A technique for simultaneous *in situ* MAS NMR and on-line gas chromatographic studies of hydrocarbon conversions on solid catalysts under flow conditions

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A new technique is introduced allowing simultaneous *in situ* MAS NMR investigations of hydrocarbon conversions on solids under flow conditions and on-line gas chromatography. For adsorption of methanol on zeolite HBeta, equal amounts of adsorbed molecules were determined by both analytical methods. Studying the synthesis of methyl tertiary-butyl ether (MTBE) on zeolite HBeta using an MAS NMR rotor reactor, a constant yield of MTBE of $Y_{mtbe} = 27\%$ was obtained up to a weight hourly space velocity of 1.4 h^{-1}. The variation of the reaction temperature led to a simultaneous change of the ^{13}C MAS NMR signals of isobutoxy species and of the yield of MTBE determined by on-line gas chromatography which indicates that isobutoxy species act as chemically active compounds. In this first application, the new *in situ* technique has demonstrated its advantage for a simultaneous investigation of compounds with a long residence time on the catalyst surface and of compounds rapidly leaving the catalyst surface.

Keywords: *in situ* MAS NMR flow probe, on-line gas chromatography, synthesis of MTBE, zeolite HBeta, Brønsted acid sites, methanol adsorption, alkoxy species

1. Introduction

Starting in 1989 [1], *in situ* MAS NMR spectroscopy has been developed to a useful tool for the study of chemical reactions catalyzed by solids. In most of the *in situ* MAS NMR techniques applied during the last decade, samples in gas-tight MAS NMR rotors or fused in glass ampoules were used [2,3]. The reaction conditions in these samples are comparable with those in a batch reactor. An interesting approach is the temperature-jump relaxation MAS NMR technique with sample heating by laser pulses which is suitable for the study of reaction kinetics under batch conditions [4]. In 1995, a MAS NMR equipment for *in situ* investigations of the conversion of hydrocarbons on solid catalysts under flow conditions was introduced in this laboratory [5]. This equipment consists of a MAS NMR rotor with an axially placed tube inserted into the rotor via a hole in the rotor cap. This tube allows an injection of carrier gas loaded with reactant molecules into the MAS NMR rotor reactor during the NMR experiment. In 1996, Goguen and Haw [6] described a similar *in situ* MAS NMR system in which the reactant flow, introduced on top of the MAS rotor, has to pass a Torlon disk before it reaches the catalyst inside the MAS rotor and flows back to the top or through the catalyst bed. Very recently, MacNamara and Raftery [7] described a magic angle probe allowing *in situ* NMR investigations under flow conditions and at pressures up to 13.8 MPa. Applying a step motor, the sample is rotated in steps of 120° around an axis in the magic angle with typical rates of 3–5 Hz [7]. Finally, the group of Haw introduced a pulse-quench reactor for *in situ* MAS NMR studies under flow conditions [8]. With this technique, irreversible reactions can be rapidly stopped by quenching with liquid nitrogen. After quenching, the samples are transferred into a precooled probe and studied with MAS NMR spectroscopy.

In a number of studies, the *in situ* MAS NMR flow probe [5] was applied to investigate the fate of catalytically active sites and the formation of coke during the conversion of propan-2-ol on zeolites HY and LaNaY [9], the adsorption of methanol on zeolites HZSM-5, HBeta and HY [10,11] and the synthesis of MTBE on zeolite HBeta [12]. In 1997, Raftery et al. [13] used the injection technique for a selective enhancement of ^1H MAS NMR signals of solid catalysts by a spin polarization transfer from laser-polarized xenon to surface protons. Goguen et al. [14] and Xu et al. [15] applied the pulse-quench reactor to investigate the mechanism of methanol-to-gasoline conversion and the formation of benzenium ions on zeolite HZSM-5. In all of these investigations, *in situ* MAS NMR spectroscopy under flow conditions has demonstrated its advantages for the study of OH groups, adsorbate complexes, stable carbocations and the formation of coke deposits. In the present paper, an equipment is described which allows simultaneous *in situ* MAS NMR investigations under flow conditions and on-line gas chromatographic studies of heterogeneous reaction systems. In a first application, the new *in situ* technique has been used for a quantitative investigation of the adsorption of methanol and of the synthesis of methyl tertiary-butyl ether (MTBE) on zeolite HBeta. MTBE, an octane booster in unleaded gasoline, is industrially synthesized

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from methanol and isobutene on Amberlyst-15, a sulfonic acid resin [16]. Recently, Collignon et al. [17] observed yields of MTBE on zeolite HBeta comparable with those obtained on Amberlyst-15. Applying temperature-jump relaxation MAS NMR spectroscopy, Mildner et al. [18] investigated the synthesis of MTBE on a boron pentasil zeolite. In this work, the synthesis of MTBE on zeolite HBeta has been investigated by the new *in situ* technique consisting of a MAS NMR flow probe coupled with an on-line gas chromatograph. Using the above-mentioned method, the influence of the modified residence time of the reactant molecules and of the reaction temperature on the yield of MTBE and on the ^{13}C MAS NMR spectra of the reaction system inside a MAS NMR rotor reactor has been studied.

2. Experimental

Zeolite Beta with the unit cell composition of $Na_{3.8}Al_{3.8}Si_{60.2}O_{128}\cdot nH_2O$ was synthesized according to [19]. The ammonium form of this zeolite was prepared by four-fold ion exchange at $T = 353$ K in a surplus of a 0.4 M NH_4NO_3 solution leading to an exchange degree of 99%. The sample was characterized by AES, XRD, ^{29}Si and ^{27}Al MAS NMR spectroscopy. Zeolite HBeta was obtained after heating the ammonium form sample in vacuum with a rate of 20 K/h up to the final temperature of 673 K and evacuating it at this temperature for 12 h at a pressure below 10^{-2} Pa. For the MAS NMR investigations, 200 mg of calcined zeolite HBeta was filled into a 7 mm MAS NMR rotor under dry nitrogen using a glove box. Applying a special tool, the calcined powder sample was pressed to a catalyst bed shaped like a hollow cylinder. The methanol adsorption experiments and the synthesis of MTBE were performed with CH_3OH (me), Fluka, No. 65542, and isobutene (ib), Messer Griesheim, No. 0483300357.

The MAS NMR flow probe used in this work is based on a 7 mm Bruker MAS NMR probe equipped with an injection system, as described in [5]. The carrier gas, loaded with reactant molecules in a saturator, is injected into the MAS NMR rotor reactor via a tube with an outer diameter of 1.8 mm. The catalyst bed has the shape of a hollow cylinder and rotates around the fixed injection tube. A second tube with an outer diameter of 3.0 mm serves as exhaust for the reaction products (figure 1). Both, the injection tube and the exhaust tube are inserted into the rotor via an axially placed hole (diameter 3.2 mm) in the rotor cap. Via the former tube, the reactant molecules are injected into the MAS NMR rotor. The reaction products leave the rotor at the top via the exhaust tube. This exhaust tube is connected with the sampling loop of an on-line gas chromatograph (figure 2). A flow inducer works as exhaust pump and ensures a constant flow of the product molecules from the MAS NMR rotor reactor via the sampling loop to a cold trap.

After purging the MAS NMR turbine with dry nitrogen, the hole in the rotor cap is opened and the injection and exhaust tubes are inserted into the MAS NMR rotor reactor

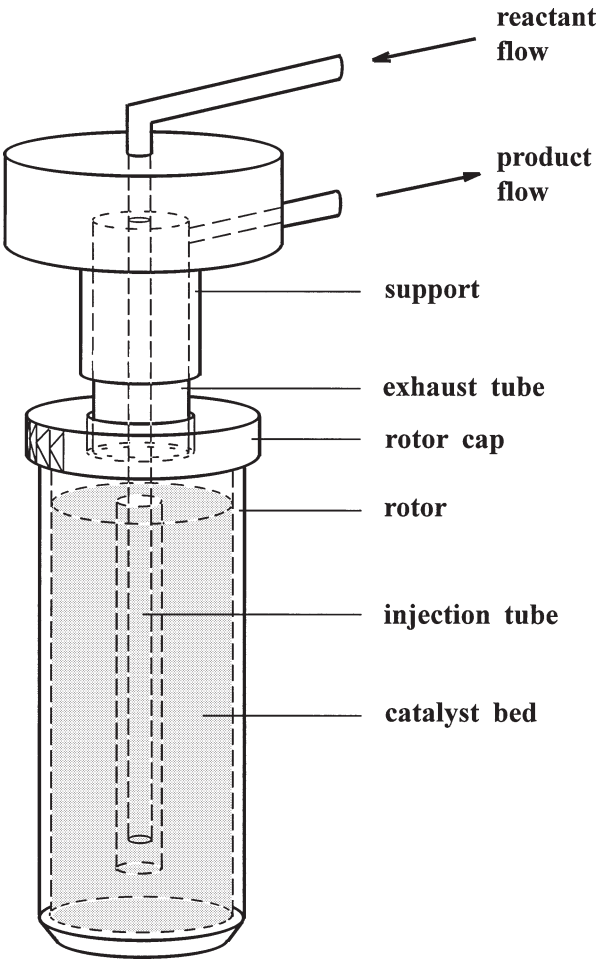

Figure 1. Design of the modified MAS NMR rotor with axially placed tubes for the injection of reactant molecules and the exhaust of reaction products.

filled with the calcined catalyst. Carrier gas is used for the bearing and driving of the MAS NMR rotor reactor. A glass bell acts as gas-tight housing of the MAS NMR turbine. Therefore, neither humidity nor other impurities can enter into the MAS NMR rotor reactor during the *in situ* experiments.

NMR investigations were performed on a Bruker MSL 400 spectrometer at resonance frequencies of 400.1 and 100.6 MHz for ^{1}H and ^{13}C nuclei, respectively, and with a sample spinning rate of 2.8 kHz. The ^{13}C MAS NMR spectra were recorded after direct excitation with ^{1}H decoupling and with reactant molecules having ^{13}C isotopes in natural abundance. For each ^{1}H and ^{13}C spectrum, free induction decays of 25 and 720, respectively, were accumulated with a repetition time of 10 s. The amounts of adsorbed molecules were determined by comparing the ^{1}H MAS NMR intensities with that of an external intensity standard (dehydrated zeolite HY with an exchange degree of 35%).

The reaction products were analyzed by a gas chromatograph HP 5890 (Hewlett Packard) equipped with a DB-WAX column (J&W Scientific) with a length of 30 m and an inner diameter of 0.25 mm. The exhaust flow of the

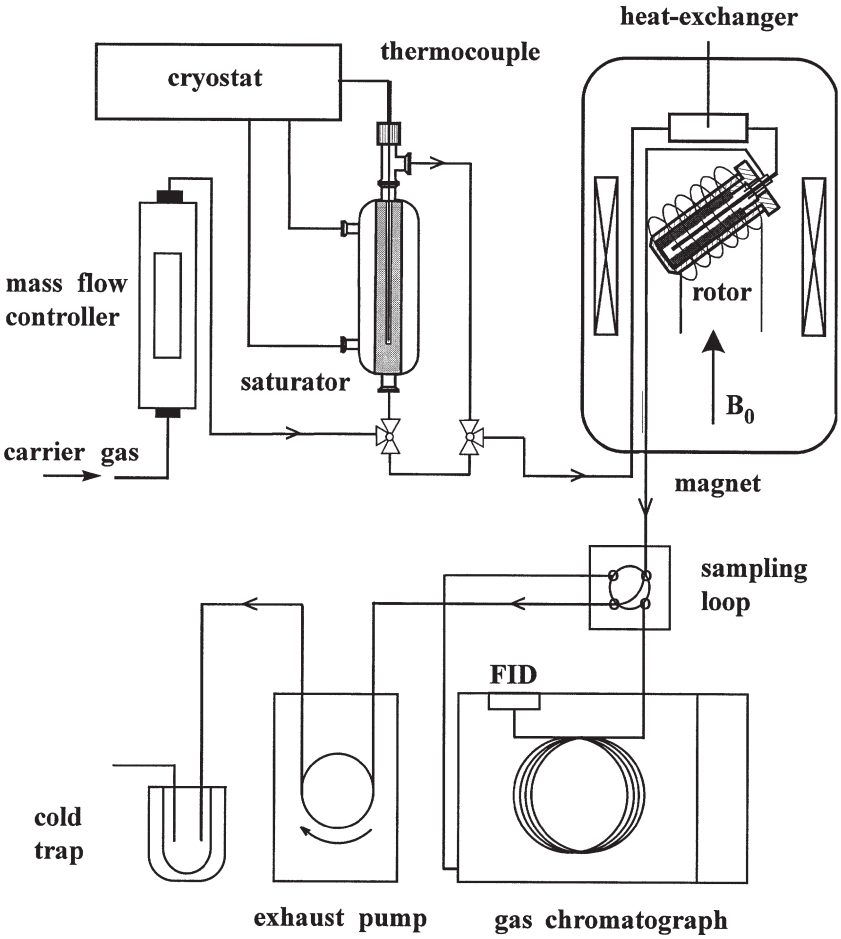

Figure 2. Scheme of an *in situ* MAS NMR flow probe coupled with a sampling loop and an on-line gas chromatograph.

MAS NMR rotor reactor was sampled and analyzed in steps of 4 min in the adsorption experiment and of 10 min during the catalytic experiments. A commercial flow inducer (ISMATEC MCP 6.05) which is connected with the sampling loop ensured an exhaust flow of 13 ml/min. The reactant flow rates were adjusted by the carrier gas (dry nitrogen) flow rate, the temperature-dependent partial pressure, p_{me}, of methanol in the saturator, and, in the case of MTBE synthesis, by the flow rate of isobutene. The 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.

3. Results and discussion

3.1. Simultaneous ^{1}H MAS NMR and on-line gas chromatographic investigation of methanol adsorption on zeolite HBeta

Before starting the adsorption experiments, the carrier gas loaded with methanol was injected into the MAS NMR flow probe equipped with an empty rotor. In this way, the response delay of the on-line gas chromatograph coupled with the MAS NMR flow probe was determined. In addition, this measurement gave the maximum amplitude

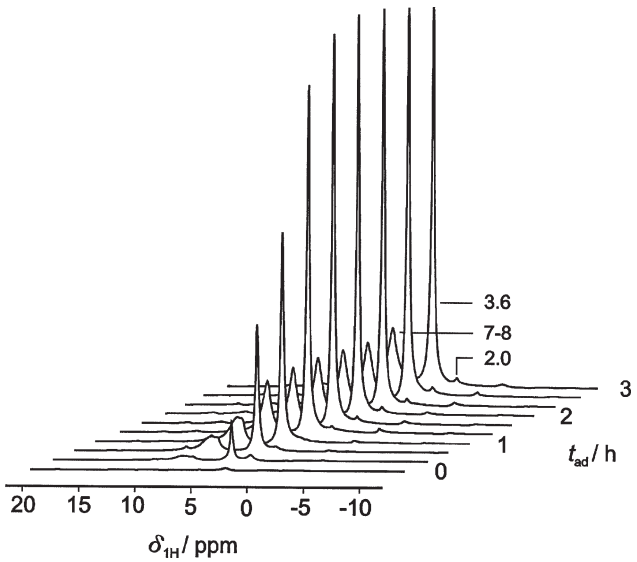

Figure 3. ^{1}H MAS NMR spectra of calcined zeolite HBeta, recorded before ($t_{ad} = 0$) and during ($t_{ad} > 0$) adsorption of methanol by an injection of carrier gas (nitrogen, 4.7 ml/min) loaded with methanol (methanol pressure $p_{me} = 50.8$ mbar) into the MAS NMR rotor.

of the break-through curve recorded during the adsorption of methanol on zeolite HBeta. Figure 3 shows the ^{1}H MAS NMR spectra of dehydrated zeolite HBeta ob-

tained before ($t_{ad} = 0$) and after ($t_{ad} > 0$) starting the adsorption of methanol. The spectrum of the unloaded zeolite HBeta ($t_{ad} = 0$) consists of weak signals at 2.0 and 4–5 ppm due to silanol groups and bridging OH groups (SiOHAl) [11,20], respectively. With progressive adsorption of methanol, signals of methyl groups and hydroxyl protons contributing to adsorbate complexes can be observed at 3.6 and 7–8 ppm [11], respectively. These signals increase until saturation is reached after an adsorption time of about 2 h. According to theoretical and experimental investigations, the low-field signal at 7–8 ppm is caused by hydroxyl protons of methanol molecules bound via hydrogen bonds at the zeolite framework [10,11,21,22].

The simultaneous analysis of the exhaust of the MAS NMR flow probe by on-line gas chromatography led to the break-through curve shown in figure 4(a) (filled squares). The curve formed by the filled circles was obtained by an injection of the reactant flow into the empty MAS NMR rotor (*vide supra*). The difference of the integrals of these two curves corresponds to the amount of methanol molecules adsorbed on zeolite HBeta at the adsorption time t_{ad}. In figure 4(b), these amounts of adsorbed methanol molecules are plotted as a function of adsorption time (open circles). The curve described by the filled circles corresponds to the amounts of adsorbed methanol molecules, determined by a quantitative evaluation of the ^{1}H MAS NMR spectra in figure 3. Considering the experimental accuracies of *in situ* ^{1}H MAS NMR spectroscopy under flow conditions (±10%) coupled with on-line gas chromatography, the amounts of adsorbed methanol molecules determined by both methods (figure 4(b)) agree well.

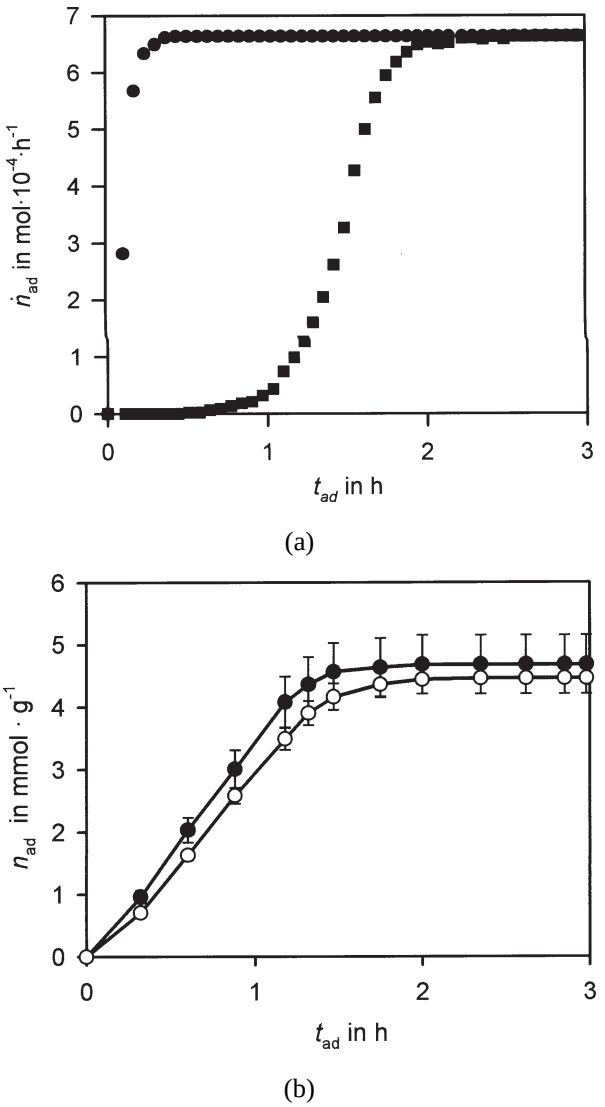

Figure 4. Break-through curve obtained for adsorption of methanol on calcined zeolite HBeta by on-line gas chromatography (a) using the equipment shown in figure 2 ((•) empty rotor, (■) rotor filled with calcined zeolite HBeta). In (b), the amounts of adsorbed methanol molecules, n_{ad}, determined by *in situ* ^{1}H MAS NMR spectroscopy under flow conditions (filled circles) and on-line gas chromatography (open circles) are plotted as a function of the adsorption time t_{ad}.

3.2. Simultaneous ^{13}C MAS NMR and on-line gas chromatographic studies of MTBE synthesis on zeolite HBeta

In the following experiment, the influence of the modified residence time on the yield of MTBE on zeolite HBeta in a spinning MAS NMR rotor reactor was investigated applying a MAS NMR flow probe coupled with an on-line gas chromatograph. To allow a comparison of the obtained results with those in the previous study [12], the measurements were carried out at a reaction temperature of 333 K and with $\dot{n}_{me}/\dot{n}_{ib} = 2:1$. Figure 5 shows the yields of MTBE, Y_{mtbe}, obtained with modified residence times between $W/F_{ib} = 2$ and 150 g h/mol. For modified residence times between $W/F_{ib} = 40$ and 150 g h/mol, the yield of MTBE is constant and exhibits a value of $Y_{mtbe} = 27\%$. The strong decrease of the Y_{mtbe} value, found for modified residence times smaller than $W/F_{ib} = 40$ g h/mol (WHSV = 1.4 h^{-1}), indicates a strong limitation of reaction kinetics by reactant transport processes inside the catalyst bed. The yield of MTBE on zeolite HBeta obtained

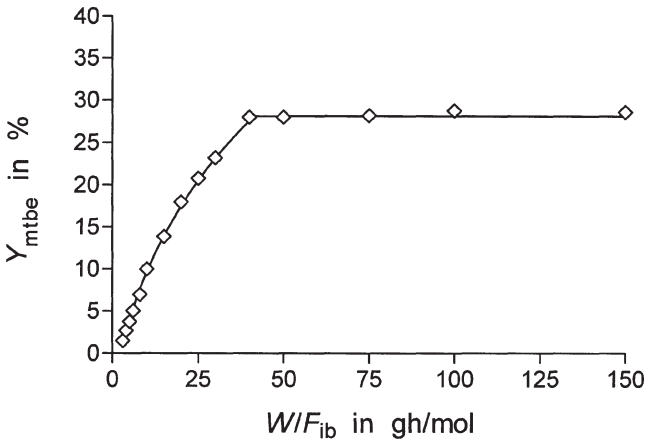

Figure 5. The yields of MTBE, Y_{mtbe}, obtained on zeolite HBeta at a reaction temperature of 333 K with a molar methanol/isobutene feed ratio of $\dot{n}_{me}/\dot{n}_{ib} = 2:1$ and modified residence times between $W/F_{ib} = 2$ and 150 g h/mol.

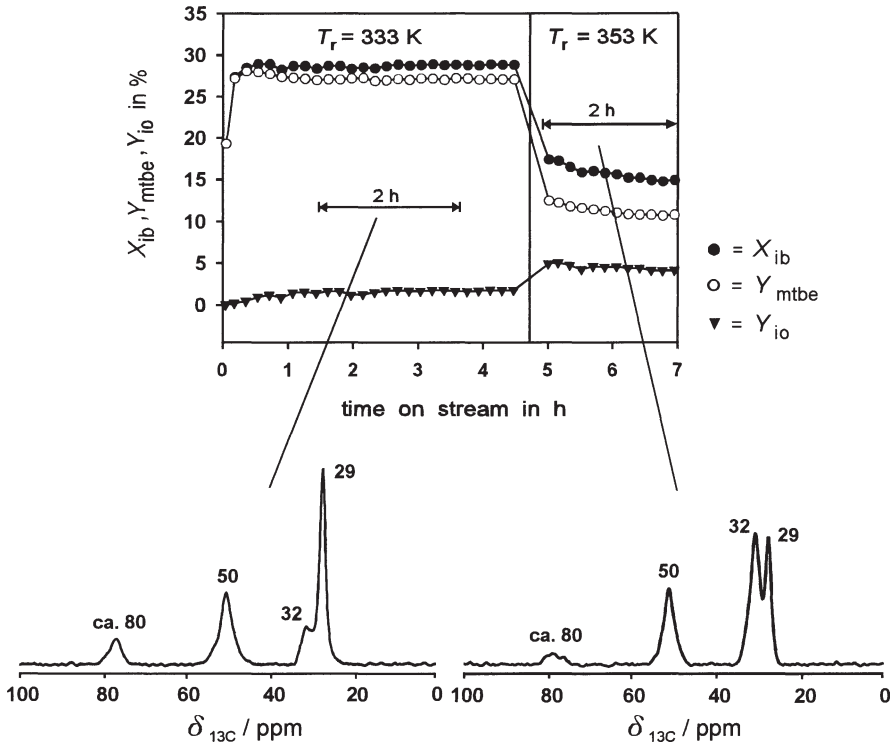

Figure 6. Conversion of isobutene, X_{ib}, and yields of MTBE, Y_{mtbe}, and isobutene oligomers, Y_{io}, on zeolite HBeta (top) obtained with a molar methanol/isobutene feed ratio of $\dot{n}_{me}/\dot{n}_{ib} = 2:1$, a modified residence time of $W/F_{ib} = 150$ g h/mol and at reaction temperatures of $T_r = 333$ K (left) and 353 K (right). The *in situ* ^{13}C MAS NMR spectra (bottom) recorded after reaching the steady state were obtained with reactants having ^{13}C isotopes in natural abundance.

with a non-spinning MAS NMR rotor reactor in a closed reactor tube was found to be equal to that in a fixed-bed reactor [9]. Therefore, the difference in the yields of MTBE obtained for $W/F_{ib} = 75$–150 g h/mol using a fixed-bed reactor ($Y_{mtbe} = 42$–45%, see [12]) and using a spinning MAS NMR rotor reactor ($Y_{mtbe} = 27\%$, this work) is due to the different flow conditions outside the catalyst bed.

In figure 6 (top), the values of X_{ib}, Y_{mtbe} and Y_{io} are plotted as a function of time on stream. At a reaction temperature of $T_r = 333$ K, an isobutene conversion of $X_{ib} = 29\%$ and a yield of MTBE 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 is due to the temperature-dependent chemical equilibrium. The *in situ* ^{13}C MAS NMR spectra shown in figure 6 (bottom) were recorded after reaching the steady state at $T_r = 333$ K (left) and 353 K (right). Both spectra consist of signals at 29, 32, 50 and ca. 80 ppm. The signals at 32 and 50 ppm are caused by methyl groups of isobutene oligomers and physisorbed methanol [12], respectively. According to Aronson et al. [24] and Stepanov et al. [25], the signal at 80 ppm can be explained by tertiary carbon atoms of isobutoxy species formed at the zeolite framework. The methyl groups of these alkoxy species are responsible for the signal at 29 ppm [24,25]. Since neither signals of isobutene (22, 109 and 145 ppm [12,26]) nor of MTBE (26, 46 and 73 ppm [12,26]) were observed in the ^{13}C MAS NMR spectra, 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 (figure 6, bottom, left) shows a weak signal of methyl groups of isobutene oligomers at 32 ppm and a strong signal of methyl groups of isobutoxy species at 29 ppm. The latter signal is accompanied by the signal of tertiary carbon atoms of isobutoxy species at 80 ppm. After raising the reaction temperature from 333 to 353 K (figure 6, bottom, right), the signal at 32 ppm increases significantly which indicates a higher formation of isobutene oligomers at this temperature. This finding agrees well with the higher yield of isobutene oligomers found by on-line gas chromatography (figure 6, top, right). In addition, a significant decrease of the signals of isobutoxy species at 29 and 80 ppm can be observed, simultaneously, with a decrease of the yield of MTBE from 27 to 11%.

4. Conclusions

A new technique allowing simultaneous *in situ* MAS NMR spectroscopic and on-line gas chromatographic investigations of heterogeneously catalysed reactions was applied to study the adsorption of methanol and the synthesis of methyl tertiary-butyl ether on zeolite HBeta. For adsorption of methanol on zeolite HBeta, a good quantitative agreement of the amounts of adsorbed molecules determined by both methods was found. By *in situ* ^{13}C MAS NMR spec-

troscopy of the synthesis of MTBE on zeolite HBeta, a simultaneous variation of the amount of isobutoxy species and the yield of MTBE was found indicating that alkoxy species play a role as chemically active compounds. This is an impressive demonstration of the possibilities of *in situ* MAS NMR spectroscopy under flow conditions coupled with on-line gas chromatography for the study of active surface compounds in heterogeneous catalysis.

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