Contribution to the study of framework modification of SAPO-34 and SAPO-37 upon water adsorption by thermogravimetry

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Abstract

The adsorption–desorption of water vapor in SAPO-34 and SAPO-37 is followed in isobar conditions ($P_{H_2O} = 17.6$ mbar) by thermogravimetry at temperatures from 20°C to 400°C. The phenomenon is reversible in SAPO-34 but not in SAPO-37. The rise in water uptake is the highest at around 60–70°C, i.e. in range where an attack of the frameworks was previously reported. The reversibility (or not) of water adsorption–desorption uptake is linked to this reversible (or not) framework modification. The kinetics of desorption in SAPO-34 is strongly slowed down between 40°C and 60°C. This suggests that the full restructuration of the framework requires some time (700 min in the experimental conditions used). The morphology of the crystals of the two SAPOs is unchanged upon hydration but template-free SAPO-34 crystals become progressively destroyed in the electron beam of an electron microscope. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

SAPO-37 and SAPO-34 (structures of faujasite and chabasite, respectively) are very stable at high temperature even in the presence of water vapor [1,2]. By contrast severe modifications occur in the temperature range 50–100°C in non-dry atmosphere and the two zeolites behave differently. Hydration at room temperature of the template-free materials gives for SAPO-37 an irreversible loss of crystallinity seen by XRD [1,3] and IR spectroscopy [3–5] while SAPO-34 is reversibly modified as evidenced by XRD [3,6,7]

and MAS NMR of ^{29}Si [6,7], ^{27}Al [6,8,9] and ^{31}P [4]. It was proposed that SiOHAl bonds are broken upon adsorption of water in the template-free SAPOs. In SAPO-34 a large part of them is restored by desorption above around 100°C [2,6,7]. This instability of SAPOs with regard to water is in contrast with the case of SiAl zeolites stable up to around 450–500°C, i.e. before any dealumination starts.

The aim of the present paper is to study the isobar equilibrium of water vapor adsorption and desorption at various temperatures (thermodynamic and kinetic aspects) in order to get information on the attack of the SAPO framework by water vapor. Results are analyzed with regard to previously published data [1,9].

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2. Experimental

SAPO-37 was synthesized in the presence of tetra-methyl and tetrapropylammonium hydroxides (TMA-OH and TPAOH, respectively) as already described [1] and SAPO-34 was prepared using tetraethylam-monium hydroxide (TEAOH) as template [6,7]. Their formula are $Si_{0.14}Al_{0.48}P_{0.38}O_2$ and $Si_{0.09}Al_{0.49}P_{0.42}O_2$, respectively. XRD studies [1,7] were conducted to characterize the two SAPOs. The isobar curves of water adsorption at a water vapor pressure of 17.6 mbar (1 mbar=10^2 Pa) were performed on samples pretreated at 600°C (in order to remove the templates). The pretreatments were carried out in situ in the thermobalance used for all the experiments [10]. The heating at 600°C for 10 h under either a pressure of 100 mbar of oxygen or 400 mbar of air was fol-lowed by evacuation at the same temperature for 6 h. Two kinds of procedures were used for the water vapor adsorption isobar study. In the first one the zeolite was slowly cooled down to room temperature in vacuum. The sample was then contacted with the 17.6 mbar pressure of water until equilibrium was reached. In the second procedure the sample was cooled to 400°C in vacuum and contacted with the water vapor at this temperature. After the equilibrium was reached the temperature was decreased by 20°C (or 10°C) steps to room temperature. At each step the equilibrium was obtained with the 17.6 mbar water pressure. The iso-bar desorption curves were obtained by heating and increasing temperatures by 20°C (or 10°C) steps up to 200°C, the equilibrium being reached at the constant vapor pressure at each temperature. A further isobar adsorption experiment was conducted as previously from 200°C to room temperature. The amount of water adsorbed at each equilibrium point was expressed as m in gram per gram of activated SAPO (g g^{-1}). The amount adsorbed after half an hour (see text) was chosen as the reference to express the percentage of saturation by water reached at each point of the isobar.

The morphology of the materials was checked with a scanning electron microscope Jeol type JSF 6400 F.

3. Results and discussion

3.1. Adsorption kinetics at 25°C (isobar conditions)

Isobar and isotherm kinetics plots of adsorption as a function of time $m=f(t)$ (Fig. 1(1)) are smooth and do
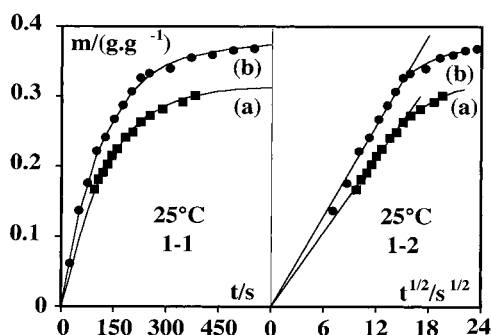

Fig. 1. (1) Isotherm kinetics of water vapor adsorption as a function of time: (a) SAPO-34, (b) SAPO-37. (2) Classic law of adsorption kinetics: (a) SAPO-34, (b) SAPO-37.

not show any break. The two materials behave dif-ferently with regard to the amount of water adsorbed m. It is smaller for SAPO-34 than for SAPO-37. After half an hour (not seen in Fig. 1(1)), SAPO-34 and SAPO-37 absorb 0.321 and 0.375 g g^{-1}, respectively. After a longer adsorption time (from 3 to 24 h) the amount of adsorbed water reaches 0.329 and 0.440 g g^{-1}, respectively. The values after half an hour, m_S, are considered as a pseudo-saturation. In what follows the percentage of this saturation amount (or percentage of hydration) is used to compare the samples.

Normalized kinetic plots follow the classic law $\gamma=f(t^{1/2})$ ($\gamma=m/m_S$) in a wide range of relative uptakes, i.e. γ from 0 to 0.82 (82% of hydration; $m=0.265$ g g^{-1}) for SAPO-34 and to 0.87 (87% of hydration; $m=0.325$ g g^{-1}) for SAPO-37 (Fig. 1(2)).

Previous studies showed that after rehydration at room temperature, SAPO-34 loses 50% of its crystal-linity [2,6,7] while SAPO-37 becomes fully amor-phous [1].

3.2. Isobar adsorption–desorption between 400°C and 20°C

3.2.1. Equilibrium curves for adsorption–desorption cycles

The template-free materials first treated at 600°C and then evacuated at 400°C were contacted with water vapor. The results obtained at this temperature show a very small hydration percentage 7.6% for SAPO-34 (Fig. 2) and 2% for SAPO-37 (Fig. 3). These values remain constant down to 150°C for
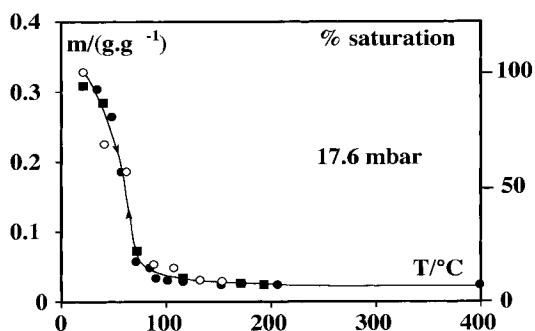
Fig. 2. Water vapor adsorption–desorption isobar equilibrium of SAPO-34 as a function of temperature ((●) first adsorption; (○) first desorption; (■) second adsorption).

SAPO-34 and 180°C for SAPO-37. Between 150°C and 80°C, the amount of water adsorbed is small for SAPO-34 while it increases for SAPO-37. At 80°C the percentage of hydration is 15% for SAPO-34 and 24% for SAPO-37. Below this temperature the water adsorption increases strongly for the two samples to reach the maximum value at room temperature.

The desorption curves obtained by increasing the temperature from room temperature to 200°C show a different behavior for the two samples. For SAPO-34 the adsorption–desorption curves are superimposed (Fig. 2) indicating a reversible phenomenon while the process is not reversible for SAPO-37 (Fig. 3, adsorption curve a, and desorption curve b). This non-reversibility for SAPO-37 is confirmed by a second adsorption study between 200°C and room temperature which gives a completely different curve
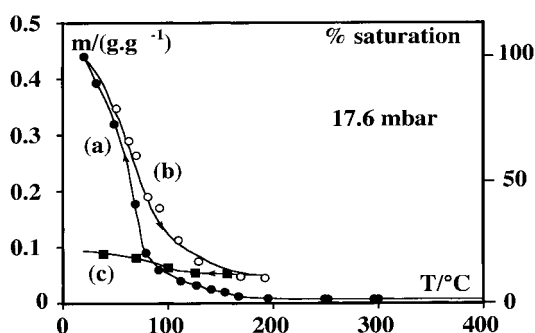
(Fig. 3, curve c). The second adsorption in SAPO-34 is superimposed to the first one. This is in line with a total reversibility. It may be noted that exactly identical results are obtained for the desorption curves whether the previous adsorption was carried out as described in Figs. 2 and 3 at decreasing temperatures or at 25°C (Fig. 1).

These isobar results of water vapor adsorption–desorption confirm the reversibility (SAPO-34) or not (SAPO-37) of the modification of the frameworks by water seen by various techniques [1–9]. In addition they show that the water uptake increases sharply below around 100°C where these modifications were observed. It was suggested [1] that liquid water present in this temperature range could be more destructive than the gas phase.

A comparison with SiAl zeolites shows differences between the two types of materials. At first the hydration–dehydration cycles are usually reversible in SiAl zeolites. Secondly to reach the same percentage of hydration a higher temperature is required for SiAl zeolites than for SAPOs. For instance 50% hydration is obtained at 120°C for 4A or 13X [11] and as low as 60–70°C for the SAPOs.

3.2.2. Adsorption–desorption kinetics

A time Δt is required to reach between two temperatures the mass equilibrium with the thermobalance at each point of the isobars in Figs. 2 and 3. The plot of water uptake m as a function of t ($t=\Sigma\Delta t$) gives Figs. 4 and 5, for the adsorption (curves a and c) and for the desorption (curves b). Several differences are

Fig. 3. Water vapor adsorption–desorption isobar equilibrium of SAPO-37 as a function of temperature (a: (●) first adsorption; b: (○) first desorption; c: (■) second adsorption).
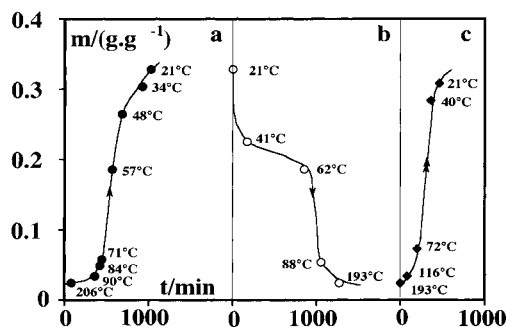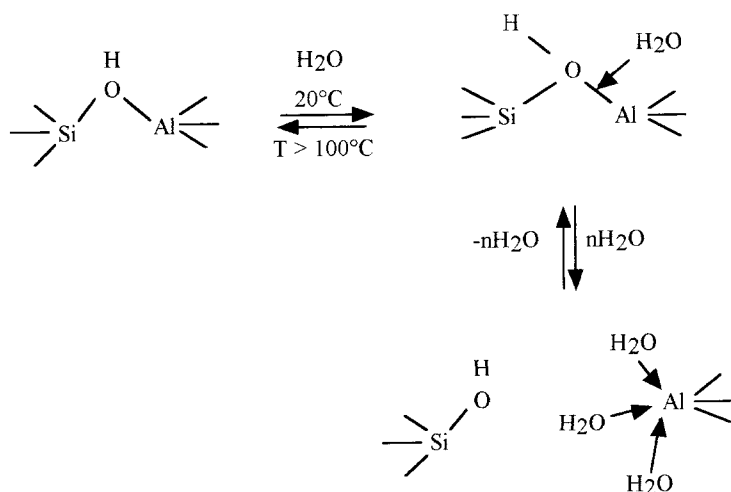

Fig. 4. Isobar equilibrium of water vapor adsorption–desorption cycles as a function of added up equilibrium times at given temperatures for SAPO-34 (a: (●) first adsorption; b: (○) first desorption; c: (■) second adsorption).

noted between the two SAPOs. Firstly water vapor adsorption and desorption are faster in SAPO-34 than in SAPO-37. For instance curves a, Figs. 4 and 5, show that to reach the equilibrium at 33–34°C, around 950 min are required for SAPO-34 and around 2500 min for SAPO-37. This may reflect the time needed for the full attack of the SAPO-37 framework [1,3] opposed to the opening of a few bonds in SAPO-34 [2,6,7]. Secondly the desorption is smooth for SAPO-37 but not for SAPO-34 in the range 40–60°C (Figs. 4 and 5, curves b). It was checked that the crystallinity is not restored in SAPO-37 upon water vapor desorption while it is recovered in SAPO-34 between 50°C and 100°C as seen in an X-ray heating chamber [2,6,7]. Then curve b, Fig. 5, describes the desorption of water from an amorphous solid while curve b, Fig. 4, shows that in SAPO-34 the desorption of water in the range 40–60°C is slowed down. This corresponds in this temperature range to the healing of defects created by the opening of SiOHAl bonds as described previously [2,6,7] by the following reactions:
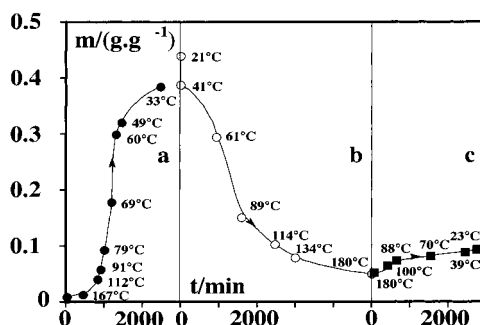

Fig. 5. Isobar equilibrium of water vapor adsorption–desorption cycles as a function of added up equilibrium times at given temperatures of SAPO-37 (a: (●) first adsorption; b: (○) first desorption; c: (■) second adsorption).

curves a and c) like the most time consuming modifications in the framework had taken place during the first hydration. It was checked in the X-ray heating chamber that the crystallinity is again decreased during the second adsorption but that it is fully reversible for several adsorption–desorption cycles.

Time is needed (around 700 min) in the present experimental conditions to reconstruct the Si and Al environment seen in MAS NMR [4,6–9]. A third difference between the two SAPOs is the quite longer time for the second hydration in SAPO-37 (Figs. 4 and 5, curves c). It is anyway very limited in this amorphous solid. For SAPO-34 the second hydration is about twice as much faster than the first one (Fig. 4,

In summary the isobar studies presented show a strong kinetic effect linked to the attack and reconstruction of the framework in SAPO-34 in the range 40–60°C.

3.3. Morphology study

The SEM micrographs of as synthesized and template-free SAPOs are given in Figs. 6 and 7. After the
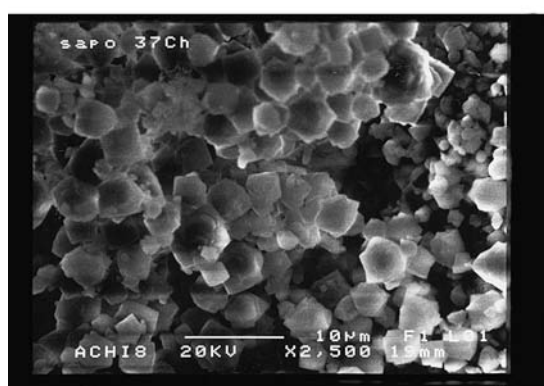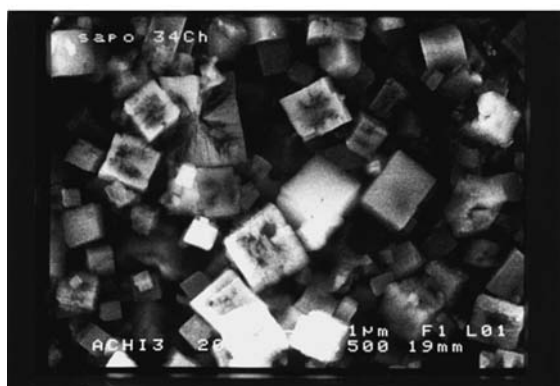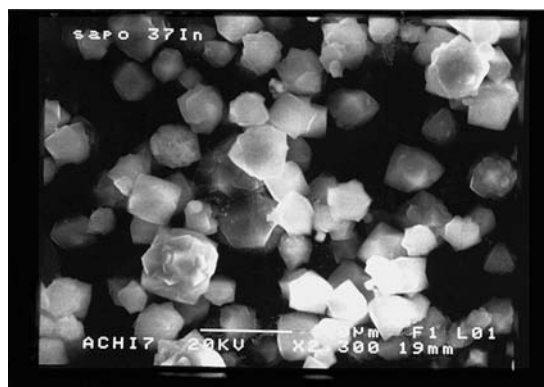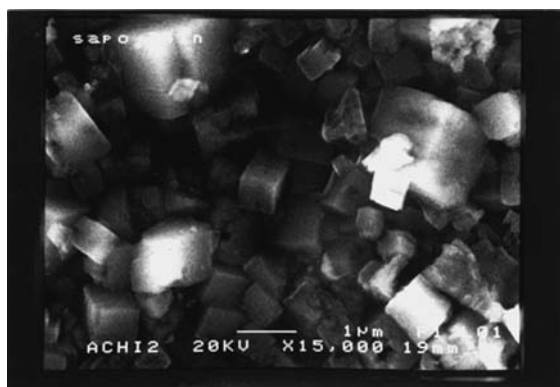
Fig. 6. SEM micrographs of SAPO-34: (above) as synthesized, (below) rehydrated template-free sample.

Fig. 7. SEM micrographs of SAPO-37: (above) as synthesized, (below) rehydrated template-free sample.

removal of the template the samples were kept at ambient atmosphere and at room temperature. Hence a rehydration occurs.

No difference is observed for SAPO-37 (Fig. 7) between the as synthesized (Fig. 7(a)) and the rehydrated template-free material (Fig. 7(b)). The amorphisation observed in XRD and confirmed in the present study does not induce a collapse of the external shape. By contrast crystals of the template-free SAPO-34 (Fig. 6(b)), but not of the as synthesized sample (Fig. 6(a)), show very large holes which seem to grow with the time in the electron beam. The attack by water vapor on the SiOHAl bonds at room temperature appears to make the crystal more fragile. This suggests that a metastable phase is formed which may be transformed back to the SAPO-34 framework upon dehydration or may collapse in an electron beam. With SAPO-37 the interaction with water of the template-free material gives a stable amorphous phase changed neither by dehydration nor by bombardment of electrons.

4. Conclusion

The interaction of water with template-free SAPO-34 or SAPO-37 is different. This suggests than one must be careful about the presence of water vapor in conducting any experiment with these materials. More generally one may expect that other SAPOs or other members of the AlPO family may be unstable in the presence of water vapor below $100°C$. This will depend on the structure considered and on the topological density, the more stable materials having the highest topological density [5].

Acknowledgements

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