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Multinuclear NMR Studies on the Thermal Stability of SAPO-34

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Thermal stability and the effect of water-coordination of a silicoaluminophosphate, SAPO-34, were investigated on the basis of multinuclear NMR studies. Crystalline silicoaluminophosphates (SAPOs) have been found as a new family of synthetic molecular sieves. The expected applications of SAPOs are as adsorbents and catalysts. Thermal stability is one of the crucial factors in applying SAPOs as automotive exhaust catalysts. ^{27}Al-, ^{29}Si-, and ^{31}P-NMR spectra and XRD as a function of temperature showed the microporous structure of SAPO-34 to be stable up to 1000°C. The effect of water-coordination on the ^{27}Al- and ^{31}P-NMR spectra also showed the adsorptive properties of SAPO-34 to be stable up to 1000°C. In this paper, SAPO-34 was found to be promising as an automotive exhaust catalyst with a microporous structure and high heat resistance.

INTRODUCTION

Crystalline silicoaluminophosphates (SAPOs) have been found as a new family of synthetic molecular sieves (*1*). By incorporating of silicon into an aluminophosphate framework, SAPOs show the catalytic property of solid acids (*2*). The expected applications of SAPOs are as adsorbents and catalysts, because there exist many design parameters in crystal structure and crystal chemistry (*3–5*).

One of the crucial factors for an applied catalyst, especially for an automotive exhaust catalyst, is thermal stability. Under extreme conditions, automotive exhaust catalysts are exposed to heat of 1000°C. Therefore, some automotive exhaust catalysts are required to be stable at temperatures up to 1000°C. Conventional zeolites are usually stable below approximately 850°C (*6*). Since SAPOs are expected to be thermally stable at 1000°C (*1*), they are promising catalysts for automotive exhaust gases. A preliminary experiment for NOx conversion featured SAPO-34.

The thermal stability of SAPO-34 is discussed from the basis of a study of the local structures and adsorptive properties of water mainly by solid-state NMR. In actual use, some elements are supported on SAPO-34. We considered the thermal stability of both element and support, but that of the support was considered foremost in this paper. The use of multinuclear solid-state NMR techniques permits analysis of the local structure in crystalline and amorphous silicoaluminophosphates. Studies of the framework structure and acidic properties of SAPOs by NMR were reported previously (*2, 7–10*). We focus on the thermal stability of SAPO-34 using multinuclear NMR.

Blackwell and Patton have shown that the adsorption of water causes a remarkable change in the ^{27}Al-NMR spectra (*8*). On the basis of this fact, the change in the ^{27}Al- and ^{31}P-NMR spectra caused by the adsorption–desorption of water was also investigated to study the effect of thermal annealing at temperatures up to 1100°C on the adsorptive properties of SAPO-34. This dy-

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namic feature of the coordination at aluminum sites (*8*) was also observed at phosphorus sites in this work.

EXPERIMENTAL

SAPO-34 was synthesized hydrothermally according to published methods (*11*). The material was crystallized at 200°C from a reactive mixture containing aluminum-isopropoxide, phosphoric acid, silica sol (Si : Al : P = 0.1 : 0.5 : 0.4), and tetraethylammoniumhydroxide as a template. The product was calcined in fresh air at 550°C to remove the template. The chemical composition of the calcined product was $(Si_{0.08}Al_{0.50}P_{0.42})O_2$. This composition was obtained by X-ray photoelectron spectroscopy with a VG ESCALAB mkII. The calcined SAPO-34 was subjected to heat treatment at temperatures of 800, 900, 1000, and 1100°C, for 2 h in an ambient atmosphere.

The NMR spectra were obtained on a Bruker MSL300 NMR spectrometer operating at a field of 7 T using the magic-angle-spinning (MAS) technique, and occasionally cross-polarization (CP) technique was used under the Hartmann–Hahn condition. ^{27}Al-, ^{31}P-, and ^{29}Si-NMR spectra were recorded at 78.21, 121.50, and 59.62 MHz, respectively. Spinning speeds of 2.5 kHz were used for ^{29}Si and 3.5 kHz for ^{27}Al and ^{31}P. The chemical shifts of the ^{27}Al-, ^{31}P-, and ^{29}Si-NMR were referred to external $Al(H_2O)_6^{3+}$ in $AlCl_3$ aqueous solution, external H_3PO_4 (85%), and external tetramethylsilane, respectively. Recycle times were 6, 30, and 90 s for ^{27}Al, ^{31}P, and ^{29}Si, respectively, which were chosen to avoid sautration effect. Short pulses ($< \pi/12$) were used for ^{27}Al spectra to ensure that they were quantitatively reliable (*12*, *13*). All the samples were equilibrated with the saturated water vapor of a NH_4Cl solution before packing into NMR-MAS rotors, except for dehydrated samples. The dehydration was carried out by heating samples in a vacuum at 180°C for 15 h. The samples were rehydrated by keeping with the saturated water vapor of NH_4Cl solution. X-ray powder diffraction data were recorded on a Rigaku RU-200 X-ray diffractometer with Co-Kα X-rays. The surface area was measured with a Shimadzu surface area analyzer using the BET method.

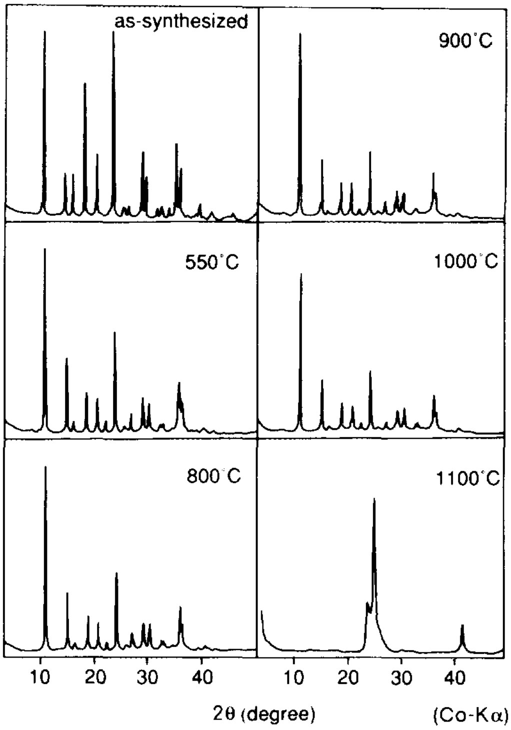

FIG. 1. X-ray powder diffraction patterns of hydrated SAPO-34 heated at each temperature.

RESULTS AND DISCUSSION

Figure 1 shows the X-ray powder diffraction patterns of the samples heated at each temperature. After removal of the template no effective change in the X-ray powder diffraction pattern was observed for the sample heated at temperatures up to 1000°C, while a distinct pattern change was recorded for the sample heated at 1100°C. This indicates that SAPO-34 retains its long-range order after heat treatment at temperatures as high as 1000°C.

The ^{27}Al-MAS-NMR spectra of the samples hydrated after the heat treatment at each temperature are shown in Fig. 2. As-synthesized SAPO-34, containing the template, showed a single line. After the template was removed, two broad lines at 44 and −13 ppm were observed for the samples heated at temperatures up to 1000°C, while a single narrow line at 40 ppm for the sample heated at 1100°C was observed. This indicates that SAPO-34 retained its short-range order around Al after heat treatment at temperatures as high as 1000°C.

The line at −13 ppm was found to disappear on dehydration and to be restored by rehydration of the dehydrated line, as is typically shown for the sample heated at 1000°C in Fig. 3. Careful analysis of the two lines showed that a nearly quantitative intensity transformation between the two lines occurred in the dehydration–hydration process. A single line of the dehydrated sample broke up into two lines upon hydration. The presence of water molecules produced different aluminum environment. After rehydration two lines collapsed into the single line. This spectral change occurred reversibly. Hydroxyl groups in SAPO-34 still remain in this dehydration process (*2*, *14*). The line at −13 ppm was strongly cross-polarized to protons by $\{^1H-^{27}Al\}$ CP-MAS, as shown in Fig. 4. This indicates that the Al atoms giving the line at −13 ppm have a strong interaction with water. The interaction between Al and the water molecule did not change after heat treatment at temperatures as high as 1000°C.

The ^{31}P-MAS-NMR spectra of the SAPO-34 hydrated after being heated at various temperatures are shown in Fig. 5. The sample heated at temperatures up to 1000°C showed a rather broad and asymmetrical line. The chemical shifts observed in the figure are characteristic of tetrahedral phosphorus. This asymmetrical line remained unchanged when the sample was heated at temperatures up to 1000°C, but it changed

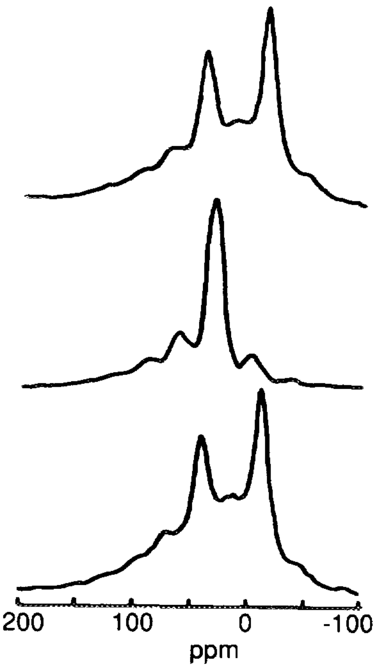

FIG. 3. ^{27}Al-MAS-NMR spectra of SAPO-34 heated at 1000°C: bottom, hydrated; middle, dehydrated; top, rehydrated.

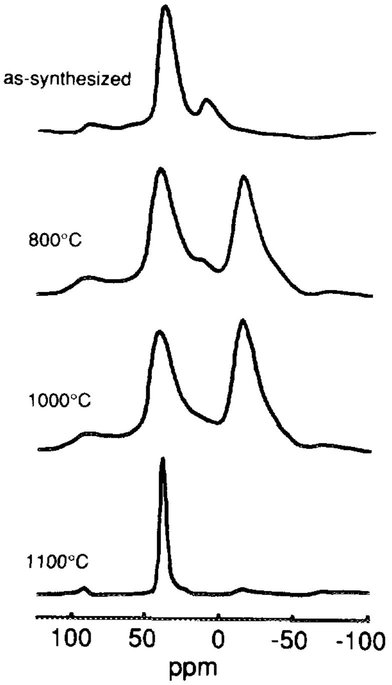

FIG. 2. ^{27}Al-MAS-NMR spectra of hydrated SAPO-34 heated at each temperature.

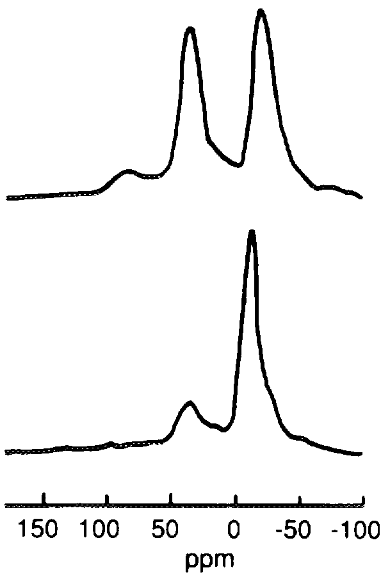

FIG. 4. ^{27}Al-NMR spectra of hydrated SAPO-34 heated at 1000°C: bottom, CP-MAS; top, MAS.

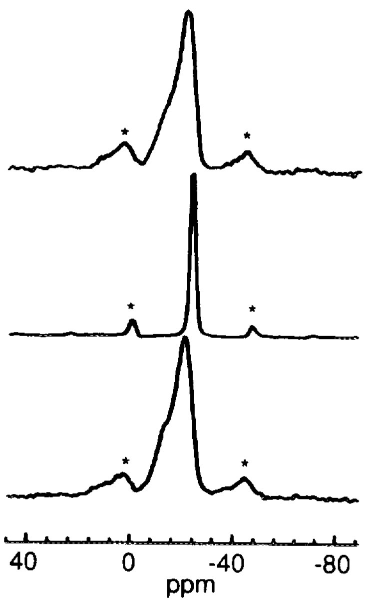

FIG. 6. ^{31}P-MAS-NMR spectra of hydrated SAPO-34 heated at 1000°C: bottom, hydrated; middle, dehydrated; top, rehydrated (*, spinning side band).

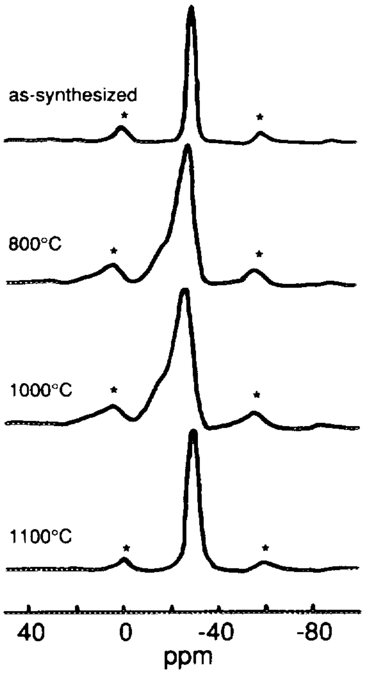

FIG. 5. ^{31}P-MAS-NMR spectra of hydrated SAPO-34 heated at each temperature (*, spinning side band).

into a sharp and symmetrical line when heated at 1100°C. On the other hand, as-synthesized SAPO-34 containing the template showed a single sharp and symmetrical line, which implies the asymmetrical line came from the adsorption of water molecules in the micropores of SAPO-34. This indicates that SAPO-34 retained its short-range order around phosphorus after heat treatment at temperatures as high as 1000°C.

Figure 6 shows the ^{31}P-MAS-NMR spectra of the sample hydrated after being heated at 1000°C, dehydrated, and rehydrated after the dehydration. This spectral change clearly indicates that the asymmetrical line resulted from the water molecule coordination to part of the P atoms in SAPO-34. Upon dehydration, the asymmetrical and broad line was changed into a symmetrical and rather sharp line. The line of the hydrated sample and that of the dehydrated sample have the same intensity. The water molecule coordination is consistent with the observations in a {^{1}H–^{31}P} CP-MAS experiment (Fig. 7). A downfield shoulder of the

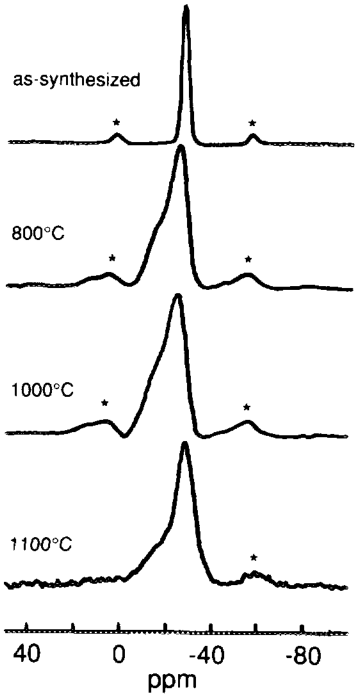

FIG. 7. ^{31}P-CP-MAS-NMR spectra of hydrated SAPO-34 heated at each temperature (*, spinning side band).

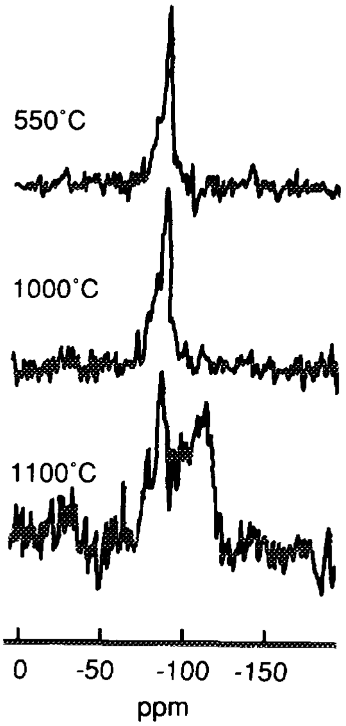

FIG. 8. ^{29}Si-MAS-NMR spectra of hydrated SAPO-34 heated at each tmeperature.

asymmetrical line was found to be more enhanced than the upfield line; part of the P atoms giving the downfield shoulder interacted tightly with water molecule. On the other hand, as-synthesized SAPO-34, containing the template, showed only one sharp line in a {^{1}H–^{31}P} CP-MAS and a MAS experiment; no hydrogen atoms were located closely to the P atom of SAPO-34.

^{29}Si-MAS-NMR spectra are shown in Fig. 8. No spectral change were caused by heat treatment at temperatures up to 1000°C. The local structures around the Si atom also remained unchanged when SAPO-34 was heated at 1000°C. Because of a poor signal-to-noise ratio, however, no further discussion was possible in this work.

The above studies on ^{27}Al-, ^{31}P-, and ^{29}Si-NMR and X-ray powder diffraction studies clearly indicate that SAPO-34 retained short-range order as well as long-range order even after heat treatment at temperatures as high as 1000°C in air. To corroborate this result, specific surface areas of SAPO-34 heated at given temperatures were measured by the BET method, and the results are given in Table 1. The specific surface area remained effectively unchanged for the samples heated at temperatures up to

TABLE 1

Specific Surface Areas of SAPO-34 Heated at Various Temperatures

Temperature (°C)	Specific surface area (m^{2}/g)
As-synthesized	20
550	224
800	217
900	238
1000	184
1100	17

1000°C. However, a distinct reduction of the specific surface area was observed for the sample heated at 1100°C. This fact implies that the microporous structure was destroyed by heat treatment at 1100°C. The change in the specific surface area with the heating temperature was consistent with the structural change in SAPO-34, as described above.

The resonance at −13 ppm in the ^{27}Al-NMR spectra (Figs. 2 and 3) ranged in an octahedral coordination. The resonance in the octahedral range has been also observed in SAPO-37 and is attributed to extralattice aluminum from the partial destruction of the framework (*2*). In the case of SAPO-34 this does not imply that part of the Al atoms is out of the crystalline framework of SAPO-34 because of the reversible spectral change in the dehydration–hydration process. Blackwell and Patton have assigned this resonance to the tetrahedral framework of the ^{27}Al species with secondary coordination of water (*8*). The chemical shift has been assumed to come from alternation of the Al nuclear symmetry and/or distortion of the neighboring framework geometry. The dynamic feature of the line in the hydration–rehydration process indicates that the local structures around the Al sites in SAPO-34 remain unchanged even after heat treatment at 1000°C.

MAS and CP-MAS ^{31}P-NMR experiments indicate that the local structure around the P sites in SAPO-34 remain unchanged even after heat treatment at 1000°C, as shown in Figs. 6 and 7. The asymmetrical line observed in the hydrated SAPO-34 likely consists of two resonance lines separated into two Gaussian lines, as shown in Fig. 9. Each line had a different line width but the same intensity. The broader Gaussian line at −19 ppm will result from tetrahedral P sites with additional coordination of the water molecule, and the narrower line at −28 ppm will result from tetrahedral P sites without the additional coordination.

The NMR studies indicate that there exist two types of tetrahedral sites for both the Al and P atoms in SAPO-34. However, the silicon incorporation was not sufficient to be consistent with these results. By neglecting the silicon incorporation, there is only one crystallographic type of T (= Al, P) site in the dehydrated framework (*6*, *15*). It is implied that there was only one kind of tetrahedral T (= Al, P) site for the dehydrated sample, but it split into two different chemical shifts with an intensity ratio of about 1 : 1 for the hydrated sample. This discrepancy may be solved by assuming that water molecules adsorb or coordinate either on the Al site or the P site randomly. The distance between the adjacent sites will be too short to accommodate two water molecules on adjacent sites. It is unlikely that another water molecule could adsorb on the site adjacent to the sites with water molecules adsorbed. Thus, there appear to be two types of T sites, for both the Al and P atoms in SAPO-34; one has a strong interaction with water and the other does not.

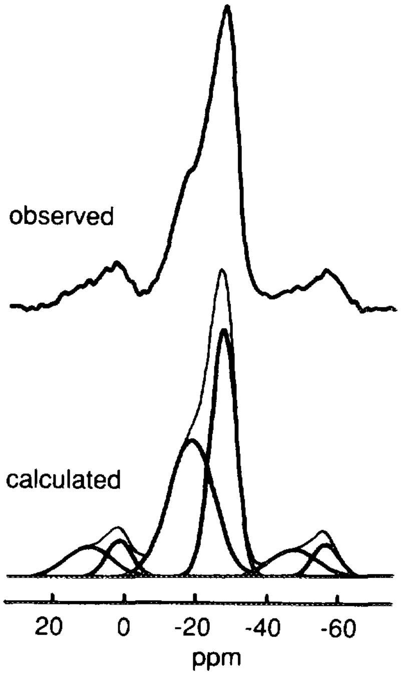

FIG. 9. Deconvolution of ^{31}P-MAS-NMR spectrum of hydrated SAPO-34 heated at 1000°C.

CONCLUSIONS

The microporous structure of SAPO-34 was mainly by NMR found to be thermally stable at temperatures as high as 1000°C. The adsorptive properties of water also remained unchanged for SAPO-34 heat-treated at temperatures up to 1000°C. In this study, SAPO-34 was found to be a promising catalyst with a microporous structure and high heat resistance.

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