Effect of the rehydration on the acidity and catalytic activity of SAPO molecular sieves

Chr. Minchev [a,1], Ya. Neinska [a], V. Valtchev [b], V. Minkov [a], T. Tsoncheva [a],
V. Penchev [a], H. Lechert [c] and M. Hess [c]

[a] *Institute of Organic Chemistry, Sofia 1113, Bulgaria*
[b] *Institute of Applied Mineralogy, Sofia 1000, Bulgaria*
[c] *Institute of Physical Chemistry, University of Hamburg, Germany*

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The structural changes occurring in the template-free SAPO-5 and SAPO-34 upon the rehydration are reversible and do not affect their acidity and catalytic activity. The rehydrated SAPO-37 loses irreversibly a considerable part of its initial crystallinity, surface area, acidity and catalytic activity. Nevertheless the remaining acid centers are stable against dehydration–rehydration cycles.

Keywords: SAPO-5; SAPO-34; SAPO-37; rehydration, acidity; catalytic activity

1. Introduction

It is well known that the removal of the template and subsequent rehydration affects the crystal structure of the different SAPO materials [1]. Depending on the type of the crystal structure, reversible or irreversible phase transitions, loss of crystallinity and/or changes in coordination of some framework Al upon rehydration are observed. In the case of SAPO-5 [1] and SAPO-34 [1,2] the rehydration leads to the formation of octahedral aluminium as recently shown by MAS NMR. Subsequent dehydration of the same samples restores the initial tetrahedral coordination of Al. On the other hand, XRD data reveal that the rehydration of SAPO-37 results in irreversible structure distortion associated with the formation of extra framework Al atoms [1,3–5].

The purpose of this work is to compare the features of silicoaluminophosphate molecular sieves like SAPO-5, SAPO-34 and SAPO-37, which differ considerably in the stability of their structure TO-bonds towards water. The main point of the investigation is to elucidate to what extent the structural changes under rehydration influence the sample acidity and catalytic activity in such acid catalyzed reactions like toluene disproportionation and methanol conversion [6].

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[1] To whom correspondence should be addressed.

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2. Experimental

2.1. SAMPLE PREPARATION

SAPO-5, SAPO-34 and SAPO-37 were synthesized according to ref. [7] by using tripropylamine, tetraethylammonium hydroxide, tetrapropylammonium hydroxide and tetramethylammonium hydroxide, respectively. The preparation of the samples including some alterations in the original procedure is described elsewhere [8]. The as-made samples were calcined in air at the following conditions: heating up to 874 K for 4 h and 2 h at 873 K in a muffle oven. The template free samples were rehydrated at 293 K for 23 h in an exsiccator with a saturated solution of calcium nitrate (55% R.H.).

In the case of the samples designated as SAPO-5I, SAPO-37I or SAPO-34I the template removal was performed in situ in a flow reactor in order to avoid any contact with ambient humidity before the catalytic or adsorption measurements. The samples were heated in flowing air at a rate of 4 K/min up to 873 K, then cooled down at room temperature in nitrogen or helium stream. High purity gases were used.

The content of Al, Si and P was determined by conventional chemical analysis and by EDAX.

2.2. INSTRUMENTAL

XRD patterns were measured with an iso Debyeflex 1000 diffractometer using Cu K_α or Co K_α radiation. A drying box and a special folio have been used in some XRD experiments to avoid any contact of the calcined samples with water vapour at room temperature. The IR spectra (1400–300 cm^{-1}) were recorded with a Specord M 80 spectrophotometer in KBr pellets. The scanning electron micrographs were taken with a SEM 519/D 805 Philips apparatus combined with a PV-9900 EDAX-Terminal. The surface area measurements were carried out on a Sorptomatic unit from Carlo Erba at liquid nitrogen temperature. Before these measurements the template-free samples were heated at 573 K under vacuum for 24 h. The adsorption of ammonia (30 kPa, in He stream at 423 K and TPD up to 873 K) was measured as already described [9].

2.3. CATALYTIC MEASUREMENTS

The toluene disproportionation was carried out in a continuous flow reactor at 723 K. The WHSV was 0.54 h^{-1} and the nitrogen/toluene molar ratio 2.5. The conversion of methanol was performed in a flow apparatus at atmospheric pressure in a He flow [10]. The experiments were carried out at 423–723 K with a WHSV of 1.5 h^{-1}.

Table 1
Characteristics of the samples

No.	Sample	Chem. composition			BET surf. area	Absorption bands[a] (cm^{-1})								
		(Al	Si	P)O$_2$	(m^2/g)									
1	SAPO-5	0.42	0.09	0.49	304	1112vs	–	704m	560ms	–	468s	–	–
2	SAPO-34	0.44	0.10	0.46	500	1113vs	–	644s	–	532s	483s	–	389ms
3	SAPO-37I[b]	0.42	0.20	0.27	399	1057vs	775m	670m	565ms	532ms	485m	456m	380m
4	SAPO-37II[c]	0.42	0.20	0.38	146	1110vs	–	–	–	–	478ms	–	–

[a] vs=very strong; s=strong; ms=medium strong; m=medium; w=weak.

[b] SAPO-37I template decomposed in situ.

[c] SAPO-37II rehydrated, total loss of crystallinity by XRD.

3. Results and discussion

3.1. CHARACTERIZATION OF THE AS-MADE AND THE CALCINED SAMPLES

Some characteristics of the samples under investigation are presented in table 1. The X-ray data, the results for the surface area and the lattice vibration spectra indicate that all as-made samples are highly crystalline. These results are in agreement with the data reported by other authors for SAPO- 5 [7,11] and SAPO-37 [12].

The scanning electron micrographs confirm the good crystallinity of all materials. The SAPO-5 crystals have a hexagonal cross-section of about 10 μm. Octahedral crystals about 10 μm in size in the case of SAPO-37 and isometric ones of about 1–2 μm for SAPO-34 are observed.

The XRD patterns of the template-free samples recorded in the absence of ambient humidity exhibit slight modifications in intensity of some reflections. The intensity ratio of some peaks changes after calcination as already described in ref. [7]. In addition the IR-vibrational spectra recorded immediately after the template removal show that the structure of the samples is preserved (fig. 1–3).

By contrast, the stability of the rehydrated template-free SAPO samples shows substantial differences. In the case of SAPO-5 and SAPO-34, the presence of water considerably influences the XRD patterns which exhibit strong loss of crystallinity

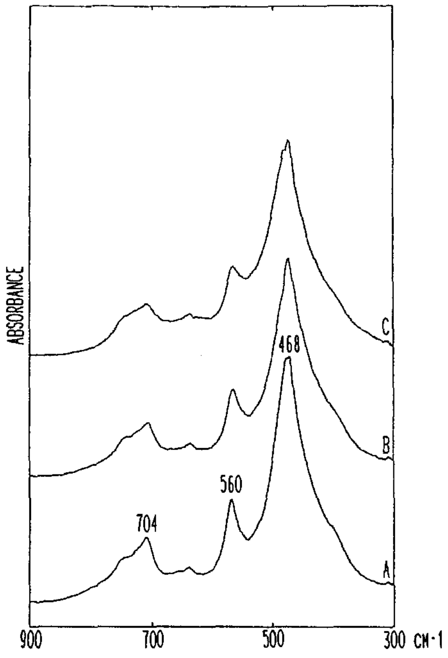

Fig. 1. Infrared spectra of SAPO-5: (A) after template removal; (B) after rehydration, 24 h; (C) sample (B), after storage for 3 years.

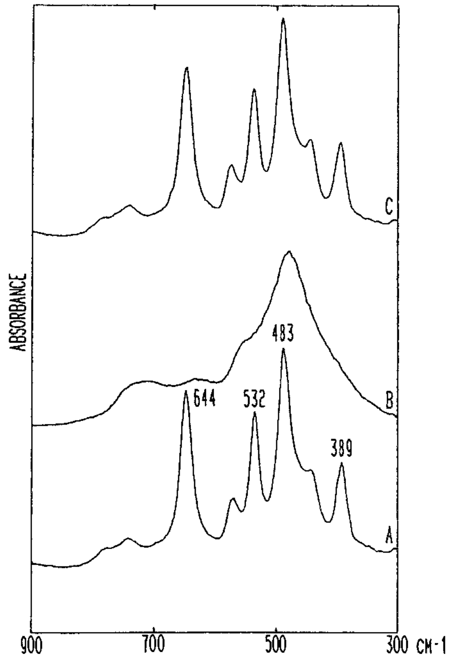

Fig. 2. Infrared spectra of SAPO-34: (A) after template removal; (B) after rehydration, 24 h; (C) sample (B) after dehydration at 823 K.

(figs. 4 and 5). The rehydrated SAPO-37 become totally amorphous to X-rays. There are differences in the behaviour of the same samples after additional thermal treatment at 823 K. The calcination completely restores the initial XRD patterns of SAPO-5 and SAPO-34, while the structural changes for SAPO-37 are irreversible. The different stability of the samples towards rehydration–dehydration cycles is confirmed also by IR data depicted in figs. 1–3. In the case of SAPO-5 and SAPO-34, adsorbed water causes an almost reversible decrease in intensity or even disappearing of some bands corresponding to the framework vibrations. These results are in accordance with the NMR-evidence for reversible change of the coordination of some Al in the framework [1].

With SAPO-37 irreversible transitions are observed (fig. 3). The adsorption capacity of this sample (table 1) decreases considerably, which is obviously due to a pore blockage by amorphous material. Nevertheless the crystals preserve their initial morphology (fig. 6). SEM micrographs do not show any splits on the faces of the octahedral crystals.

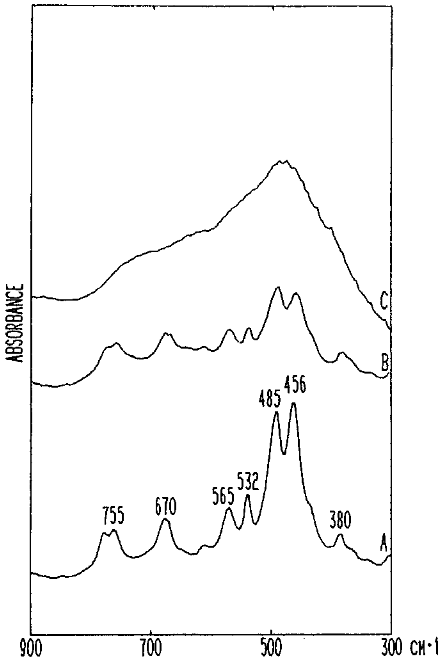

Fig. 3. Infrared spectra of SAPO-37: (A) as made; (B) sample (A) after treatment at 623 K; (C) after template removal and rehydration.

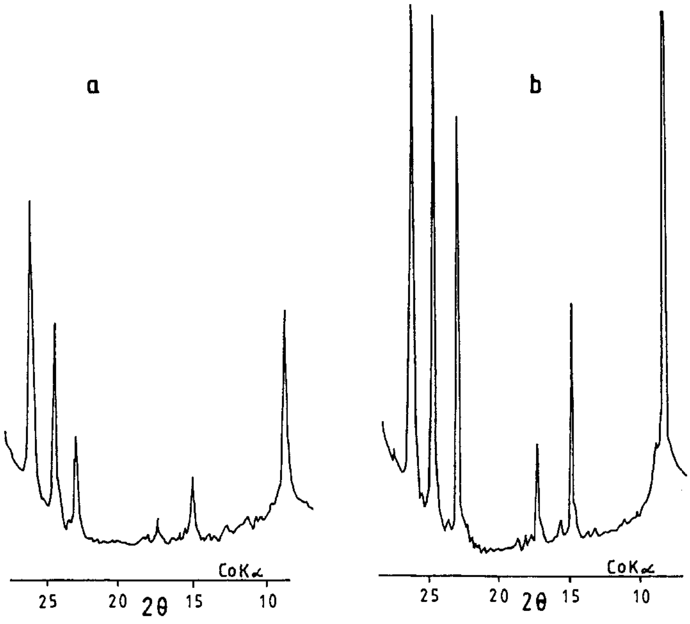

Fig. 4. XRD patterns of SAPO-5. (a) Calcined and rehydrated 24 h; (b) as (a), after dehydration at 823 K.

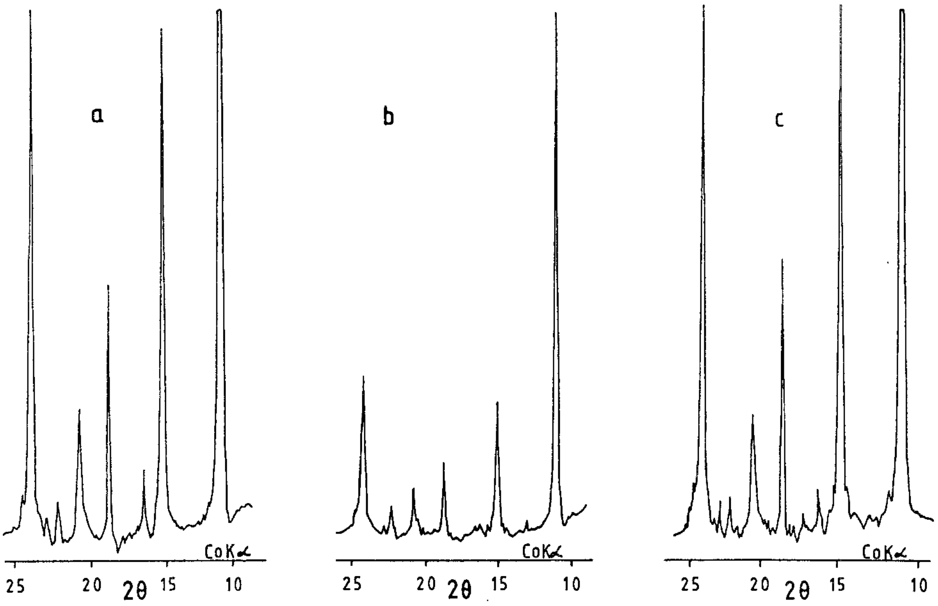

Fig. 5. XRD patterns of SAPO-34. (a) Calcined at 873 K; (b) as (a), after rehydration 24 h; (c) as (b), after dehydration at 823 K.

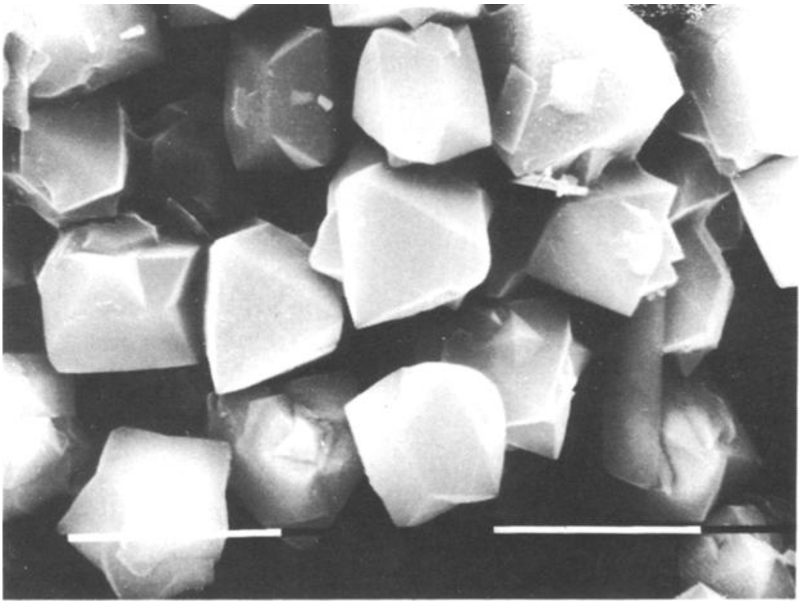

Fig. 6. SEM micrograph of the template-free, rehydrated SAPO-37. Scale bar = 10 μm.

Table 2
Thermodesorption of ammonia, adsorbed at 420 K

Sample No.	Type of sample	Treatment before the ammonia adsorption	Temperature of TPD-peaks (K)		Ammonia (mmol/g)	
					I	II[a]
1	SAPO-5	873 K in air, rehydration, 823 K in He	503	–	0.44	–
2	SAPO-5I	in situ: 873 K in air, 823 K in He	503	–	0.40	0.41
3	SAPO-34	873 K in air, rehydration, 823 K in He	503	673	1.20	–
4	SAPO-34I	in situ: 873 K in air, 823 K in He	503	673	1.36	1.34
5	SAPO-37I	in situ: 873 K in air, 823 K in He	520	–	0.80	–
6	SAPO-37II	sample 5 rehydrated 24 h, 823 K in He	520	–	0.42	0.42

[a] Before the second TPD experiment (II) the sample was rehydrated 24 h at room temperature.

3.2. ACIDITY

The results obtained for the different SAPO structures (table 2) are in good agreement with some literature estimations of the number and the strength of the acid sites in SAPO-5 [13–16], SAPO-34 [16] and SAPO-37 [17]. The total amount of ammonia adsorbed decreases in the sequence: SAPO-34 > SAPO-37 > SAPO-5. Two TPD peaks of ammonia appear in the case of SAPO-34 reflecting the occurrence of centers differing in acid strength. As seen in table 2, there are no considerable differences in the acidity of the various samples SAPO-34 (Nos. 3, 4) and SAPO-5 (Nos. 1, 2) in dependence on the conditions of pretreatment and/or rehydration. In the case of SAPO-37, however, the rehydration leads to almost twofold reduction of the adsorbed amount of ammonia. Thus the acidity measurements confirm that water affects strongly the crystal structure of SAPO-37 causing irreversible changes. It is noteworthy that about 50% of the acidity of the parent SAPO-37 sample is preserved after rehydration. This effect will be discussed again in the catalytic section.

3.3. CONVERSION OF METHANOL

All SAPO samples under investigation showed catalytic activity in the methanol conversion. According to the shift of the temperature dependence of dimethyl ether/DME/yield, the following sequence of activity is observed: SAPO-34 ≫ SAPO-37I > SAPO-5 > SAPO-37II. From fig. 7 and table 2 it is to be seen that there is a good agreement between the catalytic activity of the samples in the DME formation and their acidity as evaluated by ammonia thermodesorption.

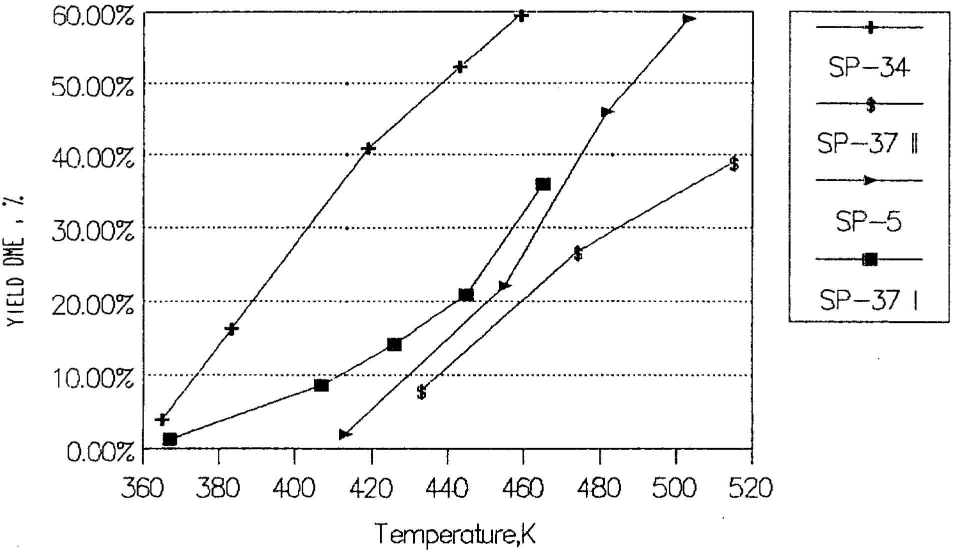

Fig. 7. Temperature dependence of yield of dimethyl ether (DME) on different SAPO samples.

Obviously, the reversible structural changes occurring after rehydration–dehydration cycles in SAPO-5 and SAPO-34 do not affect significantly their acidity and catalytic activity. On the other hand, some results with the SAPO-37 sample point out that the rehydration of the calcined sample leads to an irreversible reduction of both activity (fig. 7) and acidity (table 2).

3.4. DISPROPORTIONATION OF TOLUENE

The catalytic activity of the SAPO samples differs in a wide range depending on their structural and acidic properties. Unlike to methanol conversion, SAPO-34 shows no activity in disproportionation. Obviously this effect is caused by the rather small pore size of the SAPO-34 structure. The results depicted in fig. 8 show in accordance with the data discussed above that the SAPO-37I sample is superior to the other SAPOs in disproportionation activity. Moreover, the slight increase of the conversion with the time on stream is very similar to the induction period observed in the case of toluene [18] or ethylbenzene [19] conversion over modified faujasites. Probably, in both cases a modification of the active centers under the impact of the reaction medium is taking place. It is to be pointed out that the rehydrated SAPO-37II sample shows a much lower activity in the disproportionation reaction than the parent SAPO-37 catalyst. In the same time the reduction in activity is more pronounced than one would expect considering the changes in acidity (table 2).

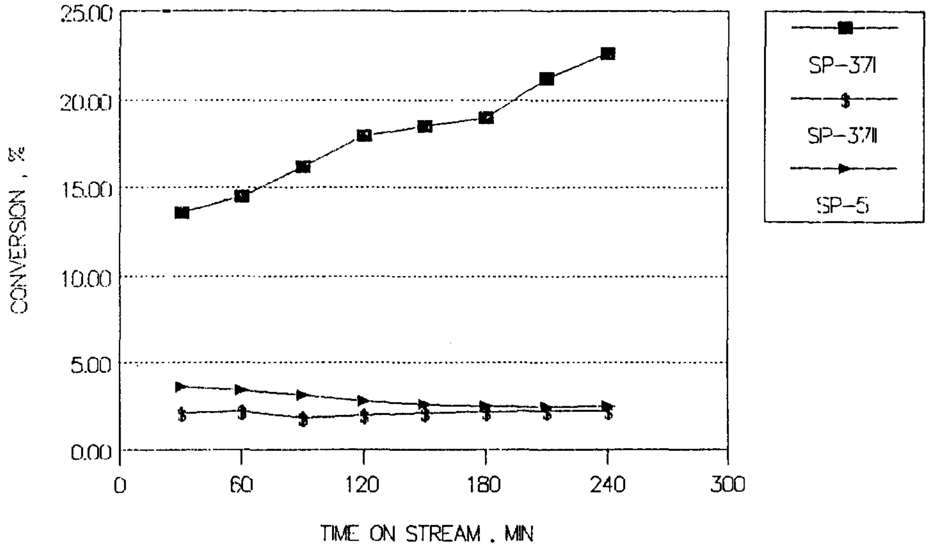

Fig. 8. Toluene conversion on different SAPO samples versus time on stream.

3.5. GENERAL COMMENTS

The structural changes occurring in the template-free SAPO-5 and SAPO-34 upon rehydration are reversible and do not affect substantially their acidity and catalytic activity.

Upon the same treatment, according to XRD SAPO-37 irreversibly loses its crystal structure. Nevertheless the rehydrated sample retains about 40–50% of the adsorption capacity, acidity and catalytic activity in methanol conversion of the original SAPO-37. It is to be pointed out that the number of these acid centers remains practically unchanged during several consecutive cycles of ammonia desorption, rehydration at room temperature and ammonia adsorption. It might be suspected from these results that the remaining acidity originates from some regions, which possess particular stability against dehydration–rehydration cycles (table 2). MAS NMR data of other authors [20] support this hypothesis, since a large part of Al-tetrahedra has been found still intact even in a completely destroyed SAPO-37. Surprisingly, the catalytic activity in toluene disproportionation is reduced in a greater extent than the acidity and hence can be regarded as more sensitive to the structural alterations and to the presence of extra lattice species. The aforementioned effect could be associated with the new environment and/or with the changes in the accessibility of the active sites remaining after the framework damage. It is not excluded that the rehydration affects at first the strong acid centers which contribute to the catalytic activity in toluene disproportionation and are probably located at the boundaries of different domains [21] or Si-islands [22].

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