

Solid-state ^{139}La NMR Investigation of Lanthanum-exchanged Y Zeolites

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The line shape of solid-state ^{139}La NMR spectra is sensitive to the local symmetry of the La ion sites: investigation of calcined La-exchanged Y zeolites reveals sharp and broad signals corresponding to La ions located in supercages and in small cages, respectively.

This work is motivated by the well established statement that lanthanum contributes greatly to the thermal stability of Y zeolite catalysts.¹⁻⁷ This high stability has been attributed to the presence of polynuclear cations in the sodalite cages containing oxygen-bridge La ions such as those presented in Fig. 1,²⁻⁷ but the precise nature of the species responsible for this stability is still not understood. However, there have been few reports on ^{139}La NMR.⁸⁻¹² This is due to the fact that ^{139}La is a spin $I = 7/2$ nucleus with a large electric quadrupolar moment and a small magnetogyric ratio, but fortunately with 99.9% natural abundance. This nucleus is very sensitive to its surrounding electric-field-gradient^{8,9} (EFG). Its lineshape depends strongly on the asymmetry parameter (η) and the quadrupolar coupling constant (e^2qQ/h) of the EFG tensor. To illustrate such effects we first studied three polycrystalline samples: $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{LaCl}_3 \cdot \text{ca. } 6\text{H}_2\text{O}$ and $\text{La}(\text{OH})_3$ with triclinic, monoclinic and hexagonal symmetry, respectively. Measurements were then performed on La-exchanged Y zeolites.

The starting material was Union Carbide LZ Y-64 (a 70% ammonium-exchanged Y zeolite). Its framework Si/Al ratio determined by ^{29}Si NMR was 2.43. A typical La exchange consisted in stirring *ca.* 10 g of zeolite in 0.5 dm³ of a 0.1 mol dm⁻³ solution of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at room temperature (RT) for 24 h. The sample was filtered, washed with distilled water and dried in a stream of air overnight (Sample 1). Chemical analysis gave the following anhydrous unit cell composition: $(\text{NH}_4)_{17}\text{La}_{13}(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}$. Sample 1 was then put in an alumina crucible and calcined in a muffle furnace for 1 h at 320 °C (Sample 2). Finally, Sample 2 was exchanged once again with a 1 mol dm⁻³ solution of NH_4NO_3

at RT for 24 h (Sample 3). The crystallinity of these samples was checked by X-ray diffraction.

^{139}La NMR spectra were recorded at $\nu_0 = 56.5$ MHz with a Bruker MSL-400 multinuclear spectrometer using a t_1 - τ - t_3 spin-echo sequence with complex phase cycling.¹³ The amplitude of the pulse, $\omega_{rf}/2\pi = 25$ kHz, and the associated $\pi/2$ pulse length, $t_{90^\circ} = 10$ μs , were determined using a solution of LaCl_3 . The acquisition parameters were: pulse lengths $t_1 = t_3 = 2.5$ μs , interpulse duration $\tau = 10$ μs , an acquisition delay of 8 μs , a recycle time of 500 ms and a dwell time of 1 μs . All spectra were referenced to an external standard of saturated aqueous lanthanum chloride. Fig. 2 shows static spectra of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{LaCl}_3 \cdot \text{ca. } 6\text{H}_2\text{O}$, and $\text{La}(\text{OH})_3$. These lineshapes are typical of second-order quadrupolar broadening (linewidth often over 100 kHz). This explains why Lutz

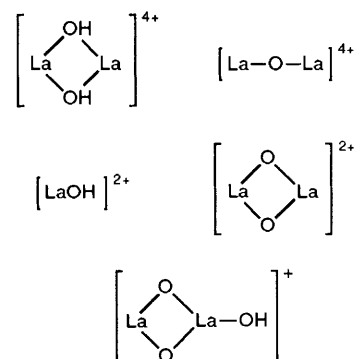


Fig. 1 Configurations of lanthanum atoms located in small cages of Y zeolites

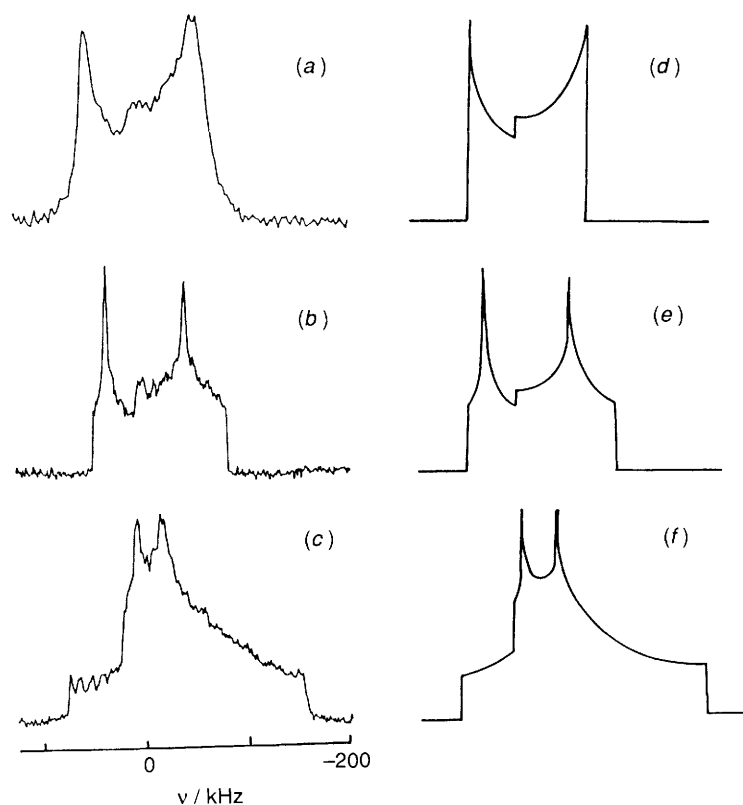


Fig. 2 Static ^{139}La NMR spectra of (a) $\text{La}(\text{OH})_3$, (b) $\text{LaCl}_3 \cdot \text{ca. } 6\text{H}_2\text{O}$, and (c) $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$; the corresponding computer simulated spectra are in (d), (e) and (f), respectively

Table 1 ^{139}La quadrupolar coupling constant (e^2qQ/h) and asymmetry parameter (η)

Compound	$(e^2qQ/h)/\text{MHz}$	η	Ref.
$\text{La}(\text{OH})_3$	20.5 ± 0.5	0.05 ± 0.05	
$\text{LaCl}_3 \cdot \text{ca. } 6\text{H}_2\text{O}$	23.7 ± 0.5	0.40 ± 0.05	
$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$	23.8 ± 0.5	0.80 ± 0.05	11
LaY, La in supercage	$8.2^a \pm 0.8$		
La in small cage	$26.0^a \pm 2$		
LaCl_3	$15.3^b \pm 0.003$	0	15, 16
$\text{LaMg}(\text{NO}_3)_5$	$13.1^b \pm 0.003$	0	15

^a The value is determined using eqn. (1), or eqns. (5) and (9) in ref. 17. ^b The sample was a single crystal. The value was deduced from the splitting of NMR lines.

and Oehler¹² did not succeed in detecting them with low-field equipment. (The second-order linewidth is inversely proportional to the static magnetic field). Spectra were simulated by the usual procedure.¹⁴ In Table 1 are reported the values of e^2qQ/h and η of ^{139}La in our samples as well as those in the literature. Our results concerning $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ are in agreement with those found by Kunwar *et al.*¹³ Apparently, water molecules modify the EFG tensor around the La site. For example, the NMR parameters of La in a single crystal of LaCl_3 are $e^2qQ/h = 15.3$ MHz and $\eta = 0$ whereas in $\text{LaCl}_3 \cdot \text{ca. } 6\text{H}_2\text{O}$, they become 23.7 MHz and 0.4, respectively.

Chemical analysis shows that 13 La^{3+} per unit cell are incorporated into the zeolite but remain in the supercages because of their hydration sphere. The hydrated La^{3+} ion radius is 3.96 Å whereas the free diameter of the entrances to the network of small cavities is 2.4 Å. Fig. 3(a) shows the ^{139}La spectrum of Sample 1. A single but symmetric line appears at $\delta -34$ ppm. Its full linewidth at half maximum ($\nu_{1/2}$) is 15 kHz. Naturally, we assign it to lanthanum cations located in the supercages. When the zeolite is heated to about 320°C, the hydration sphere is lost (the Pauling radius of La^{3+} is 1.15 Å)

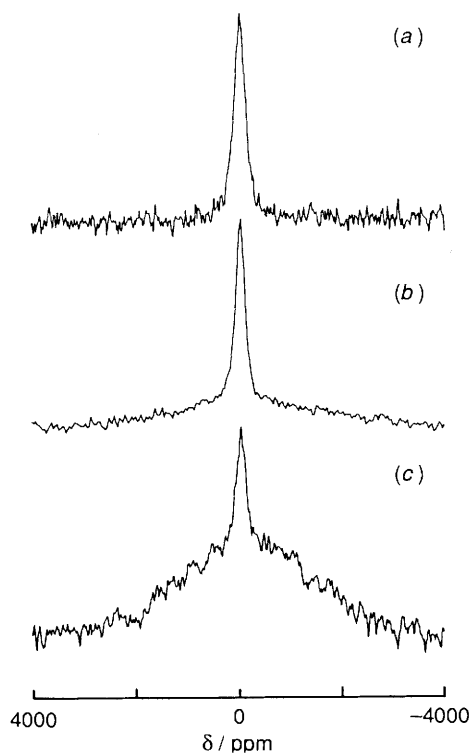


Fig. 3 Static ^{139}La NMR spectra of (a) Sample 1, (b) Sample 2 and (c) Sample 3

and some of the lanthanum cations migrate into the sodalite cages. Fig. 3(b) represents the ^{139}La spectrum of Sample 2. There are two lines: one sharp (La in supercages) superimposed on a very broad but symmetric line of low amplitude which we assign to lanthanum atoms located in small cages. These results are consistent with previous reports²⁻⁷ that La ions migrate into the small cages during calcination. The broad

line has not a well defined second-order quadrupolar powder pattern which means that La atoms are not located in a unique environment but in several, as indicated in Fig. 1. Finally, Fig. 3(c) represents the ^{139}La spectrum of Sample 3. Compared to the broad line whose linewidth is $\nu_2 = 150$ kHz, the line corresponding to La ions located in supercages decreases in intensity. This is consistent with the partial replacement of La ions in the supercages by NH_4^+ cations during exchange. As both lines are symmetric, it is not easy to determine the value of η . However, assuming a Gaussian lineshape, e^2qQ/h of these two lines can be estimated from the relationship eqn. (1).¹⁷ Applying the two extreme values of η , the quadrupolar coupling constant of La in the supercage and in a small cage are calculated and reported in Table 1. They have the same order of magnitude as La compounds containing water molecules.

$$(e^2qQ/h)^2 = \frac{2940 \nu_0 \nu_2}{\sqrt{(23/7) \log 4 [I(I+1) - 3/4](1 + \eta^2/3)}} \quad (1)$$

^{139}La NMR spectroscopy appears to be a good method for following the migration of this cation into the small cages of Y zeolite. However, it remains difficult to determine exactly where the La is: in the sodalites or/and in hexagonal prisms.

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