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A comparative study of methyl-*tert*-butyl ether synthesis on zeolites HY, HBeta, HBeta/F and HZSM-5 by in situ MAS NMR spectroscopy under flow conditions and on-line gas chromatography

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Abstract

Investigating the formation of methyl-*tert*-butyl ether (MTBE) on zeolites HY, HBeta, HBeta/F and HZSM-5 by in situ ^{13}C MAS NMR spectroscopy under flow conditions, signals of alkoxy species have been observed at 77–90 ppm. On-line gas chromatographic analysis of the reactant and product molecules leaving the MAS NMR rotor reactor yielded that the formation of these alkoxy species is in line with high yields of MTBE and vice versa. Methanol adsorption experiments performed by in situ ^{1}H MAS NMR spectroscopy under flow conditions indicated that methanol molecules adsorbed on the highly active zeolite HBeta are characterized by a low protonation degree. Based on the experimental results of in situ MAS NMR spectroscopy and on-line gas chromatography, a mechanism of the synthesis of MTBE on acidic zeolites is proposed in which the reaction of isobutene with bridging OH groups leading to the formation of isobutoxy species with 'carbenium-like properties' plays a key role. ©2000 Elsevier Science B.V. All rights reserved.

Keywords: Methyl-*tert*-butyl ether; Acidic zeolites; In situ MAS NMR spectroscopy; Flow conditions; Alkoxy species

1. Introduction

On account of its high octane number (RON 114), methyl-*tert*-butyl ether (MTBE) has found an increasing application as an additive for reformulated fuels. The current industrial synthesis of MTBE by methanol and isobutene use sulfonated ion-exchange resins such as Amberlyst-15 as catalyst. These processes are performed in the liquid phase at temperatures in the range of 323–353 K and with methanol/isobutene molar feed ratios of higher than 1 : 1 [1]. Since 1987, a number of investigations on the synthesis of MTBE in gas phase using acidic zeolites as catalysts were published [2–7]. Most of these studies were stimulated by the high MTBE selectivity of zeolites and their thermal stability. Very recently, Collignon et al. [7] studied MTBE synthesis on zeolite HBeta and found that this material is significantly more active than all other zeolites.

According to Stuewe et al. [8], the initial step in the formation of MTBE on sulfonated ion-exchange resins like Amberlyst-15 is the protonation of methanol molecules adsorbed on sulfonic acid groups. The further steps consist of the protonation of isobutene by methoxonium ions and the formation of stable tertiary carbenium ions. Then, these carbenium ions react with nucleophilic methanol molecules, and after the deprotonation of the intermediates, MTBE is formed. It was the intention of the present work to prove

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whether this mechanism starting with the protonation of methanol is valid for the formation of MTBE on acidic zeolites. As a new approach, in situ MAS NMR spectroscopy under flow conditions was applied.

In the last decade, in situ MAS NMR spectroscopy has been developed into a useful tool for the study of the fate of catalytically active sites, surface complexes formed by reactants, intermediates and the deactivation of solid catalysts. In a number of experimental and theoretical works, the interaction of methanol with Brønsted acid sites of zeolites and model clusters was investigated [9–16]. Applying ab initio methods, Haase and Sauer [12,13] calculated the ^{1}H NMR chemical shifts of hydroxyl protons in model clusters which consist of one methanol molecule interacting with one bridging OH group. For (i) neutral two-fold hydrogen bonded methanol molecules and (ii) methoxonium ions, the authors predicted ^{1}H NMR shifts of 10.8 and 17.4 ppm, respectively. However, the state of methoxonium ion was found to be a transition structure for the proton transfer from one framework oxygen atom to a neighboring one via the adsorbed methanol molecule. In the time scale of ^{1}H MAS NMR spectroscopy performed at elevated temperatures, the rapid exchange of hydroxyl protons between the states (i) and (ii) and methanol molecules in the gas phase (1.6 ppm [17]) leads to a single signal at the center of gravity of all compounds. At low coverages, only contributions of states (i) and (ii) have to be considered. Therefore, a higher ^{1}H NMR chemical shift corresponds to a higher probability that the methanol molecules pass the state (ii) of methoxonium ions which here is denoted as higher 'protonation degree'.

First, in situ MAS NMR investigations of the synthesis of MTBE on zeolites were performed by Mildner et al. [18]. In this study, the temperature-jump relaxation MAS NMR technique was applied to investigate the kinetics of the formation and decomposition of MTBE on a boron pentasil zeolite [18]. In a very recent work, the synthesis of MTBE on zeolite HBeta was studied by in situ MAS NMR spectroscopy under flow conditions [19]. In the ^{13}C MAS NMR spectra recorded after reaching the steady state, signals of alkoxy species were observed at 77–90 ppm and the question arose whether these compounds play a key role in the formation of MTBE on acidic zeolites. In the present work, therefore, acidic zeolites with different numbers of Brønsted acid sites and with sites characterized by different acid strengths have been investigated using in situ MAS NMR spectroscopy under flow conditions. In some of these experiments, a direct analysis of the reaction products leaving the MAS NMR rotor reactor was performed by on-line gas chromatography. This technique allows to correlate signals observed by in situ MAS NMR spectroscopy with catalytic data determined by on-line gas chromatography (see [20]).

2. Experimental

Amberlyst-15 (Aldrich Chemical Co. Ltd., No. 21.638-0) applied as reference catalyst and silica gel (Fluka, No. 60740) used as adsorbent were commercial products. In Table 1, the zeolites applied as catalysts and the references of the synthesis recipes are given. The ammonium forms of the zeolites were prepared by four-fold ion exchange at 353 K in a surplus of 0.1 M (NH_4Y) or 0.4 M (NH_4ZSM-5, NH_4Beta, NH_4Beta/F) aqueous solution of NH_4NO_3. After ion exchange, the zeolite powder was washed

Table 1
Synthesis procedures, chemical compositions (AAS, ICP-AES), amounts of silanol (n_{SiOH}) and bridging OH groups (n_{SiOHAl}) of zeolite catalysts, the total amounts of OH groups, n_{OH}, and the deprotonation energies, ΔE_{DP}, of acidic bridging OH groups determined applying the method of Sachsenroeder et al. [28] (see text)

Catalyst	Synthesis	Chemical composition	n_{SiOH} (mmol/g)[a]	n_{SiOHAl} (mmol/g)[a]	n_{OH} (mmol/g)	ΔE_{DP} (kJ/mol)[b]
HY	[c]	$H_{46.9}Na_{6.4}Al_{53.3}Si_{138.7}O_{384}$	0.08	4.05	4.13	120
HBeta	[21]	$H_{3.8}Al_{3.8}Si_{60.2}O_{128}$	0.85	0.90	1.75	145
HBeta/F	[21]	$H_{3.8}Al_{3.8}Si_{60.2}O_{128}$ + 0.5 wt.% NH_4F	0.35	0.85	1.20	170
HZSM-5	[22]	$H_{4.2}Al_{4.2}Si_{91.8}O_{192}$	0.15	0.75	0.90	170

[a] Experimental accuracy ±0.5 mmol/g.
[b] Experimental accuracy ±15 kJ/mol.
[c] Commercial product purchased from Union Carbide Corp., Tarrytown, NY, USA.

in demineralized water and dried at room temperature. Zeolite NH_4Beta/F was obtained by treating zeolite NH_4Beta with NH_4F as described in [23]: zeolite NH_4Beta was added to a desired quantity of 0.1 M solution of NH_4F and stirred overnight at 323 K to dryness which resulted in a zeolite with 0.5 wt.% NH_4F. All zeolite samples were characterized by AES, ICP-AES, XRD, ^{27}Al and ^{29}Si MAS NMR spectroscopy. No signals of extra-framework aluminum atoms were found in the ^{27}Al MAS NMR spectra of the hydrated samples after cation exchange and calcination.

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). In the experiments performed with a fixed bed reactor, 200 mg of the catalyst were calcined at 673 K for 12 h (Amberlyst-15 at 373 K) in a flow of dry nitrogen gas. If indicated, the in situ MAS NMR flow probe was directly coupled with an on-line gas chromatograph allowing an analysis of the reaction products leaving the MAS NMR rotor reactor (see [20]). In these experiments, 200 mg of the catalyst was calcined in vacuum as described below and filled into a 7 mm Bruker MAS NMR rotor under dry nitrogen using a glove box. As given in Table 2, modified residence times of $W_{CAT}/F_{IB} = 150$ g h/mol and $W_{CAT}/F_{IB} = 75$ g h/mol, reaction temperatures of $T = 333$ K and $T = 353$ K and methanol/isobutene molar feed ratios of $\dot{n}_{ME}/\dot{n}_{IB} = 2:1$ and $\dot{n}_{ME}/\dot{n}_{IB} = 1:1$ were applied.

The MAS NMR investigations were performed on a Bruker MSL 400 spectrometer at resonance frequencies of 400.1 MHz for ^{1}H and 100.6 MHz for ^{13}C nuclei. The measurements were carried out with sample spinning rates of ca. 2.5 kHz for 7 mm MAS NMR rotors and ca. 10 kHz for 4 mm MAS NMR rotors. ^{13}C MAS NMR spectra were obtained after direct excitation and with proton decoupling. For each ^{1}H and ^{13}C MAS NMR spectrum, free induction decays of 25 and 720 were accumulated, respectively, with a repetition time of 10 s in both cases. Prior to the NMR investigations, the samples were heated in vacuum with a rate of 20 K/h up to the final temperature of 673 K (HY) or 723 K (HZSM-5, HBeta, HBeta/F). At these temperatures, the samples were calcined for 12 h at a pressure below 10^{-2} Pa. The amounts of OH groups given in columns 4 and 5 of Table 1 were determined by comparing the total ^{1}H NMR intensities with that of an external standard (dehydrated zeolite HNaY with an exchange degree of 35%) and after a decomposition of the ^{1}H MAS NMR spectra. ^{1}H MAS NMR studies of the acid strength of zeolite OH groups were performed at low temperature ($T = 150$ K) after loading the calcined samples with perchloroethylene, $Cl_2C{=}CCl_2$ (Fluka, No. 86970), using a vacuum line. Subsequently, the samples were sealed in glass ampoules with an outer diameter of 3.0 mm fitting into 4 mm MAS NMR rotors.

Table 2
Yields, Y_{MTBE}, and selectivities, S_{MTBE}, of MTBE obtained in a fixed bed reactor (f.b.) or in an MAS NMR rotor reactor (r.r.) after a time on stream of 8 h and applying the molar methanol/isobutene feed ratios, $\dot{n}_{ME}/\dot{n}_{IB}$, the reaction temperatures, T (K), and the modified residence times, W_{CAT}/F_{IB} (g h/mol), given in columns 3–5

Catalyst	Reactor	$\dot{n}_{ME}/\dot{n}_{IB}$	T	W_{CAT}/F_{IB}	Y_{MTBE}	S_{MTBE}
HY	f.b.	1 : 1	353	75	0.08	1.00
	f.b.	2 : 1	333	150	0.05	1.00
	f.b.	2 : 1	353	150	0.15	1.00
	r.r.	2 : 1	333	150	0.02	0.95
	r.r.	2 : 1	353	150	0.07	0.98
HBeta	f.b.	1 : 1	333	75	0.41	0.91
	f.b.	2 : 1	333	150	0.45	0.90
	f.b.	2 : 1	353	150	0.21	0.48
	r.r.	2 : 1	333	150	0.27	0.93
	r.r.	2 : 1	353	150	0.11	0.49
HBeta/F	f.b.	1 : 1	333	75	0.38	0.90
	f.b.	2 : 1	333	150	0.47	0.91
	f.b.	2 : 1	353	150	0.17	0.75
	r.r.	2 : 1	333	150	0.25	0.94
HZSM-5	f.b.	1 : 1	353	75	0.15	1.00
	f.b.	2 : 1	333	150	0.09	1.00
	f.b.	2 : 1	353	150	0.19	1.00
	r.r.	2 : 1	333	150	0.07	1.00
Amberlyst-15	f.b.	1 : 1	333	75	0.38	0.97
	f.b.	2 : 1	333	150	0.47	1.00
	f.b.	2 : 1	353	150	0.20	0.83

Prior to the in situ ^{13}C MAS NMR studies of the synthesis of MTBE on zeolites HY and HBeta under batch conditions, a mixture of methanol (ME), CH_3OH (Fluka, No. 65542), and isobutene (IB), i-C_4H_{10} (Messer Griesheim, No. 795.03039), was adsorbed at partial pressures of 14 and 7 mbar, respectively, on the calcined samples filled into an MAS

NMR rotor. During the loading, the rotor was connected to the vacuum line. Subsequently, the MAS NMR rotor was sealed with a gas tight rotor cap. The in situ ^{1}H MAS NMR adsorption experiments were performed by injecting nitrogen gas loaded with methanol, CD_3OH (99.0 at.%, Riedel-deHaën, No. 09057) into a MAS NMR rotor via an axially placed injection tube (see [24,25]). During the in situ ^{13}C MAS NMR investigations of the synthesis of MTBE under flow conditions, nitrogen gas loaded with a methanol/isobutene feed (vide supra) was injected into the MAS NMR rotor reactor. Generally, all ^{13}C MAS NMR measurements were performed using reactant molecules with ^{13}C isotopes in natural abundance.

3. Results and discussion

3.1. Characterization of Brønsted acid sites

The quantitative characterization of Brønsted acid sites of the zeolite catalysts was performed by ^{1}H MAS NMR spectroscopy. The ^{1}H MAS NMR spectra of calcined zeolites HY, HBeta, HBeta/F and HZSM-5 recorded at $T = 295$ K consist of signals at ca. 2 ppm and at ca. 4 ppm due to silanol groups (SiOH) and bridging OH groups (SiOHAl) [26,27], respectively. The quantitative evaluation of the intensities of these signals yielded the amounts of SiOH (n_{SiOH}) and SiOHAl groups (n_{SiOHAl}) summarized in columns 4 and 5 of Table 1. According to these values, zeolite HY is the catalyst with the highest amount of bridging OH groups, while zeolite HBeta is characterized by the highest amount of silanol groups. Treatment of zeolite NH_4Beta with NH_4F and subsequent calcination led to a decrease in the amount of silanol groups by more than 50% (see zeolite HBeta/F). This indicates a partial fluorination of silanol groups in zeolite HBeta/F.

The acid strength of bridging OH groups was determined using the method proposed by Sachsenroeder et al. [28]. According to this method, the deprotonation energy, ΔE_{DP}, of hydroxyl groups can be calculated via the adsorbate-induced resonance shift of the hydroxyl protons after loading the samples with perchloroethylene leading to the values summarized in column 7 of Table 1 (see also [29]). Considering these values, the bridging OH groups of zeolite HY have the lowest acid strength while zeolite HZSM-5 is the catalyst with the strongest acid sites. Interestingly, fluorination of zeolite HBeta with NH_4F leads to bridging OH groups with an acid strength comparable to that of bridging OH groups in zeolite HZSM-5.

3.2. Synthesis of MTBE on solid acids studied by on-line gas chromatography

The intention of the on-line gas chromatographic investigations was to prove whether the zeolites under study show catalytic activities comparable to those described in the literature [7]. Furthermore, reaction parameters suitable for in situ MAS NMR investigations under flow conditions should be found and the influence of the reactor type — fixed bed reactor and spinning MAS NMR rotor reactor — on the yield of MTBE should be clarified.

In Fig. 1, the yields of MTBE, Y_{MTBE}, on Amberlyst-15 and on zeolites HY, HBeta, HBeta/F and HZSM-5 are depicted as a function of time on stream. These investigations were carried out with a molar methanol/isobutene feed ratio of $\dot{n}_{ME}/\dot{n}_{IB} = 2:1$, a modified residence time of $W_{CAT}/F_{IB} = 150$ g h/mol and at reaction temperatures of $T = 333$ K (Fig. 1a) and $T = 353$ K (Fig. 1b). At the reaction temperature of $T = 333$ K, the yield of MTBE obtained on the zeolites HBeta and HBeta/F is comparable with that on Amberlyst-15. Zeolite HY with the largest amount of acidic bridging OH groups and zeolite HZSM-5 with the strongest acid sites show significantly lower yields of MTBE than zeolites HBeta and HBeta/F, which agrees with the results of Collignon et al. [7]. The decrease in the yield of MTBE on Amberlyst-15 and on zeolites HBeta and HBeta/F after raising the reaction temperature to $T = 353$ K (Fig. 1b) is due to limitations of the chemical equilibrium (see [7]).

In all on-line gas chromatographic investigations, the steady state was reached after a time on stream of ca. 1 h and no deactivation was observed up to a time on stream of 8 h. Hence, there is a period of at least 6 h allowing in situ MAS NMR spectroscopic studies of the steady state of the heterogeneously catalyzed reaction. In Table 2, the yields and selectivities of MTBE obtained in a fixed bed reactor (f.b.) are compared with those obtained in a spinning MAS NMR rotor reactor (r.r.). The latter measurements were

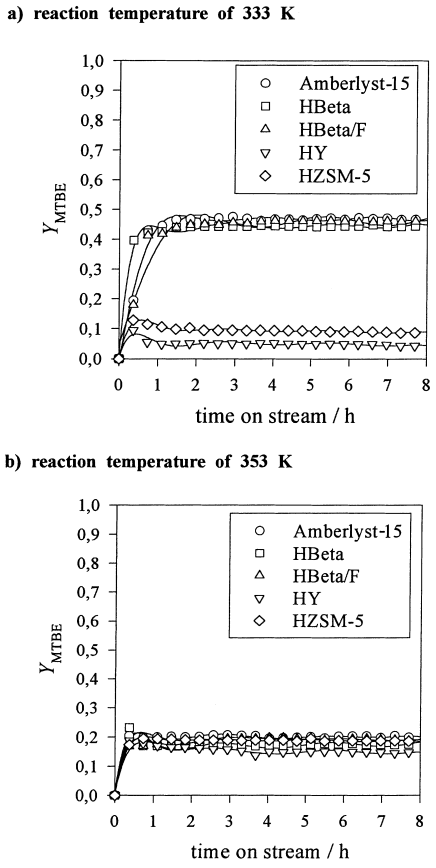

Fig. 1. Yields of MTBE, Y_{MTBE}, obtained on dehydrated Amberlyst-15 and on calcined zeolites HY, HBeta, HBeta/F and HZSM-5 in a fixed-bed reactor with a modified residence time of $W_{CAT}/F_{IB} = 150$ g h/mol, a molar methanol/isobutene feed ratio of $\dot{n}_{ME}/\dot{n}_{IB} = 2:1$ and at reaction temperatures of $T = 333$ K (a) and $T = 353$ K (b).

performed using an MAS NMR flow probe directly coupled with an on-line gas chromatograph. For all zeolites under study, lower yields of MTBE were obtained with the spinning MAS NMR rotor reactor in comparison with the fixed bed reactor. This may be due to the different flow conditions in the two reactor types. In the fixed bed reactor, the carrier gas loaded with reactant molecules flows through the catalyst bed, while in the rotor reactor, it flows along the inner surface of the catalyst bed shaped as a hollow cylinder. However, same characteristic differences of the catalytic activities of zeolites HY, HBeta, HBeta/F and HZSM-5 were found for the synthesis of MTBE in these two types of reactors.

3.3. Adsorption of methanol on Brønsted acid sites studied by ^1H MAS NMR

The interaction of the reactant methanol with hydroxyl groups in zeolites HY, HBeta, HBeta/F and HZSM-5 was studied by injecting nitrogen loaded with CD_3OH into the MAS NMR rotor reactor filled with the calcined catalyst (see [10]). With increasing loading, the spectra were dominated by strong low-field signals due to hydroxyl protons contributing to methanol adsorbate complexes. In Fig. 2, the resonance positions of these ^{1}H MAS NMR low-field signals obtained after adsorption of methanol on zeolites HY, HBeta, HBeta/F and HZSM-5 are depicted as a function of the amount of methanol molecules loaded per OH group, n_{ME}/n_{OH} (n_{OH}: total amount of OH groups). At room temperature, the rapid exchange of hydroxyl protons of (i) two-fold hydrogen bonded methanol molecules and of (ii) methanol molecules passing the state of a methoxonium ion leads to a single signal at the centre of gravity of these components. Since at low loadings all methanol molecules are adsorbed on Brønsted acid sites, a higher ^{1}H NMR chemical shift of the low-field signal corresponds to a higher 'protonation degree' of the methanol molecules. Considering the curves in Fig. 2 at low loadings, the methanol adsorbate complexes on zeolite HZSM-5 show the highest chemical shift, while the adsorbate complexes on zeolite HBeta are characterized by a low chemical shift. Considering the low catalytic acitivity of zeolite HZSM-5 in the

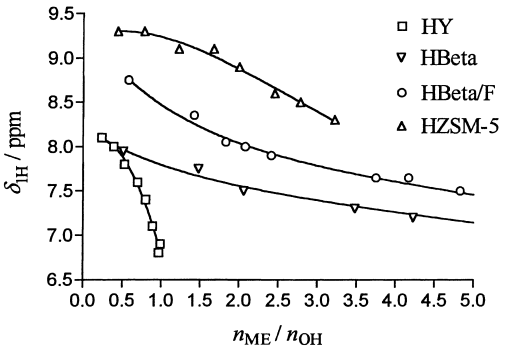

Fig. 2. ^{1}H MAS NMR shifts of the low-field lines occurring after adsorption of CD_3OH on calcined zeolites HY, HBeta, HBeta/F and HZSM-5 plotted as a function of the amount of methanol molecules per OH group, n_{ME}/n_{OH} (n_{OH}: total amount of OH groups).

synthesis of MTBE in comparison with that of zeolite HBeta (see Fig. 1), it seems to be questionable whether the protonation of methanol molecules plays a key role in this reaction.

Interestingly, the methanol adsorption capacities of zeolites HBeta and HBeta/F are significantly higher than those of zeolites HY and HZSM-5 (Fig. 2). The ^{1}H MAS NMR spectra recorded during the adsorption of methanol on zeolites HBeta and HBeta/F clearly show that silanol groups also act as adsorption sites. Therefore, the large number of methanol molecules weakly physisorbed on silanol groups in zeolites HBeta and HBeta/F act as a reservoir of reactant molecules in the synthesis of MTBE.

3.4. In situ ^{13}C MAS NMR investigations of the synthesis of MTBE on zeolites under batch conditions

In situ MAS NMR investigations under batch conditions allow to optimize experimental parameters and to determine the ^{13}C NMR chemical shifts of adsorbed reactant and product molecules. In addition, the influence of the reaction modus — batch or flow conditions — on the NMR spectroscopically observed signals can be studied.

According to previous investigations, the ^{13}C NMR shift of methanol molecules adsorbed on zeolites covers a range of 50–53 ppm [9,10,30,31]. To prevent chemical conversions, the chemical shifts of isobutene and MTBE were determined by adsorption on non-acidic solids such as silica gel (Fig. 3a and b) and zeolite NaY (Fig. 3c). According to these investigations, adsorption on zeolite NaY leads to resonance positions equal to those observed for silica gel. The ^{13}C MAS NMR spectra of isobutene consist of signals due to methyl groups at 22 ppm, tertiary carbon atoms at 109 ppm and methylene groups at 145 ppm (Fig. 3a). Adsorption of MTBE causes signals of tertiary butyl groups at 26 ppm, methyl groups at 48–49 ppm and tertiary carbon atoms at 73 ppm (Fig. 3b and c).

Synthesis of MTBE on zeolites was studied with samples prepared by adsorption of a mixture of methanol and isobutene ($n_{ME}/n_{IB} = 2:1$) on the calcined zeolites filled into an MAS NMR rotor. The ^{13}C MAS NMR spectra shown in Fig. 3d and e were recorded during heating the samples at $T = 353$ K and $T = 333$ K, respectively. The strong signal at 50 ppm

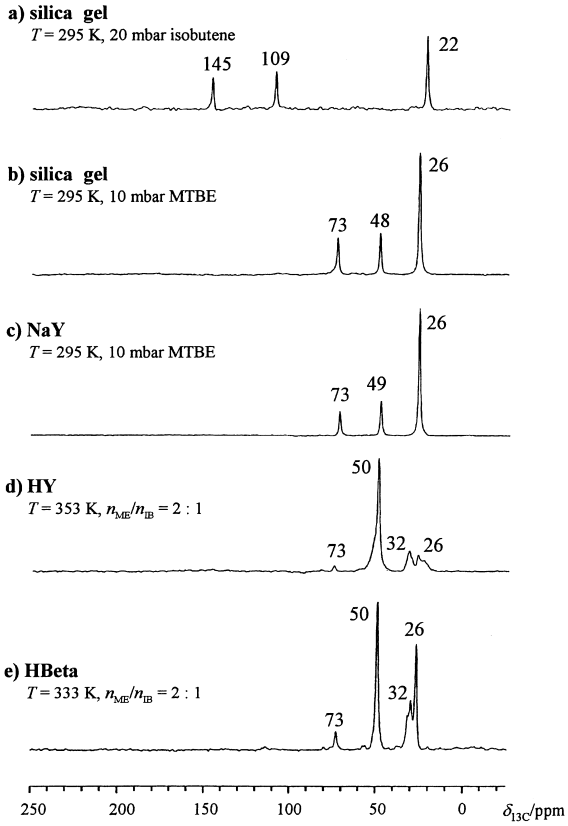

Fig. 3. ^{13}C MAS NMR spectra of isobutene on calcined silica gel (a), of MTBE on calcined silica gel (b) and zeolite NaY (c) and of a mixture of methanol and isobutene on calcined zeolites HY (d) and HBeta (e). The adsorption of the methanol/isobutene mixtures was performed with partial pressures of $p_{ME} = 14$ mbar, $p_{IB} = 7$ mbar. After the adsorption, the MAS NMR rotors were sealed with gas tight caps. The spectra were recorded at temperatures of $T = 295$ K (a–c), $T = 353$ K (d) and $T = 333$ K (e).

dominating the ^{13}C MAS NMR spectrum of zeolite HY (Fig. 3d) is due to methanol. The signal at 32 ppm agrees with that observed by Lazo et al. [32] after the adsorption of isobutene on zeolite HY and HZSM-5 under batch conditions. It indicates the formation of isobutene dimers or oligomers with methyl groups having chemical shifts of 30–32 ppm [33]. The remaining signals at 26 and 73 ppm correspond to resonance positions of the tertiary butyl groups and tertiary carbon atoms of MTBE, respectively. The signal of the methyl groups of MTBE at 48–49 ppm is overlapped by the strong signal of methanol at 50 ppm. In agreement with the high catalytic activity of zeolite HBeta in the synthesis of MTBE (see

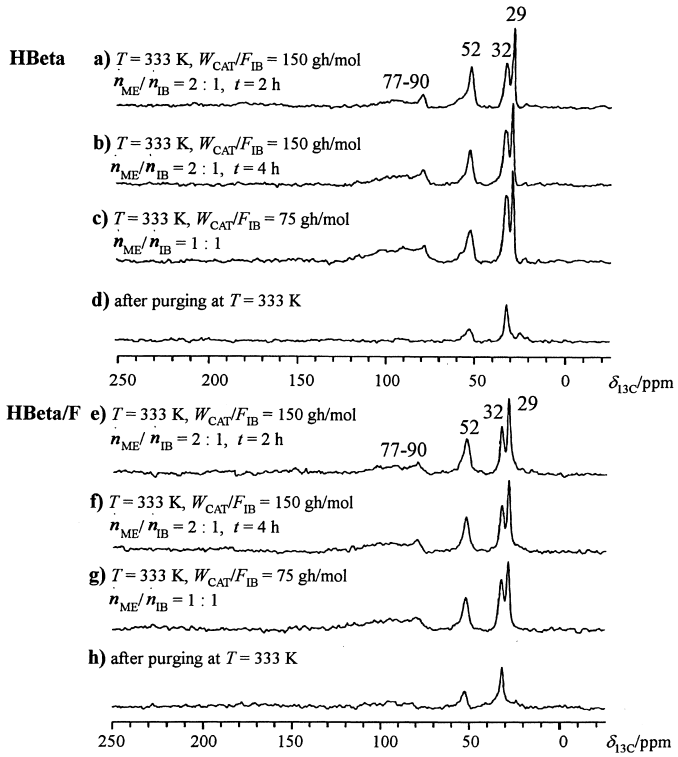

Fig. 4. ^{13}C MAS NMR spectra recorded in the steady state of the synthesis of MTBE on calcined zeolites HBeta (a–c) and HBeta/F (e–g) with the modified residence times, W_{CAT}/F_{IB}, and the molar methanol/isobutene feed ratios, $\dot{n}_{ME}/\dot{n}_{IB}$, given in the text and after purging these catalysts with dry nitrogen (d and h).

Table 2), the spectrum of this zeolite (Fig. 3e) shows significantly stronger signals at 26 and 73 ppm due to the reaction product MTBE. Again, the signal at ca. 32 ppm is a hint for the formation of isobutene oligomers. In agreement with earlier studies of the conversion of isobutene on acidic zeolites HY and HZSM-5 under batch conditions [32], no signals in the vicinity of 77–81 ppm were found. ^{13}C MAS NMR signals at these resonance positions would be a hint for the formation of alkoxy species [32,34,35].

3.5. In situ ^{13}C MAS NMR investigations of the synthesis of MTBE on zeolites under flow conditions

The ^{13}C MAS NMR spectra shown in Fig. 4 were recorded in the steady state of the synthesis of MTBE applying reaction conditions equal to those used for the fixed bed reactor (see Table 2). Two of the observed signals agree with those found in the spectra recorded under batch conditions: the line at 52 ppm due to strongly adsorbed methanol molecules and the line at 32 ppm caused by methyl groups of isobutene oligomers and dimers. The chemical shifts of the signals at 29 and 77–90 ppm are too high for them to be assigned to methyl groups of the tertiary butyl compounds and to tertiary carbon atoms, respectively, of MTBE (compare Fig. 3b,c and e). The absence of signals at 26 and 73 ppm indicates that the residence time of MTBE molecules inside the MAS NMR rotor reactor is short in comparison with their longitudinal relaxation time. According to the literature [32,34,35], isobutoxy species formed by the adsorption of 2-methyl-2-propanol on zeolite HZSM-5 cause a signal of tertiary carbon atoms at ca. 77–81 ppm. The chemical shift of the methyl groups of these species of 29 ppm corresponds to the resonance position of the high-field signals in Fig. 4. Therefore, the signals appearing at 29 and 77–90 ppm can be attributed to alkoxy species. The disappearance of the signals at 29

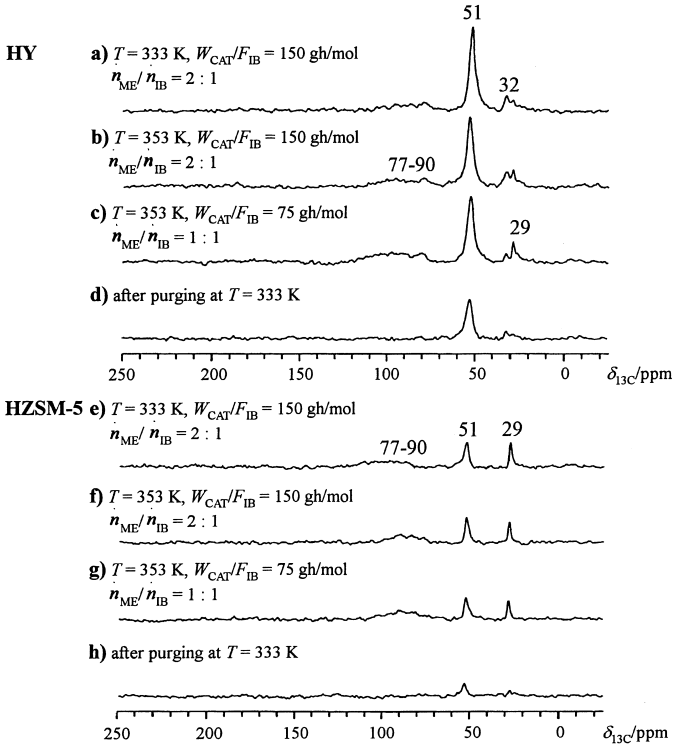

Fig. 5. ^{13}C MAS NMR spectra recorded in the steady state of the synthesis of MTBE on calcined zeolites HY (a–c) and HZSM-5 (e–g) with the modified residence times, W/F_{IB}, and molar methanol/isobutene feed ratios, $\dot{n}_{ME}/\dot{n}_{IB}$, given in the text and after purging these catalysts with dry nitrogen (d and h).

and 77–90 ppm (Fig. 4d and h) after purging zeolites HBeta and HBeta/F with dry nitrogen gas is a hint for a low chemical stability of these alkoxy species. This finding agrees with the fact that neither in the present work nor that by Lazo et al. [32] were signals of isobutoxy species observed in ^{13}C MAS NMR spectra recorded under batch conditions. Considering the high acid strength of Brønsted sites in zeolite HZSM-5 (Table 1, column 7), its ability of physisorbing methanol (Fig. 2) and the formation of isobutoxy species observed by in situ ^{13}C MAS NMR spectroscopy (Fig. 5e–g), the low yield of MTBE indicates restrictions in the reactant diffusion in this zeolite. This is in line with the increase of Y_{MTBE} found for zeolite HZSM-5 at the reaction temperature of $T = 353$ K.

Comparing the ^{13}C MAS NMR spectra recorded during the synthesis of MTBE on zeolites HBeta and HBeta/F (Fig. 4a–c and e–g), no significant differences in the relative NMR intensities occur. The spectra recorded at different times on stream (Fig. 4a and b and e and f) as well as those recorded with different methanol/isobutene feed ratios (Fig. 4b and c and f and g) show nearly the same isobutoxy signals. In all these cases, the yields of MTBE (see Table 2) vary only in a small range. On the other hand, the ^{13}C MAS NMR spectra recorded in the steady state of the synthesis of MTBE on zeolites HY and HZSM-5 (Fig. 5) show significantly weaker signals of alkoxy species than the spectra of zeolites HBeta and HBeta/F. While in the spectrum of zeolite HY, obtained at a reaction temperature of $T = 333$ K, only weak signals can be found at 29 and 77–90 ppm, the increase in the reaction temperature to $T = 353$ K leads also to an increase in the intensities of these signals (Fig. 5a and b). This is in line with the higher yield of MTBE determined by on-line gas chromatography (see Table 2). For zeolite HZSM-5 (Fig. 5e–g), the weak signals at 29 and 77–90 ppm observed at $T = 333$ K and the absence of the signal at 32 ppm are in line with the low yield

of MTBE at this reaction temperature and the high MTBE selectivity, respectively, of zeolite HZSM-5.

Since the NMR spectroscopic observation of isobutoxy species on zeolites HY, HBeta, HBeta/F and HZSM-5 is in line with the yields of MTBE determined by on-line gas chromatography, it can be assumed that isobutoxy species play a key role in the formation of MTBE on zeolites. On account of the low energy barrier for a transformation of alkoxy species into carbenium ions, Aronson et al. [34] called them 'species with carbenium-like properties'. This assignment is supported by quantum-chemical investigations published by Kazansky [36] and van Santen [37]. In a further step, the methanol molecules react with the isobutoxy/isobutyl cation compounds leading to the formation of MTBE. On zeolites HBeta and HBeta/F, this reaction step is promoted by the large reservoir of methanol molecules weakly adsorbed at internal OH groups.

4. Conclusions

By in situ MAS NMR spectroscopy of the steady state of MTBE synthesis on zeolites HY, HBeta, HBeta/F and HZSM-5, the formation of alkoxy species bound on framework oxygen atoms was observed. The occurrence of ^{13}C MAS NMR signals at 29 and 77–90 ppm due to these species correlate with the yield of MTBE determined by on-line gas chromatography. In the ^{13}C MAS NMR spectra of highly active zeolites, such as zeolites HBeta and HBeta/F, the signals of alkoxy species were found to be stronger than those in the spectra of zeolites having a lower activity, such as zeolites HY and HZSM-5. The alkoxy species can be removed by purging the catalysts with dry nitrogen. Under batch conditions, these species could not be detected. Therefore, it was concluded that alkoxy species observed by in situ ^{13}C MAS NMR spectroscopy at 29 and 77–90 ppm are characterized by a low chemical stability. Based on these results and the low 'protonation degree' of methanol molecules adsorbed on the highly active zeolites HBeta and HBeta/F, a mechanism for the formation of MTBE on acidic zeolites is proposed in which the initial step consists of a reaction of isobutene with bridging OH groups leading to the formation of alkoxy species with 'carbenium-like properties'.

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