS NMR) technique has been developed very rapidly. In contrast to conventional bearing gas heating, laser heating^{2–5} and inductive heating⁴ can abruptly change the temperature of the sample. A temperature or feed switch is necessary to observe the time dependence of reactions which take place within about 10 s. *In situ* MAS NMR studies can be performed in open gas flow rotors^{6,7} or in sealed samples.^{2–5} The former method is more equivalent to a gas flow reactor than the use of sealed samples, but it needs a pulsed feed, in order to observe the time dependence of fast reactions, which until now has not been realized.

The design of the laser-heated MAS NMR probe, e.g., the point of impact of the laser beam on the rotor and the heat conductivity of the rotor materials used, has a great influence on temperature gradients, the maximum temperature, and the heating rate. The Bruker laser probe with the sample under study in a sealed glass tube inside the boron nitride (BN) ceramic container gives a maximum temperature of 530 °C, a maximum deviation from the mean Celsius temperature of ±10%, and a maximum heating rate of 20 K s⁻¹.⁵

The *stop-and-go* technique was introduced in ref 5, in order to monitor the time development of irreversible reactions at high temperatures during the *go* period by means of ¹H MAS NMR. The ¹³C MAS NMR spectrum of the reaction state after the *go*

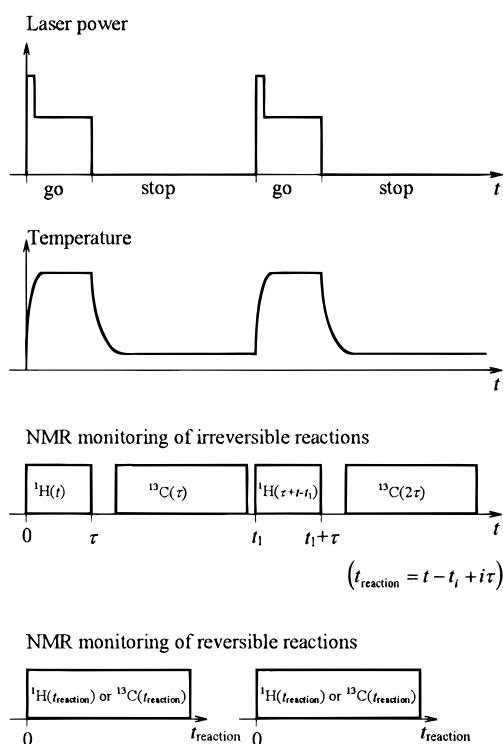


Figure 1. Schematic representation of laser power, sample temperature, and NMR acquisition during two stop-and-go cycles.

period is acquired at room temperature during the *stop* period; cf. Figure 1. The only purpose of stop-and-go cycles in this study is the improvement of the signal-to-noise ratio. Multiple scans of the free induction decay (FID) were commonly used for pulse NMR experiments. First, accumulation increases the signal-to-noise ratio. Second, phase-cycled scans are necessary for averaging some electronic effects and for the application of most pulse sequences. If the state of the system is changing too fast for the acquisition of multiple scans, which characterize only one time-dependent state of the reaction, the accumulation and phase cycling can be realized by multiple repetition of the heating-cooling cycle, provided a reversible system is considered. This will be shown in this paper.

Methyl *tert*-butyl ether (MTBE) has become heavily utilized

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(1) Haw, J. *In situ* NMR. In *NMR Techniques in Catalysis*; Bell, A. T., Pines, A., Eds.; Marcel Dekker: New York, 1994; p 139.

(2) Ernst, H.; Freude, D.; Mildner, T. *Chem. Phys. Lett.* **1994**, 229, 291–296.

(3) Ferguson, D. B.; Krawietz, T. R.; Haw, J. F. *J. Magn. Reson.*, **A** **1994**, 109, 273–275.

(4) Ferguson, D. B.; Haw, J. F. *Anal. Chem.* **1995**, 67, 3342–3348.

(5) Ernst, H.; Freude, D.; Mildner, T.; Wolf, I. *Solid State NMR* **1996**, 6, 147–156.

(6) Hunger, M.; Horvath, T. *J. Chem. Soc., Chem. Commun.* **1995**, 1423–1424.

(7) Goguen, P.; Haw, J. F. *J. Catal.* **1996**, 161, 870–872.

as an octane number boosting additive for gasolines. Zeolites H-Y,^{8–10} H-ZSM-5,^{9,10} and H-BZSM-5¹¹ are known to be suitable for the MTBE synthesis. An overview for this kind of reaction is given in ref 11. In the present study a boron pentasil zeolite is used, in which a reversible reaction of MTBE takes place during several heating cycles. The details of MTBE formation in zeolites are still not well understood, though some facts seem to be clear: H-ZSM-5 is very suitable for the high-temperature formation of MTBE because of its excellent selectivity toward MTBE.¹⁰ The efficient methanol adsorption decreases the probability of oligomerization by effectively competing for the acid sites.^{8,9} The present paper is devoted to the study of the dynamics under nonequilibrium conditions, because the adsorption/desorption behavior of the reactants strongly influences the process.

Experimental Section

Materials and Samples. The synthesis of the boron pentasil zeolite was described in ref 12. The zeolite ($\text{SiO}_2/\text{B}_2\text{O}_3 = 40$) was pretreated by heating 8 mm deep layers of zeolite in thin glass tubes with 3 mm outer diameter at a rate of 10 K h^{-1} under vacuum. After the samples were maintained at $400 \text{ }^\circ\text{C}$ and at a pressure of less than 10^{-2} Pa for 24 h, they were loaded at room temperature with 8–16 molecules of MTBE per unit cell. A 1:1 mixture of isobutene (IB) and methanol ^{13}C enriched or deuterated was loaded onto the zeolite for the ^{13}C NMR experiments or for the improvement of the resolution of the ^1H NMR experiments, respectively. Special care was taken, in order to prove the reversibility of the temperature-jump relaxation experiments:¹³ 10 temperature cycles precede each NMR experiment. Weak changes of intensities take place during the first two temperature cycles.

NMR Spectroscopy. The resonance frequencies of the Bruker MSL spectrometer were 300 and 75.4 MHz for ^1H and ^{13}C , respectively. The spinning rate of the samples in the laser-heated high-temperature MAS probehead is 1–3 kHz.

The heating was performed by a CO_2 laser with a maximum power of 50 W (wavelength $10.6 \pm 0.1 \mu\text{m}$). The 3 mm glass ampule was located in a BN container inside the rotor. A more detailed description of the experimental setup is given in ref 5. The temperature in the sample could be measured using a ^{207}Pb (lead nitrate) chemical shift thermometer.^{4–5,14–16} The maximum deviation from the mean temperature in the sample is $\pm 10 \text{ K}$ at $120 \text{ }^\circ\text{C}$. The lead nitrate chemical shift thermometer requires a relatively long measuring time, which makes it less suitable for dynamic temperature measurements; therefore, a ^1H thermometer (hydrated H-ZSM-5 zeolite in a fused glass ampule) was used. The temperature dependence of the ^1H MAS signal was calibrated in the relevant temperature range by means of the lead nitrate chemical shift thermometer. Figure 2 shows on the left-hand side the calibration of the ^1H chemical shift thermometer, i.e., the temperature dependence of the chemical shift of the hydrated H-ZSM-5 zeolite. On the right-hand side of the figure, the chemical shift in a dynamic experiment with a final temperature of $140 \text{ }^\circ\text{C}$ is shown. At the beginning of the measurement the maximum laser power is used for 5 s, and it is then reduced to an appropriate value. It can be seen in

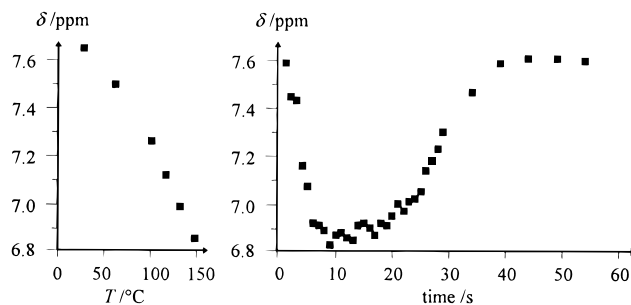


Figure 2. ^1H MAS NMR measurements on a sample containing hydrated H-ZSM-5 zeolite. Left: dependence of the chemical shift on the static temperature. Right: dynamic experiment using a 20 s laser pulse.

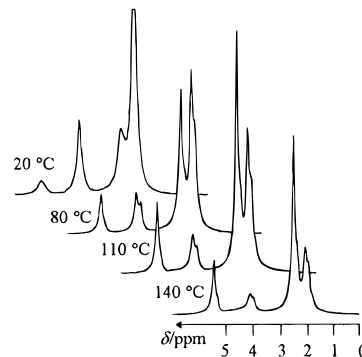


Figure 3. ^1H MAS NMR spectra of the boron pentasil zeolite loaded with 8 ± 2 MTBE molecules per unit cell.

Figure 2 that the final temperature is reached after 6 s and remains constant until the laser is switched off after 20 s. One computer controls the start of both the laser heater and the NMR acquisition.

Results and Discussion

Figure 3 shows the temperature dependent ^1H MAS NMR spectra of the MTBE/zeolite system at room temperature (before heating), at $80 \text{ }^\circ\text{C}$, at $110 \text{ }^\circ\text{C}$, and at $140 \text{ }^\circ\text{C}$. These spectra were measured in thermal equilibrium after keeping the samples for more than 10 min at the given temperature. The spectra consist of four lines due to CH_2 groups of isobutene (4.8 ppm), $-\text{OCH}_3$ groups of MTBE (3.4 ppm), *tert*-butyl CH_3 groups of MTBE (1.4 ppm), and CH_3 groups of isobutene (1.8–2.3 ppm). The CH_3OH signals could not be observed at spinning frequencies of 1–3 kHz. This is not surprising, since for adsorbed methanol^{8,9} the correlation time of the motion can be on the order of magnitude of a rotation period, which causes a drastic broadening of the MAS NMR signal.¹⁷ The change of equilibrium concentrations upon increasing temperature, cf. Figure 3, shows an increasing IB concentration. This is in agreement with thermal equilibrium values calculated,^{10,18} which tend toward IB and methanol, when the temperature increases. At room temperature a concentration ratio of MTBE to IB of 3:2 in the sealed sample has been obtained; cf. Figure 3 (top).

In order to determine the mole fraction of one species from the relative intensity of the corresponding signal in the spectrum, the total intensity of all signals must be constant, except a weak change due to the Curie factor. Unfortunately, if the sample is heated to $140 \text{ }^\circ\text{C}$ or higher for a longer time, a significant loss of signal intensity is observed. This can be explained by some immobile byproducts, most probably oligomers of isobutene such as the isomers of octene. These can be formed in the

(8) Kogelbauer, A.; Goodwin, J. G., Jr.; Lercher, J. A. *J. Phys. Chem.* **1995**, *99*, 8777–8781.

(9) Kogelbauer, A.; Nikolopoulos, A. A.; Goodwin, J. G., Jr.; Marcelin, G. *J. Catal.* **1995**, *152*, 122–129.

(10) Nikolopoulos, A. A.; Oukaci, R.; Goodwin, J. G., Jr.; Marcelin, G. *Catal. Lett.* **1994**, *27*, 149–157.

(11) Hölderich, W. F. In Proceedings of TOCAT 1, Tokyo, Japan; Yoshida, S., et al., Eds.; 1990; *Catalytic Science and Technology*, Kodancho Ltd., 1991; Vol. 1, pp 31–46.

(12) Hölderich, W. F.; Götz, N.; Hupfer, L., BASF AG. DE 3722891 = US-PS 4891451, July 10, 1987.

(13) Atkins, P. W. *Physical Chemistry*, 4th ed.; Oxford University Press: Oxford, 1990.

(14) Mildner, T.; Ernst, H.; Freude, D. *Solid State NMR* **1995**, *5*, 269–271.

(15) Bielecki, A.; Burum, D. P. *J. Magn. Reson., A* **1995**, *116*, 215–220.

(16) Van Gorkom, L. C. M.; Hook, J. M.; Logan, M. B.; Hanna, J. V.; Wasylishen, R. E. *Magn. Reson. Chem.* **1995**, *33*, 791–795.

(17) Fenzke, D.; Gerstein, B. C.; Pfeifer, H. *J. Magn. Reson.* **1992**, *98*, 469–474.

(18) Tejero, J.; Cunill, F.; Izquierdo, J. F. *Ind. Eng. Chem. Res.* **1988**, *27*, 338–343.

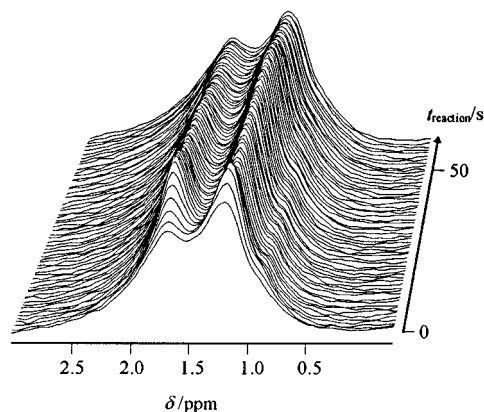


Figure 4. Stack plot of ^1H MAS NMR spectra of the zeolite loaded with 16 ± 4 molecules of isobutene and 16 ± 4 molecules of deuterated methanol per unit cell.

sealed samples. In this case, the total signal intensity decreases due to very broad signals, which are nonvisible in our spectra; cf. Figure 3 (bottom). This effect can be avoided by limiting the laser pulse length. E.g., after a period consisting of 32 laser pulses with a duration of 20 s for each and a maximum temperature of 150 °C, no loss in the total intensity was observed.

The temperature jump creates a nonequilibrium, and a change of the state toward equilibrium can be observed. The recording of one complete heating and cooling cycle by means of several scans (FIDs) equidistant in time is denoted as one transient scan. Figure 4 shows the time-resolved ^1H MAS NMR spectra of an experiment at 116 °C. A total of 32 transient scans have been accumulated along with the NMR phase cycle "cyclops". During one transient scan, 60 FIDs were recorded with a repetition time of 1 s. The final temperature in the sample is reached after ca. 5 s. Identical laser pulses of 32 s duration were applied for each transient scan followed by 5 min relaxation of the system at room temperature. The difference between the relative concentrations of MTBE and IB at room temperature as shown in Figures 3 and 4 is due to the pressure dependent value of the equilibrium constant and the different loading of the samples.

A 1:1 mixture of IB and deuterated (99%) methanol was used for the measurements of the concentration–time dependencies. This reduces the ^1H – ^1H intermolecular dipolar interactions, and the $-\text{OCH}_3$ signal of MTBE at 3.4 ppm vanishes. It turned out that the time dependencies of the concentrations of all observed signals are not influenced by the initial deuteration of methanol.

The spectrum between 1.0 and 2.5 ppm is sufficient for the observation of the reactions, but a fitting procedure of the line shape in the CH_3 region is necessary, in order to obtain the intensities of the individual signals. Figure 5 shows as an example the ^1H MAS NMR spectrum of the CH_3 groups after 4 s, the fit obtained, and a deconvolution. The latter is presented in order to demonstrate that, besides the clearly resolved signal of the *tert*-butyl CH_3 groups of MTBE at 1.4 ppm, the signal of the CH_3 groups of IB consists of two lines at 1.8 and 2.3 ppm, which will be denoted as components 1 and 2, respectively. The value of the chemical shift of isobutene CH_3 groups without intermolecular interaction can be taken from the literature as 1.7 ppm.¹⁹ Therefore, component 2 seems to be more strongly adsorbed than component 1. However, a resonance shift due to a chemical exchange between CH_2 and CH_3 groups cannot

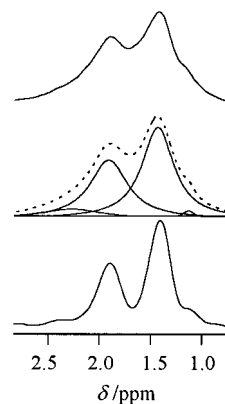


Figure 5. ^1H MAS NMR spectrum ($t_{\text{reaction}} = 4$ s) of a zeolite loaded with 16 ± 4 molecules of isobutene and 16 ± 4 molecules of deuterated methanol per unit cell (top), the separation into 4 lines and the dashed sum of the 4 lines (middle), and a deconvolution by artificial prolongation of the FID (bottom).

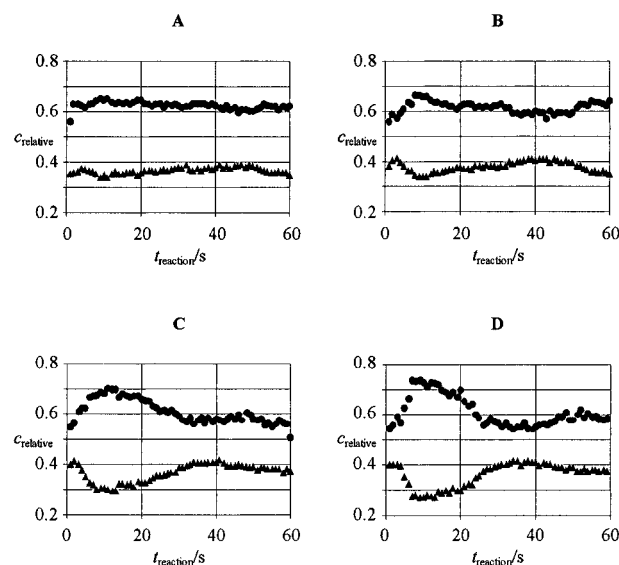


Figure 6. Time dependent concentrations of MTBE (triangles) and isobutene (circles) in experiments with final temperatures of 100 °C (A), 116 °C (B), 132 °C (C), and 148 °C (D). The corresponding laser pulse lengths are 40, 32, 25, and 20 s, respectively.

be excluded. For further considerations we do not distinguish between the two components. The weak signal at 1.1 ppm remains unchanged in time. It can be explained by an ether species, which is unable to react. The complete time dependence of the concentrations of MTBE and IB monitored in four experiments (A–D) with final temperatures of 100, 116, 132, and 148 °C adjusted by appropriate laser power are given in Figure 6. The laser pulse lengths of the experiments A–D were shortened from 40 to 32 to 25 to 20 s, respectively, in order to avoid side reactions. The corresponding durations for cooling the sample (cf. Figure 2) were 12, 15, 20, and 27 s, respectively.

The relative concentrations of MTBE and IB are adjusted to 1 only at the time $t = 10$ s. Therefore, the values for $t \neq 10$ s do not necessarily complement each other to 1 for two reasons: the inaccuracy of the experimental values obtained and the time dependence of the intensities, which may occur by the reversible formation and decomposition of NMR-invisible species. The relatively slight deviation of the sums for $t \neq 10$ s shows the limited influence of both effects.

The change of concentrations upon time, see Figure 6, is discussed for $t > 3$ s, since the total intensity of all spinning center bands is slightly increasing during the first 3 s due to an intensity flow from the spinning sidebands. The concentration

(19) Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der organischen Chemie*; Georg Thieme Verlag: Stuttgart, NY, 1987; p 172.

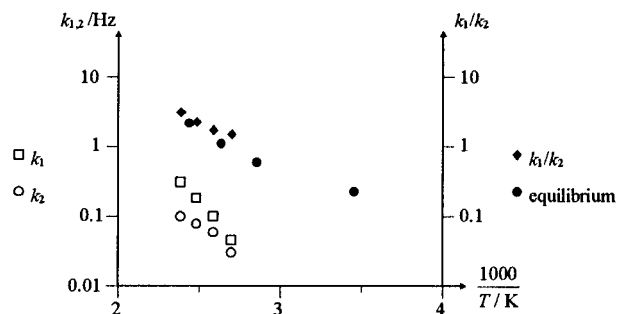


Figure 7. Arrhenius plot of the reaction rates k_1 (open squares) and k_2 (open circles) for the reaction of MTBE to IB plus methanol and the reverse reaction, respectively. The full diamonds correspond to the ratio k_1/k_2 . The values represented by the full circles were obtained independently by evaluation of the concentrations in the chemical equilibrium.

of MTBE decreases within about 10 s to a minimum. The consecutive slight increase during the heating period is due to nonequilibrium effects, which are mainly caused by a temperature exchange during the reaction. If the period is prolonged to about 1 min, the system has reached its equilibrium state at the given temperature. A similar behavior can be observed during the cooling period: A maximum occurs due to nonequilibrium effects. At the end of the time scale in Figure 6 the system goes back to the room temperature state.

The reaction of MTBE to isobutene and methanol can be described by the equation



Figure 7 shows the Arrhenius plot of the decomposition rate k_1 and the formation rate k_2 of MTBE. The mole fractions obtained in the time interval $4 \text{ s} \leq t_{\text{reaction}} \leq 10 \text{ s}$ were used for the fit with solutions of eq 5.

We start with the kinetic equation for the concentrations c :

$$\frac{dc_{\text{MTBE}}}{dt} = -k_1 c_{\text{MTBE}} + k_2^* c_{\text{IB}} c_{\text{MeOH}} \quad (2)$$

Provided, that in the system under study no byproducts were formed, for any time the concentrations of methanol and IB are equal and the sum of the concentrations of MTBE and IB remains constant. That means

$$c_{\text{IB}} = c_{\text{MeOH}} \quad \text{and} \quad c_{\text{MTBE}} + c_{\text{IB}} = c_0 \quad (3)$$

From eq 2 one obtains with the mole fraction $x = c_{\text{MTBE}}/c_0$

$$\dot{x} = -k_1 x(t) + k_2 (1 - x(t))^2 \quad \text{with} \quad k_2 = k_2^* c_0 \quad (4)$$

The value of k_2 depends on the loading of the sample, but not on the time dependent concentrations. The solution is given by

$$x(t) - x_\infty = \frac{au}{u - (u - a) \exp(ak_2 t)} \quad (5)$$

$$u = x_0 - x_\infty, \quad a = \frac{k_1 \left[1 + \frac{4k_2}{k_1} \right]^{1/2}}{k_2},$$

$$x_\infty = 1 + \frac{k_1}{2k_2} \left(1 - \left[1 + \frac{4k_2}{k_1} \right]^{1/2} \right)$$

The value of x_0 denoted the start value after the heating period. The value of x at $t = 10 \text{ s}$ was used as an approximation for

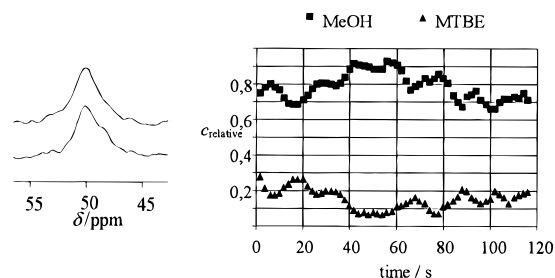


Figure 8. ^{13}C MAS NMR data of a boron pentasil zeolite loaded with 16 ± 4 molecules of isobutene and 16 ± 4 molecules of ^{13}C -enriched methanol per unit cell. The final temperature, which was reached after about 5 s, is $116 \text{ }^\circ\text{C}$. The duration of the laser pulse was 50 s. Left: as an example two proton-decoupled spectra for $t_{\text{reaction}} = 16 \text{ s}$ (bottom) and 44 s (top). Right: time dependent relative concentrations of MTBE (triangles) and methanol (squares) for the same experiment.

the equilibrium value x_∞ . This approach is similar to the temperature-jump relaxation method described in ref 13.

The apparent energies of activation of the values $k_1(T)$ and $k_2(T)$ are $51 \pm 5 \text{ kJ mol}^{-1}$ and $32 \pm 3 \text{ kJ mol}^{-1}$, respectively. The values of energy were denoted as apparent energies, since this MAS NMR experiment concerns a closed system, which is neither an isotherm nor an isobar system. The temperature and pressure in the sealed sample even change after the temperature jump due to processes like sorption and reaction. The temperature in the sample obviously changes, if the heat of reaction cannot be carried off fast enough. The observed change from decomposition to formation of MTBE during the heating (or cooling) period can be explained in this way.

Figure 7 also gives ratios $k_1(T)/k_2(T)$. The ratio denoted by diamonds was obtained from the values of k_1 and k_2 in the figure, whereas the full circles were derived from the equilibrium concentrations, which are taken from Figure 3. The similarity of nonequilibrium values (diamonds) and equilibrium values (full circles) shows that the experimental value which is used for x_∞ allows a good modeling.

After loading of IB and ^{13}C -enriched methanol in a ratio of 1:1, the same ^1H MAS NMR spectra as in Figure 3 (top) could be observed. The $-\text{OCH}_3$ signal of MTBE at 3.4 ppm splits due to the $^{13}\text{C}-^1\text{H}$ coupling. This is a further confirmation that the MTBE formation and decomposition upon decreasing and increasing temperature, respectively, does not depend on the starting state, generated by loading either MTBE or IB/methanol. The system depends only on its temperature and pressure.

This finding is in good agreement with experimental results obtained in a fixed bed reactor and in an autoclave. Using, e.g., a weakly acidic boron pentasil zeolite at about $100 \text{ }^\circ\text{C}$ and 30 bar, MTBE is formed from IB and methanol in 90% yield.²⁰ A side product could be bisisobutene. However, this can be suppressed by lowering the temperature below $70 \text{ }^\circ\text{C}$,²¹ resulting in selectivities for MTBE up to 95%. Such an experiment could be carried out either in an autoclave batchwise or in a tube reactor under a continuous stream.

On the other hand, at higher temperatures such as $200 \text{ }^\circ\text{C}$, MTBE as the starting material is cleaved over potassium containing boron pentasil zeolite to IB with 99.9% selectivity and to methanol with 99.8% selectivity at a conversion of 15%. If the temperature is raised to $315 \text{ }^\circ\text{C}$, the conversion can be increased to approximately 100% without any drop in selectivity.

The ^{13}C MAS NMR spectrum (cf. Figure 8, bottom) consists of the $-\text{OCH}_3$ groups of MTBE and methanol at 48 and 50.5

(20) Klotz, M. R.; Amoco Corp. US 4.584.415, April 22, 1989.

(21) Daniels, J. A.; Steward, A., ICI Comp. EP 55.045, Dec 19, 1986.

ppm, respectively. Taking into consideration that only methanol but not IB has been enriched in ^{13}C , it can be concluded that the carbon nuclei of the methanol molecules do not distribute over all possible carbon positions of MTBE or IB. The fact that only the $-\text{OCH}_3$ group of MTBE is affected by the initially enriched methanol molecules gives evidence that this O–C bond is never cracked during the reaction.

The same conclusion can be obtained if the 1:1 mixture of IB and 99% deuterated methanol is considered. The $-\text{OCH}_3$ signal of MTBE at 3.4 ppm cannot be observed in the spectra at room temperature and at higher temperatures as well. Only one deuteron coming from the $-\text{OD}$ group can distribute over the other positions in IB and MTBE (*tert*-butyl group). Therefore, from the location of the labeled nuclei, it can be concluded that during the reaction the entire $-\text{OCH}_3$ group is transferred from MTBE to methanol and back.

Proton-decoupled ^{13}C MAS NMR spectra of the zeolite loaded with IB and ^{13}C -enriched methanol in an experiment of 50 s at 116 °C are given on the left-hand side in Figure 8. Labeled IB was not available. A total of 400 transient scans with a 5 min delay have been accumulated. The difference between the chemical shifts of the $-\text{OCH}_3$ groups of MTBE and methanol observed at 48 and 50.5 ppm, respectively, is sufficient for a discrimination and a line fit for the two compounds. The concentration-time dependence for methanol and MTBE is presented on the right-hand side of Figure 8. The change from decomposition to formation of MTBE during the heating (or cooling) period is more pronounced compared to Figure 6. For ^{13}C or ^1H MAS NMR experiments we used methanol enriched in ^{13}C or ^2H , respectively. Therefore, small deviations in the loading can occur. Also a different void volume in the small glass ampules can change the conditions in the batch reactor. It should be noted that, for these spectra, which monitor for the first time the evolution of a system by ^{13}C MAS NMR in steps of 2 s, the total measuring time was about 40 h.

Conclusions

Temperature-switched MAS NMR offers the possibility to study molecules in zeolites under nonequilibrium conditions. This allows the introduction of the “temperature-jump relaxation” technique, which is well-known in the field of homogeneous reactions, into the field of heterogeneous catalysis.

For reversible reactions, like the MTBE formation/decomposition in a zeolite, the response of the system to a temperature pulse can be recorded by a number of FIDs, equidistant in time. A multiple of these transient scans is combined with NMR phase cycles and accumulated. This offers the possibility of obtaining time-resolved MAS NMR spectra of sufficient signal-to-noise ratio for both ^1H and ^{13}C NMR.

The concentration of MTBE does not approach monotonously the equilibrium value after a temperature jump. More or less pronounced oscillations take place after the temperature jump and can be observed by ^{13}C and ^1H MAS NMR spectroscopy.

Apparent energies of activation of 51 ± 5 and 32 ± 3 kJ mol^{-1} were in the temperature range between 100 and 150 °C obtained for the decomposition and formation rates of MTBE, respectively.

The experiments with boron pentasil zeolite loaded with labeled methanol (deuterated or ^{13}C enriched) and IB show that during the reaction the entire $-\text{OCH}_3$ group is transferred from MTBE to methanol and back.

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