

CALORIMETRIC STUDY OF THE ACIDITY OF A NEW FAMILY OF MESOPOROUS CATALYSTS

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Abstract

Thermally stable mesoporous aluminophosphates (AIPO) and silicoaluminophosphates (SAPO) were prepared at room temperature in the presence of a cationic surfactant and an organic base. These materials possess high surface areas and regular mesopores of approximately 35 Å diameter. By contrast to microporous crystalline aluminophosphate molecular sieves, mesoporous compounds are amorphous and characterized by Al/P ratios greater than 1. These particularities are responsible for a strong Lewis acidity, as evidenced by ammonia adsorption microcalorimetry. Mesoporous materials are more acidic than the microporous analogues and the amount of strong acid sites increases with the silicon content.

Keywords: acidity, AIPO, calorimetry, mesoporous catalysts, SAPO

Introduction

Since their discovery by Mobil researches in 1992 [1], mesoporous silica-based molecular sieves have been the matter of an increasing interest, both on a fundamental level and for their potential applications in filtration, separation and catalysis.

These materials possess specific properties essentially due to their pore diameter and pore size distribution together with very high surface areas and reasonable thermal stability. Mesoporous silicas and aluminosilicates are synthesized under mild conditions from gels containing inorganic species and a long-chain organic structure directing agent, generally alkyltrimethylammonium cations with chain lengths in C₈ to C₁₆. The formation of the regular porous structure is supposed to proceed by a liquid crystal templating mechanism. The comprehension of the mechanism of their formation allowed the synthesis of similar materials based on different oxides (TiO₂, ZrO₂, Al₂O₃) or sulfides [2-4]. As for zeolites, aluminophosphate (AIPO₄) molecular sieves have also been widely studied crystalline microporous materials. However, several attempts to prepare mesostructured aluminophosphates have failed and most of the products were lamellar [5, 6]. It is only recently that two groups managed to prepare mesoporous aluminophosphate (AIPO) and silico-aluminophosphate

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(SAPO) molecular sieves and showed that the template could be eliminated without damaging the mesoporous structure [7, 8]. By contrast to microporous AlPO_4 materials, mesoporous AlPO_4 s and SAPOs can be obtained within a broad range of P/Al ratios [9].

Typically, P/Al is smaller than one, which indicates the presence of pure alumina domains in the materials. Moreover, incorporation of silicon increases the Al/P ratio, as well as the fraction of 4-coordinated Al and P species in the materials.

Since $\text{P/Al} \neq 1$, the framework is not electrically neutral and mesoporous AIPO materials probably possess interesting and new acido basic properties that do not exist in microporous compounds. Moreover, these properties more likely depend on the presence of silicon atoms in the framework.

In the present paper, we report on the characterization of various mesoporous AIPO and SAPO materials. The solids were prepared at room temperature following a method similar to that reported by Luan *et al.* [9] and were stable after removal of the organic template. Preliminary results about their physico chemical characteristics and their acidity as studied by adsorption microcalorimetry are presented.

Experimental

Synthesis

The various materials were prepared from gels containing aluminium isopropoxide (Aldrich), orthophosphoric acid (Rhône-Poulenc), cetyltrimethylammonium chloride (CTMACl, Aldrich), tetramethylammonium hydroxide (TMAOH, Aldrich) and silicon ethoxide (TEOS, Aldrich). In a typical preparation, a first solution was obtained by dissolving 0.1 mol $\text{Al}(\text{O}i\text{Pr})_3$ in H_3PO_4 (0.1 mol) and H_2O (1 mol) at 50°C . A second solution was obtained by adding 0.3 mol CTMACl to 5 mol of water. This solution may contain silica (TEOS), in which case it is stirred for several hours at room temperature to allow the complete hydrolysis of TEOS.

Stirring was maintained for 3 to 4 days at room temperature and the solid was then recovered by centrifugation, washed with deionized water and air-dried at room temperature.

Various samples have been prepared with Si/P ranging from 0 to 0.2 whilst the P/Al ratio remained equal to 1.

The elimination of the occluded organics was performed by calcination in N_2 at 450°C followed by air at 500°C for 12 h.

Characterization

XRD patterns were collected using a Philips PW 1710 diffractometer with CuK_α radiation in the range of $2-10^\circ$ (2θ).

N_2 adsorption/desorption isotherms were measured on a CATASORB apparatus. Samples were first evacuated at 250°C overnight prior to nitrogen adsorption. The specific surface area was obtained from the linear part of the BET equation. The pore

size distribution was calculated with the BJH method using the desorption branch of the isotherm.

Solid state NMR spectra were obtained on a BRUKER DSX 400 spectrometer at a spinning rate of typically 12 kHz. ^{29}Si , ^{27}Al and ^{31}P chemical shifts were referred to TMS, $\text{Al}(\text{H}_2\text{O})_6^{3+}$ and H_3PO_4 , respectively.

Ammonia was chosen as probe molecule to perform calorimetric and volumetric gas-solid titration of the acid sites of the samples. Ammonia (Air Liquide, purity > 99.9%) was purified by successive freeze-thaw pumping cycles before use. The samples (~100 mg) were put in quartz calorimetric cells and pretreated at 400°C with a 2°C min⁻¹ increase rate under vacuum overnight.

The ammonia heats of adsorption were measured in a differential heat flow microcalorimeter of Tian-Calvet type, C80 from Setaram. The adsorption temperature was maintained at 150°C in order to limit physisorption. A glass volumetric line linked to the calorimetric cells permitted the introduction of successive small doses of ammonia onto the samples until a final equilibrium pressure of 133 Pa was obtained. The equilibrium pressure relevant to each adsorbed amount was measured by means of a differential pressure gauge (Datametries).

While microcalorimetry is a very efficient method for the determination of the number and strength of sites, it is not suitable to distinguish specifically between Brønsted and Lewis acidic sites. It must be associated to infrared spectroscopy measurements to discriminate accurately both types of sites. The infrared spectra of adsorbed pyridine were recorded using a BRUKER Vector 22 FTIR spectrometer.

Results and discussion

Synthesis

Luan *et al.* [9] have recently reported that the pH of the starting gel is a critical factor to obtain hexagonal mesoporous aluminophosphate molecular sieves. In the present case, the crystallinity of the materials, reflected by the intensity and width of XRD peaks was optimum when the synthesis was performed at pH=8. For different pH values, either lamellar compounds or less ordered solids were obtained.

Table 1 Physicochemical properties of the samples

Solid	Molar composition					S/ m ² g ⁻¹	Dp/ Å
	Gel		Solid				
	Al/P	Si/P	Al/P	Si/P	Si/Al		
AIPO	1	0	1.19	0	0	763	34
S0.25APO	1	0.05	1.24	0.07	0.06	819	35
S0.5APO	1	0.1	1.3	0.17	0.13	745	35
SI APO	1	0.2	1.27	0.28	0.22	889	33

S: surface area obtained by the BET method ; Dp: pore diameter obtained by the BJH method

The physicochemical properties of our solids are given in Table 1. The molar composition is given for both the gel and the solid after calcination.

Chemical analysis of the various samples shows that the Al/P ratio is not equal to 1 as it is in the case of microporous AlPO_4 systems with frameworks made of strictly alternating AlPO_4 and PO_4 tetrahedra. The Al/P ratio increases with incorporation of silicon, suggesting that Si preferentially substitutes for P.

Surface areas are relatively high and similar to those obtained for silica-based MCM-41 materials. The surface does not seem to depend on the silicon content in the material.

Characterization

The X ray powder pattern of as synthesized SAPO material is typical of mesoporous structures with a d_{100} spacing of about 39 \AA (Fig. 1a). The presence of peaks at $2\theta=3.9$ and 4.5 , which can be indexed as (110) and (200) in a hexagonal lattice indicate a long range order for mesopores, as already observed for MCM 41 [1]. The pattern is not significantly modified after calcination. The most intense peak is slightly shifted in agreement with a small contraction of the pores.

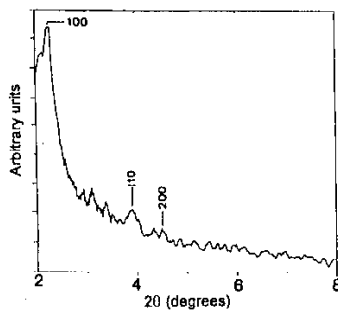


Fig. 1a Powder XRD pattern of the as-synthesized mesoporous S0.25APO material

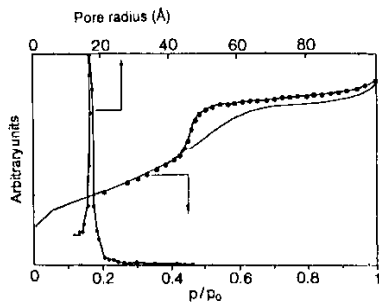


Fig. 1b Pore radius distribution and nitrogen adsorption isotherm of S0.25APO

The N_2 adsorption/desorption isotherm are typical irreversible type IV isotherms with a hysteresis loop (Fig. 1b). The isotherm is very similar to that observed on MCM-41 and characterizes a mesoporous material with relatively well defined pores. The step at $p/p_0=0.4$ corresponds to the capillary condensation within the pores. The desorption branch of the isotherm can be used to estimate the pore size distribution using the Kelvin equation. For our materials, relatively narrow pore size distributions were observed, with a maximum at ca 35 Å. The pore diameter did not depend on the chemical composition of the samples, particularly the Si content.

All samples were characterized by solid state NMR. ^{27}Al NMR spectra of as-synthesized materials show essentially two lines at ca 4 and 39 ppm, assigned to AlO_6 and AlO_4 species respectively (Fig. 2).

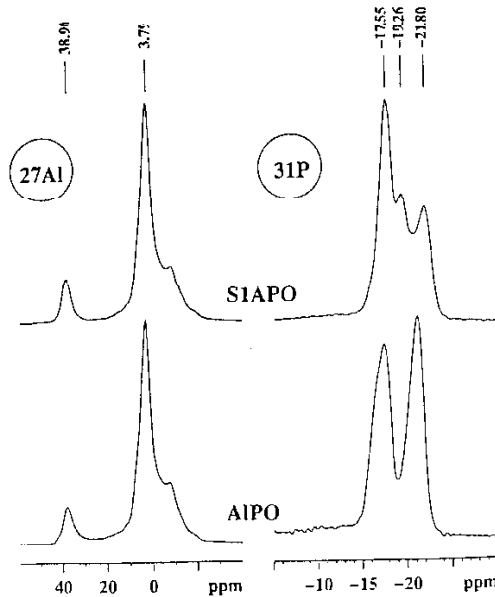


Fig. 2 Solid state MAS NMR spectra (^{27}Al and ^{31}P) of the as-synthesized SIAPO and AIPO samples

The intensity of the line at ca 4 ppm represents more than 90% of the spectrum intensity, indicating that the majority of Al species are octahedrally coordinated. ^{31}P NMR spectra show several lines in the -10, -20 ppm range. The line around -20 ppm has been attributed to P (4 Al) units, i.e. PO_4 tetrahedra linked to aluminium via 4 oxygen bridges [9]. Low field peaks between -10 and -20 ppm probably result from partially hydroxylated phosphorus species, as already observed in microporous materials.

Calcination of the materials drastically modifies both ^{27}Al and ^{31}P NMR spectra (Fig. 3). The ^{27}Al spectrum still shows an intense line at ca 4 ppm but peaks at 34 and 63 ppm are also observed. These peaks, which can be assigned to 5 and 6-coordinated Al species, respectively, indicate a condensation of Al species upon calcination. Similar conclusions can be drawn from the ^{31}P NMR spectra. After calcination, a single line is observed at -28 ppm, typical of P (4 Al) units in aluminophosphates.

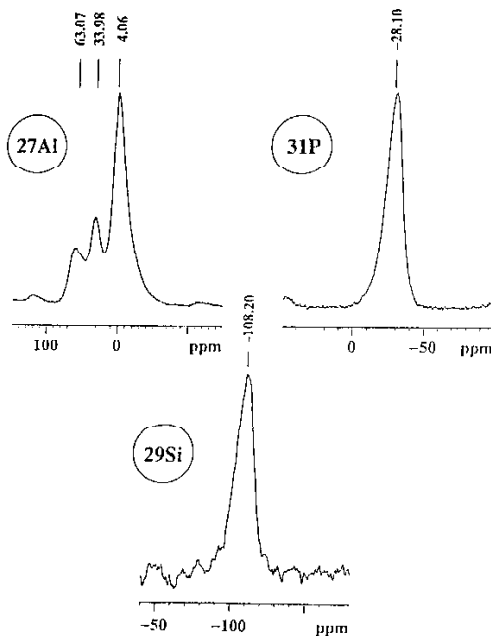


Fig. 3 Solid state MAS NMR spectra (^{27}Al , ^{31}P and ^{29}Si) of the calcined S1APO sample

^{29}Si NMR can be used to evaluate the dispersion of silicon species in the AlPO framework. At low Si contents, a weak signal is observed around -90 ppm, typical of isolated Si (4 Al) species in aluminophosphate molecular sieves. When the silicon content is increased, a line at -108 ppm is observed, typical of polycondensed Si species, which suggests the presence of SiO_2 domains in the materials.

Microcalorimetry

Adsorption microcalorimetry of a basic probe molecule such as ammonia has already proved to be a powerful technique for characterizing the number, strength and strength distribution of the acid sites of solids [10]. However, to our knowledge only few studies concerning the acidity of mesoporous materials have been reported in the literature [11–13].

Figure 4 represents the differential heats of adsorption vs. the ammonia uptake for the various AIPO and SAPO mesoporous samples. The acid site strength distribution is very heterogeneous, as evidenced by the sharp and continuous decrease of the heat curve as a function of the coverage. The initial heats are very high, ranging from 330 to 170 kJ mol^{-1} . For S1APO and S0.5APO samples, despite the low accuracy on the first point of the curves due to the experimental device, the following points are still ranging in a domain of very high heats of adsorption (between 200 and 250 kJ mol^{-1}), which indicates the presence of either impurities or extraframework Lewis species. However the amount of very strong acid species is small compared to the total acidity of the samples. In the domain of very strong acidity ($>150 \text{ kJ mol}^{-1}$) the strength of the samples is in the order $\text{AIPO} < \text{S0.25APO} < \text{S0.5APO} < \text{S1APO}$, which is consistent with the chemical composition (the strength increases with the Si/Al ratio). The curves are all very close in the domain of medium and weak sites ($<100 \text{ kJ mol}^{-1}$).

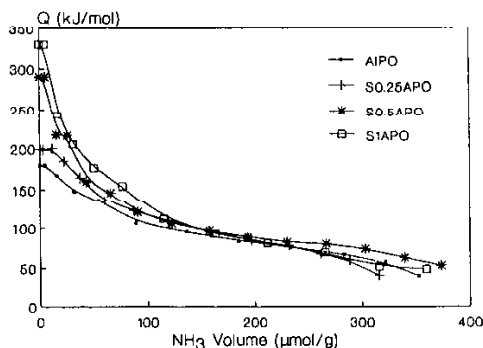


Fig. 4 Differential heats of ammonia adsorption vs. coverage for the various AIPO and SAPO samples

The acidity of the mesoporous materials has been compared to other microporous classical SAPO and AIPO samples (Figs 5 and 6). In Fig. 5, the mesoporous AIPO curve of differential heats is plotted together with the corresponding curve of an AIPO-5 sample ($P/Al=1$). It can be observed that the classical material is much less acidic than its mesoporous analogue, and this occurs in the whole domain of strength despite a similar number of total acid sites.

In Fig. 6 the S1APO mesoporous sample has been compared to a classical SAPO-5 (with 1.85 Si per unit cell and a $\text{Si}/(\text{Si}+\text{Al}+\text{P})$ ratio of 0.077). It can be seen that at low coverage ($<100 \mu\text{mol g}^{-1}$) the mesoporous material displays much higher heats of ammonia adsorption, but at higher coverage the classical SAPO-5 sample shows stronger and more numerous acidic sites.

Kosslick *et al.* [12] have used ammonia to probe the acidic properties of substituted MCM-41 type mesoporous silicates. They found initial heats of ammonia chemisorption around 185 kJ mol^{-1} for an Al-substituted mesoporous silicate, which

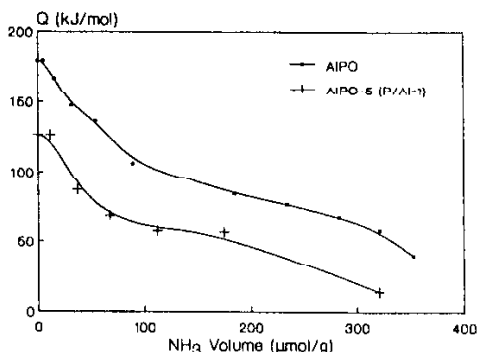


Fig. 5 Differential heats of ammonia adsorption vs. coverage for mesoporous AIPO and a classical AIPO-5

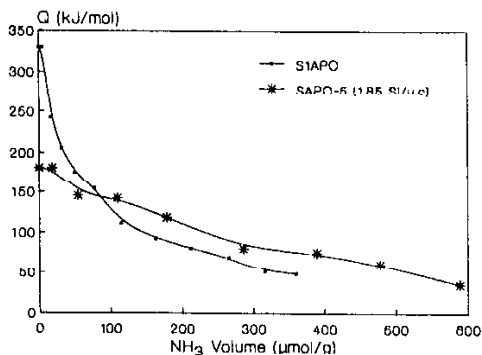


Fig. 6 Differential heats of ammonia adsorption vs. coverage for SIAPO and a classical SAPO-5

is relatively close to the value measured for our mesoporous AIPO sample. Also, a classical SAPO-5 was reported by Stach *et al.* [14] to have initial heats of ammonia adsorption around 140 kJ mol^{-1} .

Infrared spectra of adsorbed pyridine show that SIAPO essentially contains strong Lewis acid sites (Fig. 7). Brønsted acid sites characterized by an adsorption band at 1545 cm^{-1} are not significant, in agreement with ^{29}Si NMR data which indicated a low dispersion of silicon species in the material. Therefore, the increase of initial adsorption heat with the Si content in the samples cannot be correlated with the formation of Brønsted acid sites but rather with modifications of the chemical composition, particularly the Al/P ratio. Actually, Fig. 4 shows that the initial heat increases with the Al/P ratio, suggesting that the acidity results from the excess of Al species in the framework. Such a strong acidity does not exist in microporous compounds where Al/P=1.

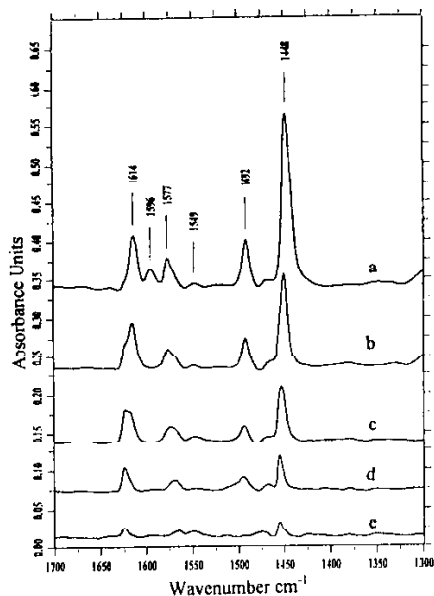


Fig. 7 Infrared spectra of pyridine adsorbed on S1APO after evacuation at 25°C a), 100°C b), 200°C c), 300°C d) and 400°C e)

Conclusions

Mesoporous aluminophosphates and silicoaluminophosphates were prepared at room temperature by using a cationic surfactant. These materials are stable after removal of the organics by calcination at 500°C and exhibit high surface areas and pore diameters of approximately 35 Å. All solids possess Al/P ratios greater than 1, and this ratio was found to increase with incorporation of silicon in the precursor gel. These materials are thus completely different from crystalline microporous aluminophosphates, for which Al/P=1. Moreover, most of the aluminum species are octahedrally coordinated, even after calcination at high temperature. The specific framework composition provides mesoporous materials with a distinct population of strong Lewis acid sites, the strength and number of which are higher than those observed by ammonia adsorption on microporous AIPO and SAPO molecular sieves.

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