## Study of surface species on solid catalysts by <sup>2</sup>H solid-state NMR

**Spectroscopic background:** <sup>2</sup>H nuclei have a spin of I = 1 and a quadrupole moment of  $Q = 0.286 \times 10^{-30} \text{ m}^2$ . Therefore, <sup>2</sup>H NMR signals of deuterium atoms on the surface of solids are affected by quadrupolar interactions. Due to the low natural abundance of the <sup>2</sup>H isotope of 0.0115 % and a sensitivity in comparison with <sup>1</sup>H nuclei (1.0) of 1.1 x 10<sup>-6</sup> in this state, <sup>2</sup>H solid-state NMR spectroscopy of deuterium atoms of solid-state NMR, see lectures "Solid-State NMR Spectroscopy" for Bachelor students or PhD seminars, accessible via the link "Lectures for Students".

Applications of <sup>2</sup>H MAS NMR spectroscopy for the study of deuterated surface hydroxyl groups on solid catalysts or the kinetics of reactions catalyzed by these sites are rare. **Fig. 1a** shows the <sup>2</sup>H MAS NMR spectrum of an **aluminum-containing mesoporous SBA-15 material** ( $n_{Si}/n_{AI} = 9$ ), which was deuterated by saturation of the dehydrated sample with D<sub>2</sub>O and subsequently dehydrated at *T* = 473 K for 2 h (D-[AI]SBA-15) [1]. Due to the quadrupolar interactions of the surface OD groups, spinning sidebands (asterisks) occur at  $\delta_{2H} = \pm 407$  ppm ( $v_{rot} = 25$  kHz,  $v_0 = 61.4$  MHz) from the position of the central line at  $\delta_{2H} = 2$  ppm. Since the chemical shielding



Fig. 1

of <sup>2</sup>H nuclei is comparable with the shielding of <sup>1</sup>H nuclei, the above-mentioned chemical shift value corresponds to that of surface SiOH groups on SBA-15 (see Table 1 in Section "method 1"). In Ref. [1], mesoporous D-[Al]SBA-15 material was utilized as solid catalyst for the vapor-phase Beckmann rearrangement of cyclohexanon oxime ( $C_6H_{10}NOH$ ) and cyclododecanone oxime ( $C_{12}H_{22}NOH$ ). This reaction is important for the production of nylon-6 fibres via  $\varepsilon$ -caprolactam [2-4]. In the <sup>2</sup>H MAS NMR spectrum recorded after adsorption of cyclohexanone oxime on D-[Al]SBA-15 (Fig. 1c), a low-field signal occurs at  $\delta_{2H}$  = 12 ppm, which hints at the protonation of the adsorbed reactant molecules. As indicated by the weak signal in the shift range of SiOD groups ( $\delta_{2H} \cong 2$  to 3 ppm) in comparison with **Fig. 1b**, most of these surface groups are accessible for cyclohexanone oxime. Because of the pore diameter of D-[AI]SBA-15 of ca. 9 nm [1], also the larger cyclododecanone oxime molecules can diffuse into the mesopores. Accordingly, a signal at  $\delta_{2H}$  = 10 ppm with a weak shoulder  $\delta_{2H} \cong 14$  ppm occur in **Fig. 1d**, which are caused by the protonation of cyclododecanone oxime molecules. However, the weaker decease of the <sup>2</sup>H MAS NMR signal of SiOD groups in Fig. 1d compared with that upon adsorption of cyclohexanone oxime in Fig. 1c hints at a restricted accessibility of these surface sites in the mesopores of D-[AI]SBA-15 for the larger oxime molecule [1].

In Ref. [5], <sup>2</sup>H MAS NMR spectroscopy was utilized for investigating the **double-bond-shift reaction of** *n***-but-1-ene**-*d***8** (CD<sub>2</sub>=CDCD<sub>2</sub>CD<sub>3</sub>) to *n*-but-2-ene on a zeolite H-FER ( $n_{Si}/n_{AI} = 47$ ) with cation exchange degree of ca. 3 % by the temperature-dependent change of the <sup>2</sup>H MAS NMR signal intensities. **Fig. 2** shows a stacked plot



Fig. 2

of <sup>2</sup>H MAS NMR spectra of deuterated *n*-but-1-ene-*d*8 on zeolite H-FER, recorded at T = 333 K during reaction times of 5 min to 18.5 h. The <sup>2</sup>H MAS NMR signals at  $\delta_{2H} = 1.0, 2.0, 5.0, and 5.9$  ppm correspond to CD<sub>3</sub>, CD<sub>2</sub>, =CD<sub>2</sub>, and –CD= groups of *n*-but-1-ene-*d*8, respectively. During the reaction, all <sup>2</sup>H MAS NMR signals of *n*-but-1-ene decrease in intensity, whereas the signal at  $\delta_{2H} = 1.7$  ppm due to the methyl groups of *n*-but-2-ene increases. By <sup>2</sup>H MAS NMR studies of the double-bond-shift reaction in the temperature range of T = 300 to 373 K and quantitative evaluation of the signal intensities of the CD<sub>3</sub> groups of *n*-but-1-ene, an activation energy of the double-bond-shift reaction shift reaction of  $E_A = (9.8 \pm 1.1)$  kcal/mol was determined [5].

The good resolution of the <sup>2</sup>H MAS NMR spectra in **Fig. 2** is supported by an enhanced mobility of reactant molecules at elevated temperatures, which leads to a partial averaging of the quadrupolar interactions of the <sup>2</sup>H nuclei. There are different approaches for the study of the dynamics of <sup>2</sup>H-containing molecules. One of these is the **temperature-dependent analysis of the** *T*<sub>1</sub> **and** *T*<sub>2</sub> **relaxation times** [6-9]. Examples are the study of the mobility of benzene molecules in zeolites Na-EMT and K-L [6] and in the metal-organic framework ZIF-8 [7] or of *n*-hexane in silicalite [8]. In a much broader manner, however, the dynamics of <sup>2</sup>H quad-echo NMR spectra [7, 10-13].

<sup>2</sup>H quad-echo NMR spectra are symmetric with respect to the Larmor frequency  $v_0$  and the dominant features of the shapes of their signals are two strong peaks separated by the **quadrupole splitting of (3/4)** $C_{\rm Q}$  and two shoulders separated by (3/2) $C_{\rm Q}$ , where  $C_{\rm Q} = e^2 q Q/h$  is the quadrupole coupling constant (**Fig. 3a**). For deuterium atoms, e.g. bonded to tetrahedral carbon atoms (CD<sub>3</sub> groups) in polycrystalline organic solids, the quadrupole splitting (3/4)· $C_{\rm Q}$  is usually 120 to 130 kHz and the asymmetry parameter  $\eta_{\rm Q}$  is close to zero [7, 10].

If a CD<sub>3</sub> group of an organic molecule rotates rapidly with the correlation time  $\tau_{rot} \ll \{(3/4)\cdot 2\pi\cdot C_Q\}^{-1}$  around the threefold axis, the shape of the <sup>2</sup>H NMR signal is not changed, but the quadrupole splitting is reduced (**Fig. 3b**), according to the following equation [7, 10]:

$$(3/4) \cdot C_{Q,1} = (3/4) \cdot C_Q \cdot \{(1/2)(3\cos^2\beta_1 - 1)\}$$
(1)

where  $\beta$  is the angle between the C-D bond and the rotation axis. In the case of an ideal tetrahedral geometry of the rotating CD<sub>3</sub> group, i.e. with  $\beta_1 = 109.5^{\circ}$ , a  $C_{Q,1}$ 

value of  $(1/3) \cdot C_Q$  follows. Typical values of the reduced quadrupole splitting are  $(3/4) \cdot C_{Q,1} \cong 35$  to 40 kHz [7, 10].

If for a CD<sub>3</sub> group, which rotates rapidly around the threefold axis, a second rapid rotation exists around another axis, which is tilted at an angle  $\beta_1$  with respect to the first axis (e.g. the C-O bond), the quadrupole splitting is further decreased (**Fig. 3c**) to the value of  $(3/4) \cdot C_{Q,2}$  with [7, 10]:

$$(3/4) \cdot C_{Q,2} = (3/4) \cdot C_{Q,1} \cdot \{(1/2)(3\cos^2\beta_2 - 1)\}$$
(2)

For  $\beta_2 \cong 109.5^\circ$ , the  $C_{Q,2}$  value is  $(1/9) \cdot C_Q$  and the quadrupole splitting is  $(3/4) \cdot C_{Q,2} \cong$ 12 to 14 kHz. Similarly, in the case of a third rotation, e.g. around a jump axis with  $\beta_3$ = 109.5°, there will be a further decrease of the quadrupole splitting and the  $C_{Q,3}$ value is  $(1/27) \cdot C_Q$  (**Fig. 3d**) [7, 10].



simulated <sup>2</sup>H quad-echo NMR spectra

For a **rapid isotropic reorientation** with a correlation time  $\tau_c \ll \{(3/4) \cdot 2\pi \cdot C_Q\}^{-1}$ , the quadrupole splitting is averaged to zero and a Lorentzian signal occurs. In this case, the width  $\Delta v_{1/2}$  at half-height of this signal is given by [10]:

$$\Delta v_{1/2} = (3\pi/20) \cdot C_{Q}^{2} \cdot \{3\tau_{c} + 5\tau_{c}/(1+\omega_{0}^{2}\tau_{c}^{2}) + 2\tau_{c}/(1+4\omega_{0}^{2}\tau_{c}^{2})\}$$
(3)

where  $\omega_0 = 2\pi v_0$  and  $v_0$  is the Larmor frequency of the deuterium nuclei.

To study the **dynamics of** *n*-butane-*d*10 in the 10-ring pores of zeolite H-ZSM-5 (structure-type MFI), <sup>2</sup>H quad-echo NMR spectra were recorded in a temperature range of T = 123 to 383 K. In **Fig. 4**, the experimental spectra are presented together with their simulations [11]. The signal shapes reflect the reorientations of the C-D bonds of the *n*-butane-*d*10 molecules inside the zeolite pores. In *n*-butane-*d*10, there are two types of non-equivalent C-D bonds due to the CD<sub>2</sub> and CD<sub>3</sub> groups. The total signal shape is, therefore, a sum of signals from these two groups. The change of the signal shapes with temperature reflects the motions in which the CD<sub>2</sub> and CD<sub>3</sub> groups are involved. Any fast molecular motion averages the initial Pake doublet of the rigid CD<sub>2</sub> and CD<sub>3</sub> groups (see **Eqs. (1) and (2)**), characterized by a <sup>2</sup>H quadrupole coupling constant of  $C_Q \cong 170$  kHz and an asymmetry parameter  $\eta \cong 0.33$ . The <sup>2</sup>H quad-echo NMR signal of the CD<sub>3</sub> groups gives a signal shape with smaller quadrupole coupling constant than that of CD<sub>2</sub> groups, since the CD<sub>3</sub> groups are additionally involved in a three site jump rotation around the C-CD<sub>3</sub> bond. The experiments show that the *n*-butane-*d*10 molecules in H-ZSM-5 are highly mobile



## <sup>2</sup>H quad-echo NMR of *n*-butane-*d*10 in H-ZSM-5

Fig. 4

even at T = 123 K, since the quadrupole coupling constant is already strongly averaged ( $C_Q(CD_2) \approx 31$  kHz). On the other hand, even at the highest temperature, the spectrum does not collapse to a single Lorenzian signal. Therefore, *n*-butane molecules in the pore system of H-ZSM-5 must be confined in such a manner that their motion is always ordered and no isotropic reorientation occurs [11].

As indicated by the spinning sidebands (asterisks) in the <sup>2</sup>H MAS NMR spectrum of the mesoporous D-[AI]SBA-15 materials in **Fig. 1a**, the thermal mobility of surface OD groups on this catalyst (and on H-form zeolites, see Ref. [1]), recorded at room temperature, is characterized by  $\tau_c >> 1/\nu_{rot}$ , where  $\nu_{rot}$  is the MAS frequency. Therefore, Pake doublets in the <sup>2</sup>H quad-echo NMR spectra of these solid catalysts are not affected by thermal mobility, but an overlap of Pake doublets due to different types of surface OD groups may occur. This problem was solved by a method, which was demonstrated for the first time in Ref. [14]. According to this method, a G( $t_1, t_2$ ) array is created by separating the different MAS echoes in the free induction decay of the <sup>2</sup>H MAS NMR data set. The decays of the different MAS echoes correspond to the time domain  $t_2$ , and the decays of all echo amplitudes correspond to the time domain  $t_1$ . The twofold Fourier transformation of G( $t_1, t_2$ ) leads to the array F( $\nu_1, \nu_2$ ), which is a two-dimensional (2D) spectrum with highly resolved MAS NMR signals along the  $\nu_1$  dimension and the static NMR signals along the  $\nu_2$  dimension. In **Fig. 5**, the **contour plot of a 2D evaluation of the** <sup>2</sup>H **MAS NMR spectrum of** 



2D contour plot of a <sup>2</sup>H MAS NMR spectrum

Fig. 5

dealuminated zeolite D,Na-Y/92 (cation exchange degree of 92 %) is shown [15]. In this contour plot, the perpendicular  $v_1$  dimension corresponds to the well-resolved Si(OD)AI, AIOD, and SiOD central lines of the <sup>2</sup>H MAS NMR spectrum, while along the horizontal  $v_2$  dimension, the static <sup>2</sup>H NMR spectrum (i.e. Pake doublets) is plotted. Via this contour plot, each Pake doublet for the different central lines can be separated (see dashed lines). For the Si(OD)AI signal, a Pake double with a quadrupole splitting of  $v_a = 168$  kHz occurs, which corresponds to a <sup>2</sup>H quadrupole coupling constant of  $C_Q = (4/3) \cdot v_a = 224$  kHz [15]. In a similar manner, the quadrupole

Material	Species	C <sub>Q</sub> / kHz	ηα	Refs.
rigid <i>n</i> -hexane- <i>d</i> 14	$CD_3$ and $CD_2$	ca. 170	0.33	[7]
rigid methyl groups	$CD_3$	120 to 130	0.0	[7], [10]
rapid rotation of methyl groups, around one C <sub>3</sub> axis	$CD_3$	35 to 40		[7], [10]
twofold rapid rotation of methyl groups, e.g. around two $C_3$ axes	$CD_3$	12 to 14		[7], [10]
D,Na-X/50 ( $n_{\rm Si}/n_{\rm Al} = 1.4$ )	Si(OD)Al	236±10	0.10±0.05	[15], [16]
D,Na-Y/85 ( <i>n</i> <sub>Si</sub> / <i>n</i> <sub>Al</sub> = 2.4)	Si(OD)Al	236±10	0.06±0.05	[15], [16]
D,Na-Y/92 ( $n_{\rm Si}/n_{\rm Al} = 3.1$ )	Si(OD)Al	224±10	0.13±0.05	[15], [16]
	AIOD	67±5	0.2±0.05	[15], [16]
	SiOD	< 65		[15], [16]
D-Rho ( $n_{\rm Si}/n_{\rm Al} = 3.5$ )	Si(OD)Al	251		[20]
D-Y $(n_{\rm Si}/n_{\rm Al} = 9)$	Si(OD)Al	234, 236	0	[21], [22]
D-Mordenite ( $n_{\rm Si}/n_{\rm Al}$ = 13)	Si(OD)Al	240	0	[22]
	SiOD	65	0	[22]
D-ZSM-5 ( $n_{\rm Si}/n_{\rm AI} = 22$ )	Si(OD)Al	208±10	0.15±0.05	[15], [16]
D-ZSM-5 ( $n_{\rm Si}/n_{\rm Al} = 34$ )	Si(OD)Al	225	0	[22]

## Table 1

splittings of  $v_b = 50$  kHz and  $v_c \ll 49$  kHz for the AIOD and SiOD signals correspond to <sup>2</sup>H quadrupole coupling constants of  $C_Q = 67$  kHz and  $C_Q \ll 65$  kHz, respectively [15]. **Table 1** gives a survey on the <sup>2</sup>H quadrupole coupling constants  $C_Q$  and asymmetry parameters  $\eta$  of the above-mentioned OD groups of solid catalysts and of some other deuterium-containing catalysts and compounds described in literature.

For studying the interaction of bridging hydroxyl groups (Si(OH)Al) in zeolite H-ZSM-5 with methanol at low-temperatures, CH<sub>3</sub>OD was adsorbed on the dehydrated catalyst at T = 77 K and subsequently investigated by <sup>2</sup>H quad-echo NMR spectroscopy at T = 85 K [17]. The <sup>2</sup>H quad-echo NMR spectrum in Fig. 6, bottom, consists of a large Pake doublet with a quadrupole splitting of ca. 170 kHz ( $\nu_a = \delta_a \cdot \nu_0 = 2800$  ppm · 61.4 MHz) and a small Pake doublet with a quadrupole splitting of ca. 100 kHz ( $\nu_b = \delta_b \cdot \nu_0 = 1700$  ppm · 61.4 MHz). These quadrupole splittings correspond to <sup>2</sup>H coupling constants of  $C_Q \cong 230$  kHz and  $C_Q \cong 140$  kHz, respectively [17]. While the large Pake doublet is caused by OD groups of rigidly adsorbed CH<sub>3</sub>OD molecules ( $C_Q \cong 230$  kHz), the small Pake doublet is due a weak H/D exchange between the OD groups of CH<sub>3</sub>OD molecules and bridging OH groups of the zeolite H-ZSM-5, occurring despite the low temperature and leading to some



Si(OD)AI species ( $C_Q \cong 140$  kHz). The <sup>2</sup>H quad-echo NMR spectra recorded upon stepwise heating to room temperature (**Fig. 6, middle and top**) show a narrowing of the signals. This signal narrowing indicates an enhanced mobility of the deuterons of all contributing OD groups, in agreement with the effect of a decreasing correlation time  $\tau_c$  in **Eq. (3)**.

In a review on parameters of deuterium atoms in **hydrogen bonds (OD**<sup>...</sup>**O)** of solids, a **relationship between the** <sup>2</sup>**H quadrupole coupling constants**  $C_{Q}$  and the O-O **distances**  $R_{O-O}$  of these bonds was demonstrated [18]. Utilizing additional experimental data [19], **Fig. 7** shows the dependence of the  $C_{Q}$  values on the O-O distance  $R_{O-O}$  [17]. Accordingly, the <sup>2</sup>H quadrupole coupling constant of  $C_{Q} \cong 140$ kHz of deuterated bridging hydroxyl groups of the zeolite under study (Si(OD<sup>...</sup>O)AI) corresponds to an O-O distance to the next nearest oxygen atom of rigidly adsorbed methanol molecules of  $R_{O-O} \cong 0.25$  to 0.26 nm [17]. Similarly, the <sup>2</sup>H quadrupole coupling constant of  $C_{Q} \cong 230$  kHz of deuterium atoms in rigidly adsorbed CH<sub>3</sub>OD molecules (CH<sub>3</sub>OD<sup>...</sup>O) corresponds to an O-O distance to the next nearest oxygen atom of the zeolite framework of  $R_{O-O} \cong 0.28$  to 0.29 nm [17].



Fig. 7

Finally must be added that determination of correct and reproducible <sup>2</sup>H quadrupole coupling constants  $C_Q$  and <sup>2</sup>H chemical shifts of hydroxyl groups on solid catalysts, such as zeolites, require a suitable preparation of the sample material, i.e. calcination of at least T = 673 K, and a transfer of the calcined samples into the NMR sample tubes or MAS rotors without contact to air for omitting rehydration. Otherwise, too

small and wrong <sup>2</sup>H quadrupole coupling constants for Si(OD)Al groups, such as  $C_Q$  = 100 kHz for Si(OD)Al groups in a deuterated H-Y zeolite (D-Y) [23] (compare with values of **Table 1**), and wrong isotropic chemical shifts, such as  $\delta_{2H}$  = 6.4 ppm for SiOH groups, also in a deuterated H-Y zeolite (D-Y) [23] (compare with values of Table 1 in Section "method 1"), are obtained.

*Catalyst preparation:* Most of the deuterated adsorbate and reactant molecules utilized for <sup>2</sup>H solid-state NMR studies in the research field of heterogeneous catalysis are commercially available. A suitable method for the preparation of deuterium-exchanged hydroxyl groups on solid catalysts is the saturation of the dehydrated samples with D<sub>2</sub>O and subsequent dehydration at T = 473 K for 2 h [1, 15, 16]. The final dehydration is required for omitting a rapid exchange between surface hydroxyl groups and water molecules, which would hinder the resolution of <sup>2</sup>H solid-state NMR signals. This dehydration and the subsequent handling of the dehydrated samples can be performed by using the same set-up and procedure as described in Section "method 1".

<sup>2</sup>*H* solid-state NMR studies: The <sup>2</sup>H MAS NMR spectra of D-[Al]SBA-15 in Fig. 1 were measured with a Bruker MSL 400 spectrometer at the resonance frequency of  $v_0 = 61.4$  MHz, utilizing a 2.5 mm Bruker MAS NMR probe, and with a sample spinning rate of  $v_{rot} = 25.0$  kHz. The spectra were recorded after excitation with single pulses of 4.0 µs (ca. 75°) and a repetition time of 2 s [1]. For the conditions of recording the spectra in Fig. 2, see Ref. [5]. The <sup>2</sup>H quad-echo NMR spectra in Figs. **4, 5, and 6** and were measured as described in Refs. [10] and [11], i.e. with quadrature-detected quadrupole echoes, utilizing a  $\Theta_1(\pm x) - \tau_1 - \Theta_2(y) - \tau_2 - t$  pulse sequence. The pulse durations  $\Theta_1$  and  $\Theta_2$  were 4.0 to 4.5 µs,  $\tau_1 = 30$  µs,  $\tau_2 = 36$  µs, and the repetition time was 2 s. The contour plot in Fig. 5 was created as described in Ref. [14] and in the text of this Section. Chemical shifts are referenced to liquid D<sub>2</sub>O ( $\delta_{2H} = 4.8$  ppm).

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