SHORT PAPER

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Estimation of potential Brønsted acid site concentration in microporous SAPO-5[†]

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An ammonium-exchange treatment followed by a Kjeldahl ammonium ion measurement was used to estimate the total potential Brønsted acid site concentration in silicon-substituted AlPO-5 microporous aluminophosphates.

Keywords: potential Brønsted acid site, silicoaluminophosphate

Silicoaluminophosphate (SAPOs) are a class of microporous catalysts considered in terms of silicon substitution into the corresponding aluminophosphate (AlPO) framework.[1,2] According to this chemical modification SAPO materials acquire potential acidic and catalytic activities.[3] The acid properties of silicoaluminophosphates strongly depend on the Si content, siting and ordering in the lattice.[4,5] When a source of silicon is introduced in to the reaction mixture of an aluminophosphate, substitution of Si into the AlPO structural framework may occur. Silicon theoretically can substitute for aluminium or phosphorus or both. If the silicon substitutes for aluminium, the charge on the framework will be positive, giving rise to anion exchange properties. Substitution of silicon for phosphorus will result in an anionic framework similar to zeolite molecular sieves. No net charge in the framework will be observed if both aluminium and phosphorus are simultaneously equally substituted with silicon atoms. The ability to exchange cations as well as the observed acid activity in SAPO materials indicates that the silicon does, indeed, substitute for phosphorus.

SAPO-5 is an interesting microporous silicoaluminophosphate because of its large pore size and unique structure.[2] For SAPO-5 there is evidence for substitution of silicon for phosphorus and also substitution of two silicon atoms for a pair of aluminium and phosphorus atoms.[6] It has been shown that the composition of SAPO-5, and therefore its acidity, can be changed over a wide range of silicon incorporation according to synthesis factors such as the type of the template, the silicon source and the crystallisation temperature.[7–9] However, little has been done to correlate the concentration of the total potential Brønsted acid sites generated during synthesis and the synthesis factors. In this work, we introduce a fast, easy and reliable method of estimating the concentration of potential Brønsted acid sites in SAPO-5. We will examine this method for the SAPO-5 samples synthesised with two different silicon sources and with different silicon contents.

Synthesis gels were prepared according to procedures previously described.[10] Aluminum isopropoxide and orthophosphoric acid (85% Merck) were used as sources of aluminum and phosphorus respectively. Either fumed silica (Aerosil, Degusa, Switzerland) or tetraethyl orthosilicate (98% Acros) was added to the synthesis gel as the source of silicon. Triethylamine was used as the template. In all cases the molar gel composition can be represented by :

$1.0\ Al_2O_3 : 1.0\ P_2O_5 : x\ SiO_2 : 2\ TEA : 50\ H_2O$ ($x = 0.01, 0.03, 0.05, 0.10, 0.15, 0.20$)

Crystallisation was performed in static conditions in a stainless steel autoclave lined with PTFE , heated in an oven at 190°C for 12 hours. Products were characterised by XRD (Philips PW1840) and EDX/SEM (Philips XL 30). SAPO-5 samples were calcined in air at a rate of 2°C/min up to 550°C and kept at this temperature for 5 hours to remove the template. The calcined samples were converted into the ammonium form by ion-exchange. For the exchange, about 2g of the calcined SAPO-5 sample was added to 100 ml of a solution of 1 molar ammonium chloride, refluxed at 80°C for 5 hours twice. The solid samples were separated by centrifugation after each step of reflux treatment and washed with hot deionised water several times. The ammonium forms of SAPO-5 samples then were analysed by the Kjeldahl method for the determination of ammonium ion concentration.

By this method, all of the potential acid sites in NH_4SAPO-5 samples can be measured. The amount of NH_3 evolved should coincide with that of the acid sites. The results are shown in Table 1. All the SAPO-5 samples are designated by the silicon source used (A for Aerosil and T for tetraethyl orthosilicate) and by the nominal silicon content (amount of Si in the synthesis gel in atomic ratio). The real silicon content of the samples as determined by EDX/SEM is shown in the Table 1.

Increasing the silicon content in the SAPO-5 frameworks causes a concomitant increase in the ammonium concentration (*i.e.* potential Brønsted acid sites) in both Aerosil-based and TEOS-based NH_4SAPO-5 samples. However, the ammonium concentration is always much higher in the samples synthesised with TEOS compared with those synthesised with Aerosil (Table 1). This clearly shows that the the use of tetraethyl orthosilicate as a silicon source leads to an increase in potential Brønsted acid sites in NH_4SAPO-5. The merit of using TEOS for synthesising acidic SAPO-5 was previously claimed by Wang *et al.*[11] and Xiao *et al.*[9] from their NH_3–TPD studies. Our results show that for lower silicon content there are higher acid sites per Si atom incorporated (Table 1, NH4]/Si). This indicates that for lower silicon content, Si substitutes predominately for phosphorus. It appears that at

Table 1 Ammonium contents

NH_4SAPO-5	Si%(EDX/SEM)[a]	$[NH_4^+]$[b]	$[NH_4^+]$/Si
1A	0.75	0.06	0.08
1T	0.96	0.12	0.12
3A	2.36	0.15	0.06
3T	2.86	0.28	0.098
5A	4.05	0.26	0.06
5T	4.28	0.41	0.096
10A	7.95	0.32	0.04
10T	8.73	0.49	0.056
15A	10.65	0.38	0.036
15T	11.30	0.57	0.050
20A	12.86	0.42	0.033
20T	13.84	0.62	0.045

[a] In atomic percent.

[b] In mmole/g.

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higher silicon content a combination of mechanisms, substitution of one Si atom for one P atom and substitution of two Si atoms for a pair of Al and P atoms takes place. This confirms the model advanced by Dwyer and coworkers so far.[6] Concentration of the acid sites in our NH_4SAPO-5 samples with Si in the range 1–5% is very close to the results reported for HSAPO-5 samples measured by temperature programmed desorption of ammonia.[5] Therefore, the concentration of potential acid sites obtained by our method may give a good estimation of acid site concentration in this type of material.

We found that the higher acidity gained for SAPO-5 samples synthesised with TEOS and with higher silicon content is related to their higher thermal stability due to incorporation of silicon in the framework. These samples acquire higher pore volumes and lower extra-framework aluminum after calcination.[12]

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