Sorption of methanol on zeolite HBeta investigated by in situ MAS NMR spectroscopy

Michael Hunger* and Thomas Horvath

Institute of Chemical Technology I, University of Stuttgart, D-70550 Stuttgart, Germany

Received 17 June 1997; accepted 24 September 1997

Methanol adsorption and desorption experiments were performed on acidic zeolites applying a new in situ MAS NMR technique. ^{1}H MAS NMR spectra of dehydrated zeolites were recorded during injection of nitrogen gas loaded with methanol into the MAS rotor. The spectra indicated that in zeolite HBeta also silanol groups are involved in the adsorption of methanol which is in contrast to the behaviour of SiOH groups in zeolites HZSM-5 and HY. The desorption experiments show that about 70% of the methanol molecules contributing to adsorbate complexes in zeolite HBeta are weakly hydrogen-bonded at silanol groups.

Keywords: zeolite HBeta, Brønsted sites, methanol adsorption, solid state NMR spectroscopy

1. Introduction

A number of papers published in the last decade [1–8] focused on adsorbate complexes formed by adsorption of methanol on acidic zeolites. The corresponding investigations were initiated by the development of the methanol to gasoline (MTG) and the methanol to olefin (MTO) processes [9]. Recently, the application of zeolites as catalysts for the synthesis of methyl tertiary-butyl ether (MTBE), which is the most largely used additive for unleaded gasolines, has improved this interest [10–12]. The industrial production of MTBE is carried out in liquid phase over sulfonic acid resins (e.g., Amberlyst-15) at temperatures in the range of 323–343 K and methanol/isobutene molar feed ratios of higher than 1 : 1 [13]. Sulfonic acid resins are quite performing catalysts, but lead to a number of undesirable by-products (e.g., diisobutenes, tertiary-butyl alcohol, dimethylether) [14], generate corrosion problems [15] and require, due to the high methanol/isobutene molar ratios, a recycle operation [13]. Therefore, in different approaches zeolites HY, H-omega, H-mordenite and HZSM-5, partially after dealumination and treatment with triflic acid or ammonium fluoride, were tested as catalysts for the synthesis of MTBE in gas phase [10–12]. However, for all of these zeolites the maximum MTBE yield was found at temperatures between 353 and 383 K. Due to the thermodynamic limitation of the chemical equilibrium [16], the most active catalysts are those which work at lower temperatures like Amberlyst-15. Very recently, Collignon et al. [12] studied MTBE synthesis on zeolites HBeta with Si/Al ratios between 13.2 and 194.2. They found that zeolites HBeta are significantly more active than all other types of zeolites. Applying a zeolite HBeta with the Si/Al ratio of 25.7, a maximum MTBE yield of ca. 50% was derived at 333 K. This high catalytical activity was explained by the large external surface (211–240 m^2/g) of the zeolites HBeta used [12]. Investigating the MTBE synthesis on zeolites HZSM-5 and HY, Kogelbauer et al. [10] 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 importance of adsorbate complexes formed by adsorption of methanol molecules for the activity of zeolite in MTBE synthesis. These adsorbate complexes prevent an oligomerization of isobutene by blocking the acid sites and act as protonating agent themselves [10].

In the present work methanol adsorption and desorption experiments were carried out on zeolite HBeta using a new in situ MAS NMR technique [17,18]. The calcined zeolite samples were exposed to a continuous flow of nitrogen gas loaded with methanol during the MAS NMR measurements which led to a continuous uptake of these molecules. Furthermore, the desorption behavior was studied in a flow of dry nitrogen gas at elevated temperatures. The important advantage of this approach is the combination of quantitative investigations of methanol adsorption and desorption and of NMR spectroscopic studies on adsorbate complexes. To ensure a concentration of bridging OH groups (SiOHAl) which allows their suitable observation by NMR spectroscopy, a zeolite Beta with the Si/Al ratio of 16.0 was used. The behavior of this sample was compared with those of a zeolite HZSM-5 (Si/Al = 22.0) described in ref. [8] and a zeolite HY (Si/Al = 2.6) studied in the present work.

* To whom correspondence should be addressed.

© J.C. Baltzer AG, Science Publishers

2. Experimental

The parent zeolite NaY was a commercial product of Union Carbide (Tarrytown, NY) with a unit cell composition $Na_{53.3}Al_{53.3}Si_{138.7}O_{384}\cdot nH_2O$. The 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 ref. [19]. The hydrogen forms of the zeolites Y and Beta were prepared by fourfold ion exchange at the temperature of $T = 353$ K in a surplus of 0.1 and 0.4 M aqueous solution of NH_4NO_3, respectively. The cation exchange degree reached by this way was 88% for zeolite Y and 99% for zeolite Beta. After exchange the zeolite powder was washed in demineralized water, dried at room temperature, and characterized by AES, XRD, ^{27}Al and ^{29}Si MAS NMR spectroscopy. No signals of extra-framework aluminium atoms were found in the ^{27}Al MAS NMR spectra of the hydrated samples. Before the ^1H MAS NMR investigations the powder material was heated in vacuum with a rate of 20 K/h up to the final temperature of 673 K. At this final temperature the samples were calcined for 12 h at a pressure below 10^{-2} Pa.

The NMR investigations were carried out on a Bruker MSL 400 spectrometer. For the in situ adsorption of methanol on the calcined samples the injection equipment described in refs. [17,18] was applied. During these experiments nitrogen gas (6 ml/min) loaded with CD_3OH (99.0 atom% D, Th. Geyer) was led into a commercial 7 mm MAS NMR Bruker rotor via an axially placed injection tube. This tube was inserted into the rotor through an axial hole in the rotor cap. Finally, the carrier gas left the rotor via an annular gap in the rotor cap. Before the injection the nitrogen gas was loaded in a saturator with methanol at a partial pressure of 6×10^3 Pa. The ^1H MAS NMR spectra were recorded at a resonance frequency of 400.13 MHz with a sample spinning rate of 3 kHz. For each spectrum 50 free induction decays with a repetition time of 10 s were accumulated. The adsorption experiments were carried out at room temperature ($T = 293$ K) within a time of 120 min. The desorption of methanol was performed in a flow of dry nitrogen gas (6 ml/min) at temperatures between 293 and 383 K. Starting at $T = 293$ K the temperature was increased in steps of $\Delta T = 10$ K. The ^1H MAS NMR spectra were recorded 30 min after raising the temperature. The concentrations of the OH groups in the calcined zeolites were determined comparing the total ^1H MAS NMR intensities with that of an external intensity standard (dehydrated zeolite HY with a cation exchange degree of 35%) and after a decomposition of the spectra. The numbers of methanol molecules adsorbed on the calcined zeolites were derived using the spectrum of the unloaded zeolites HBeta and HY as intensity standard. Curie's law was applied for a correction of the NMR intensities at elevated temperatures. The decomposition of the spectra were carried out using the Bruker software WINFIT.

3. Results

The different OH groups in calcined and unloaded zeolites HBeta and HY were investigated by ^1H MAS NMR spectroscopy using samples fused in glass ampoules and a sample spinning rate of 14 kHz. The ^1H MAS NMR spectra of these zeolites shown in figure 1 consist of signals between 1.3 and 2.2 ppm due to silanol groups (SiOH) and between 3.9 and 4.8 ppm caused by bridging OH groups (SiOHAl) [21,22]. The weak signal appearing at 6.5 ppm in the spectrum of dehydrated zeolite HBeta (figure 1a) can be explained by residual ammonium ions [22]. The concentrations of SiOH and

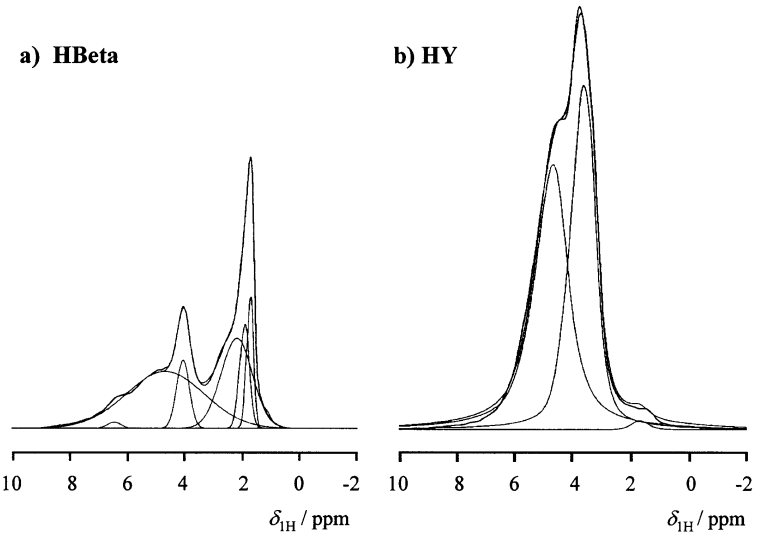

Figure 1. ^1H MAS NMR spectra of calcined (673 K) zeolites HBeta (a) and HY (b), recorded at a resonance frequency of 400.13 MHz with a sample spinning rate of 14 kHz.

Table 1
The total numbers of zeolite OH groups (column 3) and the numbers of SiOH (column 4) and SiOHAl groups (column 5) in unloaded zeolites and of methanol molecules adsorbed on the zeolites in saturation after 120 min at 323 K (column 6). The values given in columns 3–6 were derived by ^{1}H MAS NMR spectroscopy using the absolute intensity mode and an external intensity standard. The experimental accuracy is ±10%

Zeolites	Si/Al [a]	$n_{zeol.OH}/m_{zeolite}$ (mmol/g)	$n_{SiOH}/m_{zeolite}$ (mmol/g)	$n_{SiOHAl}/m_{zeolite}$ (mmol/g)	$n_{CD_3OH}/m_{zeolite}$ (mmol/g)
HZSM-5 [b]	22	0.90	0.15	0.75	3.0
HBeta	16	1.75	0.85	0.90	13.0
HY	2.6	4.13	0.08	4.05	4.5

[a] Derived by ^{29}Si MAS NMR spectroscopy.
[b] Ref. [8].

SiOHAl groups in dehydrated zeolites HBeta and HY studied in the present work and of zeolite HZSM-5 used in ref. [8] are given in columns 3–5 of table 1.

In a previous paper a new in situ adsorption method was applied for ^{1}H MAS NMR investigations of the interaction of CD_3OH molecules with bridging OH groups in dehydrated zeolite HZSM-5 [8]. This technique allows the quantitative evaluation of the adsorption process and a simultaneous spectroscopical observation of hydroxyl groups contributing to the formation of adsorbate complexes. In figure 2 (open circles) the ^{1}H MAS NMR shifts of these hydroxyl groups in zeolite HZSM-5 are depicted as a function of the number of adsorbed methanol molecules (taken from ref. [8]). The curve shows a maximum ^{1}H MAS NMR shift of 9.2 ppm after adsorption of about 0.5 mmol CD_3OH per gram zeolite. This resonance position strongly decreases with adsorption of further methanol molecules. Figure 3 shows the ^{1}H MAS NMR spectra recorded during in situ adsorption of CD_3OH on dehydrated zeolites HBeta at the same conditions as applied for zeolite HZSM-5. Already after adsorption of about 1 mmol CD_3OH per gram zeolite HBeta a low-field signal can be observed which is due to the hydroxyl groups contributing to adsorbate complexes. This signal increases with adsorption of further methanol molecules. At the same time the signals of bridging OH groups as well as of silanol groups decrease indicating that both types of hydroxyl groups interact with adsorbate molecules. This behavior is in contrast to that observed during adsorption of methanol on zeolites HZSM-5 (see figure 2 in ref. [8]) and HY (not shown) where the adsorbate molecules preferentially interact with bridging OH groups.

In figure 2 the ^{1}H MAS NMR shifts of hydroxyl groups contributing to the adsorbate complexes in zeolites HBeta and HY are plotted as a function of the number of adsorbate molecules. After adsorption of 1 mmol CD_3OH per gram powder material the hydroxyl groups in zeolites both HBeta and HY show shift values of about 8 ppm. However, after further adsorption of methanol molecules, the curves described by the ^{1}H MAS NMR shifts of hydroxyl protons show significantly different slopes. The curve described by the resonance positions of hydroxyl protons of the adsorbate complexes in zeolite HY is similar to that observed for these hydroxyl groups in zeolite HZSM-5 but lies by about 1 ppm to smaller values (figure 2, open rectangles and circles). In contrast, the ^{1}H MAS NMR shifts of hydroxyl protons contributing to adsorbate complexes in zeolite HBeta vary only from 7.8 to 6.9 ppm. In addition, the adsorption capacity of zeolite HBeta of 13.0

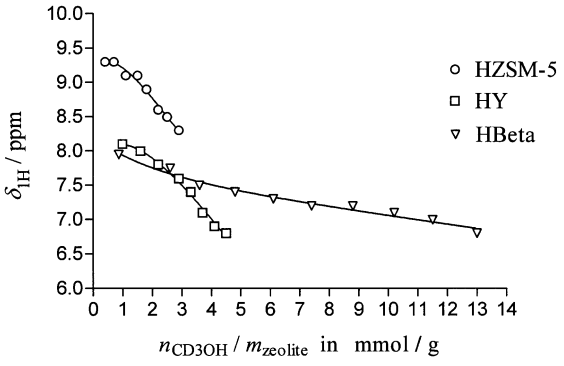

Figure 2. ^{1}H MAS NMR shifts, δ_{1H}, of hydroxyl protons contributing to methanol complexes in zeolites HZSM-5 (given in ref. [8]), HY and HBeta (this paper) derived by in situ adsorption of CD_3OH, depicted as a function of the methanol loading ($n_{CD_3OH}/m_{zeolite}$).

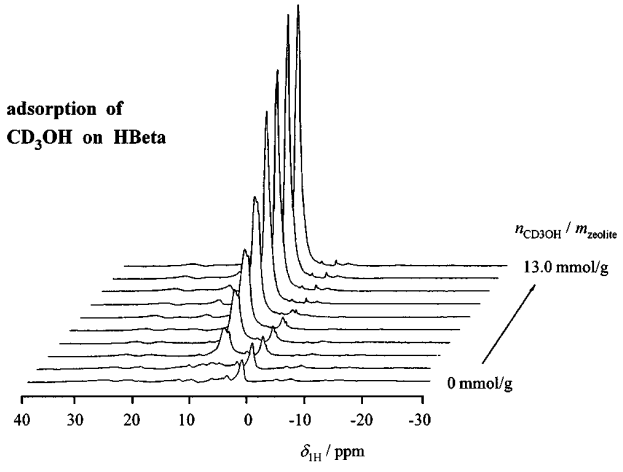

Figure 3. ^{1}H MAS NMR spectra of calcined zeolite HBeta, recorded during in situ adsorption of methanol at 293 K within a time of 120 min. The calcined zeolite HBeta was exposed to a flow of nitrogen gas loaded with CD_3OH (partial pressure of 6×10^3 Pa).

mmol CD_3OH per gram powder material (figure 2, open triangles) exceeds those of zeolites HZSM-5 and HY by a factor of about three (figure 2, circles and rectangles).

After in situ adsorption of methanol molecules on zeolites HBeta and HY the desorption of these molecules in a flow of dry nitrogen gas and at temperatures between 293 and 383 K was investigated. The above-mentioned temperature range was chosen since it includes the optimum reaction temperature of the MTBE synthesis of ca. 333 K. The ^{1}H MAS NMR spectra of zeolite HBeta loaded with 13.0 mmol CD_3OH per gram powder material, recorded after increasing the temperature in steps of $\Delta T = 10$ K are shown in figure 4. The dominating low-field signal of hydroxyl groups contributing to adsorbate complexes decreases with increasing desorption temperature and a rising signal of silanol groups can be observed at ca. 2 ppm. The ^{1}H MAS NMR intensities recorded during desorption of methanol were used to determine the numbers of methanol molecules remaining on the zeolite at different desorption temperatures. In figure 5 the numbers of remaining methanol molecules were plotted as a function of the desorption temperature. For a better illustration, these values are given in numbers of methanol molecules per zeolite OH group ($n_{CD_3OH}/n_{zeol.OH}$). Starting with adsorbate complexes consisting of 7.5 methanol molecules per zeolite OH group at 293 K, the increase of the temperature up to 383 K led to a desorption of about 70% of the methanol molecules. At 383 K, the remaining adsorbate complexes consist of 2 methanol molecules per bridging OH group. Desorption at 333 K, which corresponds to the optimum reaction temperature of the MTBE synthesis, results in adsorbate complexes consisting of about 3.5 methanol molecules per zeolite OH group.

The maximum number of methanol molecules adsorbed on zeolite HY at 293 K was determined to 4.5 mmol CD_3OH per gram powder material which corresponds to 1.1 CD_3OH per bridging OH group (see columns 4 and 5 of table 1). Purging of this sample with dry nitrogen gas at temperatures between 293 and 383 K led to no measurable desorption of the adsorbate molecules. Hence, methanol molecules adsorbed on zeolite HY are essentially stronger bonded than in zeolite HBeta.

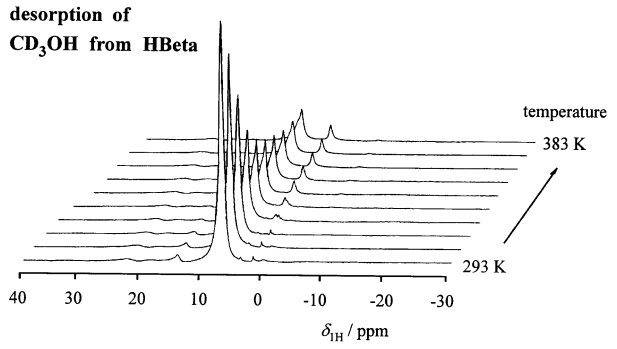

Figure 4. ^{1}H MAS NMR spectra of zeolite HBeta loaded with 13.0 mmol CD_3OH per gram powder material, recorded during in situ desorption of methanol in a flow of dry nitrogen at temperatures between 293 and 383 K.

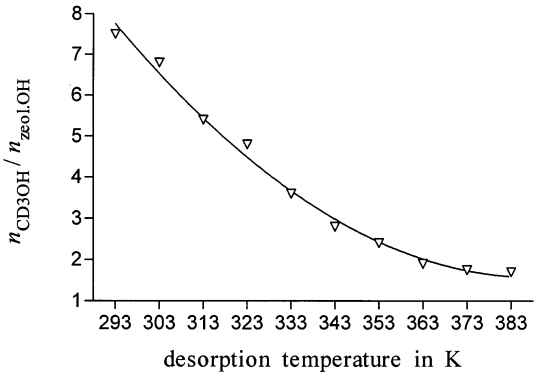

Figure 5. Numbers of methanol molecules per zeolitic OH group ($n_{CD_3OH}/n_{zeol.OH}$) remaining on zeolite HBeta after desorption in a flow of dry nitrogen gas at temperatures between 293 and 383 K. These values were derived evaluating the intensities of the spectra shown in figure 4.

4. Discussion

The concentrations of the SiOHAl groups in zeolites HZSM-5, HY and HBeta which differ by a factor of more than 5 correlate well with the Si/Al ratios of these samples (table 1, columns 2 and 5). In addition, also the concentrations of SiOH groups at framework defects and the outer surface of the zeolite particles show significant differences. While the concentration of silanol groups in zeolites both HZSM-5 and HY amounts to 1.0 ± 0.5 mmol SiOH per gram powder material, the concentration of these OH groups in zeolite HBeta is about a factor eight higher (table 1, column 4). This high density of silanol groups is a remarkable peculiarity of zeolite HBeta. Also in previous ^{1}H MAS NMR studies of dehydrated zeolite HBeta [22,23] strong signals of SiOH groups were observed. In zeolites HZSM-5 such high densities of silanol groups were found for those materials which were synthesized with cationic structure directing template molecules [24]. In the absence of anions, the positive charges of the cationic template molecules are compensated by non-closed framework bonds like $\equiv$Si–O$^-$. During burning off the template molecules, these framework defects are transformed into SiOH groups [25]. The zeolite HBeta studied in the present work was prepared with tetraethylammonium cations as structure directing compound. Therefore, the above-mentioned mechanism of the defect formation in zeolite ZSM-5 may also be valid in zeolite HBeta.

In ref. [8] the adsorption of methanol on dehydrated zeolite HZSM-5 was studied with in situ MAS NMR spectroscopy. The saturation of the zeolite sample with

methanol was performed within 120 min at 293 K which led to an adsorption of four CD_3OH molecules per SiOHAl group (0.75 mmol SiOHAl per gram zeolite) corresponding to 10.5 g methanol per 100 g zeolite [8]. This adsorption capacity agrees well with the value of 9.9 g methanol per 100 g zeolite HZSM-5 determined by Kofke et al. [2] using a Cahn microbalance at the same temperature and confirms the quantitative reliability of the NMR spectroscopic adsorption technique.

The maximum chemical shift of the hydroxyl protons contributing to adsorbate complexes in zeolite HZSM-5 was observed after adsorption of about 0.5 mmol CD_3OH per gram powder material and amounts to 9.2 ppm (figure 2). According to quantumchemical calculations of Haase and Sauer [6] these adsorbate complexes consist of a neutral methanol molecule (10.8 ppm) which is two-fold hydrogen-bonded to a bridging OH group. The protonated state of the adsorbed methanol molecule (17.4 ppm [6]) occurs only as transition state. At a temperature of 153 K, the mobility of the methanol molecules is frozen which results in ^{1}H MAS NMR spectra consisting of two separate sideband patterns due to the two hydrogen-bonded hydroxyl groups [8]. At room temperature, the high mobility of methanol molecules averages the sideband patterns to a narrow ^{1}H MAS NMR signal. The mean isotropic chemical shift of these hydroxyl protons is affected by a rapid exchange of hydrogen-bonded methanol molecules and free methanol molecules in the zeolitic pore system [8,20]. Since the hydroxyl protons of non-bonded methanol molecules have a chemical shift of ca. 1.6 ppm [4], the rapid exchange of hydrogen-bonded and non-bonded methanol molecules leads to a high-field shift of the mean resonance position.

The chemical shift of the low-field ^{1}H MAS NMR signals of adsorbate complexes observed immediately after starting the adsorption experiments amounts to 9.2 ppm for zeolite HZSM-5 and ca. 8 ppm for zeolite HBeta and HY (figure 2, open circles and rectangles). In all of these cases the low-field ^{1}H MAS NMR signals are caused by hydroxyl protons of adsorbate complexes consisting of a single methanol molecule which interacts via hydrogen bonds with a zeolite OH group. In zeolites HZSM-5 and HY a preferential interaction of methanol molecules with bridging OH groups was found. The ^{1}H MAS NMR shifts of the hydroxyl protons contributing to these complexes in zeolites HZSM-5 and HY differ by about 1 ppm (figure 2) which may be caused by differences in the local geometry of bridging OH groups or by global effects of the compositions of these zeolites. In both cases, the adsorption of further methanol molecules led to a strong decrease of the mean chemical shift of the hydroxyl protons contributing to adsorbate complexes. This fact can be explained by the above-mentioned rapid exchange with non-bonded methanol molecules. After reaching the saturation, about 4.0 and 1.1 methanol molecules per bridging OH group (table 1) were adsorbed on zeolites HZSM-5 and HY, respectively.

The ^{1}H MAS NMR shift of hydroxyl protons contributing to the first adsorbate complexes formed on zeolite HBeta agrees with that observed for zeolite HY (figure 2, open triangles and rectangles). Hence, also in zeolite HBeta the first adsorbate complexes consist of a single methanol molecule hydrogen-bonded to a bridging OH group. A further adsorption of methanol induces a decrease of the mean resonance position of the hydroxyl protons contributing to adsorbate complexes (figure 2, open triangles). However, this resonance shift is significantly smaller than that found for zeolites HZSM-5 and HY (figure 2, open circles and rectangles). After adsorption of more than 3 mmol CD_3OH molecules per gram zeolite, an interaction of methanol molecules with silanol groups was spectroscopically observed (figure 3). At 293 K the saturation of zeolite HBeta was reached after adsorption of 7.5 methanol molecules per zeolite OH group (SiOHAl and SiOH) which indicates that in zeolite HBeta significantly larger adsorbate complexes are formed than in zeolites HZSM-5 and HY (maximum 4 methanol molecules per zeolite OH group). A second difference in the behavior of zeolites HZSM-5, HY and HBeta was exposed by the desorption experiments. These experiments show that the methanol molecules adsorbed on zeolite HBeta are significantly weaker bonded than those adsorbed on zeolite HY. After raising the desorption temperature to 333 K, which corresponds to the reaction temperature of the MTBE synthesis, the adsorbate complexes remaining on zeolite HBeta consist of about 3.5 methanol molecules per zeolite OH group.

5. Conclusions

Significant differences were observed in the adsorption of methanol on zeolites HZSM-5, HY and HBeta. On zeolites HZSM-5 and HY the methanol molecules are preferentially adsorbed on bridging OH groups and form adsorbate complexes consisting of maximum 4 methanol molecules per zeolite OH group at room temperature. For zeolite HBeta, an adsorption of methanol on silanol groups and an adsorption capacity of up to 7.5 methanol molecules per zeolite OH group were found. The methanol molecules contributing to the adsorbate complexes in zeolite HBeta are weakly hydrogen-bonded and represent, therefore, a reservoir of activated reactant molecules in those heterogeneously catalyzed reactions which use methanol as educt molecules. This interesting property of zeolite HBeta may explain the high MTBE yields found by Collignon et al. [12].

Acknowledgement

The authors gratefully acknowledge financial support

by Deutsche Forschungsgemeinschaft, Max-Buchner-Forschungsstiftung and Fonds der Chemischen Industrie.

References

[1] M.T. Aronson, R.J. Gorte and W.E. Farneth, J. Catal. 98 (1986) 434.
[2] T.J.G. Kofke, R.J. Gorte and W.E. Farneth, J. Catal. 114 (1988) 34.
[3] G. Mirth, J.A. Lercher, M.W. Anderson and J. Klinowski, J. Chem. Soc. Faraday Trans. 86 (1990) 3039.
[4] M.W. Anderson, P.J. Barrie and J. Klinowski, J. Phys. Chem. 95 (1991) 235.
[5] J.D. Gale, C.R.A. Catlow and J.R. Carruthers, Chem. Phys. Lett. 216 (1993) 155.
[6] F. Haase and J. Sauer, J. Am. Chem. Soc. 117 (1995) 3780.
[7] J. Limtrakul, Chem. Phys. 193 (1995) 79.
[8] M. Hunger and T. Horvath, J. Am. Chem. Soc. 118 (1996) 12302.
[9] C.D. Chang, *Hydrocarbons from Methanol* (Dekker, New York, 1983).
[10] A. Kogelbauer, A.A. Nikolopoulos, J.G. Goodwin Jr. and G. Marcelin, J. Catal. 152 (1995) 122.
[11] A.A. Nikolopoulos, A. Kogelbauer, J.G. Goodwin Jr. and G. Marcelin, J. Catal. 158 (1996) 76.
[12] F. Collignon, M. Mariani, S. Moreno, M. Remy and G. Poncelet, J. Catal. 166 (1997) 53.
[13] A.K.K. Lee and A. Al-Jarallah, Chem. Econ. Eng. Rev. 18 (1986) 25.
[14] M. Vila, F. Cunill, J.P. Izquierdo, J. Gonzalez and A. Hernandez, Appl. Catal. 117 (1994) L99.
[15] T. Takesono and Y. Fujiwara, US Patent 4.182.913 (1980).
[16] J. Tejero, F. Cunill and J.F. Izquierdo, Ind. Eng. Chem. Res. 27 (1988) 338.
[17] M. Hunger and T. Horvath, J. Chem. Soc. Chem. Commun. (1995) 1423.
[18] M. Hunger and T. Horvath, J. Catal. 167 (1997) 187.
[19] J. Perez-Pariente, J.A. Martens and P.A. Jacobs, Appl. Catal. 31 (1987) 35.
[20] M. Hunger and T. Horvath, Ber. Bunsenges. Phys. Chem. 99 (1995) 1316.
[21] M. Hunger, S. Ernst, S. Steuernagel and J. Weitkamp, Microporous Mater. 6 (1996) 349.
[22] M. Hunger, Solid State Nucl. Magn. Reson. 6 (1996) 1.
[23] L.W. Beck and J.F. Haw, J. Phys. Chem. 99 (1995) 1076.
[24] M. Hunger, D. Freude, T. Fröhlich, H. Pfeifer and W. Schwieger, Zeolites 7 (1987) 108.
[25] M. Hunger, J. Kärger, H. Pfeifer, J. Caro, B. Zibrowius, M. Bülow and R. Mostowicz, J. Chem. Soc. Faraday Trans. I 83 (1987) 3459.