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Incorporation of Silicon into AlPO-5 Framework Sites: Higher Thermal Stability and Lower Extra-Framework Aluminum Concentration

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Abstract

Diffuse reflectance spectroscopy was used to investigate the structural modification of AlPO-5 microporous aluminophosphate synthesized in the presence of a silicon source and subjected to calcination in air. Extra-framework aluminium species, formed upon calcination and expulsion of aluminium from the framework, are detected by DRS because they are involved in aluminium-oxygen charge transfer transitions. Impregnation of the calcined AlPO-5 and SAPO-5 samples with ethanolic acetylacetone converted all the extra-framework aluminium atoms with distorted symmetry to a highly ordered symmetry, as evidenced by a distinct and well-defined 280 nm band in the DR spectra. The intensity of the 280 nm absorption band in AlPO-5 is much higher than those of all SAPO-5 samples with different silicon content. This is an indication of the presence of a considerably higher amount of extra-framework aluminium in AlPO-5. Washing the acetylacetone treated samples with hot ethanol leads to extraction of some of the complexed aluminium. The progress of extraction could be monitored by both DR and UV-vis spectrophotometry.

Introduction

SAPO-5 is the most investigated silico-aluminophosphate because of its unique features such as a 12-ring circular large pore opening of 7.3 Å [1,2] and ease of synthesis. It has been observed that SAPO-5 samples with different silicon contents show a higher degree of crystallinity and adsorption capacity following calcination compared to that of AlPO-5 [3]. This indicates a good thermal stability of the SAPO-5 due to incorporation of Si in the AlPO-5 framework sites. Sinha *et al.* also found that silicon has a promoting as well as a stabilizing effect on the AlPO-5 structure [4]. Several previous studies on SAPO-5 characterization also report higher pore volumes or BET surface area for SAPO-5 compared to that of AlPO-5 [5–8] and for SAPO-5 with increasing silicon contents [9]. In none of these reports have the differences between the calcined AlPO-5 and SAPO-5 from the point of view of thermal stability and porosity been investigated. The pore volume measurements seem to suggest that more Al, Si or P may be removed from the framework of AlPO-5, resulting in either partially blocked pores or the presence of amorphous materials in the samples.

The extra-framework aluminum atoms, formed during calcination of AlPO-n materials, can be studied and discriminated from framework aluminum atoms by MASNMR techniques [10–14]. ^{27}Al MASNMR has been widely used to determine the occurrence of aluminum atoms with different coordination number in these types of materials. But due to large quadrupole effects there are discrepancies among the results. Aluminophosphate molecular sieves have a high aluminum content and quadrupole broadening is most prominent in molecular sieves with higher aluminum content [15]. Therefore, diffuse reflectance spectroscopy can be used as an alternative or complementary technique to identify and to estimate extra-framework aluminum in zeolites and aluminophosphate molecular sieves [16, 17]. The chemical shifts in the ^{27}Al MASNMR spectrum depends primarily on the coordination of aluminum with respect to the oxygens and diffuse reflectance spectra could also provide such information.

Our aim in this contribution is to quantify the extent of extra-framework aluminium produced in both AlPO-5 and SAPO-5 upon calcination. We will indicate that a much larger amount of extra-framework aluminium atoms are produced in the AlPO-5 compared to SAPO-5 samples. We used diffuse reflectance spectroscopy for quantification of the extra-framework aluminium following the impregnation of the solid with acetylacetone.

Experimental

Sample preparation

AlPO-5 and SAPO-5 samples were prepared by hydrothermal synthesis methods described in the patent literatures [18, 19]. The AlPO-5 sample was synthesized from aluminium isopropoxide (Fluka, No. 06251) as the source of

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the aluminium and phosphoric acid (Merck) as the source of phosphorus in the synthesis gel. Triethylamine was used as template. SAPO-5 samples were prepared by the same procedure used for AlPO-5 except that some tetraethylorthosilicate (Merck, No. 800658) was added to the synthesis gel. This source of silicon proved to be the best reactant for synthesizing SAPO-5 with more silicon substitution and higher catalytic activities [20, 21]. The final molar composition of the gel was as follows:

$$1Al_2O_3 : 1P_2O_5 : xSiO_2 : 2TEA : 50H_2O,$$

where TEA stands for triethylamine and x represents the moles of silica source present per mole of Al_2O_3 or P_2O_5 and has a value from zero (AlPO-5) to 0.2 (SAPO-5) in our study. The crystallization was performed by heating the gel in a Teflon (PTFE) vessel inside a 100 mL stainless-steel autoclave. The reacting gel was heated at 180 °C for 12 h but AlPO-5 was heated for a longer time (15 h) at the same temperature to obtain highly crystalline products. After cooling the autoclave, the crystalline product was separated from the mother liquor by centrifugation. The samples were dried and then heated in a muffle furnace in air at a rate of approximately 2 °C per minute up to 550 °C and kept at this temperature for 5 h to remove the occluded template. The calcined samples were kept in a dessicator over P_2O_5.

For the impregnation treatment, 1.00 g of dried and powdered calcined sample of AlPO-5 or SAPO-5 was added to 3.0 mL of a solution of acetylacetone in ethanol (38%), separately. The samples were left in contact with acetylacetone solution for 4 h. After this time, the samples were washed with hot deionized water several times and then dried at room temperature in a stream of dry air. Some of the samples containing the aluminium acetylacetonate complex were treated with hot ethanol. The solid sample was added to 30 mL ethanol and stirred for 3 h at 50 °C. Then the solid was separated from the solution by filtration, washed several times with hot deionised water, dried and used for the DRS studies. The filtrate was analysed for extracted aluminium complex by a UV-vis spectrophotometer.

Characterization

X-ray diffraction measurements were performed on a Philips PW 1840 diffractometer with Cu-Kα radiation at room temperature. XRD patterns were recorded using an automatic divergence slit system.

Quantitative analysis of the materials was carried out using energy dispersive X-ray analysis (EDX) coupled to a Philips XL 30 scanning electron microscope.

Pore volume measurements were performed on a Sibata SA-1100 rapid surface area apparatus with nitrogen as an adsorption gas at liquid nitrogen temperature. Samples were first degassed at 250 °C for 1.5 h, prior to gas adsorption.

Diffuse reflectance spectra were recorded by a Shimadzu UV-2100 spectrophotometer, equipped with an integrating sphere assembly. A special cell, loaded with the solid sample and covered by a quartz window, was used in all measurements. All the spectra were recorded at room temperature against barium sulfate and plotted in terms of absorbance.

Table 1. The nominal and determined silicon content and pore volume of the samples

Sample	Si (%)	Si (EDX)	Pore volume (cm^3/g)
AlPO-5	0.0	0.00	0.101
SAPO-5/1	1.0	0.96	0.117
SAPO-5/5	5.0	4.20	0.136
SAPO-5/10	10.0	8.70	0.149
SAPO-5/15	15.0	11.3	0.159
SAPO-5/20	20.0	13.8	0.161

The silicon contents are in atomic percent.

Results and discussion

The nominal and determined silicon contents of the samples as determined by EDX/SEM are given in Table 1. EDX analysis was made upon several crystalline parts of the samples observable by the scanning electron microscope, the mean of the separate analysis was taken. The determined silicon content of the samples indicates that increasing amounts of silicon are incorporated into the products. Although the silicon content in the products correlates with that of the gel (the nominal values), the quantity of silicon in the products is generally less than that of the gel except for SAPO-5/1 which is approximately the same. This shows that some silicon is always left in solution as the silicon loading increases and that the amount left in solution increases with the concentration of silicon in the gel.

X-ray diffraction patterns of the as-synthesized materials demonstrate the high purity and high crystallinity of the products. They belong to the AFI crystallographic designation for type-5 aluminophosphates [22]. The calcined samples preserve their purity and crystallinity upon heating at 550 °C.

All the calcined SAPO-5 samples show pore volumes greater than for AlPO-5 (Table 1). This suggests that the AlPO-5 sample contains higher amounts of non-crystalline materials compared to SAPO-5 samples. However, the XRD results of the calcined AlPO-5 and SAPO-5 samples do not show a significant difference between the AlPO-5 and SAPO-5 samples.

The DR spectra of the calcined and dehydrated AlPO-5 and SAPO-5/10 shown in Figure 1 consist of a single and relatively broad band at 240 nm. These samples are white and therefore, do not show any absorption band in the visible region of the spectra. The 240 nm band is assigned to framework and extra-framework tetrahedral aluminium atoms arising from Al-O charge transfer transitions [17]. Various parameters, such as aluminium and oxygen charge density, Al-O distances, the crystallographic position of aluminium atoms in the structure and the origin and nature of the surroundings (water molecules, organics, etc) influence the wavelength and intensity of the charge transfer band [17, 23]. The DR spectra of the calcined AlPO-5 and SAPO-5 samples do not show any significant difference between them except that the 240 nm band is less broad in the SAPO-5 samples. Calcination lowers the symmetry of the environment of the framework aluminium atoms in

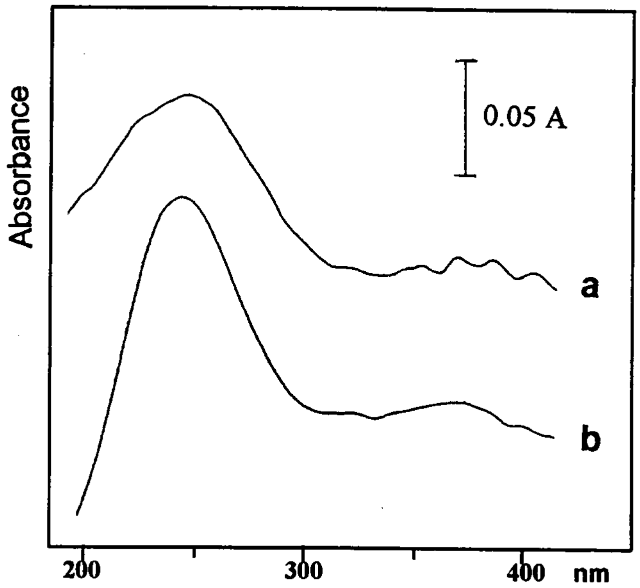

Figure 1. Diffuse reflectance spectra of calcined samples: (a) AlPO-5, (b) SAPO- 5/10.

both AlPO-5 and SAPO-5 samples but its effect is more pronounced in AlPO-5. This is in agreement with the result of the ^{27}Al MAS NMR studies of dealuminated mordenite, reported by Barras *et al.* [24]. They showed that the signal from four-coordinated aluminium is markedly broadened because of the presence of extra-framework aluminium in a distorted environment.

The acetylacetone-treated samples show a quite different feature. A distinct well-defined band at 280 nm is the result of the transformation of aluminium atoms with a distorted symmetry to those in an acetylacetonate complex in a highly ordered environment. Unlike the calcined samples, the DR spectra of acac-treated AlPO-5 and SAPO-5 samples indicate a significant difference between them. As Figure 2 shows the intensity of the 280 nm band depends strongly on the sample and its silicon content. The intensity of the 280 nm band is much higher for AlPO-5 and decreases considerably for the samples containing silicon (SAPOs). No such differentiation could be observed from the DR spectra of untreated samples. The lower intensity of this band in SAPO-5 samples is attributed to the lower amount of extra-framework aluminium in these samples. In the AlPO-5 sample more framework aluminium is expelled from their sites forming extra-framework aluminum species. Formation of these species results in either partially blocked pores or the presence of amorphous material in the sample.

Washing of the acetylacetone treated samples with hot ethanol results in a lower intensity of the 280 nm band. Figure 3 shows the effect of stepwise washing of the AlPO-5 sample. A considerable decrease in the intensity of the 280nm band was observed in every step of washing. But it is not possible to wash out all the Al(acac)$_3$ complexes from the channels and cavities of the solid, presumably because some of the aluminium atoms expelled from their sites reside in the channels of AlPO-5. Figure 4 shows sequential extraction of the aluminium acetylacetonate complex from SAPO-5/10 by successive washing with hot ethanol. A drastic decrease in the intensity of the 280 nm band shows that the majority of the Al(acac)$_3$ complex is extracted out of the solid. It should be noted that the scale of absorbance in Figures 2 and 4 are different and the amount of complexed extra-framework aluminium in SAPO-5/10 in comparison with AlPO-5 is to be assessed from Figure 2. The presence of complexed aluminium in the effluent can be observed using the conventional mode of the spectrophotometer for UV-vis scanning. Figure 5 shows the presence of the Al(acac)$_3$ complex in the filtrate identified by its well defined 280 nm band [16], similar to the one observed in the DR spectra of the acac-treated AlPO-5 and SAPO-5 samples. Virtually, no more aluminium complexes can be extracted after the second washing step of SAPO-5/10 (Figure 5c).

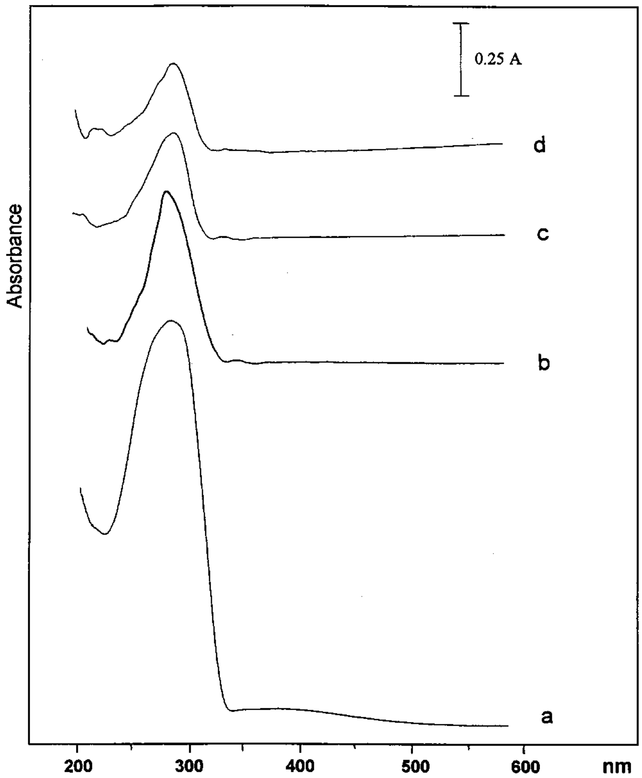

Figure 2. Diffuse reflectance spectra of acetylacetone treated samples: (a) AlPO- 5, (b) SAPO-5/5, (c) SAPO-5/10 and (d) SAPO-5/15.

The present study allowed us to quantify the promoting and stabilizing effects of SiO$_2$ on the AlPO-5 structure. Therefore, our DRS studies is a strong confirmation of the statement of Lopez *et al.* [3] and Sinha *et al.* [4] for the increased thermal stability of SAPO-5 compared to that of AlPO-5. The solid with the highest silicon content turned out to produce the lowest extra-framework aluminium and is the most stable while AlPO-5 which produces by far the greatest amount of extra-framework aluminium is the least stable.

Conclusion

Our diffuse reflectance spectrophotometric studies of the calcined AlPO-5 and SAPO-5 samples confirmed the higher

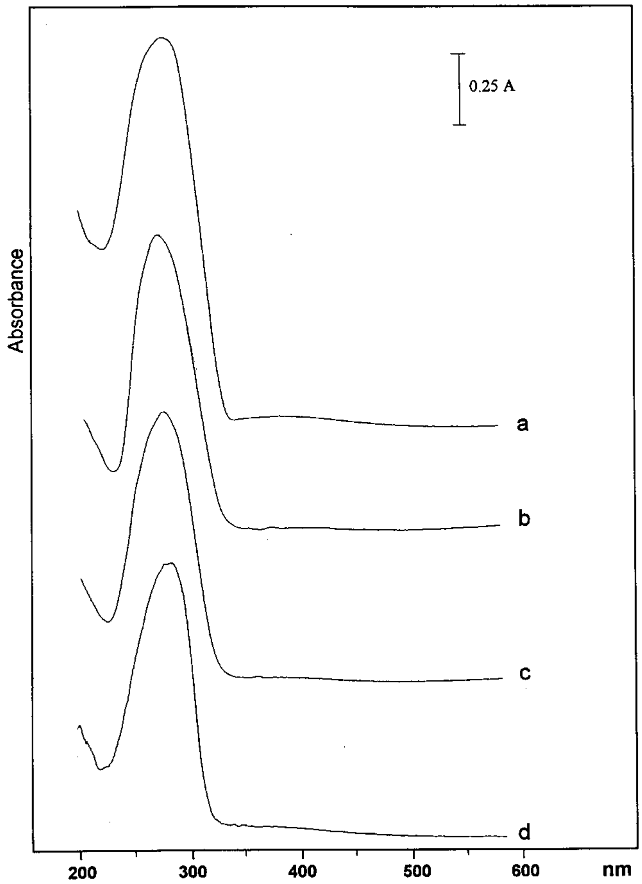

Figure 3. Diffuse reflectance spectra of acac-treated AlPO-5 at various stages of elution with hot ethanol: (a) AlPO-5, (b), (c) and (d) are after the first, second and third successive washing step, respectively.

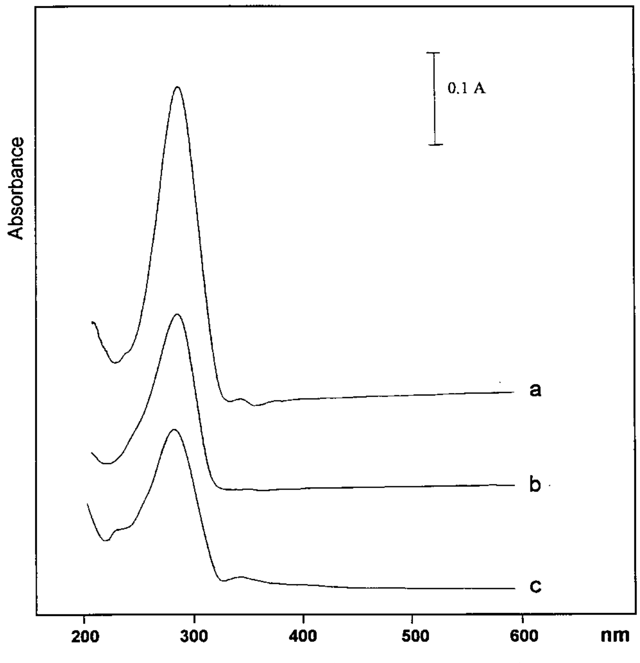

Figure 4. Diffuse reflectance spectra of acac-treated SAPO-5/10 at various stages of elution with hot ethanol: (a) SAPO-5/10, (b) and (c) are after the first and second washing step, respectively.

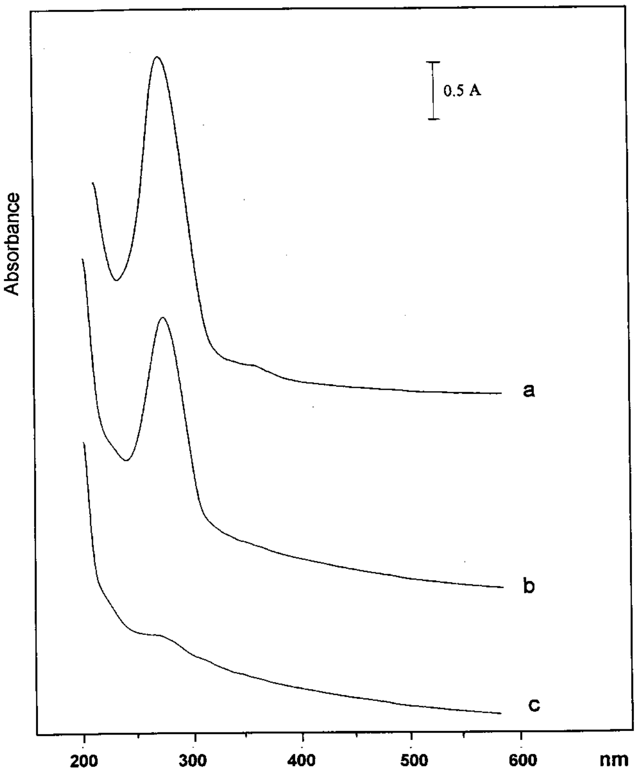

Figure 5. UV-vis spectra of the filtrate after successive washing of SAPO-5/10. (a), (b) and (c) are the first, second and third stage of washing, respectively.

thermal stability for SAPO-5 than for AlPO-5 in a quantitative manner. Acetylacetone impregnation of the calcined sample containing extra-framework aluminium leads to transformation of all of the aluminium species with distorted symmetry and different coordination number to a distinct well-defined band at 280 nm. The intensity of this band is much higher in AlPO-5 compared to those of all SAPO-5 samples with different silicon contents. This indicates much more extra-framework aluminium is produced in AlPO-5 than SAPO-5s upon calcination at 550 °C. Silicon incorporation in SAPO-5 has a stablizing effect on the AlPO-5 structure. Washing of the acetylacetone treated samples in hot ethanol will extract out some of the aluminium acetylacetonate complexes from the solid pores, as evidenced by DR and UV-vis spectra.

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