

SAPO-37: the Implications of Structure Flexibility on Acidity

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When tetrapropylammonium cations are removed from the α cavities of SAPO 37, but tetramethylammonium cations are still in the β -cages, a shift in the vibrational frequency of hydroxy groups to lower frequencies, with the corresponding appearance of stronger acid sites is observed; this is a consequence of the increase of the T–O–T' angle dimensions owing to the presence of the bulky tetramethylammonium cations.

Recent computational–chemical studies have shown the flexibility of zeolite lattices. This flexibility leads to changes in geometry of the local tetrahedra (T) and, consequently, of the T–O–T' angles which, in turn modify the acidity of the associated hydroxy groups.¹

However, to our knowledge, few experimental results have been presented to confirm the above conclusions. Recent experiments on adsorption of NH₃ over HY² indicates that framework IR bands around 800 and 1050 cm⁻¹ are shifted when ammonia is desorbed. Moreover, Peltre *et al.*³ have demonstrated that the position of the framework Al^{IV} line in the ²⁷Al MAS (magic angle spinning) NMR spectra depends on the presence of ions or adsorbates in the cages of the

zeolite, reflecting a certain degree of interaction with the framework atoms leading to deformation of the lattice. More recently, Parise *et al.*⁴ have observed abrupt changes in the cubic unit cell parameters of zeolite ρ with relocation of exchange cations upon thermal treatment, indicating that the framework of this zeolite 'possesses exceptional flexibility'.

In recent years, a new family of molecular sieves containing Si, Al and P (SAPO), have been synthesized,⁵ having different structures, some of them isostructural with known zeolites. Thus, SAPO-37, with a faujasite structure and synthesized using tetrapropylammonium (TPA) and tetramethylammonium (TMA) as templates, appears to be an interesting material from the point of view of its catalytic properties.⁶

It has been reported that when TMA and TPA templates are removed from SAPO-37, it shows a higher number of total acid sites, but with a lower acid strength, than the analogous faujasite zeolite.⁷⁻⁹

In this communication we show that if the activation of SAPO-37, through template decomposition, is carried out in such a way that TPA is removed from the α -cages, while an

Table 1 Chemical composition

Sample	Molar oxide composition	Si/u.c. ^a
S37-1	(Al _{0.48} Si _{0.12} P _{0.40})O ₂	23
S37-2	(Al _{0.47} Si _{0.17} P _{0.36})O ₂	34
S37-3	(Al _{0.44} Si _{0.20} P _{0.36})O ₂	38

^a u.c. = unit cell.

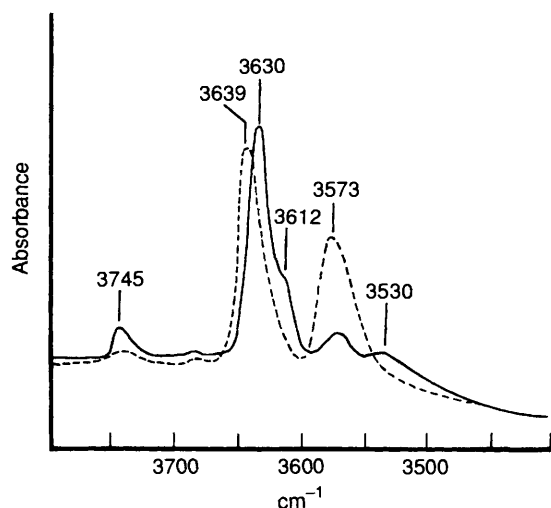


Fig. 1 IR spectra of the hydroxy groups of SAPO-37 calcined in vacuum, at 673 K —; 723 K - - -

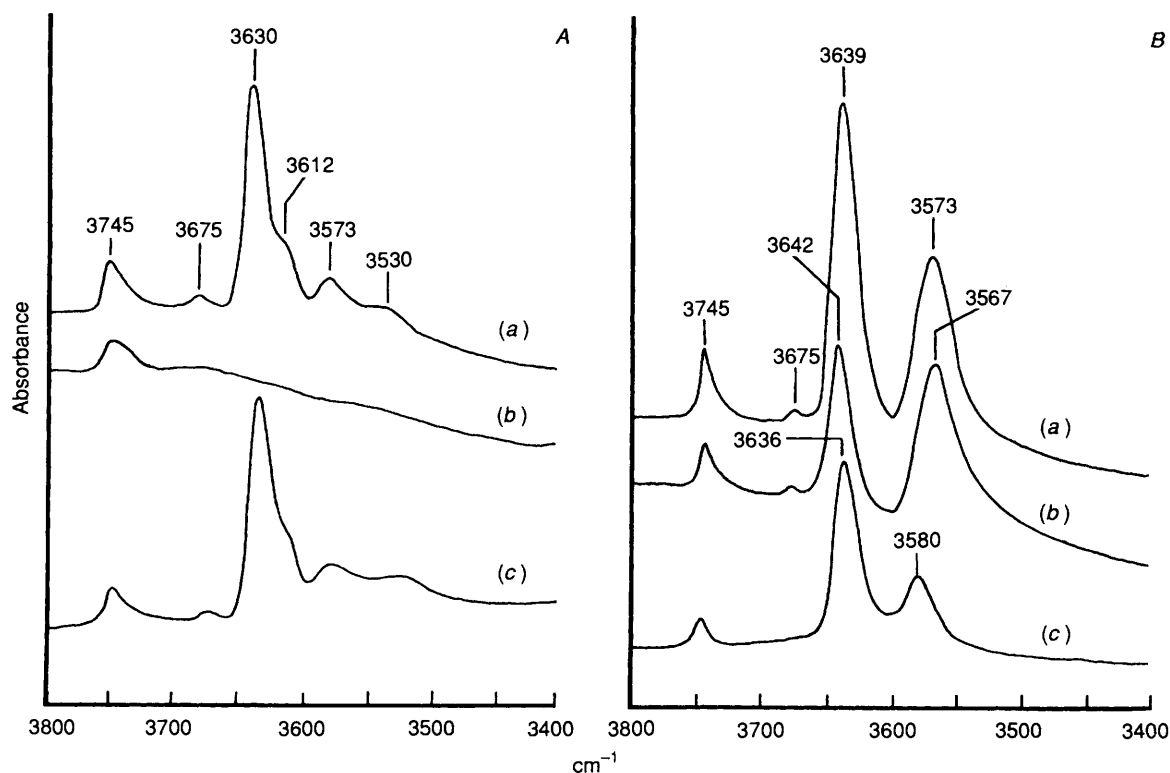


Fig. 2 IR spectra of the hydroxy groups of SAPO-37, calcined in vacuum at 673 K *A* and 723 K *B*. The different spectra correspond to: (a) calcined in vacuum; (b) after pyridine adsorption and desorption at 523 K; (c) difference spectra (a) - (b).

appreciable amount of TMA is still in the sodalite cages, unusually strong acid sites are formed. The presence of these sites can be explained on the basis of variations in the T-O-T angles owing to the presence of the bulky TMA in the sodalite cages.

SAPO-37 samples, with different silicon content, were obtained following the procedure previously described.⁶ Chemical compositions of the final products are given in Table 1.

IR spectra were obtained by using a vacuum Pyrex cell fitted with F₂Ca windows. Samples of 10 mg cm⁻² were mounted in the cell and pretreated at 673 K (*A*) or 723 K (*B*) *in vacuo* (10⁻² Pa) overnight. Pyridine (6 × 10² Pa) was admitted to the cell at room temperature and degassed for 1 h at 523, 623 and 673 K. Spectra were recorded, in all cases, at room temperature in an FTIR spectrophotometer with 2 cm⁻¹ spectral resolution.

The IR spectra of Fig. 1 indicate, in accordance with previous results,^{6,10} that when SAPO-37 is calcined at 723 K, and the templates have been removed, four hydroxy groups assigned to Si-OH (3745 cm⁻¹), POH (3675 cm⁻¹), high frequency (HF) (3639 cm⁻¹) and low frequency (LF) hydroxy bridging (3573 cm⁻¹) appear. At lower temperatures of calcination (673 K) TPA⁺ is removed, while TMA⁺, which is

Table 2 Pyridine remaining (mmol) adsorbed at different desorption temperatures on SAPO-37 samples pretreated at two temperatures

Sample	Pretreatment temperature					
	673 K			723 K		
	Pyridine desorption temperature					
	523 K	623 K	773 K	523 K	623 K	773 K
S37-1	236	49	5	192	11	<5
S37-2	257	115	27	219	27	<5
S37-3	279	131	33	268	38	<5

located in the sodalite cages, has been only partially eliminated.⁶ The spectra of SAPO-37 calcined at 673 K shows the following features: (i) two new IR bands at 3612 and 3530 cm^{-1} , assigned⁶ to HF and LF hydroxy groups interacting with remaining TMA, appear. (ii) The HF band at 3639 cm^{-1} is shifted to 3630 cm^{-1} , indicating an increase in the acidity of the corresponding hydroxy groups.¹¹

To determine if the different hydroxy groups were acidic, pyridine was admitted into the cell at room temperature and desorbed at 523 K. Spectra before and after pyridine adsorption are presented, for the samples pretreated at the two temperatures, in Fig. 2.

There we can see that, while in the sample calcined at 673 K (Fig. 2A) all the framework hydroxy groups are acidic enough to interact with pyridine at 523 K, in the sample calcined at 723 K approximately one half of HF and one half of LF hydroxy groups are not acidic enough to interact with it (Fig. 2B). Moreover, in the sample calcined at 723 K, it seems that the HF hydroxy group band is formed by two groups of OH with well defined acid strengths. One group appearing at 3636 cm^{-1} , which reacts with pyridine [Fig. 2B(c)], and the other, with an IR band located at 3642 cm^{-1} , which does not interact with pyridine at 523 K [Fig. 2B(b)]. The two bands at 3636 and 3642 cm^{-1} overlap giving a broad band with the maximum located at 3639 cm^{-1} [Fig. 2B(a)], as was observed in the original spectrum of the hydroxy groups.

In order to quantify these observations, we have included in Table 2 the amount of pyridine remaining adsorbed at different temperatures of desorption for the SAPO samples pretreated at 673 and 723 K. The results show that, in all cases, samples pretreated at 673 K possess a higher acidity than those treated at 723 K. Moreover, these differences are bigger the higher the desorption temperature is, *i.e.* acid centres with higher acid strength.

From the results presented before it is evident that the presence of TMA⁺ templates in the sodalite cages of the zeolite enhance the acid strength of the framework hydroxy groups.

These results can be explained as follows: the TMA⁺ (6.9 Å) is larger than the void space of the Na sodalite (6.6 Å) cavity, and this will be more so considering than ALPO polymorphs have lower channel dimensions than SiO₂ polymorphs.¹ Thus, it seems reasonable to accept that the presence of TMA⁺ in the sodalite cage can produce a deformation of the structure opening the T–O–T' angles and increasing the acidity of the associated protons. This hypothesis is supported, by the fact that the T–O–T' angle of TMA–sodalite (Si:Al = 5) is 158°¹² whereas that of the Na faujasite with similar Al content is *ca.* 141°.¹³

If this is so, it should be also possible to explain in the same way, the appearance of hydroxy groups at *ca.* 3600 and 3525 cm^{-1} in USY zeolites both with very strong acidities,¹⁴ when extra-framework Al species (EFAL) are

present. Indeed, it has been shown by X-ray diffraction (XRD)¹⁵ that partially polymerized EFAL species of the type



are located in the sodalite cages of USY. These

may produce the deformation of T–O–T' bond angles in the same direction that TMA⁺ does in SAPO-37, shifting therefore the frequency of the affected hydroxy groups to lower values and generating stronger acid sites.

In conclusion, it appears that SAPO-37 is indeed a flexible structure and that the T–O–T' angle dimensions can be modified by the presence of bulky cations such as TMA⁺ in the sodalite unit. This, in turn, produces a shift in the frequency of vibration of the hydroxy groups to lower frequencies which implies the appearance of stronger acid sites.

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