Nuclear Magnetic Resonance Study of the Dealumination of an Amorphous Silica–Alumina Catalyst

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The $^{29}$Si MASNMR and $^{27}$Al NMR study of an amorphous silica–alumina catalyst and of its dealuminated forms suggests that the tetrahedral aluminium ($\text{Al}^{IV}$) is involved in $Q_4\text{[Si(Al)]}$, $Q_4\text{[Si(2Al)]}$ and possibly $Q_2\text{[SiO]_2(Al)OH}_2$ units. Species $Q_4\text{[Si(0Al)]}$ are also evidenced. Ca. 30% of the Al is tetrahedral and 70% octahedral ($\text{Al}^{III}$) in the starting material. Upon dealumination, $\text{Al}^{IV}$ is removed first, then $\text{Al}^{IV}$. The extraction of Al generates hydroxyls in $Q_2\text{[SiO]_2SiOH}$ and $Q_2\text{[SiO]_2Si(OH)2}$ units.

Amorphous silica–aluminas are of interest as acidic catalysts, and research is still progressing in the field. Some amorphous silica–alumina phase is suggested to be formed as a component of Al extraneous framework debris upon steaming of faujasite zeolite. It would eventually act as a catalyst in addition to the framework zeolite sites. The description of the active sites in these amorphous materials is still open to question. Several types of sites have been presented with main interest on the geometry of the Si–O–Al bond arrangement, e.g. a ring structure. Another approach is to characterize the different configurations of Al atoms which can be tetrahedral ($\text{Al}^{IV}$), octahedral ($\text{Al}^{III}$) or even pentahedral ($\text{Al}^{V}$) after steaming. It was shown by ESR after $\gamma$-irradiation that 30% of the aluminium of a material containing 14% Al$_2$O$_3$ was tetrahedral. The content in $\text{Al}^{IV}$ was parallel to the properties in acidic catalysis for the unsteamed solids. This species appeared to constitute the active phase. The other part of Al was assumed to be alumina.

To provide more information on the properties of amorphous silica–aluminas the present work reports $^{29}$Si and $^{27}$Al NMR studies of an amorphous material in the course of its progressive dealumination.

Experimental

Materials

A co-gelled amorphous silica–alumina provided by Ketjen and containing 14% Al$_2$O$_3$ (K-14) was dealuminated using aqueous HCl solutions. Careful washing eliminates Cl$^-$ ions. The solids are referred to as K-9.4, K-4.6, K-2.4, K-0.9 and K-0.09 the numbers giving the Al$_2$O$_3$ (%) content.

The samples were hydrated in a desiccator with saturated NH$_4$NO$_3$ before NMR measurements. The loss on ignition for all the materials is 22–24 wt %.

NMR

$^{29}$Si and $^{27}$Al solid-state NMR were performed on a Bruker MSL-400 multinuclear spectrometer at 79.5 and 104.2 MHz, respectively. Their chemical shifts are reported in ppm from external tetramethylsilane (TMS) and Al(H$_2$O)$_6$ respectively. The sign convention of high-frequency (low-field, paramagnetic, deshielded) shifts being positive is used. For conventional $^{29}$Si magic-angle spinning (MAS) spectra, radiofrequency pulses of 5 μs duration were applied with a 10 s recycle delay and a rotor spinning rate of 4 kHz. Spin-locked cross-polarization (CP/MAS) spectra were obtained with a single π/2 radiofrequency pulse, the contact time and the recycle delay for our samples were 5.5 μs, 5 ms and 10 s, respectively. $^{27}$Al static spectra were obtained with a high-power probe equipped with a 5 mm diameter solenoidal coil. MAS spectra were performed with a probe from Doty Scientific and a zirconia rotor spinning at 5 kHz. A single π/2 radiofrequency pulse was used with a repetition time of 200 ms.

Results and Discussion

$^{29}$Si MASNMR

Fig. 1 gives the $^{29}$Si MASNMR spectra of the six samples. The spectra of the starting material show ill-defined bands for all the samples is 22–24 wt %. The setting of the Hartman–Hahn condition was performed with a Q$_6$M$_8$ sample. The proton π/2 pulse length, the contact time and the recycle delay for our samples were 5.5 μs, 5 ms and 10 s, respectively. $^{27}$Al static spectra were obtained with a high-power probe equipped with a 5 mm diameter solenoidal coil. MAS spectra were performed with a probe from Doty Scientific and a zirconia rotor spinning at 5 kHz. A single π/10 radiofrequency pulse was used with a repetition time of 200 ms.

Table 1. Proposed line assignments for $^{29}$Si NMR spectra

<table>
<thead>
<tr>
<th>species</th>
<th>δ (ppm)</th>
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<tbody>
<tr>
<td>$Q^3\text{Si(0Al)}$</td>
<td>-111</td>
</tr>
<tr>
<td>$Q^4\text{SiO]_2SiOH}$</td>
<td>92</td>
</tr>
<tr>
<td>$Q^3\text{SiO]_2Si(OH)2}$</td>
<td>-102</td>
</tr>
<tr>
<td>$Q^4\text{Si(2Al]}$</td>
<td>-101</td>
</tr>
<tr>
<td>$Q^4\text{Si(OAl)}$</td>
<td>-108</td>
</tr>
</tbody>
</table>
number of Al atoms substituting Si atoms in the first layer. For Q^3 and Q^2 species, which contain one or two OH groups, the nature of the bonds in SiO or AlO is stated precisely.

The peak at \(-108, -111\) ppm is of the Q^4 type Si(OAl). The line at \(-101, -102\) ppm was shown to give the same chemical shift in zeolites \(13b\) for the two species Q^4(Si(1Al)) and Q^3 type \([\text{SiO}_2\text{SiOH}]\). The peak at \(-92\) ppm is not very intense. It may correspond to species Q^4(Si(2Al)), Q^4([\text{SiO}_2\text{AlO}]\text{SiOH}) and Q^2([\text{SiO}_2\text{Si(OH)}]_2). The absence of significant lines at lower fields suggests that no Si in Q^4 units is surrounded by 3 Al or 4 Al, that no Q^3 unit contains more than one Al (if any) and that no Q^2 unit has Al atoms.

The cross-polarization of the six samples give the spectra of fig. 2. This confirms the assignments. In all cases the peak at \(-101, -102\) ppm is greatly enhanced compared with the two other peaks showing that one of its components is due to the \([\text{SiO}_2\text{SiOH}]\) species even in the starting material. The peak at \(-92\) ppm is also slightly enhanced compared with the \(-110, -111\) ppm line. This indicates the possible existence of Q^2([\text{SiO}_2\text{Si(OH)}]_2) and Q^2([\text{SiO}_2\text{AlO}]\text{SiOH}) species.

\(^{27}\text{Al} NMR\)

The \(^{27}\text{Al} NMR\) spectra of fig. 3 show an intense peak at around 55 ppm and a second peak near 0–2 ppm for all the samples. The MASNMR spectra of K-14 and K-9.4 (fig. 3) give the same type of results with better resolved peaks. The two peaks may be assigned, respectively, to tetrahedral (55 ppm) and octahedral aluminium (0–2 ppm). None of the samples gives a peak near 30 ppm which is observed after steaming. \(^{3,10}\)
In order to obtain a more reliable evaluation of Al amounts, static NMR results of fig. 3 are used to estimate total and tetrahedral aluminium. This approach minimizes the error on Al titration. For the samples K-14 and K-9.4, it is supposed that the area of the sharp peak which is above the broad one represents the tetrahedral Al content. The amount of total and tetrahedral aluminium evaluated in fig. 4(q) shows a good relationship between the total aluminium and the Al content. This suggests that all the aluminium is titrated or at least that a constant fraction of it would be invisible. Fig. 4(b) gives the tetrahedral aluminium. It is almost constant from 14 down to 4.6% Al₂O₃. At this point the amount of octahedral Al is negligible and the decrease in Al₁V / Al₅⁺ is close to 30% which is comparable to the 20% value obtained by ESR after γ-irradiation. This is also in line with the decline of catalytic properties only at low Al contents when tetrahedral Al is removed.

Dealumination Process

The results of fig. 4 show that Al₁IV is extracted first with HCl in the amorphous silica aluminas. After removing all this Al, the tetrahedral aluminium is then taken away. The Al₁IV could exist as an aluminosilicate species as in layered structures or such as alumina formed during the synthesis of the catalyst. It was shown that Al₁IV in silicate materials with no Al₅⁺ gives an overlap of ²⁹Si chemical shifts. The selective extraction of octahedral aluminium from the present samples might disturb the arrangement of the four-coordinated species close to it (bond length and bond angles). This could contribute to the changes in the ²⁹Si MASNMR spectra for the samples K-14 to K-4.6 in fig. 1.

The removal of Al₁IV is connected directly to the Q⁺ species. In any of the materials the low intensity of the line near -92 ppm (fig. 1) and its small enhancement by cross-polarization (fig. 2) suggest that there are only small amounts of Q⁺[Si(OAl)] and Q⁺[(SiO₂)₂SiOH] or Q⁺[(SiO₂)₂Si(OH)₂] species. The last one may arise, in part, from the dealumination of the first two. The peak near -108, -111 ppm related to Q⁺[Si(OAl)] should not change its relative intensity upon dealumination since no silica migration is expected to occur in the hydrochloric solution to heal the defects created from Q⁺[Si(Al)] and Q⁺[Si(2Al)] species. It was checked that the relative area of this peak remained almost constant for samples K-4.6 to K-0.09 for which a deconvolution is possible. The dealumination would then generate hydroxyls belonging to species (SiO)₂SiOH and (SiO₂)₂Si(OH)₂. The shift from ca. -108 to ca. -111 ppm and the better resolution of lines as the dealumination proceeds suggest a more homogeneously organized arrangement of the Si(OAl) species. The line at -101, -102 ppm is the most intense of all the peaks able to characterize SiO₂ with Al neighbours. Since the chemical shifts of Q⁺[Si(Al)] and Q⁺[(SiO₂)₂SiOH] units are similar, NMR does not allow a quantitative evaluation of each species. Cross-polarization confirms the existence of the Q⁺ hydroxylated type in all the samples (fig. 2). It was checked that the relative intensity of the -101, -102 ppm peak was constant for samples K-4.6 to K-0.09. The ratio of the intensities of this peak to the -108, -111 ppm peak is then also constant and close to 0.7. This confirms the replacement of Al atoms by OH groups upon dealumination of these solids. The line at -101, -102 ppm would then comprise the (SiO₂)₂SiOH species of the starting material plus the ones created upon dealumination.

The present explanation is consistent with the presence of an active phase in catalysis involving aluminum. It was shown that for a series of acid-catalysed reactions requiring different acid strengths (cumene or n-octane cracking, (Z)-2-butene isomerization, isopropyl alcohol or ethanol dehydration) the activity decreases only when the last 20% of the aluminium atoms are removed upon dealumination of the same unsteamed materials. It can be suggested that the active phase in the K-14 and dealuminated materials consists of tetrahedral aluminium giving a chemical shift at 55 ppm. It might have similarities with an extraframework Al phase evidenced in dealuminated faujasites showing a chemical shift at 54 ppm and with the Al species giving a δ of 52 ppm³ and 56.2 ppm¹⁰ in an amorphous silica–alumina. These values have been obtained at the same Larmor frequency but have not been corrected for the second-order quadrupolar shift.

In conclusion, the present study shows that coprecipitated amorphous silica–alumina contain tetrahedral and octahedral aluminium atoms. Upon dealumination with hydrochloric acid, the Al₁IV is selectively removed, first leaving moieties with Al₁V. Beyond 70% of acid extraction the remaining Al species are only Al₁V. Their removal involves a decrease in catalytic properties. The chemical shifts of the NMR ²⁹Si bands suggests that Al₁IV is present in the form of Si(Al) and Si(2Al) species generating OH groups upon dealumination.

References