Catalysis Letters 9 (1991) 403–410

COMPARISON OF AMORPHOUS SILICA-ALUMINA AND HIGHLY DEALUMINATED HY ZEOLITE BY ^{1}H HIGH RESOLUTION MAS-NMR OF SOLIDS

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Received 4 April 1991; accepted 3 May 1991

^{1}H MAS-NMR spectroscopy reveals analogies between partly dehydrated samples of silica-alumina and strongly dealuminated HY zeolite. There is a fundamental difference between the dehydration processes of crystalline and amorphous samples. A scheme for the reactions occurring during dehydration and dehydroxylation is proposed.

Keywords: Silica-alumina, steamed HY zeolite, ^{1}H MAS-NMR

1. Introduction

The surface properties of silica-aluminas used as catalysts, catalyst supports or binders are of considerable practical interest: dealuminated HY zeolites especially are of great industrial importance. These compounds have been studied by ^{1}H high resolution NMR [1–5]. Hunger et al. [1] reported, as early as 1983, the results of a ^{1}H MAS-NMR study of a partially dehydrated home-made silica-alumina; but the main magnetic field was not high enough for a good resolution. The same group developed many ^{1}H MAS-NMR studies of zeolites, including HY zeolite, summarized in reviews [2–4]. Bronnimann et al. [5] studied commercial silica-aluminas using the more complex method of ^{1}H CRAMPS-NMR. Recently, Hunger, Freude and Pfeifer [6] published a comparative study of the same home-made silica-alumina sample [1] and of highly dealuminated HY zeolite. The authors [6] identified strong Lewis acid sites in both samples, attributing a previously discussed signal [1,5] at 6.5–7 ppm to water adsorbed on these sites. From their spectra of dehydrated but still hydroxylated samples, here denoted "anhydrous", Hunger et al. [6] described OH groups only as silanol SiOH and acidic SiO(H)Al bridging ones. Barthomeuf [7] claimed that there are "strong analogies between the phases proposed to exist in amorphous silica-alumina catalysts and in extraframework Al deposits in zeolites". This remark,

along with differences we have observed between ^1H MAS-NMR spectra for silica-alumina and highly dealuminated HY zeolite and those found by Hunger et al. [6], prompted this new comparative study of these compounds.

2. Experimental

Three commercial silica-alumina samples were used, with SiO_2/Al_2O_3 ratios (w/w) of 25/75 (two samples with different specific surface area: 250 and 337 m^2g^{-1}) and 75/25. They are denoted Si25-250, Si25-337 and Si75, respectively. These samples were partially dehydrated by slow heating to a temperature between 375 and 620 K under such conditions that the pressure is always below 1 Pa. The initial characteristics of the samples are given in table 1.

The HY zeolite was obtained from NH_4Y whose Si/Al atom number is 2.5, steamed twice, with NH_4^+ ion-exchange between the steamings, and then allowed to rehydrate. It contains only traces of framework aluminium atoms, as shown by ^{29}Si NMR and traces of sodium. The zeolite was activated in "shallow bed conditions" (12 Kh^{-1} heating to 675 K at 10^{-2} Pa, then kept under these conditions for 15 hours, the sample being less than 5 mm thick). After cooling, the samples were transferred under vacuum into thin 6 mm outer diameter side-ampoules and sealed.

Room temperature ^1H MAS-NMR measurements were carried out on a Bruker MSL400 spectrometer with a special probe. The pulse angle was well under 90° and the repetition time was 20 s. The MAS equipment for rotation (rotation frequency 3 kHz) was carefully cleaned to avoid spurious proton signals and the probe signal was subtracted from the total signal. Chemical shifts are expressed relative to TMS with the usual conventions.

3. Results

The shapes of all the spectra are qualitatively the same whatever the dehydration ratio. Examples of experimental and simulated spectra are shown in fig. 1 for Si25-337 with about 2.8 remaining OH groups per nm^2 (fig. 1A) and the steamed

Table 1
Characteristics of the commercial silica-alumina samples

Supplier	Notation	SiO_2/Al_2O_3 (w/w)	Specific surface area (m^2g^{-1})	Composition		
				SiO_2	Al_2O_3	H_2O
Condea	Si25-250	25/75	250	0.57	1.0	0.7
Rhone-Poulenc	Si25-337	25/75	337	0.57	1.0	1.0
Ketjen	Si75	75/25	460	5.1	1.0	2.0

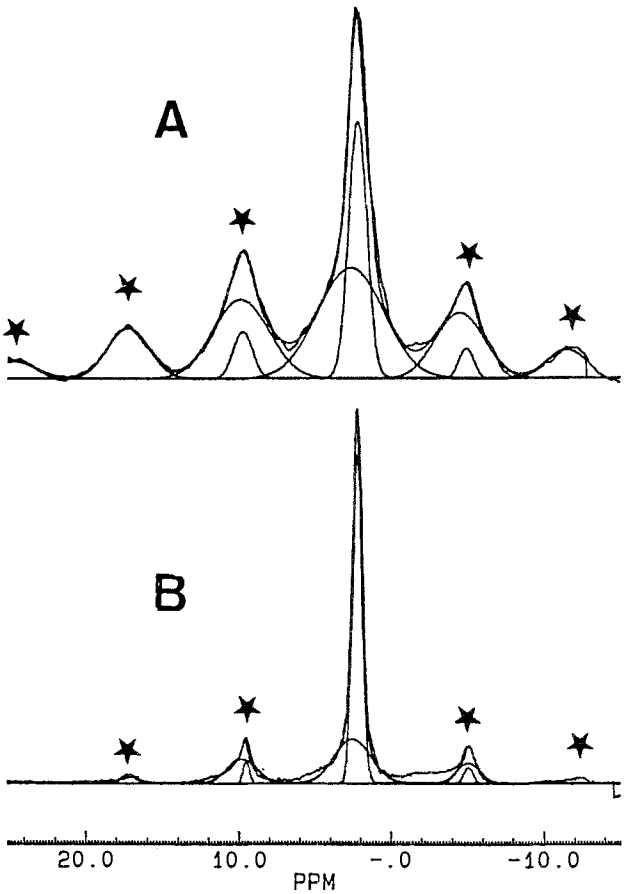


Fig. 1. Examples of ^{1}H MAS-NMR spectra (experimental, simulated and components) obtained on samples dehydrated as described in the text (*: MAS side-bands); 1A, Si25-337 with 2.8 remaining OH groups per nm^2; 1B, HY zeolite steamed twice, rehydrated and shallow-bed treated.

HY zeolite with 64 ± 32 OH groups per unit cell (fig. 1B). Neither shows a signal at 6.5 ppm characteristic of water molecules bonded to Lewis acid sites.

Careful fits indicate the presence of the following signals (fig. 1): (i) a narrow one (300 ± 80 Hz wide) with large amplitude and small spinning side bands located at 2.3 ± 0.1 ppm, characteristic of silanol groups [2–4]; (ii) a wide one (1.5 ± 0.5 kHz) with strong spinning side bands at 2.9 ± 0.5 ppm. Freude et al. [2–4] attributed signals with this last chemical shift value to AlOH groups. However, the width of their signals, though difficult to measure, is smaller than ours. We assume that the reason for the broadening of the AlOH signal is a weakening of the symmetry around the aluminium atom. The percentage of the two types of OH groups–AlOH and SiOH–depends on the sample. For the silica-alumina of fig. 1A and the zeolite of fig. 1B, approximately 80% and 50%, respectively of the hydrogen atoms are in AlOH species.

A small amount of water vapor was introduced onto the "anhydrous" HY

sample when recording the spectrum shown in fig. 2B. It contains four signals, all with low amplitude spinning side bands. Two of them are narrow Gaussian curves (both 80 ± 10 Hz) located at 1.8 ± 0.1 ppm and 4.1 ± 0.1 ppm. They are attributed to silanol and bridging acidic OH groups, respectively [2–4]. The third signal is Lorentzian and wide (1.4 ± 0.2 kHz); its chemical shift is 4.6 ± 0.1 ppm. It corresponds to protons in fast chemical exchange between mainly acidic OH groups and water molecules [2–4,8]. The fourth signal is a very small amplitude one located at about 6.3 ppm; it is probably due to water molecules on Lewis acid sites as described by Hunger et al. [6]. No signal at 2.9 ppm can be detected.

A similar spectrum (but without the 6.3 ppm signal and with slightly different chemical shift and width of the exchanging protons) was obtained for a fresh

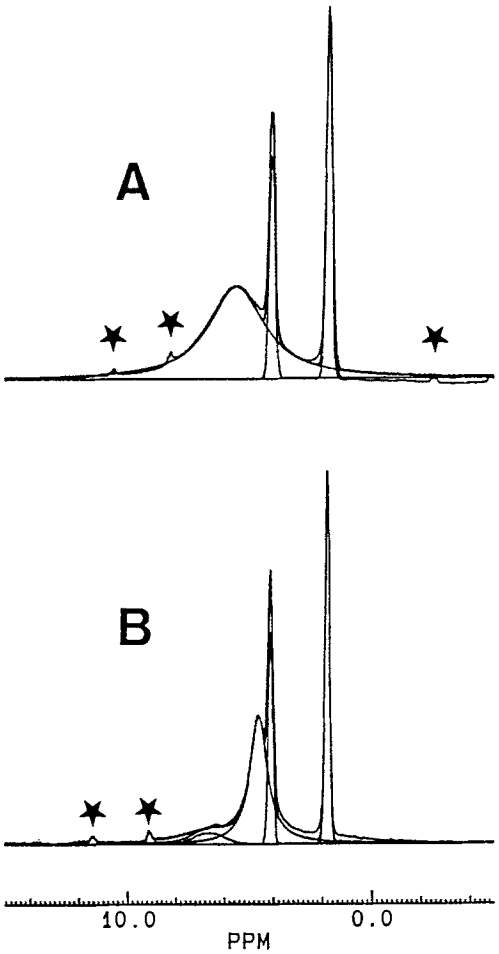
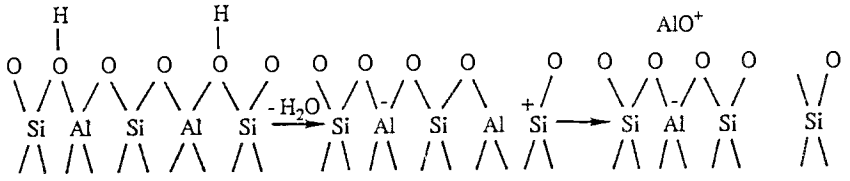


Fig. 2. ^{1}H MAS-NMR spectra (experimental, simulated and components) of partly hydrated samples (*: MAS side-bands); 2A: fresh Si25-337 sample partly dehydrated under vacuum at 300 K; 2B: HY zeolite steamed twice, rehydrated and shallow-bed treated when water vapor is allowed to reach it at 300 K.

sample prepared by dehydration under vacuum of the Si25-337 sample at 300 K (with 15 remaining equivalent OH groups per nm^2) (fig. 2A).

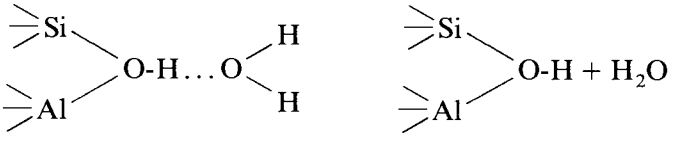
4. Discussion

We summarize the results as follows: (i) strongly steamed HY zeolite and silica-alumina samples, when dehydrated under vacuum at temperatures above 375 K contain only OH groups, which are of two sorts, silanol and AlOH ones; (ii) from the results obtained either when a few water molecules are introduced onto the "anhydrous" dealuminated HY or when a silica-alumina sample is very gently dehydrated, Si-O(H)-Al acidic groups and AlOH ones are related by dehydration-rehydration reactions. The meaning of these results is that, in "amorphous" or "amorphized" silico-aluminate acids, dehydration leads to rupture of the Si-O bonds of bridging Si-O(H)-Al groups to give AlOH groups. The phenomenon is reversible which suggests that aluminium atoms of AlOH groups remain bonded to their previous coordinated neighbours during this dehydration step. Kühl [9] proposed the following model for the dehydroxylation of HY zeolite,



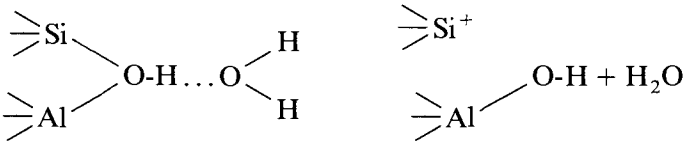
(Scheme 1)

in which tricoordinated, positively charged silicon atoms are formed in intermediates prior to the dealumination process, but he could not prove this point. Such a scheme has also been discussed by Hunger et al. [6]. Our interpretation is that, contrary to the known "shallow-bed" dehydration of well crystallized zeolites [2–4], leading to bridging acidic OH groups,



(Scheme 2)

that of "amorphous" silico-aluminate acids would be, at least partly:



(Scheme 3)

However, Al-O bond breaking in the Si-O(H)-Al groups is not excluded, leading to silanol group formation. This difference in the dehydration processes is in agreement with a recent proposal [10] that "zeolite crystals respond to "proton attack" by a global readjustement of the bond structure of the whole zeolite matrix in order to prevent major local distortions in bonding, leading to loss of long range symmetry and thus crystallinity... There would be a significant stabilization resulting from the electronic structure of the Al-O and Si-O bonds becoming more equivalent".

The difference between our proposal and that of Kühl [9], reintroduced by Hunger et al. [6], is that we claim that Si-O bond breaking occurs during dehydration before important dehydroxylation, whereas Kühl and Hunger et al. assume that it occurs during the dehydroxylation process. We expect this Si-O bond breaking at lower temperature than they do. Beran [11] calculated that the tricoordinated Si^+ ions are Lewis acids of intermediate strength. It is likely that the AlOH species occurring in the mechanism that we describe are not stable at high temperature. Dehydroxylation would create other Lewis acid centres. The dealumination process proposed by Kühl [9], where AlO^+ ions balance the still tetracoordinated $(AlO_4)^-$ groups (Scheme 1), can also occur, as well as the formation of polymeric aluminium species. Samples examined by Hunger et al. were dried at 775 K in flowing hydrogen [1] for up to 810 K in flowing nitrogen [6], and rehydrated before treatment in an open glass tube, the temperature being raised at 100 Kh^{-1} to that chosen. The Lewis acid sites that they show (chemical shift 6.5–7 ppm) are perhaps formed during these treatments. We agree with Hunger's idea that these Lewis sites remain bonded to their neighbouring atoms and are not "extracted" [6]. Under conditions where we observe the signal characteristic of AlOH groups, the width and position (2.3 ppm) of the silanol signal show small changes relative to the corresponding values for the rehydrated sample (1.8 ppm). In the "anhydrous" samples this may be due to implications of silanol protons in weak hydrogen bonds to other oxygen atoms.

5. Conclusion

First, we have shown an analogy between the extra-framework aluminium deposited in dealuminated HY zeolite and silica-alumina samples. As regards the

dehydration of their hydrated bridging OH groups under vacuum at low temperature we conclude that there is a fundamental difference between well crystallized HY zeolite and deposits in dealuminated HY samples or amorphous silica-aluminas. The process conserves the Si-O(H)-Al groups in the crystalline zeolite, but it breaks the Si-O bonds of these bridging groups in the amorphous samples. In the latter the Si-O bonds are restored by rehydration.

Acknowledgement

We thank Dr. Marie Gruia for valuable discussions.

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