HIGH-RESOLUTION PROTON MAGNETIC RESONANCE AND CATALYTIC STUDIES CONCERNING BRØNSTED CENTERS OF AMORPHOUS Al_2O_3–SiO_2 SOLIDS

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By application of the magic angle spinning (MAS) technique it was possible to observe highly resolved proton NMR spectra of the OH groups of amorphous silica–alumina. The spectra exhibit two lines at 2 and 7 ppm. The former line must be ascribed to non-acidic OH groups since it also occurs for silica and alumina. The latter line shows a maximum of intensity in the range of 20–30 wt% Al_2O_3. It must be due to acidic hydroxyl groups since the catalytic activity of the silica–aluminas measured by the cracking rate of cumene shows quantitatively the same behaviour with respect to the number of OH groups at 7 ppm.

1. Introduction

The catalytic and acidic behaviour of amorphous silica–aluminas has been studied by numerous authors [1–4]. The application of high-resolution NMR techniques (cf. ref. [5]), especially the magic angle spinning (MAS) [6] of fused sample tubes [7] enables new possibilities for the characterization of surface OH groups. In the present paper this new technique is applied to amorphous silica–alumina solids of different composition. The resonance lines of the samples under study show peaks at 7 and 2 ppm, referred to TMS. According to ref. [7] the acidic strength of the surface hydroxyl groups which are responsible for the signal at 7 ppm should be higher than that of the OH groups at 2 ppm. The aim of the present paper is to connect the intensity of the line of acidic OH groups at 7 ppm with the catalytic activity, measured by the cracking rate of cumene.

2. Experimental

A series of amorphous silica–aluminas were prepared by coprecipitation from aqueous solutions of sodium silicate (4 wt% SiO_2) and sodium aluminate (4 wt% Al_2O_3). By adding sulphuric acid, a *pH* value of 9 was adjusted. The obtained gels were filtered, washed and heated for 24 h at 120°C. Following ion exchange by a 1 M aqueous solution of ammonium sulphate, the concentration of sodium was smaller than 0.02 wt%. All samples were dried at 500°C for 2 h under flowing hydrogen. In addition, the NMR samples were rehydrated at room temperature (as a consequence of the experimental procedure) and reactivated as follows: About one gram of the powder was heated in an open glass tube under atmospheric pressure by raising the temperature with a rate of 100 K/h up to the chosen temperature. After keeping the samples for 2 h at this temperature they were evacuated for 20 h below a pressure of 10^{-2} Pa.

All NMR measurements were carried out with a home-made 60 MHz pulse spectrometer using $\pi/2$ pulses. During the high-resolution MAS experiments,

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the fused samples rotated with a speed of 2.5 kHz in a two-fold gas turbine. The magnetic dipolar coupling of surface hydroxyl protons in aluminosilicates is sufficiently low to realize a line narrowing by MAS without additional application of multiple pulse sequences. The intensities were determined without rotation by comparison of the amplitude of the free induction decay (FID) with that of a calibrated sample.

The catalytic activity was measured by the rate of cumene cracking [8] using the micro-pulse technique with gas-chromatographic analysis of the reaction products according to ref. [9].

The mean error of the relative intensities of the two lines in the highly resolved proton NMR spectra is ≈±5%. The mean error for the total amount of OH groups is ±2 OH/nm^2 and that of the resonance shifts ±0.5 ppm. Because of the latter value, correction for susceptibility [10] is not necessary.

3. Results

Fig. 1 shows the highly resolved proton NMR spectra of samples with 0, 20, 25, 50 and 100 wt% Al_2O_3. The line occurring at 1.8–2.5 ppm is attributed to OH groups of silica and γ-Al_2O_3 (see ref. [7]) with linewidths of 150 and 380 Hz, respectively. For certain amounts of Al_2O_3 another line can be observed with a resonance shift of 7 ppm (which was also confirmed by 270 MHz proton resonance) and a linewidth of 420 Hz. The relative intensity of this line is given in table 1. For some samples the two lines occurring at 2 and 7 ppm could not be separated (e.g. for 50 wt% Al_2O_3), which is marked in table 2.

Table 1 also contains values for the total number of hydroxyl groups per nm^2 using the results of proton NMR intensity and BET surface [11] measurements. The relatively large values for OH groups may be due to the fact that the samples are sintered [11] during the drying procedure at 500°C so that inner surfaces are formed which are not accessible for the nitrogen molecules used in surface area determination. By a study of H–D exchange of different silica gels it could be shown [12] that for surface areas between 185 and 350 m^2/g the relative amount of accessible hydroxyl groups is only 55–70% of the total number measured by the proton NMR intensity. The presence of molecular water can be excluded since the proton wide-line

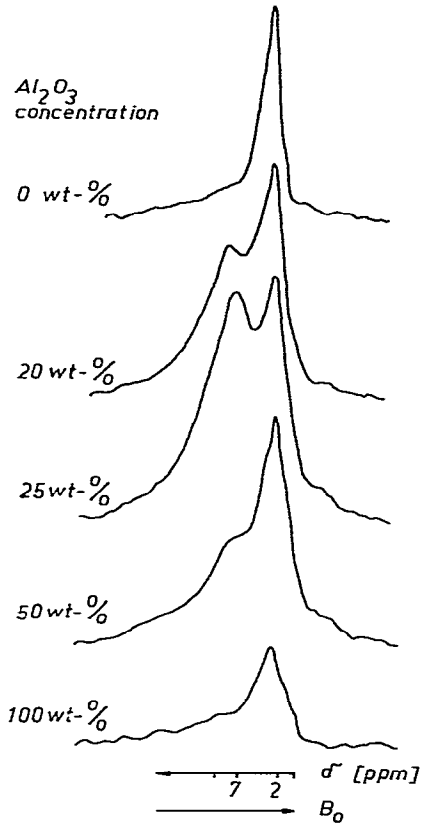


Fig. 1. Highly resolved proton NMR spectra of amorphous silica–aluminas of different composition (temperature of reactivation: 300°C).

spectrum measured at low temperatures (140 K) did not show the characteristic doublet of two-proton systems [13].

By a semilogarithmic plot of the free induction decay (FID) three components of different transverse relaxation times T_2 could be separated: (i) a T_2 of ≈20 μs due to OH groups of γ-Al_2O_3, (ii) a T_2 of ≈60–75 μs similar to the signal of structural OH groups in decationated zeolites [14], and (iii) a T_2 of ≈120–150 μs due to OH groups of silica.

Whereas separation of the components (ii) and (iii) occurring in one sample is not possible, the relative intensities p_{i} and p_{ii} or p_{i} and p_{iii} can be determined for most of the systems under study. The separation of component (i) allows in contrast to the highly resolved proton NMR (because of nearly the same value for the shift) a separate determination of the amount

Table 1
Structural and proton NMR data for amorphous aluminosilicates of different composition (reactivated at 300°C)

Concentration of Al_2O_3 (wt% Al_2O_3)	Specific surface (m^2/g)	Total number of OH groups (OH/nm^2)	Relative intensity of the line at 7 ppm relative to TMS (%)	Relative intensities of the components of FID (%)	
				p_i	p_{ii}
0	320	7 ± 2	0	0	a)
10	330	6 ± 2	a)	0	a)
20	330	9 ± 2	55 ± 5	0	a)
25	200	16 ± 2	67 ± 5	0	a)
30	200	14 ± 2	70 ± 5	35 ± 5	65 ± 5
40	185	21 ± 2	a)	65 ± 5	35 ± 5
50	210	15 ± 2	a)	66 ± 5	34 ± 5
60	220	15 ± 2	a)	86 ± 5	14 ± 5
70	230	11 ± 2	a)	90 – 100	0 – 10
80	190	16 ± 2	0 – 5	90 – 100	0 – 10
90	190	14 ± 2	0 – 5	90 – 100	0 – 10
100	350	5 ± 2	0 – 5	100	0

a) Signals are not separable.

Table 2
Comparison of the total number and of the relative amount of structural OH groups of silica–alumina (25 wt% Al_2O_3) for different pretreatments

Temperature of reactivation after rehydration (°C)	Total number of OH groups (OH/nm^2)	Relative amount of structural OH groups (%)
300	16 ± 2	67 ± 5
350	13 ± 2	30 ± 5
400	5 ± 2	0 – 10
without rehydration	14 ± 2	40 ± 5

of Al_2O_3 and SiO_2 hydroxyl groups. If p_i is plotted as a function of the relative concentration of Al_2O_3 of the silica–aluminas, the curve (fig. 2) closely resembles that published by Vaughan [14]. The amount of OH groups which give rise to the component (ii) of the FID was observed as equal to the value which follows from the line at 7 ppm in the highly resolved proton spectra.

4. Discussion

If the silica–aluminas under study be simply a mixture of separate phases (Al_2O_3 and SiO_2) and if all hydroxyl groups would be distributed randomly, the curve shown in fig. 2 should be approximately a straight line. However, the result shown in fig. 2 leads to the conclusion that OH groups of the Al_2O_3 type (FID component i) occur only at concentrations ≥30 wt% Al_2O_3.

For samples of 20 and 25 wt% Al_2O_3 the additional line at 7 ppm appears with increasing intensity in the highly resolved proton spectra (fig. 1). For very

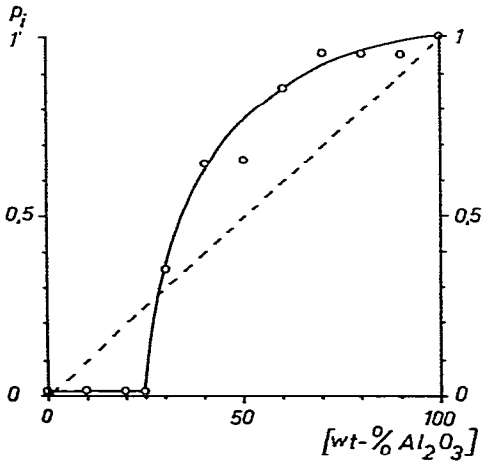
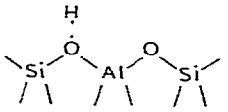


Fig. 2. Relative amount of γ-Al_2O_3 hydroxyl groups (p_i) in amorphous silica–aluminas of different composition.

small contents of aluminium the signal of these OH groups is overlapped by the foot of the signal of the silica OH groups with its centre at ≈2 ppm. It is interesting to note that for samples with small Al_2O_3 content the number of hydroxyl groups per gram at 7 ppm is approximately equal (factor 0.8) to the number of aluminium atoms (20 wt% Al_2O_3: 1.8×10^{21} OH/g at 7 ppm and 2.36×10^{21} Al/g; 25 wt% Al_2O_3: 2.2×10^{21} OH/g at 7 ppm and 2.95×10^{21} Al/g). But beginning at 30 wt% Al_2O_3 there are distinctly more aluminium atoms per gram as OH goups at 7 ppm (30 wt% Al_2O_3: 2.0×10^{21} OH/g at 7 ppm and 3.54×10^{21} Al/g; 40 wt% Al_2O_3: 1.4×10^{21} OH/g at 7 ppm and 4.72×10^{21} Al/g).

These two facts can be understood if one assumes that OH groups attached to four-fold-coordinated Al atoms give rise to the signal at 7 ppm:



The above structure is well known from the hydrogen type of zeolites [15]. OH groups of this type are denoted as structural hydroxyl groups.

As a test reaction for the catalytic activity cumene cracking was chosen [9]. However, the sample pretreatment for cumene cracking differs from that of NMR measurements: whereas the cumene cracking activity could be measured directly after the drying procedure at 500°C, the NMR samples were rehydrated and reactivated as described above. Fig. 3a shows highly resolved proton NMR spectra of an amorphous silica–alumina (25 wt% Al_2O_3) rehydrated and reactivated at 300°C, 350°C and 400°C, whereas fig. 3b shows the spectrum of the sample without rehydration. From fig. 3 and the corresponding total number of OH groups (table 2) we can state that the number of structural OH groups in the samples studied catalytically is equal to that of samples rehydrated and reactivated at ≈350°C.

Curve (a) in fig. 4 shows the rate constant (k_1) of cumene cracking for the amorphous silica–aluminas as a function of their composition. In curve (b) the relative amount of that OH group is plotted which gives rise to the line at 7 ppm in the highly resolved proton spectra or to the component (ii) in the FID (structural OH groups). A comparison of the curves shows an

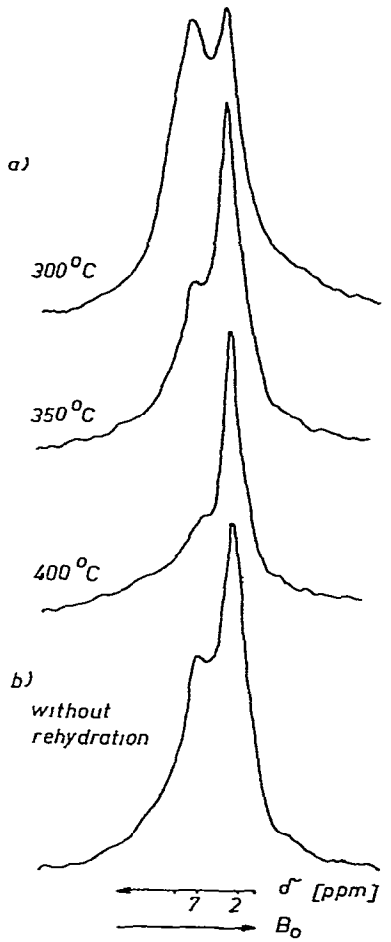


Fig. 3. Highly resolved proton NMR spectra of an amorphous silica–alumina (25 wt% Al_2O_3) for different procedures of pretreatment: (a) rehydrated and reactivated at different temperatures; (b) without rehydration.

analogous behaviour of the cumene cracking activity and the amount of structural OH groups. The maxima of both curves occur at the same composition of the amorphous silica–aluminas (≈30 wt% Al_2O_3). These results demonstrate unambiguously the predominant role which is played by the structural OH groups in catalytic reactions based on proton transfer. In contrast to the interpretation given in ref. [14], we can state that neither the SiO_2 nor the γ-Al_2O_3 OH groups possess a significant catalytic activity. The small value of the chemical shift of ≈2 ppm for these both hydroxyl types is due to low acidity [7]. The structural

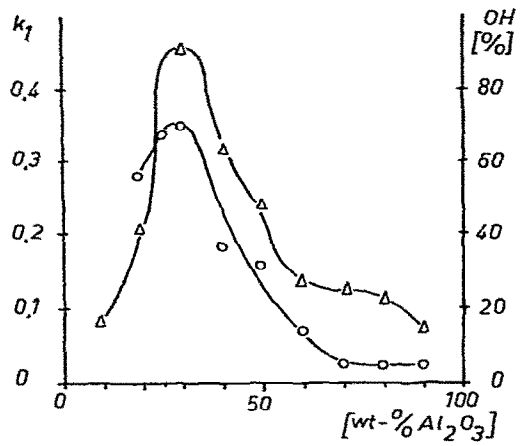


Fig. 4. Rate constant k_1 of the cumene cracking (a, ▵) and the relative amount of structural OH groups in per cent (b, o) for amorphous silica–aluminas of different composition. The values for curve (b) are taken from table 1. Curve b was measured for samples which were rehydrated and reactivated at 300°C because of better conditions for NMR measurements. The number of structural OH groups of these samples is greater by a factor of ≈2 than that of samples of curve a (approximately equal to a 350°C reactivation).

OH groups exhibit a large (7 ppm) resonance shift, they are acidic and responsible for the high catalytic activity of amorphous silica–aluminas with an Al_2O_3 content of ≈20–30 wt%.

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