Accessibility and Interaction of Surface OH Groups in Microporous and Mesoporous Catalysts Applied for Vapor-Phase Beckmann Rearrangement of Oximes

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Abstract ¹H and ²H MAS NMR spectroscopy were utilized for investigating the interaction of surface complexes upon adsorption of cyclohexanone and cyclododecanone oxime on MFI-type zeolites and [Al]SBA-15. Signals of hydrogen-bonded and protonated complexes were identified and evidenced the diffusion of cyclohexanone oxime into the micropores of silicalite-1 and ZSM-5 and limited accessibility of acid sites in [Al]SBA-15 for cyclododecanone oxime.

Keywords Beckmann rearrangement · Cyclohexanone oxime · Porous catalysts · Acid sites · Accessibility · Solid-state NMR spectroscopy

1 Introduction

Manufacturing of nylon-6 fibres requires ε -caprolactam as reactant, which is mainly produced via the liquid-phase Beckmann rearrangement reaction [1–3]. However, the conventional liquid-phase process has important disadvantages due to the production of large amounts of ammonium sulfate as by-product and the corrosive reaction medium caused by the use of sulphuric acid or oleum. Environmentally benign new processes base on the vaporphase Beckmann rearrangement of cyclohexanone oxime to ε -caprolactam on solid catalysts [4, 5]. For the vaporphase Beckmann rearrangement reaction, various zeolites, such as silicalite-1 [6], [B]ZSM-5 [7], ZSM-5 [8], MCM-22 [9], Beta [10], and [B]Beta [11], and mesoporous

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materials, like siliceous, aluminum-containing, and niobium incorporated MCM-41 [12, 13] as well as SBA-15 [14] and cross-linked TS-1 [15] have been investigated as solid acid catalysts.

A number of recent in situ spectroscopic investigations focused on the mechanism of the vapor-phase Beckmann rearrangement of oximes [12, 16-20]. In these studies, surface hydroxyl groups with different chemical properties and local structures, such as isolated SiOH groups and SiOH nests at the outer surface or pore mouth of zeolite particles or located in mesopores as well as SiOH groups in the neighbourhood of framework boron atoms and bridging OH groups (SiOHAl) in aluminum-containing materials, were discussed as catalytically active sites. Recent quantum-chemical investigations indicate that silanol groups play the key role under the above-mentioned candidates [21]. As evidenced by ¹⁵N MAS NMR spectroscopy, adsorption of cyclohexanone oxime at siliceous materials, such as silicalite-1 or siliceous mesoporous SBA-15, is accompanied by the formation of adsorbate complexes, which are hydrogen-bonded to the N-atom of the reactant cyclohexanone oxime [18–20]. In contrast, an N-protonation of the reactant was found to occur upon adsorption of this reactant at aluminum-containing materials, such as H-ZSM-5 or [A]SBA-15, covered by acidic surface sites [18-20].

Generally, hydrogen bonding and protonation of adsorbate molecules leads to characteristic low-field shifts of the ¹H MAS NMR signals caused by the contributing hydroxyl protons [22–25]. In the case of the adsorption of nondeuterated molecules, the ¹H MAS NMR signals due to hydroxyl groups on solid catalysts are overlapped by the adsorbate signals. Not all reactants of interest, however, are available in the fully deuterated state, which would solve the above-mentioned problem. On the other hand, deuteration of surface hydroxyl groups is possible and opens the way for highly resolved ²H solid-state NMR studies (²H: spin I = 1) of deuterated catalysts without and after adsorption of non-deuterated molecules. In the present work, to the best of our knowledge first ²H high-speed MAS NMR investigations of the hydroxyl groups of deuterated solid acid catalysts upon loading with adsorbate molecules have been performed. By studying solid catalysts with different chemical compositions and pore diameters upon adsorption of oximes with different molecular sizes, the accessibility and chemical interacting of surface sites were indentified.

2 Experimental

Silicalite-1 ($n_{Si}/n_{Al} = 1,700$), H-ZSM-5 ($n_{Si}/n_{Al} = 14$), and aluminum-containing [Al]SBA-15 material ($n_{Si}/n_{Al} = 9$) were prepared as described in Ref. [20]. The materials were characterized by X-ray diffraction (Bruker D8), ICP/OES (Varian), N₂-adsorption (micrometrics ASAP 2010), and solid-state NMR spectroscopy (Bruker MSL 400). The XRD patterns of these catalysts were identical with the patterns reported in the literature [26–28]. The physiochemical properties of the catalysts, such as the n_{Si}/n_{Al} ratio, concentration of surface hydroxyl groups (n_{H}), BET surface areas, pore volume, and average pore diameters are given in Table 1.

For dehydration, the catalyst materials were heated in glass tubes at a vacuum line from 298 to 393 K with a rate of 0.5 K min⁻¹ and maintained at 393 K for 3 h. Subsequently, the temperature was increased from 393 to 723 K with a rate of 1 K min⁻¹ and maintained at the final temperature for 12 h. During this time, the materials were evacuated at a pressure of $p < 10^{-2}$ mbar. Finally, the samples were cooled to room temperature and sealed in the glass tubes.

Prior to ²H solid-state NMR studies, the deuterated catalysts D-ZSM-5 and D-[A1]SBA-15 were prepared via the following procedure: The non-deuterated materials were dehydrated at 723 K according to the above-mentioned route. Upon cooling to room temperature, the samples were kept at this temperature in contact with D_2O

vapor for 1 h. Subsequently, they were dehydrated at 473 K for 2 h. Upon repeating this procedure 5 times, the materials were sealed in glass tubes. Utilizing this procedure, deuteration degrees of 50% for D-ZSM-5 and 65% for D-[A1]SBA-15 were obtained as determined by quantitative ¹H MAS NMR spectroscopy.

Partially deuterated cyclohexanone oxime-D₁₁ was prepared as follows: In a 25 ml round-bottom flask, 1.00 g of deuterated hydroxylamine-hydrochloride (ND2OD... DCl) delivered by CDN Isotopes (Lot#B218P2) was dissolved in 4.28 g of deuterated water. Subsequently, 0.86 g of sodium acetate (Riedel-de Haën) was added and the solution was heated to 313 K. Finally, 1.00 g of cyclohexanone-D₁₀ of CDN Isotopes (Lot#G126P13) was added dropwise under stirring. After the complete addition, the flask was sealed and shaken vigorously until the oxime could be precipitated as a fine white powder. This cyclohexanone oxime-D₁₁ was collected by vacuum filtration and dried in air for 24 h at room temperature. The obtained cyclohexanone oxime-D₁₁ reached a deuteration degree of 83% as determined by quantitative ¹H MAS NMR spectroscopy.

Before mixing the non-deuterated or deuterated catalysts with the deuterated or non-deuterated cyclohexanone oxime and cyclododecanone oxime, the oxime was evacuated at room temperature for 20 min. Then, the evacuated reactants were mixed with the dehydrated (vide supra) catalysts in a ratio of 1 : 1, i.e., one oxime molecule per OH group, inside a glove box purged with dry nitrogen gas. Subsequently, the catalyst/oxime mixtures were filled into 4 mm MAS NMR rotors without contact to air and heated at 393–523 K for 20 min before the solid-state NMR studies.

¹H and ²H MAS NMR spectra of the dehydrated samples before and upon mixing with cyclohexanone oxime were obtained on a Bruker MSL 400 spectrometer at resonance frequencies of 400.1 and 61.4 MHz and with sample spinning rates of 8.0 kHz using 4 mm rotors and 25.0 kHz using 2.5 mm rotors, respectively. The spectra were recorded after excitation with single pulses of the lengths of 2.1 and 4.0 μ s and with repetition times of 10 and 2 s, respectively.

Table 1 Physiochemical properties of the calcined catalysts used in this study

$n_{\rm Si}/n_{\rm Al}$	$n_{\rm H}$ /mmol g ⁻¹ *	BET surface area/m ² g ^{-1}	Pore volume/cm ³ g^{-1}	Average pore diameter/nm	
1,700	0.31	365	0.20	0.55**	
14	1.12	338	0.16	0.55**	
9	1.29	672	1.54	8.97	
	n _{Si} /n _{Al} 1,700 14 9	$ \begin{array}{ccc} n_{\rm Si}/n_{\rm Al} & n_{\rm H}/\rm{mmol}\ g^{-1}* \\ 1,700 & 0.31 \\ 14 & 1.12 \\ 9 & 1.29 \end{array} $	$n_{\rm Si}/n_{\rm Al}$ $n_{\rm H}/{\rm mmol}~{\rm g}^{-1}*$ BET surface area/m ² g^{-1}1,7000.31365141.1233891.29672	$n_{\rm Si}/n_{\rm AI}$ $n_{\rm H}/{\rm mmol}~{\rm g}^{-1}*$ BET surface area/m ² g ⁻¹ Pore volume/cm ³ g ⁻¹ 1,7000.313650.20141.123380.1691.296721.54	

* $n_{\rm H}$ values were obtained by the quantitative ¹H MAS NMR spectroscopy of dehydrated samples

** According to Ref. [26]

3 Results and Discussion

3.1 ¹H MAS NMR Investigations of Non-Deuterated Silicalite-1 and H-ZSM-5 upon Adsorption and Conversion of Partially Deuterated Cyclohexanone Oxime-D₁₁

For supporting the discussion of ²H MAS NMR spectra of the deuterated catalysts under study, at first ¹H MAS NMR investigations of the non-deuterated and unloaded as well as oxime-loaded catalysts were performed. Figure 1a shows the spectrum of dehydrated and unloaded silicalite-1 consisting of a single signal at 1.8 ppm due to silanol groups. After loading of silicalite-1 with partially deuterated (83%) cyclohexanone oxime $[C_6(H,D)_{10}NO(H,D)]$ and heating at 393-423 K (Fig. 1b, c), a strong signal occurred at ca. 2.5 ppm caused by the overlapping signals of residual ring protons (ca. 17%) in cyclohexanon oxime [29]. The lowfield signal at 9.3 ppm can be explained by the hydroxyl proton of the hydrogen-bonded oxime. The formation of these surface complexes was already observed in earlier ¹⁵N MAS NMR studies of oxime-loaded silicalite-1 [18-20]. Unfortunately, the signal of residual non-deuterated ringprotons in cyclohexanone oxime at 2.5 ppm overlaps the chemical shift range of surface hydroxyl groups of silicalite-1. This hinders the study of the effect of oxime adsorption on the corresponding signals of OH groups occurring at 1.8–4 ppm before the adsorption.

Upon heating of the silicalite/oxime mixture at 473 and 498 K (Fig. 1d, e), the signal at 9.3 ppm became weaker and another low-field signal at 12.2 ppm occurred, which indicates the formation of hydrogen-bonded ε -caprolactam [18–20]. The very small hump at ca. 14.5 ppm may be caused by few protonated ε -caprolactam molecules formed in the vicinity of the small number of framework aluminum species in silicalite-1 ($n_{Si}/n_{Al} = 1,700$). The much stronger and broad signal at ca. 6.5 ppm indicates the formation of by-products, such as ε -aminocapric acid and hydroxyl-amine [18, 20, 29]. A survey on the assigned ¹H MAS NMR signals and their chemical shift values is given in Table 2.

In contrast to silicalite-1 $(n_{\rm Si}/n_{\rm Al} = 1,700)$, the zeolite H-ZSM-5 $(n_{\rm Si}/n_{\rm Al} = 14)$ is characterized by a large number of acidic bridging OH groups causing the ¹H MAS NMR signal at 4.2 ppm in Fig. 2a. After adsorption of partially deuterated cyclohexanone oxime on H-ZSM-5 and heating at 393–423 K (Fig. 2b, c), again a strong signal of ring protons in cyclohexanon oxime appeared at ca. 2.5 ppm. Instead of the low-field signal occurring at 9.3 ppm in the spectrum of oxime-loaded silicalite-1, however, the low-field range of the spectra consists of a narrow signal at 10.4 ppm and two additional broad signals at 11.2 and 13.0 ppm. Since the intensity of the signal at



Fig. 1 ¹H MAS NMR spectra of dehydrated silicalite-1 recorded before (**a**) and upon adsorption of partially deuterated cyclohexanon oxime $[C_6(H,D)_{10}NO(H,D)]$ and heating at temperatures of 393– 523 K (**b**-f)

10.4 ppm has the same temperature-dependence like the signal at 9.3 ppm in Fig. 1b–d, it was attributed to hydrogen-bonded cyclohexanone oxime. Based on earlier ¹⁵N MAS NMR studies, the signals at 11.2–13.0 ppm are assigned to protonated cyclohexanone oxime [18–20].

Heating of the H-ZSM-5/oxime mixture to 478–523 K (Fig. 2d–f) led to a strong decrease of the signals of protonated cyclohexanone oxime (11.2 and 13.0 ppm), while few of the hydrogen-bonded reactants (10.4 ppm) remained on the catalyst indicating the low catalytic activity of the corresponding surface sites (SiOH). The most significant change in the low-field range is the appearance of a new signal at 14.2 ppm caused by the formation of protonated ε -caprolactam as observed in earlier ¹⁵N MAS NMR investigations [18]. As already discussed in the case of oxime-loaded silicalite-1, the signals at ca. 6.5 ppm are a hint for the formation of by-products (vide supra).

Summarizing can be stated that adsorption of partially deuterated cyclohexanone oxime on silicalite-1 and H-ZSM-5 via hydrogen-bonding to SiOH groups leads to ¹H MAS NMR signals at 9.3–10.4 ppm. Protonation of the cyclohexanone oxime at bridging OH groups of H-ZSM-5 is accompanied by the occurrence of signals at



Fig. 2 ¹H MAS NMR spectra of dehydrated H-ZSM-5 recorded before (a) and upon adsorption of partially deuterated cyclohexanon oxime $[C_6(H,D)_{10}NO(H,D)]$ and heating at temperatures of 393–523 K (b–f)

 Table 2
 Assignments of ¹H MAS NMR signals observed upon adsorption and conversion of cyclohexanone oxime on silicalite-1 and zeolite H-ZSM-5

$\delta_{1\rm H}$ /ppm	Assignments ^a		
1.2–2.2	Silanol groups at the external and internal surface of solid catalysts		
1.4–3.5	Ring protons of cyclohexanone oxime and <i>\varepsilon</i> -caprolactam		
3.6-4.3	Bridging OH groups of acidic zeolites		
ca. 6.5	NH ₂ groups of by-products (e.g., ε-aminocapric acid, hydroxylamine)		
9.3	Hydrogen-bonded cyclohexanone oxime on silicalite-1		
10.4	Hydrogen-bonded cyclohexanone oxime on H-ZSM-5		
12.2	Hydrogen-bonded ε-caprolactam on silicalite-1		
11.2–13.0	Protonated cyclohexanone oxime on H-ZSM-5		
14.2–14.5	Protonated ε-caprolactam on silicalite-1 and H-ZSM-5		

 $^{\rm a}\,$ Most of the assignments were made on the base of earlier $^{15}N\,MAS\,$ NMR studies

11.2–13.0 ppm. Upon conversion of this reactant to ε caprolactam, ¹H MAS NMR signals of the hydrogenbonded and the protonated reaction product can be observed at 12.2 and 14.2 ppm, respectively. In the same manner, also the interaction of non-deuterated oximes with hydroxyl groups of deuterated solid catalysts should lead to low-field ²H MAS NMR signals in the chemical shift range of

9–14 ppm indicating the accessibility of the corresponding surface sites for adsorbate molecules and their interactions.

3.2 High-Speed ²H MAS NMR Investigations of Partially Deuterated ZSM-5 and [Al]SBA-15 upon Adsorption of Non-Deuterated Cyclohexanone Oxime and Cyclododecanone Oxime

The standard technique for performing ²H solid-state NMR studies of the quadrupolar ²H nuclei with spin I = 1 in solid catalysts and adsorbate complexes in the past decades and until nowadays is the application of echo-sequences with the use of static (no sample spinning) samples (see, e.g., Refs. [30–34]). Often, this spectroscopic technique is utilized for studying motional effects in the materials under study. Similarly, the sideband intensities of ²H MAS NMR spectra recorded with small to moderate spinning rates are analyzed to obtain information on molecular mobilities [35, 36]. On the other hand, there are only very few studies utilizing high-resolution ²H MAS NMR spectroscopy for the investigation of deuterated surface hyxdroxyl groups or adsorbate complexes on solid catalysts [37–39].

Via the above-mentioned solid-state NMR techniques, the quadrupole coupling constants $C_{\rm O}$ of acid sites on solid catalysts were determined. Values of $C_Q = 208-240$ kHz for deuterated bridging hydroxyl groups (SiODAl) in zeolites [30, 37, 38] and $C_Q = 67-75$ MHz for deuterated silanol groups (SiOD) [30, 38] were obtained. The significant larger C_0 values of deuterons in SiODAl groups in comparison with those in SiOD groups are due to the effect of framework aluminum atoms in the local structure of SiODAl groups on the electric field gradient at the site of the deuterons. Since the ²H MAS NMR spectrum of OD groups with $C_{\rm O}$ values of ca. 220 kHz is characterized by a sideband pattern with an envelop having a width of ca. 330 kHz, high spinning speeds are required to decrease the number of spinning sidebands and their intensity contribution, i.e., for obtaining central lines with suitable intensities. In the present work, therefore, the ²H MAS NMR studies of deuterated catalysts before and upon adsorption of reactant were performed with the sample spinning rate of 25 kHz.

In Figs. 3 and 4, the high-speed ²H MAS NMR spectra of the zeolite D-ZSM-5 and the mesoporous material

Fig. 3 ²H MAS NMR spectra of deuterated and dehydrated zeolite D-ZSM-5 recorded before (**a**, **b**) and after adsorption of cyclohexanon oxime [C₆H₁₀NOH] (**c**) and cyclododecanone oxime [C₁₂H₂₂NOH] (**d**). While spectrum (**a**) consists of *central line* and the first *left* and *right* spinning sidebands (marked by *asterisks*), spectra (**b**–**d**) show exclusively the *central line*



Fig. 4 ²H MAS NMR spectra of the deuterated and dehydrated mesoporous D-[Al]SBA-15 material recorded before (**a**, **b**) and after adsorption of cyclohexanon oxime [C₆H₁₀NOH] (**c**) and cyclododecanone oxime [C₁₂H₂₂NOH] (**d**). While spectrum (**a**) consists of the *central line* and the first *left* and *right* spinning sidebands (marked by *asterisks*), spectra (**b**-**d**) show exclusively the *central line*

D-[A1]SBA-15 recorded before and upon adsorption of oximes are shown. In the spectra depicted in Figs. 3a and 4a, the strong effect of aluminum species in the vicinity of deuterons, such as in SiODAl groups (D-ZSM-5), on the sideband intensity is obvious. The slight intensity difference between the left and right spinning sidebands is due to the electronic filter utilized for improving the signal-to-noise ratio. In the ²H MAS NMR spectra of D-ZSM-5 and D-[A1]SBA-15 in Figs. 3b and 4b, the signals at 2 ppm and 5 ppm have to be attributed to SiOD and SiODAl groups, respectively. In comparison with the ¹H MAS NMR signals

of H-ZSM-5 in Fig. 2a, the 2 H MAS NMR signals of D-ZSM-5 in Fig. 3b have significantly larger residual line widths leading to a partial overlap of the resonances at 2 and 5 ppm.

Adsorption of cyclohexanone oxime (diameter of 0.65 nm [40]) on D-ZSM-5 is accompanied by the occurrence of a low-field ²H MAS NMR signal at 12 ppm (Fig. 3c). Assuming same interactions for adsorption of deuterated cyclohexanone oxime on non-deuterated ZSM-5 (Fig. 2b) like for adsorption of the non-deuterated reactant on the deuterated zeolite (Fig. 3c), the above-mentioned ²H MAS NMR signals at 12 ppm indicates protonation of the adsorbate molecules. In this case, the results of ²H MAS NMR spectroscopy demonstrate that a significant content of the acidic bridging hydroxyl groups (SiOHAl and SiODAl) in ZSM-5 are accessible for cyclohexanone oxime, which supports the diffusion of the adsorbate molecules into the pores of this material.

Upon adsorption of cyclododecanone oxime (diameter of 0.9 nm [41]) on D-ZSM-5, most of the deuterated hydroxyl groups do not interact with the adsorbate molecules and only a small content of the deuterated hydroxyl groups contribute to the low-field shoulder at 9-12 ppm (Fig. 3d). Considering the molecular diameters of cyclohexanone oxime and cyclododecanone oxime of 0.65 and 0.9 nm, respectively, the latter molecule do not fit into the pores of ZSM-5 and interacts exclusively with hydroxyl groups at the outer surface and at pore mouths. The lowfield shoulder in Fig. 3d covering the chemical shift range of 9-12 ppm indicates protonation of a small number of adsorbed cyclododecanone oxime molecules. Hence, some of the strongly acidic SiODAl groups of D-ZSM-5 must be accessible for cyclododecanone oxime, i.e., these few SiODAl groups are located at the outer surface of the zeolite particles or at pore mouths.

The ²H MAS NMR spectrum recorded after adsorption of cyclohexanone oxime on the mesoporous D-[Al]SBA-15 material (Fig. 4c) is very similar to that obtained upon adsorption on D-ZSM-5 (Fig. 3c). Again, a low-field ²H MAS NMR signal at 12 ppm occurs, which is a hint for protonation of the adsorbate molecule. A weak shoulder at the high-field flank of the latter signal is due to the formation of hydrogen-bonded cyclohexanone molecules. Only few surface hydroxyl groups are not accessible for the adsorbate molecules and cause the weak signal at ca. 3 ppm.

According to the pore diameter of D-[A1]SBA-15 of ca. 9 nm (see Tab. 1), cyclododecanone oxime is able to diffuse into the mesopores of the above-mentioned material. In agreement with this assumption, the ²H MAS NMR spectrum of D-[Al]SBA-15 loaded with cyclododecanone oxime shows a strong signal at 10 ppm indicating an interaction of the corresponding adsorbate molecules with surface sites via hydrogen bonding (Fig. 4d). Surprisingly, however, a large content of the surface hydroxyl groups is not accessible for cyclododecanone oxime and causes the signal intensities at ca. 3 ppm. In addition, the content of cyclododecanone oxime molecules, which are protonated upon adsorption on D-[A1]SBA-15, is much lower than for cyclohexanone oxime (signals at 12–14 ppm). Hence, a significant number of acidic hydroxyl groups on the D-[A1]SBA-15 material under study are located in small mesopores or in micropores, which are not accessible for cyclododecanone oxime molecules.

4 Conclusions

¹H MAS NMR and high-speed ²H MAS NMR spectroscopy were utilized for studying the accessibility and interaction of surface hydroxyl groups on microporous MFI-type zeolites (pore diameter of ca. 0.55 nm) and mesoporous [A1]SBA-15 material (pore diameter of ca. 9 nm) for cyclohexanone oxime and cyclododecanone oxime with molecular diameters of 0.65 and 0.9 nm, respectively. Deuteration of cyclohexanone oxime up to an H/D-exchange degree of 83% and application of this oxime as probe molecule and reactant for vapor-phase Beckmann rearrangement on silicalite-1 and H-ZSM-5 led to ¹H MAS NMR spectra with reasonable resolution in the low-field range, which is the characteristic chemical shift range of signals caused by hydrogen-bonded and protonated adsorbate complexes.

After adsorption of partially deuterated cyclohexanone oxime on silicalite-1, the ¹H MAS NMR spectra indicated the hydrogen-bonding of the surface complexes (9.3 ppm). Also upon conversion of cyclohexanone oxime to ε -caprolactam on silicalite- 1, the hydrogen bonding was the dominating interaction of the surface complexes (12.2 ppm) and only a very weak ¹H MAS NMR signal of very few protonated ε-caprolactam molecules was found (14.5 ppm). In contrast, for adsorption and conversion of cyclohexanone oxime on zeolite H-ZSM-5, mainly the ¹H MAS NMR signals due to surface complexes of protonated cyclohexanone oxime (11.2-13.0 ppm) and protonated ε -caprolactam (14.2 ppm) were observed. The above-mentioned findings for the interaction of surface complexes formed upon adsorption and conversion of cyclohexanone oxime support the result of earlier ¹⁵N MAS NMR studies on this reaction system.

As an important advantage of high-speed ²H MAS NMR studies of the deuterated catalysts loaded with non-deuterated oximes, the direct observation of surface OD groups and of the effects of adsorbate molecules are possible. In comparison with the ¹H MAS NMR spectra in this work, larger residual line widths occurred in the ²H MAS NMR spectra, which may be caused by the crucial adjustment of the magic angle in the latter case. Upon adsorption of cyclohexanone oxime on deuterated ZSM-5 and [Al]SBA-15, ²H MAS NMR signals at 12 ppm occurred, which is a hint to the formation of protonated surface complexes. For both materials under study, microporous zeolite D-ZSM-5 and mesoporous D-[Al]SBA-15 material, a significant content of the surface OD were involved in the formation of adsorbate complexes. This observation indicates that cyclohexanone oxime diffuses into the pores of the microporous zeolite ZSM-5. Adsorption of cyclododecanone oxime on D-ZSM-5, on the other hand, was found to affect only a small content of surface hydroxyl groups leading to a broad low-field shoulder at 9–12 ppm in the ²H MAS NMR spectrum. The corresponding OD groups should be located at the outer particle surface and at pore mouths. Also in the case of cyclododecanone oxime adsorption on D-[Al]SBA-15, not all OD groups are accessible for the adsorbate molecules. Especially the stronger acidic hydroxyl groups in the vicinity of aluminum atoms are located in small pores since the strong ²H MAS NMR signal at 10 ppm hints to the formation of hydrogen-bonded adsorbate complexes as dominating surface compounds.

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