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MTBE SYNTHESIS ON ZEOLITES INVESTIGATED BY *IN SITU* NMR SPECTROSCOPY

Gas phase synthesis of MTBE on zeolites HY, HZSM-5, HBeta and fluorinated zeolite HBeta/F was investigated by *in situ* ^1H and ^{13}C MAS NMR spectroscopy. Low-temperature ^1H MAS NMR spectroscopy of the zeolite catalysts, loaded with perchloroethylene, led to a strong increase in the strength of Broensted acid sites in zeolite HBeta after fluorination with ammonium fluoride. Similar results were obtained when propan-2-ol dehydration was used as a test reaction for Broensted acidity and when methyl tertiary-butyl ether (MTBE) synthesis was studied in a flow-type apparatus with on-line gaschromatographic detection of the products. *In situ* adsorption experiments showed that, especially in zeolite HBeta, a large number of partially protonated methanol clusters were formed at silanol groups. These clusters may act as a reservoir of reactant molecules in the MTBE synthesis. Signals of by-products of the MTBE synthesis on zeolites which were observed by *in situ* ^1H and ^{13}C MAS NMR spectroscopy could be assigned to diisopropyl and methyl isopropyl ether.

Introduction

A number of papers published in the past three years [1-5] focused on the application of zeolites as catalysts for the synthesis of MTBE, which is largely used as an octane booster in unleaded gasolines. The industrial production of MTBE is currently performed in the liquid phase over sulfonic acid resins (e.g., Amberlyst-15) at temperatures in the range 323 K to 343 K and methanol/isobutene molar feed ratios of higher than 1 : 1 [6]. While sulfonic acid resins are quite efficient catalysts, they lead to a number of undesirable by-products (e.g., diisobutenes, tertiary-butyl alcohol, dimethylether) [7], cause corrosion problems [8] and require, due to the high methanol/isobutene molar ratios, a recycle operation [6]. Therefore, zeolites HY, H-omega, H-mordenite and HZSM-5, partially after dealumination and treatment with triflic acid or ammonium fluoride, were tested as alternative catalysts for the synthesis of MTBE in the gas phase [1-5]. For all these zeolites, the maximum MTBE yield was found at temperatures between 353 K and 383 K. Equilibrium limitations [9] call for catalysts which are more active than Amberlyst-15. Very recently, Collignon et al. [5] studied MTBE synthesis on zeolites HBeta with n_{Si}/n_{Al} ratios between 13 and 194. These authors found that zeolites HBeta are significantly more active than all other types of zeolites. Zeolite HBeta with an n_{Si}/n_{Al} ratio of 25.7, gave a maximum MTBE yield of ca. 50 % at 333 K. This high catalytic activity was interpreted in terms of the large external surface (211 to 240 m^2/g) of the zeolites HBeta used [5]. Investigating the MTBE synthesis on zeolites HZSM-5 and HY, Kogelbauer et al. [2] observed an increase in the rate of MTBE formation by a factor of two and a suppression of by-products after preadsorption of about 2.5 methanol

molecules per zeolite OH group. This indicates the important role of adsorbate complexes formed by adsorption of methanol molecules for the activity of zeolites in MTBE synthesis. The adsorbate complexes prevent an oligomerization of isobutene by blocking the acid sites and act as protonating agent themselves [2].

In the present work zeolites HY, HZSM-5, HBeta and a fluorinated zeolite HBeta were applied as catalysts in the MTBE synthesis. The Broensted acid sites in these materials were investigated by low-temperature ^{1}H MAS NMR spectroscopy after loading the calcined samples with perchloroethylene. According to Sachsenröder et al. [10], the adsorbate-induced low-field shift of the resonance position of the hydroxyl protons is a measure for their acid strength.

Using a new MAS NMR technique [11, 12] *in situ* methanol adsorption experiments were carried out. The calcined zeolite samples were exposed to a continuous flow of nitrogen loaded with methanol vapors during the MAS NMR measurements which led to an uptake of these molecules. The important advantage of this technique is the combined quantitative information on methanol adsorption and insight into the structure of adsorbate complexes through NMR spectroscopy.

The catalytic activity of the above-mentioned zeolites was studied as well in the dehydration of propan-2-ol and MTBE synthesis in the gas phase. *In situ* ^{1}H and ^{13}C MAS NMR spectroscopy was applied to identify by-products of MTBE synthesis inside the zeolite pores.

Experimental Section

Information on the zeolite catalysts employed is given in Table 1. The hydrogen forms were prepared by fourfold ion exchange at 353 K in a surplus of 0.1 M (HY) or 0.4 M (HZSM-5, HBeta) aqueous solution of NH_4NO_3. After ion exchange the zeolite powder was washed in demineralized water and dried at room temperature. Zeolite HBeta/F was obtained by treating zeolite HBeta with NH_4F as described in reference [15]. Zeolite HBeta 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.

Table 1 Synthesis procedures, chemical compositions (AAS, ICP-AES) and OH concentrations of the zeolite catalysts under study.

Catalyst	Synthesis	Chemical composition	c_{SiOH} in mmol/g	c_{SiOHAl} in mmol/g
HY	*	$H_{46.9}Na_{6.4}Al_{53.3}Si_{138.7}O_{384}$	0.08	4.05
HZSM-5	ref. [13]	$H_{4.2}Al_{4.2}Si_{91.8}O_{192}$	0.15	0.75
HBeta	ref. [14]	$H_{3.8}Al_{3.8}Si_{60.2}O_{128}$	0.85	0.90
HBeta/F	ref. [14]	$H_{3.8}Al_{3.8}Si_{60.2}O_{128}$, + 0.5 wt.-% NH_4F	0.35	0.85

-) commercial product purchased from Union Carbide Corp., Tarrytown, NY, USA

Amberlyst-15 was a commercial product (Aldrich Chemical Co. Ltd, No. 21,638-0). All zeolite samples were characterized by AAS, 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. Before the NMR investigations, the powdered materials were heated in vacuum with a rate of 20 K/h up to the final temperature of 673 K. There, they were calcined for 12 h at a pressure below

10^{-2} Pa. The adsorption of probe molecules ($Cl_2C{=}CCl_2$) and reactants (C^*H_3OH and $(CH_3)_2C{=}CH_2$, asterisk indicates ^{13}C-enriched carbon atoms) was carried out on the calcined samples using a vacuum line. All samples applied for low-temperature ^1H MAS NMR and *in situ* ^1H and ^{13}C MAS NMR spectroscopy were sealed inside 3.2 mm glass ampoules.

The NMR investigations were carried out on a Bruker MSL 400 spectrometer. During *in situ* adsorption experiments nitrogen gas (6 cm^3/min) loaded with CD_3OH (99.0 atom-% D) was led into a commercial 7 mm MAS NMR Bruker rotor via an axially placed injection tube (see refs. [11, 12]). 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 %) after a decomposition of the spectra. The numbers of methanol molecules adsorbed on the calcined zeolites were determined using the spectrum of the unloaded zeolites as an internal intensity standard. *In situ* MAS NMR investigations were carried out on the calcined and loaded zeolite samples sealed in glass ampoules and heated inside the spectrometer at the reaction temperature.

The dehydration of propan-2-ol and the synthesis of MTBE were investigated with a flow-type apparatus and on-line gaschromatographic detection of the products. Prior to the catalytic measurements 250 mg of the catalyst were calcined for 12 h at 673 K (Amberlyst-15 at 373 K) in a flow of dry nitrogen gas. A modified residence time (W/F) of 450 gh/mol and a reaction temperature of 393 K were used for propan-2-ol dehydration. The MTBE synthesis was carried out at 333 K with $W/F_{i\text{-}b}$ = 150 gh/mol and a methanol/isobutene (i-b) molar feed ratio of 2 : 1.

Results and Discussion

Broensted acid sites of the zeolite catalysts:

In the present work ^1H MAS NMR spectroscopy was applied for a quantitative characterization of Broensted acid sites in the zeolite catalysts. The concentrations of silanol groups (c_{SiOH}) at ca. 2 ppm and bridging OH groups (c_{SiOHAl}) at ca. 4 ppm given in Table 1 were derived from a quantitative evaluation of the ^1H MAS NMR spectra of the calcined zeolites. According to these values, zeolite HY is the catalyst with the largest number of bridging OH groups. An interesting feature of zeolite Beta is the decrease of the SiOH concentration after treatment with NH_4F and calcination. This indicates a partial fluorination of SiOH groups in zeolite HBeta/F.

To determine the strength of Broensted acid sites, the method proposed by Sachsenröder et al. [10] was applied: the deprotonation energy ΔE_{DP} of hydroxyl groups was calculated via the adsorbate-induced resonance shifts of the hydroxyl protons of silanol groups ($\Delta\delta_{SiOH}$) as an internal shift standard and of the acidic OH groups under study ($\Delta\delta_{acOH}$) [10]:

$$\frac{\Delta E_{DP}}{\text{kJ/mol}} = -\frac{1}{0.00226} \cdot \log\left(\frac{\Delta\delta_{acOH}}{\Delta\delta_{SiOH}}\right) \qquad (1)$$

A suitable adsorbate molecule which has no ^1H MAS NMR signal of its own is perchloroethylene. To slow down the rapid exchange of adsorbate molecules between different adsorption sites, the ^1H MAS NMR spectra shown in Figure 1 were recorded at 150 K. The adsorbate-induced resonance shifts $\Delta\delta_{acOH}$ found by

comparing the spectra of the unloaded zeolites with those of the zeolites loaded with one molecule perchloroethylene per acidic OH group are given in column 2 of Table 2. With equation (1) and $\Delta\delta_{SiOH}$ = (0.75 ± 0.05) ppm [10] the deprotonation energies ΔE_{DP} given in column 3 of Table 2 were calculated. According to these values, zeolite HY has Broensted acid sites (*vide supra*) with the lowest acid strength. On the other hand, fluorination of zeolite HBeta leads to Broensted acid sites with the same acid strength as in zeolite HZSM-5.

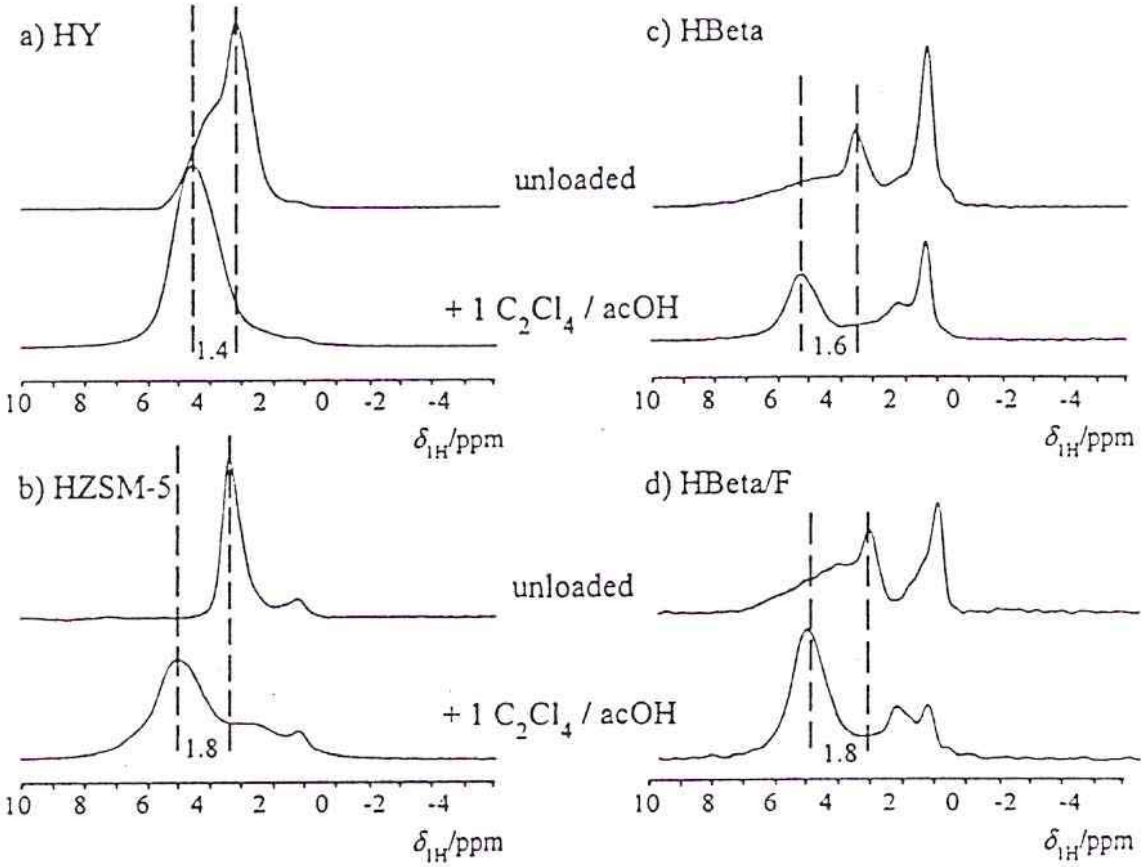

Fig. 1 Low-temperature (150 K) ^{1}H MAS NMR spectra of calcined zeolites HY (a), HZSM-5 (b), HBeta (c) and HBeta/F (d), recorded before (top) and after (bottom) loading of one molecule perchloroethylene per acidic OH group.

Table 2 Adsorbate-induced ^{1}H MAS NMR low-field shifts $\Delta\delta_{acOH}$ (accuracy ± 0.05 ppm) of the resonance positions of acidic hydroxyl protons in zeolites, corresponding deprotonation energies ΔE_{DP} (accuracy ± 5 kJ/mol), conversions $X_{p\text{-}2\text{-}ol}$ of propan-2-ol dehydration at 393 K and yields Y_{MTBE} of MTBE synthesis at 333 K (n.d.: not determined).

Catalysts	$\Delta\delta_{acOH}$ in ppm	ΔE_{DP} in kJ/mol	$X_{p\text{-}2\text{-}ol}$ in %	Y_{MTBE} in %	S_{MTBE} in %
Amberlyst-15	n.d.	n.d.	n.d.	47	100
HY	1.4	120	76	8	94
HZSM-5	1.8	170	41	9	100
HBeta	1.6	145	60	47	95
HBeta/F	1.8	170	76	46	95

Catalytic activity of the catalysts:

The conversion of alcohols is a well established reaction for the characterization of solid catalysts [16,17]. The dehydration of propan-2-ol was studied on the acidic zeolites HNaX [18], HNaY [19] and dealuminated HY [20]. The reaction was found to be first order with respect to propan-2-ol, the only products being propene, diisopropyl ether and water. The conversions $X_{p\text{-}2\text{-}ol}$ mesured on the zeolitic catalysts under study are given in column 4 of Table 2. At the chosen reaction conditions, propene was the main product. By-products like diisopropyl ether and acetone were formed with a yield of less than 2 %. Zeolite HY with the largest number of bridging OH groups (column 5 in Table 1) and zeolite HBeta/F with the largest number of strongly acidic bridging OH groups (column 5 in Table 1 and column 3 in Table 2) show the highest catalytic activity in the dehydration of propan-2-ol.

The yields and selectivities measured in the MTBE synthesis (columns 5 and 6 of Table 2) were measured after preadsorption of two molecules of methanol per Broensted acid site before the isobutene flow was started. A steady state was reached after a reaction time of 8 hours. The preadsorption of methanol was found to be an important prerequisite for the suppression of by-product formation on the zeolites. As shown in Table 2, zeolites HBeta and HBeta/F give yields of MTBE which are comparable to the one measured on Amberlyst-15. This indicates that the structure-type of zeolites may be of importance for catalysts applied in MTBE synthesis. Additional interesting aspects are the formation of methanol clusters at OH groups as a result of methanol preadsorption and of by-products inside the catalyst pores. Both aspects were investigated in the present work by the application of *in situ* MAS NMR spectroscopy.

In situ ^1H MAS NMR study of methanol adsorption:

In Figure 2 the ^1H MAS NMR spectra recorded during *in situ* adsorption of CD_3OH on dehydrated zeolites HZSM-5 and HBeta are depicted. The spectra labbelled with 0 mmol/g (bottom) correspond to those of the unloaded zeolites with signals due to silanol groups at ca. 2 ppm and of bridging OH groups at ca. 4 ppm [13]. Already after adsorption of about 1 mmol CD_3OH per gram zeolite, a low-field ^1H MAS NMR signal was observed which is due to the hydroxyl groups contributing to adsorbate complexes. This signal increases upon the adsorption of further methanol molecules. At the same time, the signals of zeolite OH groups decrease indicating their interaction with adsorbate molecules. Methanol adsorption on zeolites HZSM-5 (see Fig. 2a) and HY (not shown) leads to a preferential interaction of adsorbate molecules with bridging OH groups. Even after an adsorption time of 120 min (end of the experiment) the signal of silanol groups can still be observed in the spectra (see Fig. 2a). By contrast, methanol adsorption on zeolite Beta (see Fig. 2b) brings about a significant decrease of the signals of silanol groups which indicates an interaction with these OH groups too.

In Figure 3 the ^1H MAS NMR shifts of hydroxyl groups contributing to the adsorbate complexes in zeolites HY, HZSM-5 and HBeta are plotted as a function of the number of adsorbate molecules. The curve for zeolite HY resembles the one for zeolite HZSM-5, however, all values are lower by ca. 1 ppm. According to the results of quantum-chemical calculations published by Haase and Sauer [21], methanol

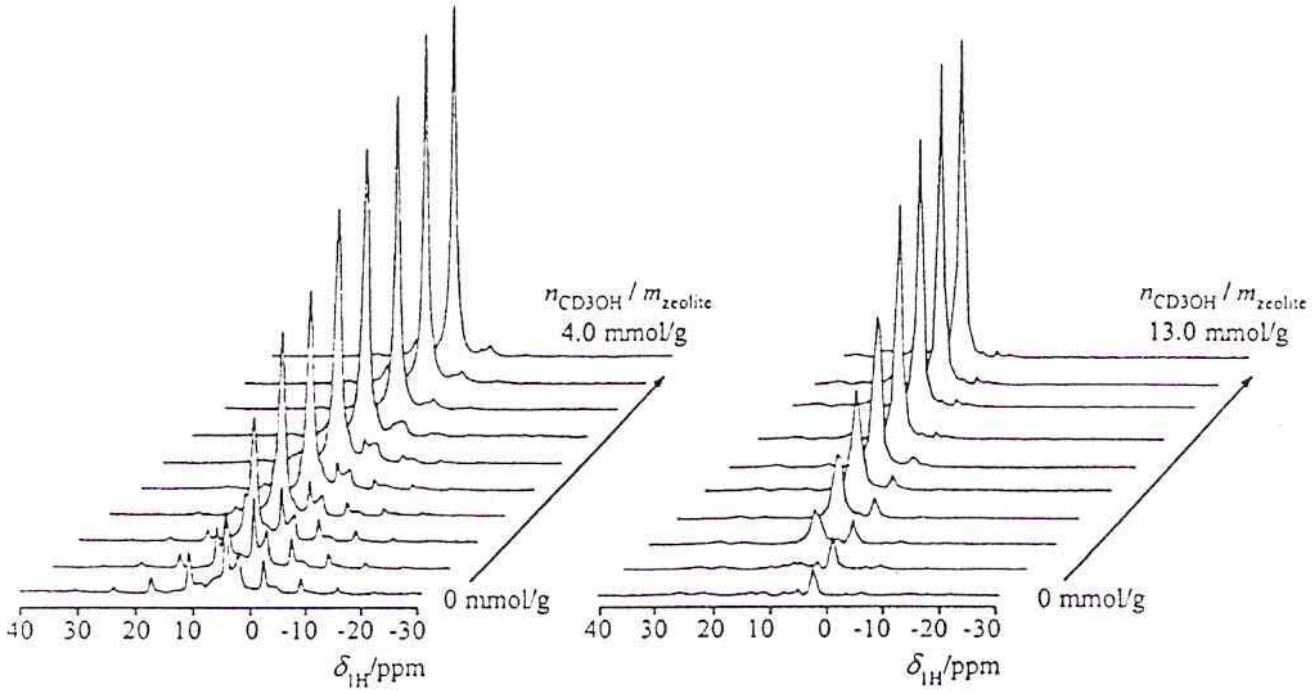

Fig 2 ^{1}H MAS NMR spectra of calcined zeolites HZSM-5 (a) and HBeta (b), recorded during *in situ* adsorption of methanol at 293 K within a time of 120 min. The calcined zeolite HZSM-5 was exposed to a flow of nitrogen gas loaded with CD_3OH (partial pressure of 6×10^3 Pa).

molecules interact with zeolite OH groups via a twofold hydrogen bonding (I). Hydrogen bound methoxonium ions exist as a transition state (II). The formation of both arrangements is coupled with a significant low-field shift of the ^{1}H MAS NMR signal of the contributing hydroxyl protons. The formation of arrangement (II) shifts the calculated resonance position of the hydroxyl protons by about 7 ppm to a lower field as in the case of complex (I). The different experimental resonance shifts of the adsorbate complexes in zeolites HY and HZSM-5 could, therefore, be explained by the stronger acid sites of the latter zeolite and a higher protonation of the methanol complexes in this material.

After adsorption of 1 mmol CD_3OH per gram powder material in the ^{1}H MAS NMR spectra of zeolites HBeta and HY low-field signals occur at ca. 8 ppm. It is only upon adsorption of further methanol molecules, that the curves have significantly different slopes. The ^{1}H MAS NMR shifts of hydroxyl protons contributing to adsorbate complexes in zeolite HBeta vary only from ca. 8 ppm to ca. 7 ppm after adsorption of up to 13.0 mmol CD_3OH per gram zeolite (Fig. 3, triangles). Hence, the first methanol molecules adsorbed on zeolites HY and HBeta form adsorbate complexes in the same partially protonated state (same ^{1}H NMR shift). Upon progressive methanol adsorption on zeolite HY, no adsorption sites are available any further resulting in a rapid exchange of methanol molecules contributing to adsorbate complexes and of free methanol molecules. This rapid exchange causes the significant decrease in the ^{1}H MAS NMR shift of the low-field signal shown in Figure 3. In zeolite HBeta, silanol groups are involved as well in the formation of adsorbate complexes (*vide supra*), and with progressive adsorption, further adsorbate complexes are formed. Since this ongoing adsorption is accompanied by a high-field shift of only 1 ppm, the adsorbate complexes formed on SiOH groups

should also be partially protonated, making them a reservoir of activated reactant molecules in the MTBE synthesis.

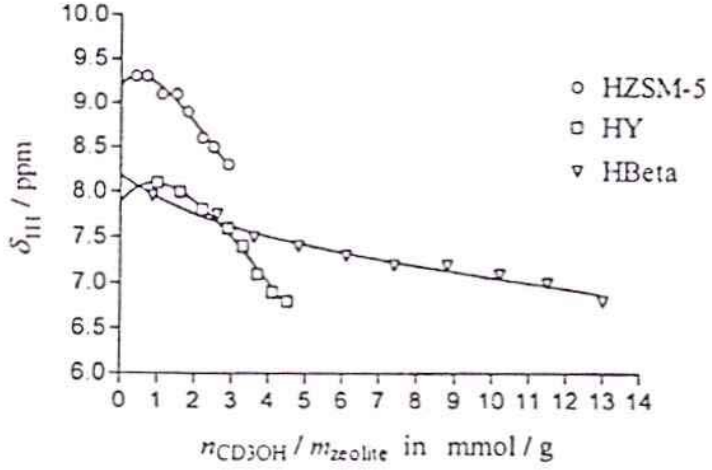

Fig. 3 ^1H MAS NMR shifts, δ_{1H}, of hydroxyl protons contributing to methanol complexes in zeolites HY, HZSM-5 (see Fig. 2a) and HBeta (see Fig. 2b) derived by *in situ* adsorption of CD_3OH, plotted as a function of the methanol loading ($n_{CD3OH} / m_{zeolite}$).

In situ ^1H and ^{13}C MAS NMR investigations of MTBE synthesis on zeolites:

In the past decade *in situ* NMR spectroscopy has been developed as a useful tool allowing the study of heterogeneously catalyzed reactions inside the catalyst pores (for a review see ref. [22]). As an example, Figure 4 shows *in situ* ^1H (left) and ^{13}C MAS NMR (right) spectra recorded during MTBE synthesis on zeolite HY at 333 K (top) and 353 K (bottom). According to these spectra, the formation of MTBE is accompanied by an increase of ^1H MAS NMR signals at 0.9 ppm to 1.1 ppm (-O-C-($C\underline{H}_3)_3$) and 3.2 ppm (-O-$C\underline{H}_3$) [23]. By *in situ* ^{13}C MAS NMR spectroscopy, the MTBE synthesis can be followed via the line at 45 ppm ($(CH_3)_3C$-O-$\underline{C}^*H_3$) [23]. The broad signal at 49 ppm is due to methanol (C^*H_3OH) [23]. Weak ^{13}C NMR signals, occurring in addition to the lines of the reactant and product molecules, i.e.

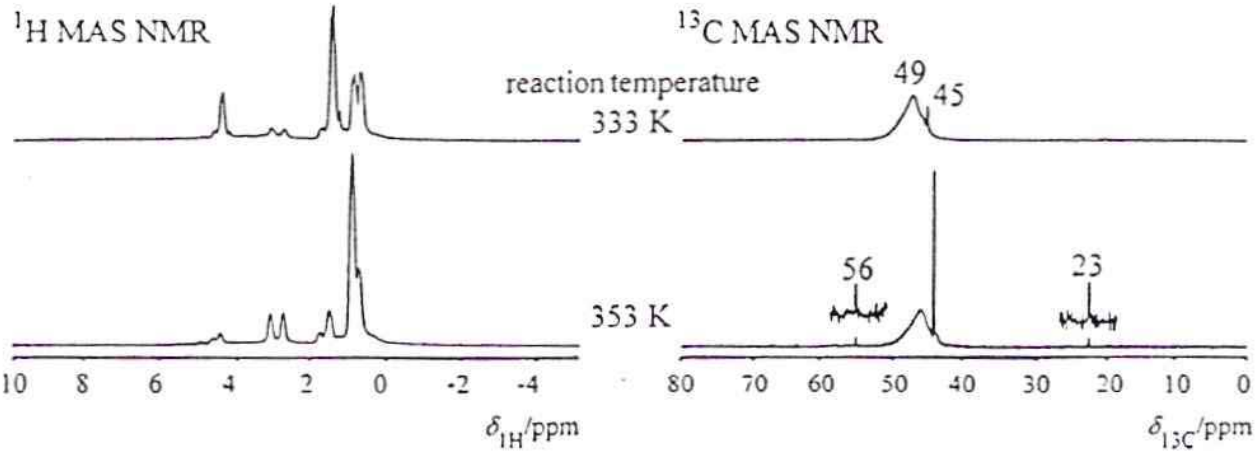

Fig. 4 *In situ* ^1H and ^{13}C MAS NMR spectra of reactants, recorded during MTBE synthesis on zeolite HY at temperatures of 333 K (top) and 353 K (bottom).

methanol, isobutene and MTBE, indicate the formation of by-products. Isobutene oligomerization leads to products with signals at 130 ppm to 140 ppm which could not be observed. Rather, the formation of small amounts of methyl isopropyl ether must be assumed leading to signals of ^{13}C-enriched carbon atoms at 23 ppm and 56 ppm [23] (Fig. 4). Further *in situ* NMR experiments under flow conditions are under way with the aim to investigate catalyst deactivation.

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