Characterization of solid catalysts by ¹⁷O solid-state NMR

Spectroscopic background: ¹⁷O nuclei have a spin of I = 5/2 and a quadrupole moment of $Q = -2.558 \times 10^{-30} \text{ m}^2$. Therefore, ¹⁷O NMR signals of oxygen atoms in solids are affected by quadrupolar interactions. Due to the low natural abundance of the ¹⁷O isotope of 0.037 % and, in this state, a sensitivity in comparison with ¹H nuclei (1.0) of 1.1×10^{-5} only, ¹⁷O solid-state NMR spectroscopy of catalysts requires an isotopic enrichment. For basic principles of solid-state NMR, see lectures "Solid-State NMR Spectroscopy" for Bachelor students or PhD seminars, accessible via the link "Lectures for Students".

Early ¹⁷O broad-line NMR spectroscopic studies of water-free aluminosilicate-type zeolites, performed without the application of MAS, led to broad quadrupole patterns corresponding to a quadrupole coupling constant of about $C_Q = 4.6$ to 5.7 MHz and 3.2 to 4.3 MHz due to oxygen atoms in Si-¹⁷O-Si and Si-¹⁷O-AI bridges, respectively. The isotropic chemical shifts were determined to $\delta_{170,iso} = 28$ to 52 ppm for Si-¹⁷O-Si and $\delta_{170,iso} = 31$ to 45 ppm for Si-¹⁷O-AI bridges [1]. Simulation of the ¹⁷O broad-line NMR spectra of aluminophosphates gave $C_Q = 5.6$ to 6.5 ppm and $\delta_{170,iso} = 61$ to 67 ppm for AI-¹⁷O-P bridges. Gallosilicates contain Si-¹⁷O-Ga bridges with $C_Q = 4.0$ to 4.8 ppm and $\delta_{170,iso} = 29$ ppm (Table 1) [2].

Nowadays, ¹⁷O solid-state NMR investigations of catalysts are performed applying the MAS, DOR, and two-dimensional (2D) MQMAS techniques [3-8]. A prerequisite for obtaining well-resolved ¹⁷O MAS, DOR, and 2D MQMAS NMR spectra is the presence of ordered local structures, such as those occurring in siliceous zeolites and in zeolites with an alternating arrangement of silicon and aluminum atoms at T-



Fig. 1

positions ($n_{\rm Si}/n_{\rm Al} = 1$). In these cases, the different signals of oxygen atoms at crystallographically non-equivalent O-sites appear as well-resolved signals in the ¹⁷O DOR NMR (**Fig. 1**) and ¹⁷O MQMAS NMR spectra (**Fig. 2**) [3]. For siliceous **zeolite FER** and utilizing ¹⁷O MQMAS NMR spectroscopy, up to 10 different signals of oxygen atoms at crystallographically non-equivalent positions in Si-O-Si bridges were found [4]. While the isotropic chemical shifts of these signals cover a range of $\delta_{170,iso} = 28.0$ to 43.1 ppm, slightly different quadrupole coupling constants in the range of $C_{\rm Q} = 5.2$ to 5.6 MHz were determined.

The significant effect of the DOR technique on the spectral resolution in comparison with the MAS technique for the study of quadrupolar nuclei is demonstrated in **Fig. 1** [3]. While the ¹⁷O MAS NMR spectrum of ¹⁷O-enriched and dehydrated zeolite Na-LSX ($n_{Si}/n_{Al} = 1$) consists of a single broad signal, the application of the DOR technique leads to a split of the spectrum into three narrow signals. The potential of the 2D MQMAS technique is demonstrated in **Fig. 2**, which shows the ¹⁷O MQMAS NMR spectrum of oxygen atoms in zeolite Na-LSX [3]. The signals obtained along the δ_2 -axis of the two-dimensional spectrum in **Fig. 2** correspond to the one-dimensional ¹⁷O MAS NMR spectrum (projection on top). These signals are affected by second-order quadrupolar signal broadening. The signals obtained along the δ_{so} -axis (projection at the left-hand side) are comparable with those in the ¹⁷O DOR NMR



Fig. 2

spectrum in **Fig 1**, **bottom**. In this dimension, the anisotropic second-order quadrupolar signal broadenings are averaged by the multiple-quantum experiment. On the right-hand side of **Fig. 2**, slices cut parallel to the δ_2 -axis at different δ_{170} values are depicted. These slices correspond to the different ¹⁷O MAS NMR signals of oxygen atoms at the crystallographically non-equivalent oxygen positions in **zeolite Na-LSX**. The simulation of these slices allows a determination of the quadrupole parameters of the corresponding ¹⁷O nuclei and led to quadrupole coupling constants of $C_{\rm Q} = 3.2$ to 3.6 MHz and chemical shifts of $\delta_{170,\rm iso} = 41.1$ to 53.6 ppm for oxygen atoms at the four crystallographically non-equivalent O-sites in zeolite Na-LSX [3]. Data obtained by 2D ¹⁷O MQMAS NMR spectroscopy of oxygen atoms at crystallographically non-equivalent oxygen positions in zeolites Na-A and Na-LSX (both $n_{\rm SI}/n_{\rm Al} = 1$) yielded a correlation between their isotropic chemical shift $\delta_{170,\rm iso}$ and the Si-O-Al bond angle β [3]:

$$\delta_{170,iso} / \text{ppm} = -0.71 \ \beta + 143.7$$
 (1)

Eq. (1) can be utilized to calculate Si-O-Al bond angles β in materials, where a determination of the local oxygen structure by X-ray diffraction is not possible.

¹⁷O solid-state NMR spectroscopic studies of non-crystalline powder materials are complicated by the distribution of the bond geometries in the local structure of the oxygen atoms and, therefore, of the ¹⁷O quadrupole parameters. By ¹⁷O spin-echo and MAS NMR experiments, the oxygen atoms in **silica**, synthesized via the sol-gel technique, were investigated [9]. The signals of oxygen atoms in the **Si-O-Si** bridges were found to be characterized by a quadrupole coupling constant of $C_{Q} = 5.3$ MHz and an isotropic chemical shift of $\delta_{170,iso} = 42$ ppm. The SiOH fragments caused signals in a wide range of C_{Q} values and at isotropic chemical shifts of $\delta_{170,iso} = 0 \pm$ **20** ppm. The behaviour of the latter signals is explained by the above-mentioned distribution of the bond geometries in the local structure of the **SiOH** fragments.

Titanium oxides, TiO₂, are extensively studied materials because they are widely employed as conventional catalyst supports [10], pigments [11], and photocatalysts [12, 13]. The two common phases are **anatase (A)** and **rutile (R)**. The rutile phase is the most stable structure of TiO₂, while the anatase phase can transform to rutile at high temperatures. Both anatase and rutile consist of TiO₆ units, which are joined together by sharing different numbers of edges - two in rutile and four in anatase. The photocatalytic activity of TiO₂ could be related to phase-junctions formed between the anatase and rutile domains, which enhance the hydrogen production in the photocatalytic water splitting [14, 15]. Therefore, the ^{16/17}O isotope exchange (OIE) on water-free pure anatase in comparison with mixed-phase TiO₂ materials, containing anatase and rutile domains as well as various surface oxygen species and phase conjunctions on the anatase and rutile domains, was studied by ¹⁷O MAS NMR spectroscopy upon a thermally induced OIE with ¹⁷O₂ gas [16]. By this way, the activation energies of the OIE were determined for the above-mentioned materials.

Fig. 3 shows the stacked plots of ¹⁷O MAS NMR spectra of pure anatase (a, TiO₂/A) and an anatase/rutile mixture (b, TiO₂/A+R) recorded upon OIE with ¹⁷O₂ gas (p = 500 mbar) at T = 773 K up to t = 80 h. The ¹⁷O MAS NMR signal at $\delta_{170} =$ 562 ppm is due to ¹⁷O atoms in pure anatase and has a signal shape according to a quadrupole coupling constant of $C_Q = 1.2$ MHz. The signal at $\delta_{170} = 596$ ppm, with a similar signal shape, is caused by ¹⁷O atoms in rutile with $C_Q = 1.8$ MHz, while surface ¹⁷O atoms of the anatase/rutile domain mixture are responsible for the signals at $\delta_{170} = 516$ ppm, 543 ppm, and 572 ppm [16].



Fig. 3

The ^{16/17}O isotope exchange (OIE) kinetics, investigated upon thermal treatments of the ¹⁷O₂ gas-loaded TiO₂ materials at T = 723 K, 773 K, and 823 K, led to the Arrhenius plots of the velocity constants k_i of ¹⁷O atoms in the pure anatase (TiO₂/A) and in anatase/rutile domains (TiO₂/A+R) shown in **Fig. 4** [16]. These plots indicate a strong decrease of the activation energy of the OIE on the **mixed-phase TiO₂/A+R**

material ($E_a = 61 \text{ kJ/mol}$ for the anatase domains and $E_a = 70 \text{ kJ/mol}$ for the rutile domains) compared with the pure anatase TiO₂/A material ($E_a = 105 \text{ kJ/mol}$). Furthermore, the very rapid increase of the ¹⁷O MAS NMR signals of surface oxygen species on the TiO₂/A+R material indicates that the OIE starts at these surface sites, which subsequently exchange their ¹⁷O atoms with ¹⁶O framework atoms in anatase and rutile domains [16].



Table 1 gives a summary of the ¹⁷O solid-state NMR parameters of the abovementioned and some additional materials. Utilizing ${}^{1}H\rightarrow{}^{17}O$ CPMAS NMR, ${}^{17}O^{-1}H$ REDOR NMR, and ${}^{1}H^{-17}O$ HETCOR NMR techniques, the study and determination of framework oxygen atoms bound to the hydroxyl protons of bridging OH groups (Si- ${}^{17}OH$ -Al) in acidic zeolites are possible [21-23]. For a broad survey on ${}^{17}O$ solid-state NMR parameters of oxygen atoms in solids, see Ref. [17] and Table 8.3 of Ref. [18].

Materials	O Species	C _Q / MHz	η_{Q}	$\delta_{ m 170}$ / ppm	Refs.
zeolite Na-A (1.0)*	Si- ¹⁷ O-Al	3.2 - 4.2	0.2	32 - 33	[1]
zeolite Na-A (1.0)*	Si- ¹⁷ O-Al	3.4	0.0	30 - 42	[3]
			- 0.3		
zeolite Na-LSX (1.0)*	Si- ¹⁷ O-Al	3.2 - 3.6	0.15	41 - 54	[3]
			- 0.4		
zeolite Na-Y (2.74)*	Si- ¹⁷ O-Si	4.6 - 5.7	0.1	44 - 46	[1]
	Si- ¹⁷ O-Al	3.1 - 4.2	0.2	31	[1]
zeolite NH ₄ -Y (2.92)*	Si- ¹⁷ O-Si	5.0 - 5.7	0.1	47 - 48	[1]
	Si- ¹⁷ O-Al	3.2 - 4.3	0.2	31	[1]

https://michael-hunger.de

zeolite H-Y (2.6)*	Si- ¹⁷ O _{2,3,4} -AI	3.7	0.2	27.5	[23]
	Si- ¹⁷ O ₁ -Al	3.5	0.3	33.3	[23]
	Si- ¹⁷ O _{2,3,4} -Si	5.3	0.1	44.0	[23]
	Si- ¹⁷ O ₁ -Si	5.1	0.3	50.0	[23]
	Si- ¹⁷ O _{2,3} H-	6.2	0.9	24.0	[22, 23]
	AI				
	Si- ¹⁷ O ₁ H-AI	6.0	1.0	21.0	[22, 23]
dealuminated Na-Y (>25)*	Si- ¹⁷ O-Si	5.2 - 5.7	0.2	45 - 47	[1]
siliceous Ferrierite (FER)	Si- ¹⁷ O-Si	5.2 - 5.6	0.1	28 - 43	[4]
			- 02		
zeolite H-ZSM-5 (25)*	Si- ¹⁷ O-Si	5.45	0.2	40.5	[22]
	Si- ¹⁷ OH-Al	5.8 - 7.0	0.5	31 - 37	[22]
			- 0.75		
zeolite Ga-Sodalite	Si- ¹⁷ O-Si	5.1 - 5.7	0.0	51 - 52	[2]
	Si- ¹⁷ O-Ga	4.0 - 4.8	0.3	29	[2]
amorphous SiO ₂	Si- ¹⁷ O-Si	5.3 - 5.7	0.0	42 - 46	[1, 9]
aluminophospate AIPO ₄ -5	Al- ¹⁷ O-P	5.7 - 6.5	0.0	61 - 63	[2]
aluminophospate AIPO ₄ -11	Al- ¹⁷ O-P	5.7 - 6.4	0.0	63 - 64	[2]
aluminophospate AIPO ₄ -17	Al- ¹⁷ O-P	5.6 - 6.3	0.0	63 - 67	[2]
			- 0.1		
TiO ₂ / Anatase	¹⁷ OTi ₃	1.2	0.6	562	[16, 20]
TiO ₂ / Rutile	¹⁷ OTi ₃	1.8	0.6	596	[16, 20]

*) $n_{\rm Si}/n_{\rm Al}$ ratio

Table 1

Catalyst preparation: The ¹⁷O enrichment of powder materials used for the NMR studies presented in Figs. 1 and 2 was performed by a treatment in a reactor with $H_2^{17}O$ vapour at T = 523 K for several hours [3]. For the studies presented in Fig. 3, the dehydrated TiO₂ materials, filled in quartz glass tubes, were loaded with 500 mbar ¹⁷O₂ gas. Upon sealing the quartz glass tubes, these samples were heated at T = 723 to 823 K for up to t = 80 h. After this treatment, the sample materials were transferred into a MAS NMR rotor without air contact inside a mini glove box (see Section "mini glove box", accessible via the link "*In Situ* Solid-State NMR Techniques"), purged with dry nitrogen gas.

¹⁷O solid-state NMR studies: The ¹⁷O DOR NMR experiments were performed at the Larmor frequency of $v_0 = 67.8$ MHz in the magnetic field of $B_0 = 11.7$ T [3]. For https://michael-hunger.de

the 2D ¹⁷O MQMAS experiments, the Larmor frequency of $v_0 = 101.7$ MHz and the external magnetic field of $B_0 = 17.6$ T were utilized [3]. The MQMAS pulse sequence consisted of two strong pulses and an additional weak z-filter pulse [19]. A total ring down delay of 7 µs after the z-filter pulse and a repetition time of t = 200 ms were used. The non-selective nutation frequency of 100 kHz was determined for a H₂¹⁷O sample at the Larmor frequency of $v_0 = 101.7$ MHz. For this rf power, the widths of the first and second pulse were adjusted for maximum signal intensity to 3.4 and 1.2 µs, respectively. The selective $\pi/2$ pulse length of the z-filter was adjusted to 50 µs [3]. The ¹⁷O MAS NMR investigations of the TiO₂ materials were performed at the Larmor frequencies of $v_0 = 54.2$ MHz upon single pulse excitation of $\pi/6$, with the repetition time of t = 0.5 s, and the sample spinning rate of $v_{rot} = 20$ kHz using a 2.5 mm MAS NMR probe. The chemical shifts were referenced to liquid H₂¹⁷O ($\delta_{170} = 0$ ppm).

References:

- H.K.C. Timken, G.L. Turner, J.-P. Gilson, L.B. Welsh, E. Oldfield, Solid-state oxygen-17 nuclear magnetic resonance spectroscopic studies of zeolites and related systems, Part 1, J. Am. Chem. Soc. 108 (1986) 7231-7235, DOI: 10.1021/ja00283a017.
- [2] H.K.C. Timken, N. Janes, G.L. Turner, S.L. Lambert, L.B. Welsh, E. Oldfield, Solid-state oxygen-17 nuclear magnetic resonance spectroscopic studies of zeolites and related systems, Part 2, J. Am. Chem. Soc. 108 (1986) 7236-7241, DOI: 10.1021/ja00283a018.
- U.-T. Pingel, J.-P. Amoureux, T. Anupold, F. Bauer, H. Ernst, C. Fernandez, D. Freude, A. Samoson, *High-field* ¹⁷O *NMR studies of the SiOAI bond in solids*, Chem. Phys. Lett. 294 (1998) 345-350, DOI: 10.1016/S0009-2614(98)00847-1.
- [4] L.M. Bull, B. Bussemer, T. Anupold, A. Reinhold, A. Samoson, J. Sauer, A.K. Cheetham, R. Dupree, A high-resolution ¹⁷O and ²⁹Si NMR study of zeolite siliceous ferrierite and ab initio calculations of NMR parameters, J. Am. Chem. Soc. 122 (2000) 4948-4958, DOI: 10.1021/ja993339y.
- [5] D. Freude, T. Loeser, D. Michel, U. Pingel, D. Prochnow, ¹⁷O NMR studies of low silicate zeolites, Solid State Nucl. Magn. Reson. 20 (2001) 46-60, DOI: 10.1006/snmr.2001.0029.
- [6] J.E. Readman, N. Kim, M. Ziliox, C.P. Grey, ¹⁷O MQMAS NMR studies of Na-A and Ca-A, Chem. Commun. (2002) 2808-2809, DOI: 10.1039/b208356f.

- [7] T. Loeser, D. Freude, G.T.P. Mabande, W. Schwieger, ¹⁷O NMR studies of sodalites, Chem. Phys. Lett. 370 (2003) 32-38, DOI: 10.1016/S0009-2614(03)00066-6.
- [8] J.E. Readman, C.P. Grey, M. Ziliox, L.M. Bull, A. Samoson, *Comparison of the* ¹⁷O NMR spectra of zeolites LTA and LSX, Solid State Nucl. Magn. Reson. 26 (2004) 153-159, DOI: 10.1016/j.ssnmr.2004.03.004.
- [9] E.R.H. van Eck, M.E. Smith, S.C. Kohn, Observation of hydroxyl groups by ¹⁷O solid-state multiple quantum MAS NMR in sol-gel-produced silica, Solid State Nucl. Magn. Reson. 15 (1999) 181-188, DOI: 10.1016/S0926-2040(99)00055-7.
- [10] M.C.J. Bradford, M.A. Vannice, Catalytic reforming of methane with carbon dioxide over nickel catalysts, Appl. Catal. A: Gen. 142 (1996) 73-96, DOI: 10.1016/0926-860X(96)00065-8.
- G. Pfaff, P. Reynders, Angle-dependent optical effects deriving from submicron structures of films and pigments, Chem. Rev. 99 (1999) 1963-1981, DOI: 10.1021/cr970075u.
- [12] A. L. Linsebigler, G. Q. Lu, J. T. Yates, *Photocatalysis on TiO₂ surfaces: Principles, mechanisms, and selected results*, Chem. Rev. 95 (1995) 735-758, DOI: 10.1021/cr00035a013.
- X. Sun, W. Dai, G. Wu, L. Li, N. Guan, M. Hunger, *Evidence of rutile-to-anatase photo-induced electron transfer in mixed-phase TiO₂ by solid-state NMR spectroscopy*, Chem. Commun. 51 (2015) 13779-13782, DOI: 10.1039/c5cc04971g.
- [14] J. Zhang, Q. Xu, Z. Feng, M. Li, C. Li, Importance of the relationship between surface phases and photocatalytic activity of TiO₂, Angew. Chem. Int. Ed. 47 (2008) 1766-1769, DOI: 10.1002/anie.200704788.
- [15] J. Zhang, Q. Xu, M. Li, Z. Feng, C. Li, UV Raman spectroscopic study on TiO₂.
 II. Effect of nanoparticle size on the outer/inner phase transformations, J.
 Phys. Chem. C 113 (2009) 1698-1704, DOI: 10.1021/jp808013k.
- X. Sun, M. Dyballa, J. Yan, L. Li, N. Guan, M. Hunger, Solid-state NMR investigation of the ^{16/17}O isotope exchange of oxygen species in pure-anatase and mixed-phase TiO₂, Chem. Phys. Lett. 594 (2014) 34-40, DOI: 10.1016/j.cplett.2014.01.014.
- [17] D. Freude, Quadrupolar Nuclei in Solid-State Nuclear Magnetic Resonance, in: Encyclopedia of Analytical Chemistry: Applications, Theory, and Instrumentation, Wiley, 2006, DOI: 10.1002/9780470027318.a6112.
- [18] D. Freude, <u>https://www.dieter-freude.de/quad-nmr</u>.
- [19] J.-P. Amoureux, C. Fernandez, S. Steuernagel, *Z filtering in MQMAS NMR*, J.
 Magn. Reson. A 123 (1996) 116-118, DOI: 10.1006/jmra.1996.0221.

- T.J. Bastow, A.F. Moodie, M.E. Smith, H.J. Whitfield, *Characterisation of titania gels by* ¹⁷O *nuclear magnetic resonance and electron diffraction*, J. Mater. Chem. 3 (1993) 697-702, DOI: 10.1039/jm9930300697.
- [21] L. Peng, Y. Liu, N. Kim, J.E. Readman, C.P. Grey, Detection of Broensted acid sites in zeolite HY with high-field ¹⁷O-MAS-NMR techniques, Nature Materials 4 (2005) 216-219, DOI: 10.1038/nmat1332.
- [22] L. Peng, H. Huo, Y. Liu, C.P. Grey, ¹⁷O magic angle spinning NMR studies of Broensted acid sites in zeolites HY and HZSM-5, J. Am. Chem. Soc. 129 (2007) 335-346, DOI: 10.1021/ja064922z.
- [23] L. Peng, H. Huo, Z. Gan, C.P. Grey, ¹⁷O MQMAS NMR studies of zeolite HY, Microporous Mesoporous Mater. 109 (2008) 156-162, DOI: 10.1016/j.micromeso.2007.04.039.