Iron-incorporation in extra-large pore molecular sieve in acid medium

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Received 17 June 1994; accepted 20 July 1994

Dedicated to the memory of Professor Paul A. Vatakencherry

An extra-large pore molecular sieve, FAPO-H1, has been synthesized in the absence of organic additives. The ESR studies show Fe^{3+} incorporation into lattice sites in addition to its presence as occluded species. A change in coordination of the occluded species is observed on room temperature dehydration.

Keywords: $AlPO_4$ molecular sieve; iron incorporation; ESR spectroscopy

1. Introduction

Organic templating agents were thought to be an indispensable additive in the synthesis of aluminophosphate molecular sieve [1]. Absence of these additives resulted in the crystallization of condensed phases. Alternatively, molecular sieves could be synthesized in the absence of organic additive to curb the cost of this additional chemical. The extra-large pore molecular sieve $AlPO_4$-H1, first reported by d'Yvoire [2], has been synthesized totally in the absence of an organic additive [3,4]. Clearfield and co-workers [5,6] have synthesized a crystalline material, $AlPO_4$-H1, in the presence of an organic additive. Their recent report, however, excludes the possibility of occlusion of amine molecules in the as-synthesized form [7]. The framework of the as-synthesized $AlPO_4$-H1 contains water molecules coordinated to the Al atom situated at the junction of the double four-membered rings (4-MR)

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[5–7]. There has been much interest in the incorporation of a hetero atom in the very large pore $AlPO_4$ molecular sieve VPI-5 [8–10]. Partial substitution of a hetero atom would create a negatively charged framework which could be protonated to form acid sites. The substitution of Si for P is unlikely to occur during hydrothermal synthesis for the plausible two reasons: (1) the absence of organic amines in the micropores which could play the crucial role of a charge compensating cation [10]; (2) an aluminosilicate fragment of the type $-Si-O-Al(H_2O)_2-$ is unlikely to occur [11]. Unlike the silicon substitution, a trivalent transition metal, e.g. Fe^{3+}, is expected to substitute for Al creating a neutral framework [12], and thus is a promising way to incorporate a hetero atom into an $AlPO_4$-H1 framework. Here we report the incorporation of iron in $AlPO_4$-H1, a first step towards the synthesis of metal–$AlPO_4$ in acid medium. The location of iron in the molecular sieve, and the changes occurring on dehydration of the sample are studied by ESR spectroscopy.

2. Experimental

Aluminium isopropoxide was hydrolysed to $Al(OH)_3$. Dilute phosphoric acid was added followed by HCl, and the mixture stirred to a homogeneous state. $FeCl_3$ solution was then added to get a highly acidic gel (pH ca. 1.0) of the composition $1.0Al_2O_3 \cdot 0.8P_2O_5 \cdot 1.0HCl \cdot 0.01Fe_2O_3 \cdot 50H_2O$. Hydrothermal treatment was carried out at 150°C under agitation, and the reaction quenched after 4 h. The final product having a pH of 4.0 was repeatedly washed with a copious amount of water and air dried. The X-ray measurement was done on a Rigaku Geigerflex diffractometer with Cu Kα radiation. The MAS NMR experiments were carried out on a Bruker MSL 300 instrument operating at 7.0 T. For the ^{27}Al spectrum, 400 free-induction-decays (FID's) were recorded using a pulse length of 2 μs and a recycle delay of 1 s at a frequency of 78.2 kHz. For the ^{31}P spectrum, 32 FID's were collected using a pulse length of 8 μs ca. 90° and a recycle delay of 15 s at a frequency of 121.4 kHz. A spinning frequency of 3.5–5 kHz was employed. The chemical shifts were measured relative to aqueous $AlCl_3$ and 85% H_3PO_4 solutions, respectively. The ESR experiments were performed in a Bruker ER-200 D X-band spectrometer using a 100 kHz field modulation.

3. Results and discussion

The X-ray diffraction pattern is shown in fig. 1. The pattern resembles that of $AlPO_4$-H1 [3,4] and there are little or no impurity phases. The ^{27}Al spectrum (fig. 2, bottom) shows a sharp signal at 39.2 ppm (ascribed to 4-coordinated species) and an additional signal in the region −11 to −20 ppm ascribed to 6-coordinated Al [3,4,8–11]. The presence of the latter signal was confirmed using different spinning

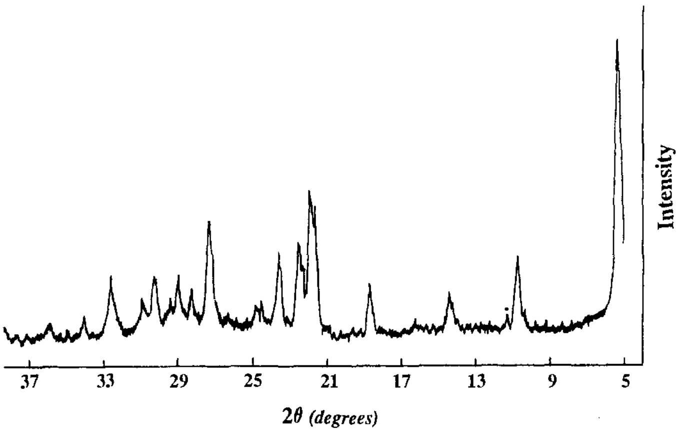

Fig. 1. X-ray diffraction pattern of as-synthesized FAPO-H1. The impurity peak is marked.

feeds. The broad diffused signal near 0 ppm arises from Al present in form of unreacted starting aluminium. A higher Al/P of 1.05 obtained by chemical analysis also suggests the presence of extraneous Al. The ^{31}P NMR spectrum shows 3 peaks at −23.3, −27.1, and −33.0 ppm in the approximate ratio of 1 : 1 : 1 (fig. 2, top). The peaks are assigned to P in double 4-MR and 6-MR, respectively [7]. Thermo-

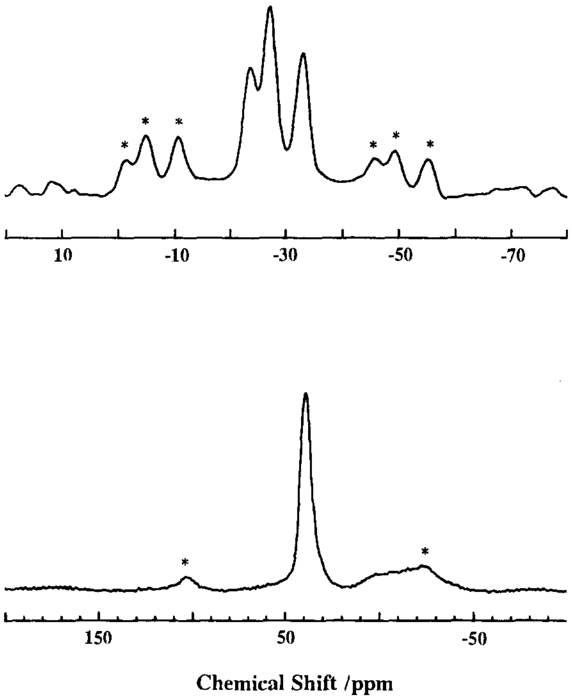

Fig. 2. ^{27}Al (bottom) and ^{31}P (top) MAS NMR spectra of FAPO-H1.

gravimetric analysis showed a weight loss of ~ 25% attributed to the loss of water molecules from the structure.

The room temperature ESR spectrum (fig. 3) shows signals at $g = 2.0, g = 4.3$ and ~ 9, and $g = 3.0$. To account for g-values near 2, the Fe^{3+} ions must be in a symmetric environment [13]. In Fe-VPI-5, the spectrum exhibited symmetric signals at $g = 2$ and 6 implying that the Fe ions mostly occupy axial sites [14]. Unlike Fe-VPI-5, in FAPO-H1 there is no signal in the region $g = 6$, hence no centres of axial symmetry are present in the sample. McNicol and Pott [15], Derouane et al. [16], Wichterlova [17], and Brucker et al. [18] have attributed the $g = 2$ signal to Fe^{3+} in O_h symmetry as hexa-aquo iron probably located in cationic positions in the channels. Since there are no cationic sites in a neutral $AlPO_4$ framework, these species are expected to reside in the channels [19,20]. The large width (>600 G) of the signal points to dipole–dipole interaction within the cavities. Signals at $g = 4.3$ and the corresponding shoulder at ~ 9 have been reported for Fe^{3+} in glasses [21], zeolites [15–18], and $AlPO_4$'s [14,19,20] described by the spin Hamiltonian [22]

$$H = D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + \beta \boldsymbol{S} \cdot \boldsymbol{g} \cdot \boldsymbol{H}, \qquad (1)$$

where D and E are the zero-field splitting (ZFS) parameters. The intense signal at $g = 4.3$ in conjunction with a shoulder at $7 < g < 11$ indicates Fe^{3+} on strongly distorted rhombic sites ($D > g\beta B$ and $\lambda = E/D = 1/3$) [14–22]. The intensity of this

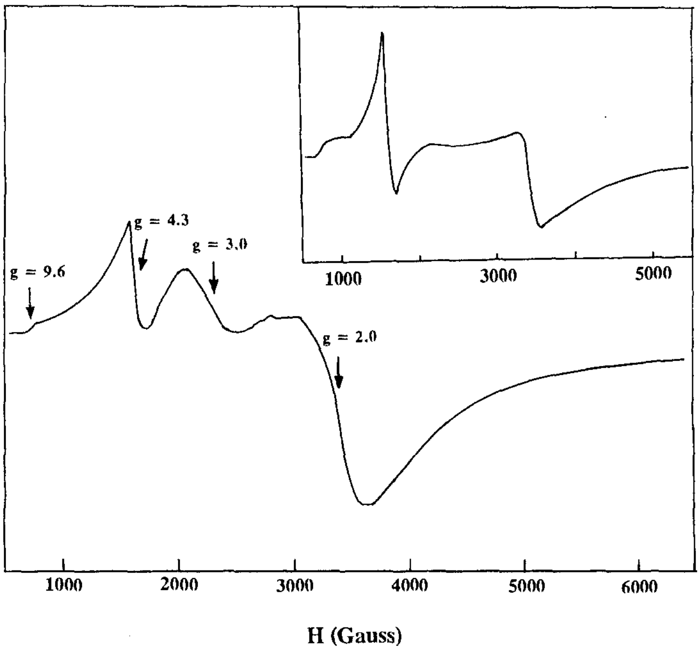

Fig. 3. ESR spectrum of FAPO-H1 at room temperature. Inset shows the spectrum at liquid nitrogen temperature.

signal is very large unlike that reported in Fe-VPI-5 [14]. Thus the location of iron in these molecular sieves differs. The signal in the region $g = 2.2$–2.8, 3.0 has been attributed to iron located in the channels as occluded phase (oxidic, hydroxidic phases) [14–18]. We identify the signal at $g = 3.0$ to Fe oxide microcrystallite precipitated on the crystal in the course of its synthesis. A liquid nitrogen temperature measurement (fig. 3, inset) enhanced the intensities of the signals at $g = 4.3$ and 9.6, and there is a concomitant reduction in the intensity for the $g = 2$ signal. The larger increase in the intensity due to the $g = 4.3$ signal masked the signal at $g = 3.0$, and hence the latter signal became unobservable. Such behaviour has been observed by others [14,18].

There have been numerous studies on the dehydration behaviour of VPI-5 [23–28]. These studies report a change in coordination/environment of the framework T-sites upon removal of the occluded water molecules. $AlPO_4$-H1 has been proven to be thermally unstable, drying at a temperature as low as 100°C induces structural transformation resulting in the formation of the stable-$AlPO_4$-8 [3,4]. It is desirable that the occluded water molecules present in the as-synthesized form [7] are removed without structural transformation, which may induce pore blocking through stacking faults [29]. We have resorted to ESR spectroscopy to study the nature of Fe in this process. A portion of the FAPO-H1 sample was evacuated at room temperature at high purity quartz tube for 24 h to obtain FAPO-H1(vac). By this procedure, all the water molecules located in the channels (except the water molecules coordinately bonded to Al) could be removed without structural transformation [27,28].

The ESR spectrum for FAPO-H1(vac.) (fig. 4) shows that the signal at $g = 2$ vanished completely. The signal at $g = 4.3$ remains unaffected with a higher intensity, even at a liquid nitrogen temperature measurement. The ESR spectrum of a physi-

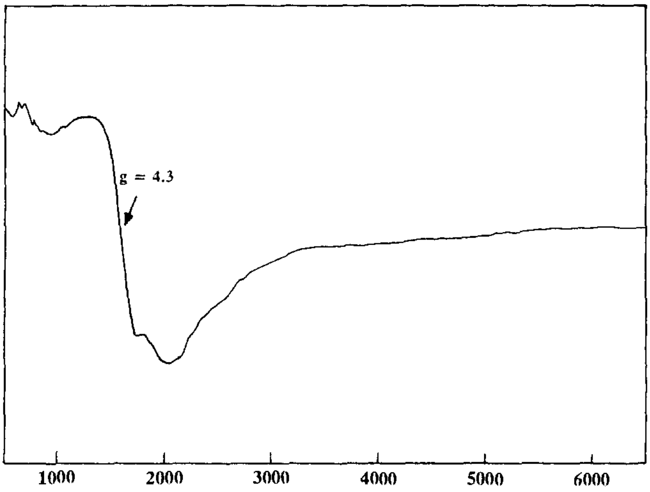

Fig. 4. A room temperature ESR spectrum of FAPO-H1 evacuated at room temperature for 24 h.

cal mixture of $AlPO_4$-H1 and $FeCl_3$ evacuated for 24 h, showed only a very broad signal of a couple of thousand Gauss wide centered at $g = 2.0$. For Fe in zeolite Y, upon dehydration in the presence of oxygen, the $g = 2$ signal vanished and the intensity of the $g = 4.3$ signal increased, reflecting the change in coordination of Fe^{3+} [17]. This process has been found to be reversible. During room temperature dehydration, in FAPO-H1, the environment of Fe changes from hexa coordination to tetra coordination. Thus the signal at $g = 2$ is unambiguously assigned to hexa-aquo complex present inside the channels of the molecular sieve.

4. Conclusion

It is possible to incorporate hetero atoms into an aluminophosphate framework in presence of an added mineral acid. The environment of the occluded Fe species in the molecular sieve is altered upon removal of the water molecules.

Acknowledgement

We are indebted to Dr. I. Balakrishnan (EIC, Trivandrum) and Dr. S.B. Liu (IAMS, Taipei) for encouraging support.

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