Characterization of lanthanum-containing catalysts by ¹³⁹La solid-state NMR

Spectroscopic background: ¹³⁹La nuclei have a spin of I = 7/2 and a large quadrupole moment of $Q = 20 \times 10^{-30} \text{ m}^2$. Therefore, ¹³⁹La NMR signals of lanthanum atoms in solids are strongly affected by quadrupolar interactions. The ¹³⁹La isotope has a natural abundance of 99.9 % and, in this state, a sensitivity of 6.1 x 10^{-2} in comparison with ¹H nuclei (1.0), making this isotope a suitable candidate for NMR studies of solids. 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".

Lanthanum-exchanged zeolites Na-Y (La,Na-Y) play an important role in the fluid catalytic cracking, one of the most widely applied petroleum refinery processes that make use of zeolites as catalyst components. Therefore, the lanthanum cation location and migration in hydrated and **dehydrated faujasite zeolites** were in the focus of numerous solid-state MAS NMR studies [1-6]. According to Ref. [7], **lanthanum cations in the sodalite cages are located on position SI'** are coordinated to three framework oxygen atoms of the six-ring window and extra-framework oxygens at position SII' (La²⁺OH, La⁺O, La²⁺O-La²⁺), while lanthanum ions at position SI are octrahedrally coordinated to six framework oxygen atoms (see **Fig. 1**) [8]. Using a point charge model [9], oxygen charges between -0.8 and -1.0 e, and the XRD data of the dehydrated La,Na-Y-68 studied in Ref. [7], quadrupole coupling constants of $C_{\rm Q} = 5.3$ to 6.6 MHz and 45 to 56 MHz were calculated for lanthanum cations located on positions SI and SI', respectively [3].



Fig. 1

In an early work [1], inorganic compounds with La-O bonds were studied by ¹³⁹La solid-state NMR spectroscopy as spectroscopic models for lanthanum cations in zeolites. One of these materials was La(OH)₃. Due to the very strong quadrupolar interactions of ¹³⁹La nuclei, these solid-state NMR investigations were performed with the spin-echo technique and without MAS (static). **Fig. 2** shows the ¹³⁹La **spin-echo NMR spectrum of La(OH)**₃, recorded at the resonance frequency of $v_0 = 56.5$ MHz ($B_0 = 9.4$ T) [1]. The experimental quadrupole pattern covers a frequency range of ca. 200 kHz and can be well-described by a quadrupole coupling constant of $C_{\rm Q} = 20.5\pm0.5$ MHz and an asymmetry parameter of $\eta = 0.05\pm0.05$ [1]. The spectrum in **Fig. 2** demonstrates that the ¹³⁹La spin-echo NMR technique is suitable for the investigation of lanthanum cations in faujasites, which are characterized by $C_{\rm Q}$ values in a similar order (*vide supra*).





The zeolite La,Na-Y, used for recording the ¹³⁹La spin-echo NMR spectra in **Fig. 3**, has 60% of the Na⁺ cations replaced by La³⁺ cations (La,Na-Y-60) [2, 3]. In the spectrum, recorded directly after the cation exchange, i.e. without subsequent dehydration (as-exchanged), a single signal (i) with a width of $\Delta v_{1/2} \cong 12$ kHz occurs. In this state of zeolite La,Na-Y-60, all lanthanum cations are fully hydrated and located in the supercages auf the faujasite structure [1, 10]. Upon dehydration at T = 433 K, the intensity of signal (i) is decreased to ca. 20 % and an additional signal with a width of $\Delta v_{1/2} \cong 150$ to 190 kHz appears. Since the

dehydration is accompanied by a migration of lanthanum cations into the sodalite cages, signal (ii) must be due to La³⁺ at positions SI', coordinated to oxygen atoms in their neighbourhood [11]. The structure-less shape of signal (ii) indicates that the corresponding lanthanum cations are involved in various local structures.



¹³⁹La spin-echo NMR

Fig. 3

Assuming a Gaussian signal shape for signals (i) and (ii), their quadrupole coupling constant C_Q can be estimated via their signal width $\Delta v_{1/2}$ [1, 12]:

$$C_{Q}^{2} = \frac{2940 v_{0} \Delta v_{1/2}}{\sqrt{(23/7) \log 4 [I(I+1) - 3/4](1 + \eta^{2}/3)}}$$
(1)

with $v_0 = 56.5$ MHz. Applying the two extreme values of the asymmetry parameter η ($\eta = 0$ and 1), quadrupolar coupling constants of $C_Q \cong 8$ MHz for the hydrated lanthanum cations in the supercages (signal (i)) and $C_Q \simeq 30$ MHz for the dehydrated lanthanum cations in the sodalite cages (signal (ii)) are obtained [3]. The latter C_Q value agrees qualitatively with the theoretical value of $C_Q = 45$ to 56 MHz, obtained via the point charge model for lanthanum cations at positions SI' (vide supra).

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Materials	C _Q / MHz	ηα	Refs.
La(OAc) ₃ (La(CH ₃ CO ₂) ₃)	11.0 ± 0.2	0.65 ± 0.05	[13]
La(OAc) ₃ (La(CH ₃ CO ₂) ₃) +2 H ₂ O	25.5	0.81	[14]
La(phen) ₂ (NO ₃) ₃ (La($C_{12}H_8N_2$) ₂ (NO ₃) ₃)	17.8	0.89	[14]
LaCrO ₃	48.0	0.15	[15]
LaGaO ₃	49.9 ± 0.2	0.05 ± 0.01	[16]
LaCl ₃ + ca. 6 H ₂ O	23.7 ± 0.5	0.40 ± 0.05	[1]
La(NO₃) ₃ + ca. 6 H ₂ O	23.8 ± 0.5	0.80 ± 0.05	[1]
	21.5 ± 1.0	0.85 ± 0.05	[13]
La(OH) ₃	20.5 ± 0.5	0.05 ± 0.05	[1]
La ₂ O ₃	58.5		[15]
zeolite La,Na-Y			
La ³⁺ in supercages (hydrated)	8.2 ± 0.8		[1]
	8.0 ± 1.0		[3]
La ³⁺ in sodalite cages (dehydrated)	26.0 ± 2.0		[1]
	30.5 ± 1.5		[3]

Table 1 gives a survey on the ¹³⁹La solid-state NMR parameters of the abovementioned zeolites La,Na-Y and some additional materials.

Table 1

Catalyst preparation: Depending on the state of the lanthanum cations in the zeolites under study, hydrated or dehydrated sample are investigated. In the case of studying dehydrated zeolites, a sample treatment as described in Section "method 1" is utilized.

¹³⁹La solid-state NMR studies: The ¹³⁹La NMR spectra in Figs. 2 and 3 were recorded with a Bruker MSL-400 spectrometer, at the resonance frequency of $v_0 = 56.5$ MHz, and using a t_1 - τ - t_2 spin-echo sequence with complex phase cycling. The pulse lengths were $t_1 = t_3 = 2.5 \mu$ s, the interpulse duration $\tau = 10 \mu$ s, and the recycle time 500 ms [1-3]. ¹³⁹La chemical shifts are often referenced to an external standard of an 1 M aqueous solution of LaCl₃ ($\delta_{139La} = 0$ ppm) [5, 6].

References:

- B. Herreros, P.P. Man, J.-M. Manoli, J. Fraissard, Solid-state ¹³⁹La NMR [1] investigation of lanthanum-exchanged Y zeolites, J. Chem. Soc., Chem. Commun. (1992) 464-466, DOI: 10.1039/c39920000464.
- [2] M. Hunger, G. Engelhardt, J. Weitkamp, Cation migration in zeolite LaNaY investigated by multi-nuclear solid-state NMR. Stud. Surf. Sci. Catal. 84A (1994) 725-732, DOI: 10.1016/S0167-2991(08)64179-8.
- M. Hunger, G. Engelhardt, J. Weitkamp, Solid-state ²³Na, ¹³⁹La, ²⁷Al and ²⁹Si [3] NMR studies of cation location and migration in LaNaY, Microporous Mater. 3 (1995) 497-510, DOI: 10.1016/0927-6513(94)00061-Y.
- [4] P. Garcia, E. Lima, J. Aguilar, V. Lara, Fractal extra-framework species in dealuminated LaY zeolites and their catalytic activity, Catal. Lett. 128 (2009) 385-391, DOI: 10.1007/s10562-008-9761-5.
- F. Schueßler, S. Schallmoser, H. Shi, G.L. Haller, E. Ember, J.A. Lercher, [5] Enhancement of dehydrogenation and hydride transfer by La³⁺ cations in zeolites during acid catalyzed alkane reactions, ACS Catal. 4 (2014) 1743-1752, DOI: 10.1021/cs500200k.
- R. Pointecouteau, P. Florian, V. Rodriguez, N. Bion, A. Demourgues, Unveiling [6] structural defects by ¹³⁹La NMR and Raman spectroscopies at the origin of surface stability for the design of cerium-based catalysts, J. Phys. Chem. C 127 (2023) 3020-3031, DOI: 10.1021/acs.jpcc.2c07034.
- [7] D.-S. Shy, S.-H. Chen, J. Lievens, S.-B. Liu, K.-J. Chao, Distribution of cations in lanthanum-exchanged NaY zeolites, J. Chem. Soc. Faraday Trans. 87(17) (1991) 2855-2859, DOI: 10.1039/ft9918702855.
- [8] H. Klein, H. Fuess, M. Hunger, Cation location and migration in lanthanumexchanged zeolite NaY investigated by X-ray powder diffraction and MAS NMR spectroscopy, J. Chem. Soc., Faraday Trans. 91 (1995) 1813-1824, DOI: 10.1039/ft9959101813.
- H. Koller, G. Engelhardt, A.P.M. Kentgens, J. Sauer, ²³Na NMR spectroscopy [9] of solids: Interpretation of quadrupole interaction parameters and chemical shifts, Phys. Chem. 98 (1994) 1544-1551, DOI: 10.1021/j100057a004.
- Q.J. Chen, T. Ito, J. Fraissard, ¹²⁹Xe-n.m.r. study of rare earth-exchanged [10] Y zeolites, Zeolites 11 (1991) 239-243, DOI: 10.1016/S0144-2449(05)80225-8.
- [11] A.K. Cheetham, M.M. Eddy, J.M. Thomas, The direct observation of cation hydrolysis in lanthanum zeolite-Y by neutron diffraction, J. Chem. Soc., Chem. Commun. (1984) 1337-1338, DOI: 10.1039/c39840001337.
- D. Freude. J. Haase, J. Klinowski, T. A. Carpenter, G. Ronikier, NMR line [12] shifts caused by the second-order quadrupolar interaction, Chem. Phys. Lett. 118 (1985) 365-367, DOI: 10.1016/0009-2614(85)80434-6.

- [13] A.R. Thompson, E. Oldfield, Solid-state scandium-45, yttrium-89, and lanthanum-139 nuclear magnetic resonance spectroscopy, J. Chem. Soc., Chem. Commun. (1987) 27-29, DOI: 10.1039/c39870000027.
- [14] M.J. Willans, K.W. Feindel, K.J. Ooms, R.E. Wasylishen, An investigation of lanthanum coordination compounds by using solid state ¹³⁹La NMR spectroscopy and relativistic density functional theory, Chem. Eur. J. 12 (2006) 159-168, DOI: 10.1002/chem.200500778.
- [15] T.J. Bastow, ¹³⁹La Nuclear magnetic resonance characterisation of La_2O_3 and $La_{1-x}Sr_xMO_3$ where M = Cr, Mn or Co, Solid State Nucl. Magn. Reson. 3 (1994) 17-22, DOI: 10.1016/0926-2040(94)90047-7.
- [16] T.J. Bastow, T. Mathews, J.R. Sellar, ${}^{69,71}Ga$ and ${}^{139}La$ NMR characterisation of LaGaO₃ and La_{1-x}Sr_xGa_{1-x}Mg_xO_{3-x}, Solid State Ionics 175 (2004) 129-133, DOI: 10.1016/j.ssi.2004.09.028.