STUDY OF BRØNSTED ACIDITY OF ZEOLITES USING HIGH-RESOLUTION PROTON MAGNETIC RESONANCE WITH MAGIC-ANGLE SPINNING

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By applying magic angle spinning to proton magnetic resonance of zeolites, two different lines were separated. Comparison of the corresponding resonance shifts with values for OH groups of other adsorbents and of organic compounds in solution showed that the signals must be due to hydroxyl groups of different acidity.

1. Introduction

As is well known, hydroxyl groups at solid surfaces may act as adsorption sites and as proton donors in heterogeneous catalytic reactions. In the latter case the surface is termed a solid acid of Brønsted type. For characterization of OH groups, mainly infrared spectroscopy has been used [1]. In some cases proton magnetic resonance [2,3], and recently ^{29}Si nuclear magnetic resonance spectroscopy, including cross-polarization techniques [4,5], have also been employed.

If the proton resonance shift can be determined, it is possible to draw conclusions concerning the bonding of protons to the oxygen atoms: a positive value, that means a shift of the resonance to lower magnetic field, corresponds to a smaller shielding by the electron shell. The value of the resonance shift for protons without an electron shell ("ideal" Brønsted acid) is 30.94 ppm relative to TMS [6]. For methanol, phenol, *m*-cresol and *m*-nitrophenol, dissolved in CCl_4, the values for the resonance shifts of the OH protons are 0.52, 4.28, 5.67 and 10.58 ppm, respectively [7], which is the same sequence as for the pK_a values of these compounds in aqueous solution (17, 9.9, 10.1 and 7.2, respectively).

For measurements of proton resonance shifts in solids it is necessary to reduce the influence of the magnetic dipole–dipole interaction and of the anisotropy of the resonance shift. For the systems under study, the most efficient method seems to be magic angle spinning (MAS) as introduced by Andrew [8] where the sample rotates with a speed of some kHz around an axis which is inclined by an angle of 54.7° with respect to the direction of the external magnetic field. For hygroscopic adsorbents the humidity of air may disturb significantly a proton magnetic resonance spectrum and that is why we had to use evacuated samples in fused glass ampoules during the MAS measurements. The technical realization was accompanied by some experimental problems. With such equipment however, it was possible to investigate, besides silica gel and γ-Al_2O_3, also zeolites.

2. Experimental

The NMR measurements were carried out with a home-made 60 MHz pulse spectrometer. The accuracy of the line positions is ±0.3 ppm. All δ values are referred to TMS and are positive if the shifts are to lower magnetic field. The rotation speed of the MAS sample was 2.5 kHz. The rotor served as a support for the fused sample tubes. In general, the samples were prepared under deep-bed (DB) conditions (c.f. ref. [9]). First of all the zeolite was heated in an open sample tube for 2 h up to a pretreatment temperature of 400°C and then evacuated carefully at this temperature for 2 further hours up to 10^{-2} Pa. The adsorption of organic compounds (see below) was car-

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ried out by distillation and controlled gravimetrically. The zeolites were prepared from a NaY with a Si/Al ratio of 2.6 (Chemiekombinat Bitterfeld, GDR) by a cation exchange of 90% with NH_4^+ and Ca^{2+} ions for DeNaY and CaNaY, respectively. The H-mordenite with a Si/Al ratio of 7.3 was decationated by treatment with HNO_3 up to a value of 87%.

The silica gel (Merck, FRG) has 3.4 OH groups per 100 $Å^2$ [10]. For zeolites we determined from the intensity of the proton magnetic resonance signal 1 ± 0.5, 0.46 ± 0.05 and 1.24 ± 0.10 hydroxyl groups per aluminium atom for DeNaY, CaNaY and H-mordenite, respectively [11].

3. Results and discussion

The results of our measurements are collected in table 1. In agreement with ref. [10], for silica gel only a single line with a width of 170 Hz and a resonance shift of 1.6 ppm could be observed. A similar line occurred in the spectra of the alumino silicates with values for the resonance shift between 1.5 and 2.5 ppm. Consequently we attribute this signal to OH groups of small acidity, like SiOH groups formed at crystal defects at the inner and outer surface of the adsorbent, and to terminal OH groups, respectively. But for some zeolites with parts of extra-lattice aluminium (for example DeNaX) it is also possible that a portion of this signal is caused by AlOH groups, as can be seen from the value for γ-Al_2O_3 in table 1. The signal with values for the resonance shift between 6.0 and 10.0 ppm corresponds to hydroxyl groups of higher acidity. Its larger line width points to a distribution of the acidity of the OH groups contributing to this signal.

A comparison of the chemical shifts in fig. 1 with those of organic molecules dissolved in CCl_4 shows that the mean value for the shift of the OH groups in zeolites is of the order of that for phenol (≈4 ppm) which seems to be in contrast with the well-known fact that the acidity of OH groups in zeolites is much greater than in phenol. It must be kept in mind however, that our comparision of chemical shifts concerns the bonding state of hydroxyl protons in an inert environment which is in general different from the state of protons during a normal measurement of acidity (acid–base interaction).

If we assume that for the same sort of hydroxyl groups (OH groups in organic molecules or at solid

Table 1
Values for the resonance shifts and line widths of the proton magnetic resonance of OH groups in various dehydrated adsorbents

Adsorbent	Loading	Relative intensity (%)	Chemical shift (ppm)	Line width (Hz)
silica gel	–	100	1.6	170
γ-Al_2O_3	–	100	2.0	290
amorphous alumino silicate	–	22	1.8	210
		78	6.0	510
DeNaY	–	15	1.7	220
		85	9.9	800
	pyridine	68	1.6	260
		32	6.0	550
CaNaY	–	60	1.5	230
		40	9.1	440
	pyridine	100	1.6	220
H-mordenite	–	50	1.8	280
		50	8.6	830
	pyridine	50	1.7	290
		50	8.4	850

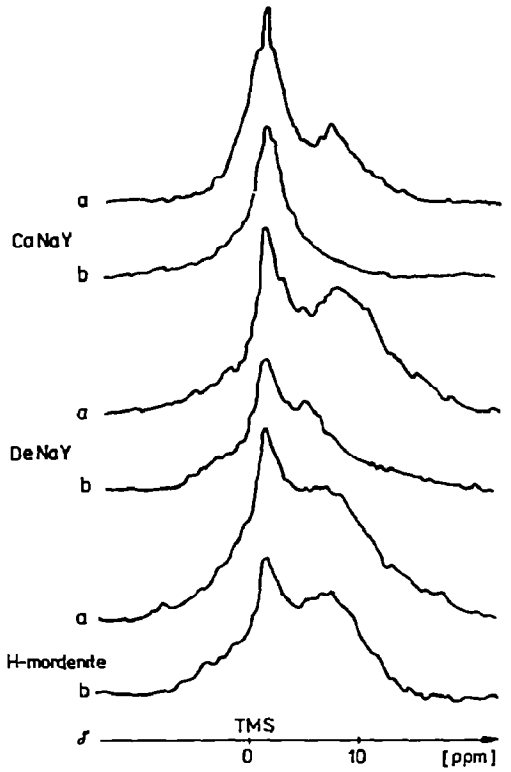

Fig. 1. Proton magnetic spectra of DeNaY, CaNaY and H-mordenite, unloaded (a) and loaded with pyridine (b).

surfaces) the values for the chemical shifts are proportional to the values for pK_a, we can use our experimental result that the shift difference of the OH groups of silica type and of more acidic hydroxyl groups is nearly equal to the shift difference between methanol and *m*-cresol ... *m*-nitrophenol. It follows from the pK_a values of organic molecules given in section 1 the difference of acidities due to such a difference of chemical shifts is $\Delta pK_a \approx 7-10$. Since the intensity of the proton magnetic resonance signal is strictly proportional to the number of OH groups (in contrast to the intensity of IR bands), the measured spectra can be interpreted as distribution functions of acidity strength.

If silica gel is loaded with deuterated acetone and pyridine, the proton magnetic resonance of the OH groups is shifted to lower magnetic fields by 6.1 and 9.6 ppm, respectively. An exchange between the hydroxyl protons and the deuterons of acetone could be observed at room temperature during a time interval of the order of 10 h. For pyridine there was no such exchange and at least three lines for the proton magnetic resonance of the OH groups occurred. Two of them are at the same position as for the unloaded surface while one is shifted to lower magnetic field. This shift can be explained by hydrogen bonds formed between the pyridine molecules and the OH groups contributing to this latter signal. Their relative number could be determined from the intensity of this signal to ≈70%.

A proton–deuteron exchange also occurred in the case of decationated zeolites Y loaded with deuterated benzene. At room temperature the mean lifetime of the hydroxyl protons with respect to a transition to the adsorbed molecules is of the order of some days. Unfortunately the value of the proton magnetic resonance shift of benzene is about the same as that for acidic OH groups, and hence it was not possible to make statements about the formation of hydrogen bonds between hydroxyl groups and benzene. It seems interesting to note however, that the OH groups which we termed as hydroxyl groups of silica type (chemical shift value of ≈1.8 ppm) do not participate in the H–D exchange in contrast to the hydroxyl groups of silica gel and the acidic OH groups of the zeolites.

A higher mobility caused by formation, diffusion, and disintegration of pyridinium ions (PyH^+) was observed for the decationated zeolite Y loaded with deuterated pyridine. The abovementioned mean lifetime amounts to about 2×10^{-5} s [12] which corresponds to a frequency of 50 kHz. This value is much greater than the width of the hydroxyl protons so that the limiting case of fast exchange [3] holds for all OH groups, which are involved in this exchange reaction. The resulting line should have a positive resonance shift due to the existence of PyH^+ in this zeolite [13–15] and due to the possible formation of hydrogen bonds between OH groups and pyridine. On the other hand the fast exchange prevents a narrowing of the line width by the MAS technique and therefore this signal should be unobservable by use of this technique at room temperature. In accordance with this interpretation, at higher temperatures because of the narrowing as in fluids (≈150°C, without MAS) a signal with a resonance shift of ≈13 ppm and a line

width of 1.1 kHz could be measured. Therefore we can say that at room temperature, only those OH groups contribute to the MAS-narrowed spectra of the zeolites loaded with pyridine, which are not influenced by pyridine. For DeNaY and CaNaY their number is less than one half of the total of OH groups [11].

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