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Methyl tertiary-butyl ether synthesis on zeolite HBeta investigated by in situ MAS NMR spectroscopy under continuous-flow conditions[1]

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Abstract

In situ MAS NMR spectroscopy was applied to investigate the synthesis of methyl tertiary-butyl ether (MTBE) over zeolite HBeta ($n_{Si}/n_{Al}=15.8$) under continuous-flow conditions. Preliminary catalytic tests with on-line gas chromatographic analysis of the reaction products revealed an activity of zeolite HBeta in the MTBE synthesis comparable with that of Amberlyst-15. By exposing the calcined zeolite, filled into an MAS NMR rotor, to a flow of nitrogen gas loaded with methanol and isobutene, the interaction of these reactant molecules with the zeolite OH groups and the dimerization and oligomerization of isobutene were studied. ^{13}C MAS NMR spectroscopy performed during the conversion of a methanol/isobutene mixture over zeolite HBeta yielded signals at 77 ppm to 90 ppm due to secondary and tertiary carbon atoms of alkoxy complexes formed at the zeolite framework. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: MTBE synthesis; Zeolite HBeta; In situ MAS NMR spectroscopy; Methanol adsorption; Isobutene dimerization; Alkoxy groups

1. Introduction

Methyl tertiary-butyl ether (MTBE) is used on a large scale as an octane booster in unleaded gasoline. The industrial production of MTBE is currently carried out in the liquid phase on sulfonic acid resins (e.g. Amberlyst-15) at temperatures in the range 323–343 K and methanol/isobutene molar feed ratios of higher than 1:1 [1]. Sulfonic acid resins are quite efficient catalysts; however, they lead to a number of undesirable by-products (e.g. diisobutenes, tertiary-butyl alcohol, dimethyl ether) [2] and cause corrosion problems [3]. Therefore, a number of papers, published in the past 3 years, focused on the application of zeolites such as HY, H-omega, H-mordenite, HZSM-5 and HBeta as alternative catalysts for the synthesis of MTBE [4–8]. In these studies, which were performed in the gas phase, a maximum MTBE yield was found at temperatures between 353 and 383 K. Equilibrium limitations [9] call for catalysts which are active at lower temperatures. Collignon et al. [8] studied MTBE synthesis on a series of zeolites

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HBeta with n_{Si}/n_{Al} ratios ranging from 13 to 194 and found that these materials are significantly more active than all other zeolite types employed. Over zeolite HBeta with an n_{Si}/n_{Al} ratio of 25.7, a maximum MTBE yield of ca 50% was obtained at 333 K. This high catalytic activity was explained by a contribution of the large external surface (211–240 $m^2 g^{-1}$) of the zeolites HBeta used as catalysts [8]. Investigating the MTBE synthesis on zeolites HZSM-5 and HY, Kogelbauer et al. [5] observed an increase in the MTBE formation rate and a suppression of by-products after preadsorption of methanol molecules. This is a hint to the important role of adsorbate complexes formed by adsorption of methanol molecules for the activity of zeolites in MTBE synthesis. These adsorbate complexes prevent an oligomerization of isobutene by blocking the strong Brønsted acid sites [5].

In the present work, a zeolite HBeta with $n_{Si}/n_{Al}=15.8$ was investigated as the catalyst in MTBE synthesis. Recently, Mildner et al. [10] and Hunger et al. [11] carried out in situ MAS NMR spectroscopy of MTBE synthesis on zeolites under batch conditions. In this work, methanol and isobutene adsorption experiments and studies of the synthesis of MTBE on zeolite HBeta were performed by applying a new MAS NMR technique allowing in situ investigations under continuous-flow conditions [12,13]. For this purpose, the calcined zeolite HBeta was exposed to a continuous flow of nitrogen loaded with the reactants during the MAS NMR experiments. The important advantage of this technique is the combined quantitative information on adsorption and conversion of reactant molecules and the insight into the fate of catalytically active sites, the structure of adsorbate complexes and catalyst deactivation. By in situ MAS NMR spectroscopy under flow conditions all species can be studied whose lifetimes inside the MAS NMR rotor reactor are large in comparison with the observation time of the applied spectroscopic method [13]. Prior to the NMR investigations, the catalytic activities of zeolite HBeta and Amberlyst-15 in MTBE synthesis were determined at atmospheric pressure and with on-line gas chromatographic analysis of the reaction products.

2. Experimental section

Zeolite Beta with the chemical composition $Na_{3.8}Al_{3.8}Si_{60.2}O_{128}$ was synthesized as described elsewhere [14]. The ammonium form was prepared by fourfold ion exchange at 353 K in a 0.4 M aqueous solution of NH_4NO_3. After ion exchange, the zeolite powder was washed in demineralized water and dried at room temperature. This material was characterized by AAS, AES-ICP, XRD, ^{27}Al and ^{29}Si MAS NMR spectroscopy. No signal of extra-framework aluminum atoms was found in the ^{27}Al MAS NMR spectra of the hydrated samples. Amberlyst-15 was a commercial product (Aldrich Chemical Co. Ltd, No. 21,638-0).

MAS NMR investigations were performed on a Bruker MSL 400 spectrometer at resonance frequencies of 400.1 MHz for ^1H and 100.6 MHz for ^{13}C nuclei and at a sample spinning rate of ca 2.5 kHz. The ^{13}C MAS NMR spectra were obtained after direct excitation and with proton decoupling. For each ^1H and ^{13}C MAS NMR spectrum, free induction decays of 25 and 720, respectively, were accumulated with a repetition time of 10 s in both cases. Prior to the NMR investigations, the ammonium form of zeolite Beta was heated in vacuum with a rate of 20 K h^{-1} up to the final temperature of 723 K. There, it was calcined for 12 h at a pressure below 10^{-2} Pa. During the in situ MAS NMR experiments under continuous-flow conditions, a nitrogen stream loaded with methanol (me), CD_3OD (99.8 at.% D, Sigma–Aldrich, No. 0483300357), CH_3OH (Fluka, No. 65542), isobutene (ib), i-C_4H_{10} (99.0 vol.%, Messer Griesheim, No. 795.03039) or a mixture of the latter two reactants (n_{me}:n_{ib}=2:1) was introduced into a commercial 7 mm MAS NMR Bruker rotor via an axially placed injection tube (see Refs. [12,13]). After a decomposition of the spectra, the concentrations of the OH groups in the calcined zeolites were determined by comparing the total ^1H MAS NMR intensities with that of an external standard (dehydrated zeolite HNaY with an exchange degree of 35%). The amounts of hydroxyl protons and methyl groups observed during the injection of reactant molecules were calculated using the

spectrum of the unloaded zeolites as intensity standard.

The catalytic activities of the catalysts in the synthesis of MTBE were investigated with a flow-type apparatus and on-line gas chromatographic analysis of the reaction products (DB-WAX column, J&W Scientific, 30 m length, 0.25 mm inner diameter). Prior to the catalytic measurements, 250 mg of catalyst powder were calcined for 12 h at 673 K (Amberlyst-15 at 373 K) in a flow of dry nitrogen gas. A modified residence time of $W/F_{ib} = 150$ g h mol^{-1}, a reaction temperature of $T_r = 333$ K and a methanol/isobutene molar feed ratio of 2:1 were applied.

3. Results and discussion

3.1. Catalytic investigations of MTBE synthesis on Amberlyst-15 and zeolite HBeta with on-line gas chromatographic analysis of the reaction products

Very recently, the synthesis of MTBE was investigated over zeolite HY ($n_{Si}/n_{Al} = 2.6$), non-modified and fluorinated zeolite HBeta ($n_{Si}/n_{Al} = 15.8$) and zeolite HZSM-5 ($n_{Si}/n_{Al} = 21.8$) in the gas phase, at atmospheric pressure and with on-line gas chromatographic analysis of the reaction products [11]. In agreement with the literature [8], the highest yields of MTBE were obtained over zeolite HBeta. Therefore, this material was chosen as the zeolite catalyst for in situ MAS NMR studies of MTBE synthesis under the continuous-flow conditions performed in the present work. As a preparatory step, the conversion of isobutene X_{ib} and the yield of MTBE Y_{mtbe} over zeolite HBeta were investigated under reaction conditions suitable for in situ MAS NMR experiments. Table 1 gives a summary of these values, determined at reaction temperatures of $T_r = 333$ K and $T_r = 353$ K and with modified residence times of $W/F_{ib} = 75$ g h mol^{-1} and $W/F_{ib} = 150$ g h mol^{-1}. As shown in columns four and five of Table 1, zeolite HBeta is as active as Amberlyst-15, but it tends to yield slightly more by-products. The degree to which this occurs depends on the reaction temperature (last column). The dimer 2,4,4-trimethyl-1-pentene was found to be the most abundant by-product at 353 K with a yield of 0.1.

Table 1
Conversions of isobutene X_{ib} and yields of MTBE Y_{mtbe} obtained during the synthesis of MTBE over Amberlyst-15 and zeolite HBeta ($n_{Si}/n_{Al} = 15.8$) with a molar methanol/isobutene feed ratio of 2:1 (T_r: reaction temperature; W/F_{ib}: modified residence time)

Sample	T_r (K)	W/F_{ib} (g h mol^{-1})	X_{ib}	Y_{mtbe}
Amberlyst-15	333	75	0.45	0.45
	333	150	0.47	0.47
	353	150	0.24	0.20
HBeta	333	75	0.45	0.42
	333	150	0.47	0.45
	353	150	0.44	0.17

3.2. In situ ^1H and ^{13}C MAS NMR studies of the adsorption of CD_3OD on zeolite HBeta under flow conditions

In previous in situ ^{1}H MAS NMR studies of the adsorption of methanol on zeolite HBeta under continuous flow conditions, CD_3OH was applied as reactant molecule; this led to a superposition of signals due to hydroxyl protons of methanol molecules and of the zeolite [15]. In the present work, the interaction of methanol with the Brønsted acid sites of HBeta was investigated by adsorption of perdeuterated methanol under reaction conditions ($T_r = 333$ K) of the MTBE synthesis by an injection of carrier gas loaded with CD_3OD into the MAS NMR rotor.

The ^{1}H MAS NMR spectra shown in Fig. 1(a) were recorded immediately before ($t_{ad} = 0$ min) and after ($t_{ad} > 0$ min) starting the injection of CD_3OD ($W/F_{me} = 75$ g h mol^{-1}) into the MAS NMR rotor. The spectrum obtained at $t_{ad} = 0$ min corresponds to that of an unloaded zeolite HBeta and consists of signals caused by silanol groups at framework defects and the outer surface (2.1 ppm) and by bridging OH groups (4.4 ppm) [16]. As shown by Koch et al. [17], a variation of the temperature within the MAS NMR probe, e.g. from 295 to 333 K, brings about a low-field shift of the ^{1}H MAS NMR signals of the zeolite OH groups by about 0.3 ppm. In our previous work [15], the amounts of silanol and bridging

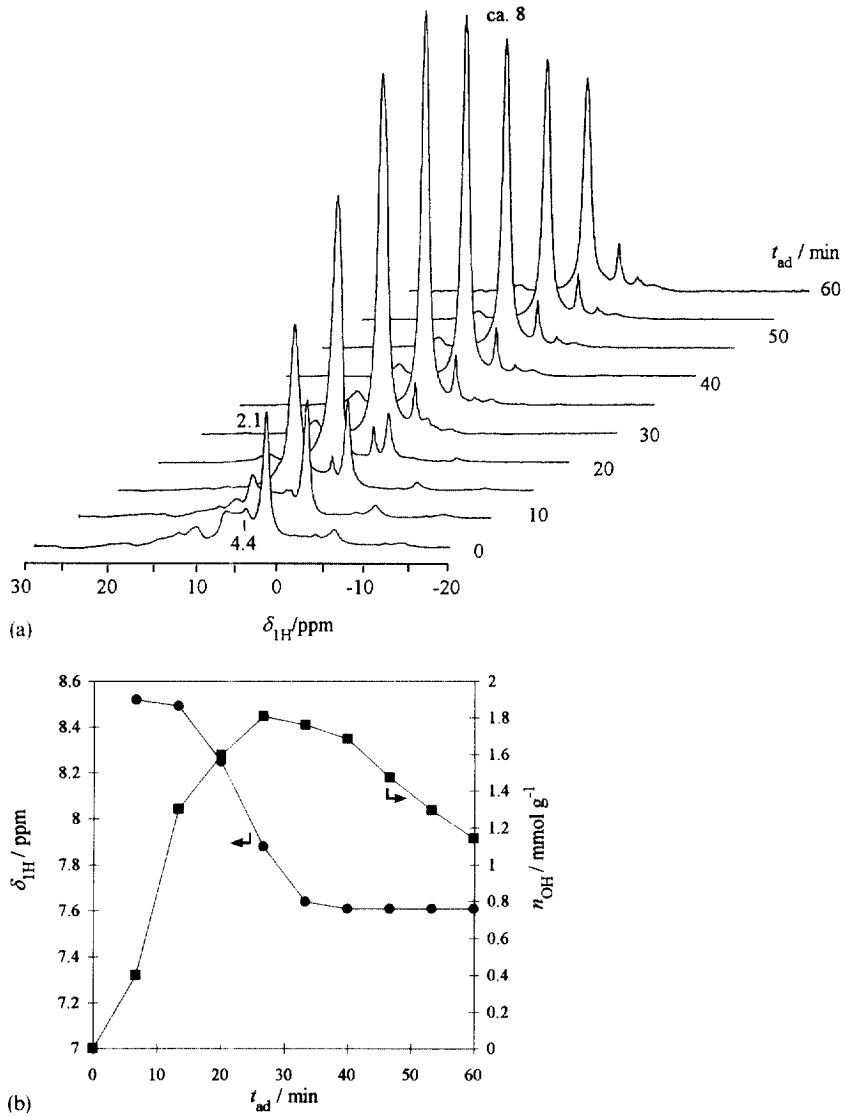


Fig. 1. ^{1}H MAS NMR spectra (a) of calcined zeolite HBeta, recorded during injection of a flow of CD_3OD with a modified residence time of $W/F_{me} = 75$ g h mol^{-1} at 333 K into the MAS NMR rotor. The graph (b) shows the ^{1}H MAS NMR shift δ_{1H} of the low-field line due to the hydroxyl protons contributing to adsorbate complexes (left) and the amount n_{OH} of these atoms (right).

OH groups in the unloaded zeolite HBeta were found to be 0.85 mmol g^{-1} and 0.90 mmol g^{-1}, respectively.

After starting the injection of CD_3OD into the MAS NMR rotor ($t_{ad} > 0$ min), two additional signals appear. One is a broad signal at ca 8 ppm due to zeolite OH groups which are involved in an interaction with adsorbate molecules. The narrow line at 3.8 ppm is caused by a small amount of hydrogen atoms in the methyl groups of CD_3OD (99.8 at.% D). At the same time, as the low-field line at ca 8 ppm increases, the ^{1}H MAS NMR signals of zeolite OH groups at 2.1 ppm and 4.4 ppm become smaller.

In Fig. 1(b), the ^{1}H MAS NMR shift (left) of the low-field line and the amounts of hydroxyl

groups contributing to this signal (right) are depicted as a function of the adsorption time. A comparison of the ^{1}H MAS NMR shifts of the low-field line recorded in the present work at 333 K (Fig. 1(b), left) with those observed at 295 K (see Ref. [15]) reveals that there is no effect of the temperature on the resonance position. As shown previously [18,19], the resonance position of the low-field line depends on a rapid exchange of hydroxyl protons of neutral hydrogen-bound adsorbate complexes, protonated methanol molecules (methoxonium ions) and undisturbed zeolite OH groups. Hence, within the temperature range from 295 to 333 K no variation occurs in the nature of complexes formed by adsorption of methanol on zeolite OH groups.

The quantitative evaluation of the ^{1}H MAS NMR low-field line at ca 8 ppm yields a maximum amount of zeolite OH groups which are involved in the interaction with adsorbate molecules of 1.8 mmol g^{-1} (Fig. 1(b), right). The comparison of this value with the total amount of silanol and bridging OH groups of the unloaded zeolite HBeta (vide supra) indicates that nearly all hydroxyl protons of both types of zeolite OH group, including the silanol groups at the outer surface of the zeolite particles, contribute to the formation of adsorbate complexes. The decrease of the low-field line after a time on stream of ca 30 min is due to an isotopic exchange of the zeolite OH groups with CD_3OD molecules leading to a partial deuteration of these hydroxyl groups.

The ^{13}C MAS NMR spectrum shown in Fig. 2(a) was recorded at $T_r = 333$ K after 1 h of methanol admittance. The signal at 49 ppm is characteristic of methanol molecules physisorbed on zeolites ([19] and Table 2). Neither signals of protonated methanol molecules (61 ppm [22]) nor signals caused by methoxy groups bound to the zeolite framework (ca 58 ppm [23]) could be observed.

3.3. *In situ ^{1}H and ^{13}C MAS NMR studies of the adsorption and reaction of isobutene on zeolite HBeta under flow conditions*

The following ^{1}H and ^{13}C MAS NMR experiments were undertaken in an endeavor to study the adsorption and reaction of isobutene on zeolite HBeta. For this purpose, the calcined zeolite HBeta, filled into the MAS NMR rotor, was exposed to a flow of nitrogen gas loaded with isobutene molecules containing isotopes in the natural abundance ($W/F_{ib} = 300$ g h mol^{-1}). The ^{1}H MAS NMR spectra shown in Fig. 3(a), section (i), were obtained at $T_r = 295$ K immediately after admitting the isobutene flow. Interestingly, neither a signal of CH_3 (1.6 ppm, Table 2) nor of CH_2 groups (4.6 ppm, Table 2) of isobutene could be observed, which indicates a short lifetime of this reactant in the zeolitic pore system. At about $t_{exp} = 10$ min, new signals appear at 0.85 ppm and 1.7 ppm which dominate the spectrum after $t_{exp} = 30$ min. Since these signals cause spinning side-bands, the correlation time τ_c of thermal motion of the corresponding species is large in

Table 2
^{1}H and ^{13}C MAS NMR shifts of reactant molecules and by-products occurring in MTBE synthesis given in the literature [20,21] or determined by adsorption on calcined (673 K) silica gel

Molecule	^{1}H MAS NMR shift (ppm)						^{13}C MAS NMR shift (ppm)					
	1	2	3	4	5	6	1	2	3	4	5	6
$\overset{1}{C}H_3OH$	3.3						49					
$(\overset{1}{C}H_3)_2\overset{2}{C}=\overset{3}{C}H_2$	1.6		4.6				22	109	145			
$\overset{1}{H_3}C-O-\overset{2}{C}(\overset{3}{C}H_3)_3$	3.2		1.3				46	73	26			
$(\overset{1}{C}H_3)_2\overset{2}{C}=\overset{3}{C}H-\overset{4}{C}(\overset{5}{C}H_3)_3$	1.6		5.2		1.0		25	135	131	32	31	
$\overset{1}{H_2}C=\overset{2}{C}(\overset{3}{C}H_3)-\overset{4}{C}H_2-\overset{5}{C}(\overset{6}{C}H_3)_3$	4.8		1.7	1.9		0.9	114	144	25	52	25	30

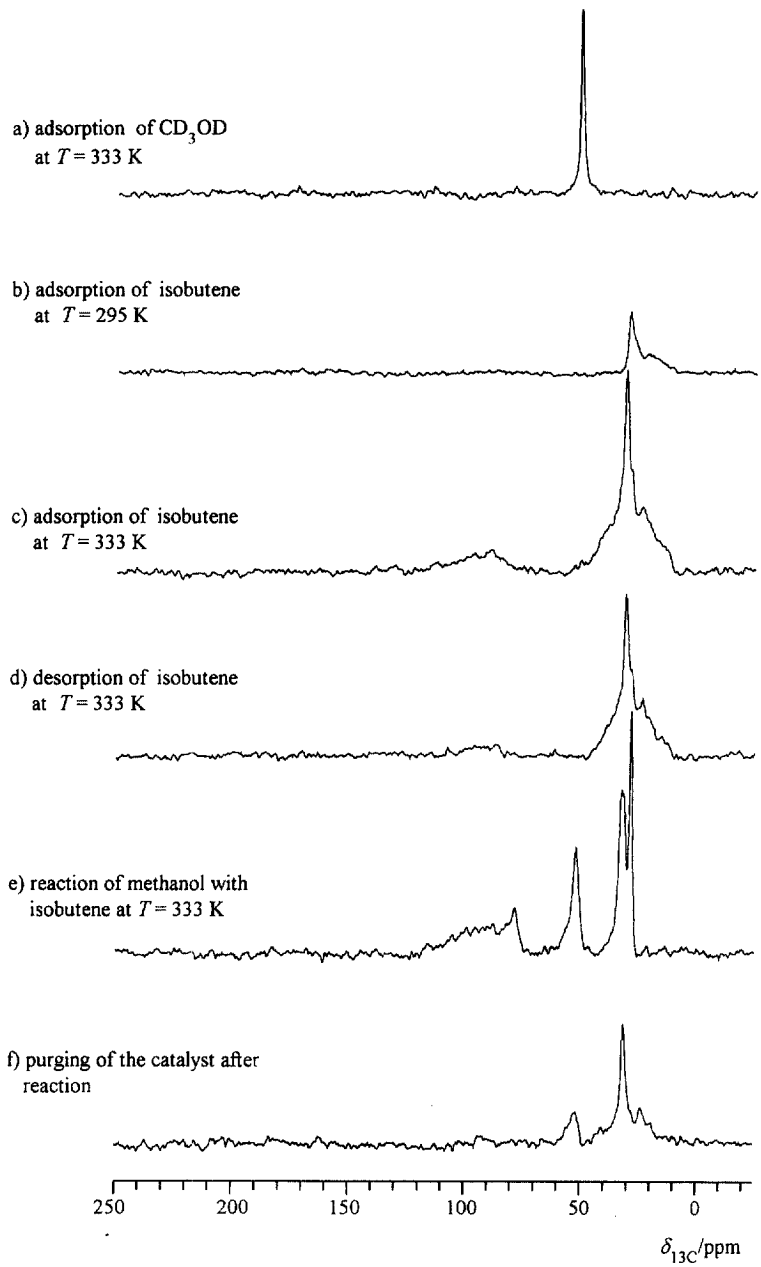


Fig. 2. ^{13}C MAS NMR spectra of calcined zeolite HBeta, recorded during injection of a flow of methanol at 333 K (a), of a flow of isobutene at 295 K (b) and of a flow of isobutene at 333 K (c) into the MAS NMR rotor and recorded after purging (dry nitrogen gas) the zeolite catalyst loaded with isobutene at 333 K for 2 h (d). The spectra shown in (e) and (f) were obtained during reaction of a methanol/isobutene mixture at 333 K and after purging (dry nitrogen gas) the catalyst at 333 K for 2 h respectively. All spectra were recorded with adsorbate and reactant molecules containing isotopes in natural abundance.

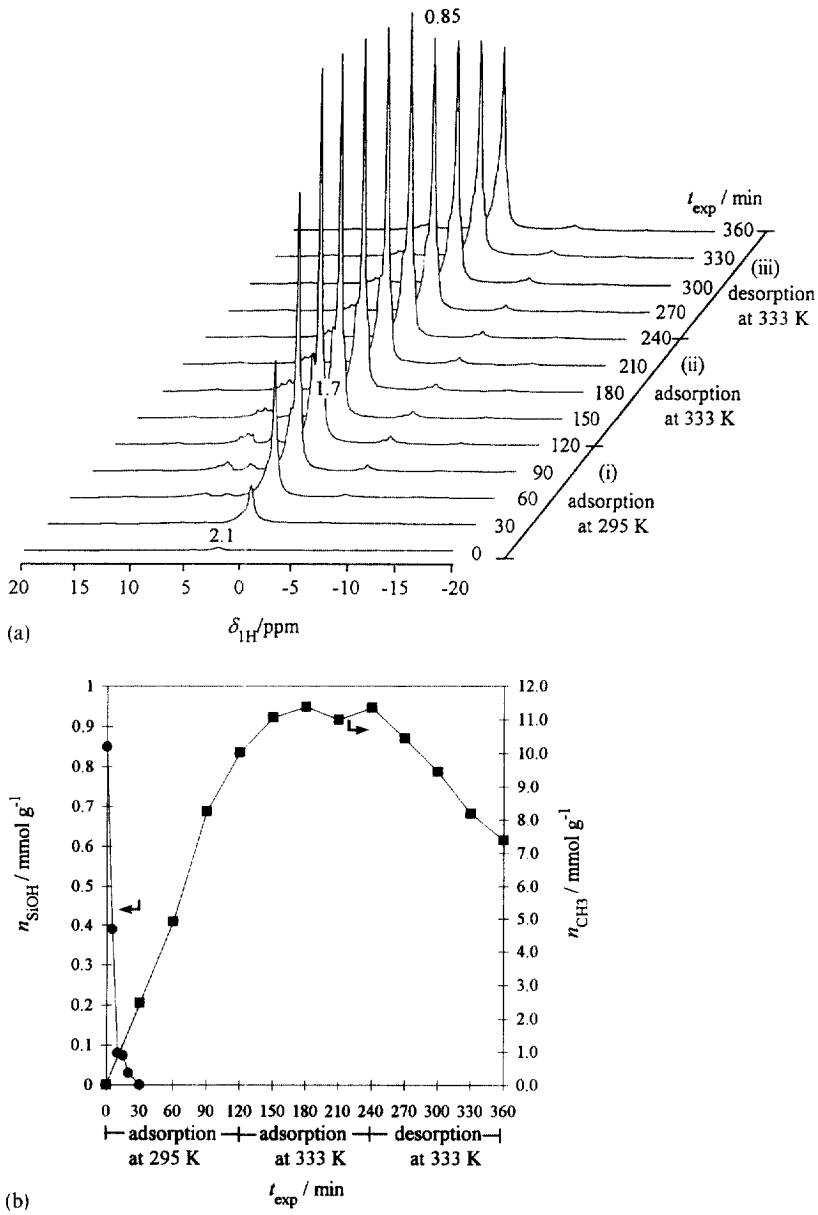


Fig. 3. ^{1}H MAS NMR spectra (a) of calcined zeolite HBeta, recorded during injection of a flow of isobutene (isotopes in natural abundance) with a modified residence time of $W/F_{ib} = 300$ g h mol^{-1} at 295 K (section (i)) and at 333 K (section (ii)) into the MAS NMR rotor. The spectra shown in section (iii) were obtained during subsequent purging (dry nitrogen gas) of the zeolite catalyst at 333 K for 2 h. In the graph (b) the amounts of methyl groups n_{CH_3} of isobutene derivatives (right) and the amounts of silanol groups n_{SiOH} which are not affected by the formation of adsorbate complexes (left) are depicted.

comparison with the reciprocal sample spinning frequency ($\tau_c > 1/\nu_{rot}$). Considering the ^{1}H MAS NMR shift values summarized in Table 2, the above-mentioned lines at 0.85 and 1.7 ppm have to be attributed to methyl groups of isobutene derivatives such as dimers (0.9–1.0 ppm and 1.6–1.7 ppm, Table 2). The amounts of these methyl groups give a measure for the amounts of

isobutene derivatives adsorbed on the zeolite. The low mobility of the above-mentioned methyl groups is due to the spatial constraints experienced by the dimerization and, even more so, the oligomerization products inside the zeolite pores. According to the amounts of methyl groups depicted in Fig. 3(b) (right), the formation of isobutene dimers has already begun at $T_r = 295$ K (section (i)). An increase in the reaction temperature to $T_r = 333$ K (section (ii)) leads to a small increase of the amount of isobutene derivatives inside the zeolite pores. After purging the catalyst for 2 h at 333 K, about 60% of the isobutene dimers remain on the zeolite (section (iii)).

Owing to the strong ^{1}H MAS NMR intensities of CH_3 and CH_2 groups of isobutene derivatives, the signals of zeolite OH groups could be evaluated only in spectra recorded during the first 30 min of the in situ MAS NMR experiment. Within this period, the silanol groups are strongly affected by adsorption and dimerization of isobutene (Fig. 3(b), left).

Fig. 2(b) shows the ^{13}C MAS NMR spectrum recorded at $T_r = 295$ K under a continuous flow of isobutene after a time on stream of 30 min. It consists of a narrow line at 31 ppm due to the methyl groups of isobutene dimers, a shoulder at 29 ppm and a broad signal at ca 20 ppm. The latter signal is caused by alkyl groups of oligomerization products [24]. The resonance positions of doubly bound carbon atoms of isobutene dimers are distributed over a range of 30 ppm (see Table 2). Since isobutene with ^{13}C in natural abundance was used, these signals have extremely weak intensities which renders their observation difficult. The increase in temperature to $T_r = 333$ K leads to an increase of the broad signals due to alkyl groups of oligomerization products and the appearance of a broad signal with a center of gravity at ca 90 ppm (Fig. 2(c)). After adsorption of propene on zeolite HY, Haw et al. [25] obtained a ^{13}C MAS NMR signal at ca 87 ppm which they assigned to secondary carbon atoms of isopropoxy groups formed at framework oxygen atoms. The tertiary carbon atoms of *tert*-butoxy complexes formed at the zeolite framework by adsorption of *tert*-butyl alcohol on HZSM-5 cause a signal at 77–81 ppm [24,26]. The large width of the signal at ca 90 ppm in Fig. 2(c) hints at contributions of both secondary and tertiary carbon atoms of alkoxy complexes formed by isobutene dimers and oligomers [24]. According to Stepanov et al. [24] and Aronson et al. [26], the methyl groups of *tert*-butoxy complexes exhibit a ^{13}C MAS NMR shift of 29 ppm, which agrees well with the resonance position of the above-mentioned high-field shoulder. The strong decrease of the broad resonance at ca 90 ppm in the ^{13}C MAS NMR spectrum recorded after purging the catalyst at $T_r = 333$ K (Fig. 2(d)) indicates that the corresponding alkoxy species are chemically unstable.

3.4. In situ ^{1}H and ^{13}C MAS NMR studies of MTBE synthesis on zeolite HBeta under continuous-flow conditions

In situ MAS NMR investigations of the conversion of a methanol/isobutene mixture on zeolite HBeta under continuous-flow conditions were performed with reactant molecules containing isotopes in natural abundance and applying reaction parameters equal to those given in line six of Table 1.

The ^{1}H MAS NMR spectra recorded immediately after starting the injection of the methanol/isobutene mixture into the preheated MAS NMR rotor (Fig. 4(a), $t_{exp} = 10$ min), show narrow signals at 1.4 ppm and 3.8 ppm caused by methyl groups of isobutene derivatives and physisorbed methanol molecules. The broad signal at 8.4 ppm originates from hydroxyl protons contributing to complexes formed by adsorption of methanol molecules on zeolite OH groups. The slightly higher chemical shift values of the above-mentioned signals in comparison with those given in Table 2 are due to different experiment temperatures (ca 0.3 ppm, vide supra) and a mutual influence of the reactant molecules inside the zeolite pores.

In Fig. 4(b), the amounts of methyl groups n_{CH_3} of adsorbed methanol molecules (left) and isobutene derivatives (right), obtained by a quantitative evaluation of the ^{1}H MAS NMR spectra, are depicted. During a period of ca 20 min after starting the reaction, the amounts of methyl groups of adsorbed methanol and isobutene deriv-

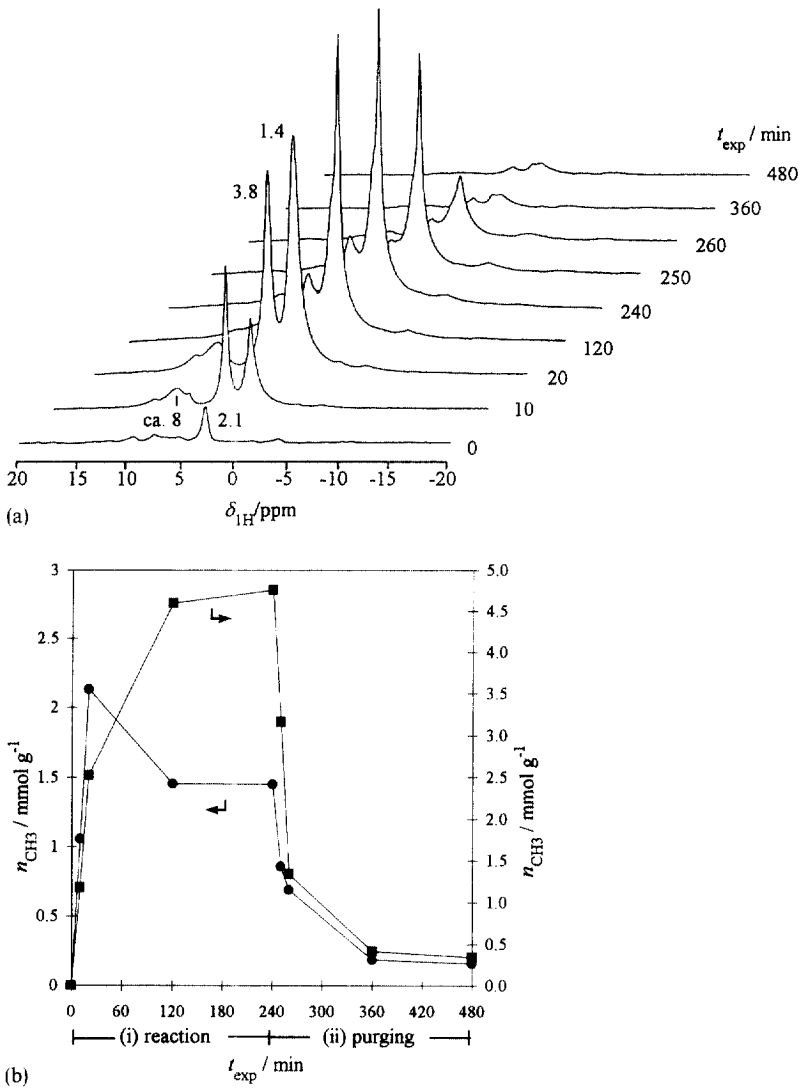


Fig. 4. ^{1}H MAS NMR spectra (a) of calcined zeolite HBeta, recorded during injection of a methanol/isobutene mixture with a modified residence time of $W/F_{ib} = 150$ g h mol^{-1} at a reaction temperature of 333 K ($t_{exp} = 0$–240 min) into the MAS NMR rotor and during purging (dry nitrogen gas) of the zeolite catalyst at 333 K ($t_{exp} = 240$–480 min). The graph (b) shows the amounts of methyl groups n_{CH_3} contributing to adsorbed methanol molecules (left) and the amounts of isobutene derivatives n_{CH_3} (right).

atives increase. At longer times on stream ($t_{exp} > 120$ min), the amounts of methyl groups of both isobutene and methanol reach a steady-state concentration. By purging the catalyst with dry nitrogen, nearly all reactants and reaction products (Fig. 4(a,b), section (ii)) were desorbed. This indicates that the conversion of a methanol/isobutene mixture on zeolite HBeta leads only to a small amount of deposits.

The ^{13}C MAS NMR spectra shown in Fig. 2(e) and Fig. 2(f) were recorded after a time on stream of 2 h and after purging the catalyst for 2 h respectively. According to the chemical shift values given in Table 2, the signals found in the former spectrum are due to physisorbed methanol molecules (49 ppm) and methyl groups of isobutene dimers (32 ppm). The strong line at 29 ppm and the broad signal at ca 90 ppm with a peak at 77 ppm hint at

the formation of a considerable amount of alkoxy complexes (vide supra). The absence of signals due to MTBE molecules indicates a short residence time of these reaction products inside the MAS NMR rotor reactor under continuous-flow conditions. This agrees with our finding in a previously published study [13].

In the ^{13}C MAS NMR spectrum recorded after purging the catalyst (Fig. 2(f)), again, the signals of alkyl silyl ether complexes (29 ppm and 77–90 ppm) are absent. This shows the low stability of the corresponding surface complexes. Owing to the low energy barrier for a transition of alkoxy complexes to carbenium ions, Aronson et al. [26] called the alkoxy complexes "a species with carbenium-like properties". Stepanov et al. [24] observed a transfer of the ^{13}C label from the CH_3 groups of *tert*-butyl alcohol adsorbed on HZSM-5 into the C–O group of the *tert*-butoxy complexes which they explained by a scrambling of carbon atoms in the *tert*-butyl carbenium ion state of this compound. They described the *tert*-butoxy complexes as intermediates of a side reaction being in a dynamic equilibrium with *tert*-butyl carbenium ions at elevated temperatures. Further in situ MAS NMR investigations have to clarify whether these complexes play a role as intermediates in the mechanism of MTBE synthesis on acidic zeolites.

4. Conclusions

Investigating the adsorption of methanol and isobutene on a zeolite HBeta ($n_{Si}/n_{Al}=15.8$) by in situ NMR spectroscopy under flow conditions, a formation of adsorbate complexes and an effect on both types of hydroxyl group, silanol and bridging OH groups, was found. This supports the assumption that silanol groups, located at the external surface of the zeolite particles, contribute to the formation of adsorbate complexes with the reactant molecules of the MTBE synthesis. ^{13}C MAS NMR spectra recorded during the conversion of a methanol/isobutene mixture on zeolite HBeta indicated the formation of alkoxy complexes. Since these complexes are, in the literature, assigned to species with carbenium-like properties, their formation may be important for the reactivity of acidic zeolites in MTBE synthesis.

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