INFLUENCE OF SILICON CONTENT AND NATURE OF THE TEMPLATE MOLECULE ON PHYSICO-CHEMICAL AND CATALYTIC PROPERTIES OF SAPO-5*

Jochen JÄNCHEN[a], Vladimir PENCHEV[b], Elke LÖFFLER[a], Barbara PARLITZ[a]
and Helmut STACH[a]

[a] *Central Institute of Physical Chemistry, Rudower Chaussee 5,*
D(O)-1199 Berlin, Germany
[b] *Institute of Organic Chemistry, Sofia 1040, Bulgaria*

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Two series of SAPO-5 molecular sieves were synthesized: (i) Using tripropylamine as a template and varying the Si content in the gel, and (ii) varying the template molecule at constant silicon content in the gel. The products were characterized physico-chemically and tested in the toluene disproportionation. It was found that the rising silica content in the synthesis gel has only little influence on the SiO_2 incorporation into the SAPO. Investigations of the acid character revealed that the concentrations of the adsorbed ammonia molecules are nearly constant and independent of the total silicon content of the crystals. The catalytic activity showed no correlation either with the silicon content of the catalysts or with the acidity measured by temperature-programmed desorption of ammonia. It is concluded that the incorporated silicon exists not only in a monomeric form and that the TPD of ammonia reflects not only the strong Brønsted acidity. The SAPO-5 sample synthesized with triethylamine possessed the strongest acidity corresponding to the highest catalytic activity. It is supposed that in the presence of TEA molecules silicon replaces mainly P atoms in the $AlPO_4$-5 framework.

The new generation of aluminophosphate-based microporous oxides ($AlPO_4$-*n*, SAPO-*n*) offers new possibilities for catalysis on molecular sieves. Mechanistically, the generation of SAPO molecular sieves may be considered in terms of silicon substitution in the corresponding $AlPO_4$ framework and consequently as a chemical modification of the aluminophosphates.[1] For SAPO-5 the atomic fraction of T-atoms occupied by silicon typically varies from 0·04 to 0·2 depending on synthesis conditions. However, in the literature some examples for atomic fractions of 0·5 and even 0·9 are also given, showing that the synthesis of true siliceous SAPO-5 is possible.[2,3]

Two substitution mechanisms are in discussion: the pair-wise substitution of two Si-atoms for one P and one Al atom as well as the occupation of phosphorus positions by silicon. Only through the latter mechanism one strong acidic center is

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generated per one silicon atom in the SAPO framework. Obviously, the mechanism of Si incorporation and the control of this process is of great importance for the appearance of catalytically active centers as well as the preparation of optimized catalysts.

Hence, we investigated the influence of the synthesis conditions on the acidic properties and the catalytic behaviour of some SAPO-5 molecular sieves. In particular, we synthesized one series of SAPO samples using the same template molecule (tripropylamine) altering the silicon content in the gel. In the second series, the chemical composition of the gel was constant and the template molecules were varied.

EXPERIMENTAL

The synthesis of $AlPO_4$-5 and of SAPO-5 were carried out according to ref.[4] with variation of the SiO_2/Al_2O_3 molar ratio between 0·42 and 0·93. For the synthesis of the second series of SAPO-5 four different template molecules were used (tripropylamine (TPA), triethylamine (TEA), tetrapropylamine hydroxide (TPAOH), diethylaminoethanol (DEAE)). The SiO_2/Al_2O_3 molar ratio was constant and corresponded to 0·42 and the molar content of the templates related to Al_2O_3 was always approximately two. Details are given in Table I.

The physico-chemical properties of the samples have been investigated by chemical analysis, X-ray difraction, IR spectroscopy, TPD of ammonia and adsorption of n-hexane. The TPD of

TABLE I

Chemical composition of gel and solid phase

Sample	Template molecule[a]	Chemical analysis (molar fraction)			
		SiO_2/Al_2O_3 (gel)	Al_2O_3	P_2O_5 (solid)	SiO_2
AP	TPA	0	0·54	0·46	0
SP 1	TPA	0·42	0·48	0·39	0·13
SP 2	TPA	0·66	0·44	0·34	0·22
SP 3	TPA	0·86	0·41	0·33	0·26
SP 4	TPA	0·98	0·48	0·39	0·13
SP 1·1	TPA	0·42	0·48	0·39	0·13
SP 1·2	TEA	0·43	0·46	0·41	0·13
SP 1·3	TPAOH	0·42	0·53	0·32	0·14
SP 1·4	DEAE	0·42	0·46	0·38	0·17

[a] TPA tripropylamine; TEA triethylamine; TPAOH tetrapropylamine hydroxide; DEAE diethylaminoethanol.

ammonia were measured in a standard apparatus with a heating rate of 10 K per min. Before TPD, the samples (200 mg) were loaded with ammonia in a helium stream (1 ml/s) at 393 K. The IR spectra were obtained in diffuse reflection at 423 K. The resolution of the spectrometer used (IRF 180) was 4 cm^{-1}. The adsorption measurements were carried our using a McBain balance at 293 K after outgassing of the samples (250 mg) at 670 K for 5 h in a high vacuum.

The toluene disproportionation was performed in a continuous flow reactor[5] at 723 K. The WHSV was 1/h and the N_2/toluene molar ratio corresponded to 10 and the H_2/toluene molar ratio to 2·5 and 10.

RESULTS AND DISCUSSION

Table I presents the results of the chemical analysis of the samples synthesized as well as the molar ratio of silica/alumina of the starting gel. (The molar ratio Al_2O_3/ /P_2O_5 in the gel was constant for all SAPO-5 samples and corresponded to one.) As can be seen from Table I a significant variation of silicon content (with the same template molecule) resulted only in a small increase of silicon content in the solid product (samples SP 1 to SP 4). Comparing the amount of silicon in the samples synthesized with different template molecules (at constant silica concentration in the gel) it can be stated that the nature of the template molecules has only a small influence on the incorporation of Si into the framework.

According to DTA data the samples are stable up to a temperature of more than 1 300 K. Results of the X-ray and IR investigations of the framework confirm a good crystallinity and a high phase purity.

Figure 1 and Table II present the results of the n-hexane adsorption measurements. In Fig. 1 selected isotherms are depicted which demonstrate the influence of the templating agent on the texture of the samples. Whereas all samples synthesized with TPA are characterized by a well established hysteresis loop, which is associated with capillary condensation in the mesopores, the n-hexane isotherm of the sample SP 1·2 shows no hysteresis loop and, consequently, possesses no mesopore system. This is demonstrated in Table II. In columns two and three are given the pore volumes of the micro- and mesopores, respectively. They were calculated according to the Dubinin equation for biporous adsorbents.[6] Some effect of the gel composition (with the same template molecule) on the mesopore volume and the pore size distribution (sample SP 2) as well as on the crystal size can be derived.

The comparatively small micropore volume of all samples (of about 0·08 to 0·09 cm^3/g, compared with a calculated volume of 0·147 cm^3/g of the ideal crystal[7]) are in disagreement with the results of the X-ray and IR measurements which prove a good crystallinity. We found this contradiction also for other one dimensional molecular sieves.[8] It can be associated with obstacles in the pores caused by crystallographic irregularities and/or amorphous residues of the synthesis in the pores. Hence, not the complete pore volume of the crystal is accessible to adsorbing molecules.

The acidic properties of the SAPO-5 samples determined by IR spectroscopy in diffuse reflection and TPD of ammonia measurements are presented in Figs 2 and 3. From the IR spectra it can be seen that (comparing the spectra of $AlPO_4$-5

TABLE II

Pore volumes of the SAPO-5 samples

Sample	Hexane adsorption capacity[a], cm^3/g micropores	Hexane adsorption capacity[a], cm^3/g mesopores	Crystal size, μm
AP	0·089	0·05	70–80
SP 1	0·093	0·065	15–20
SP 2	0·073	0·12[b]	5–7
SP 3	0·089	0·07	20–25
SP 4	0·088	0·06	30–40
SP 1·1	0·093	0·065	15–20
SP 1·2	0·080	0	8–10

[a] According to the Dubinin equation for biporous adsorbents[6]; [b] mesopores with two different pore sizes.

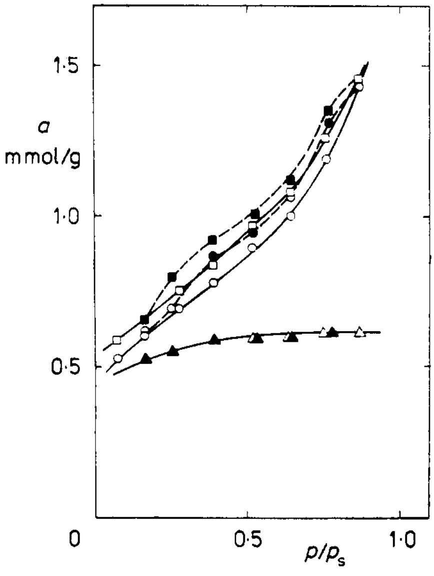

FIG. 1

Selected isotherms of the n-hexane adsorption at 293 K: *a* Adsorbed amount, mmol . g^{-1}, p/p_s relative pressure; full symbols desorption □ SP 1·1, △ SP 1·2, ○ SP 1·3 and SAPO-5) the incorporation of Si into the aluminophosphate lattice results in the appearance of bands at 3 530 and 3 620 cm^{-1} which are attributed to SiOHAl groups[9,10], i.e. to Brønsted sites. These bands are most pronounced for the sample 1·2, indicating a comparatively high concentration of bridged hydroxyl groups. They are less pronounced but comparable to each other in intensity for the sample SP 1 to SP 4. We have to conclude that the concentration of the Brønsted sites in

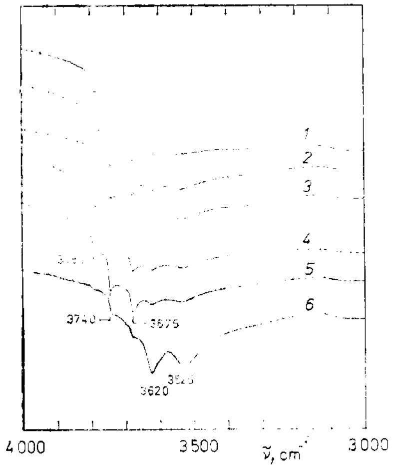

FIG. 2

IR spectra of SAPO-5 samples in diffuse reflection: *1* AP, *2* SP 1·1, *3* SP 2, *4* SP 3, *5* SP 4, *6* SP 1·2

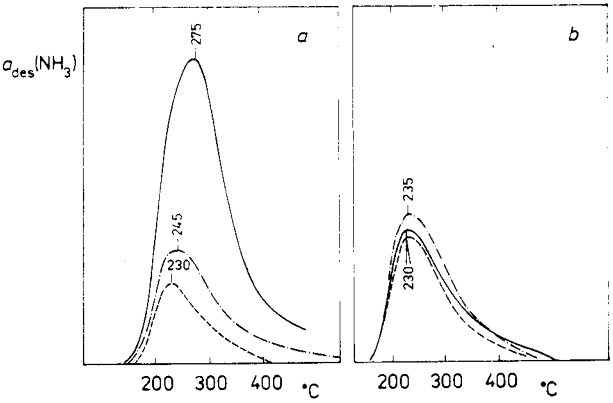

FIG. 3

TPD profiles after adsorption of ammonia at 393 K on SAPO-5 samples. The amount of desorbed NH_3 in arbitrary units. *a* SP 1·2 (———), SP 4 (-·-·-·-), AP (— — —); *b* SP 1·1 (———), SP 2 (-·-·-·-), SP 3 (— — —)

these synthesis products is nearly the same. As was to be expected for $AlPO_4$-5 (AP) no bands of strong acidic sites are found. The most distinct band of this sample at 3 675 cm^{-1} can be attributed to the less acidic POH groups.[9,10] For the SAPO-5 samples, a further terminal hydroxyl group (SiOH) was estimated at 3 740 cm^{-1}. The band at 3 785 cm^{-1} is related to AlOH groups.[9,10]

The findings from the ammonia TPD (Fig. 3) are in good agreement to the infrared spectroscopic results. The TPD profile of sample SP 1·2 distinctly differs from all the other SAPO's in concentration of the acidic sites as well as in the position of the profile maximum. Thus the desorption maximum of SP 1·2 is found at 275°C, including a shoulder at 400°C, while that of the other molecular sieves investigated is located between 230 and 245°C, indicating a less acidic character of the samples.

A distinction and a quantitative ascertainment of the number of strong and weak acidic sites, using the given TPD data, is not possible. The correct number of Brønsted sites (strong acid sites) is of high interest, due to the fact, that it corresponds to the number of isolated silicon atoms in the $AlPO_4$-5 framework. Quantitative data can be derived from calorimetric measurement of the ammonia chemisorption.

Calorimetric curves of the ammonia adsorption on an $AlPO_4$-5 and on SAPO-5 molecular sieve are presented for illustration in Fig. 4. It follows that the introduction of Si into the $AlPO_4$-5 lattice results in the formation of strong acidic sites represented by a high heat of adsorption compared with that of $AlPO_4$-5. With increasing adsorbed amount of ammonia the latter curve remains nearly constant at 50 kJ/mol. This heat of adsorption is due to the physisorptive interaction of ammonia with an uncharged $AlPO_4$-5 surface which has been found[11] for $AlPO_4$-17. Only at the beginning of the curve (at $a < 0{\cdot}2$ mmol/g) the heat seems to be increased owing to a small amount of chemisorbed ammonia molecules interacting with POH groups which is in agreement with the TPD results (see Table IV, last column). The heat curve of ammonia adsorbed on SAPO-5 seems to be similar to

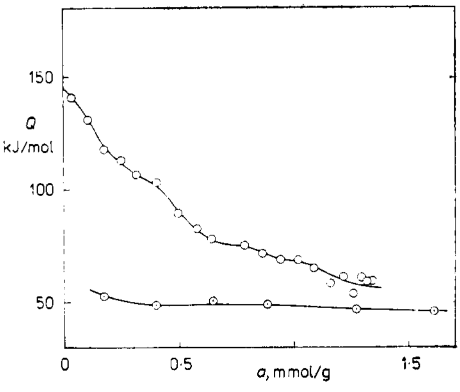

FIG. 4

Differential molar heat of adsorption of ammonia on SAPO-5 (○) and $AlPO_4$-5 (⊙) samples those found on zeolites.[12] It is characterized by more or less pronounced steps which may be associated with the interaction of ammonia with strong and weak acidic sites. It could be demonstrated[12] that the heat of ammonia adsorption higher than 80 kJ/mol is connected with the interaction of the base molecule with strong

TABLE III

Comparison of the acid strength and the OH valence stretching frequencies of some zeolites and SAPO molecular sieves

Sample	Q_0[a] kJ/mol (at $T = 423$ K)	$\tilde{\nu}$(OH) cm^{-1}	
ZSM-5	150–140	3 275[b]	3 610[c]
Mordenite	150–140	—	3 610
SAPO-34	145–135	3 610	3 627
SAPO-5	145–135	3 520	3 625
SAPO-17	130	—	3 625
HY	125	3 548	3 644

[a] Typical initial heat of ammonia chemisorption, from calorimetric measurements[12]; [b] low frequence band; [c] high frequence band.

TABLE IV

Catalytic properties of SAPO-5 samples

Sample	Toluene disproportionation at 723 K				TPD	
	N_2/toluene[a]		H_2/toluene[b]		temperature maximum	concentration of NH_3
	A[c]	S[d]	A[c]	S[d]	K	mmol/g
AP	0·9	—	0·3	—	503	0·16
SP 1	3·6	90	2·5	88	503	0·22
SP 2	8·7	88	5·1	90	508	0·22
SP 3	2·9	100	2·8	100	503	0·20
SP 4	11·1	87	5·7	94	518	0·20
SP 1·1	3·6	90	2·5	88	503	0·22
SP 1·2	18·2	85	10·2	88	548	0·61

[a] N_2/toluene = 10/1 (mol/mol); [b] H_2/toluene = 10/1 (mol/mol). [c] Activity (mole %); [d] selectivity (%) related to benzene and xylenes.

acidic sites. In this way the number of Brønsted acid sites can be estimated by calorimetric measurements.

The initial heats of chemisorption on SAPO-5 and other SAPO types as well as typical zeolite catalysts are compiled in Table III. It follows that the acid strength of SAPO-5 is lower than those of ZSM-5 and mordenite but higher than HY. Furthermore, it is seen that the acid strength of SAPO-5 is comparable with SAPO-34 and SAPO-17. The given order of the strength of the acid sites is in agreement with data from literature.[10,13,14] This correlation is in a good agreement with the relation of the high-frequency bands of the Brønsted acidic sites from IR experiments (fourth column in Table III). The high-frequency bands of SAPO-5 are between the zeolites mentioned above and comparable to SAPO-34 and SAPO-17.

Summarizing the results of the investigation of the acidic properties it can be concluded that (i) silicon atoms are incorporated in the$AlPO_4$-5 framework and (ii) especially the sample SP 1·2 contains the highest number of acid sites. It is, therefore, to be expected that the samples synthesized should show a distinct catalytic activity in acid catalyzed reactions. Table IV presents the data on toluene disproportionation at 723 K in dependence on silica content of the gel (upper part) together with the concentration of chemisorbed ammonia molecules (from TPD measurements) and the peak maximum temperature. With increasing SiO_2 content in the gel the catalytic activity increase from SP 1 to SP 2. When the silicon content of the gel is further increasing (SP 3), the catalytic activity drops and increases again (SP 4). Comparing the catalytic activity with the total number of the acid sites, no correlation is found.

Considering the concentration of strong acid sites (higher than 400°C in the TPD profiles) in detail, it seems that the more catalytically active sample SP 4 includes a comparatively higher amount of strong acidic sites. If the concentration of the strong acid sites (near 400°C of the TPD profiles) is compared with the chemically

TABLE V

Catalytic properties of SAPO-5 samples, synthetized with different template molecules

Sample	Template molecule	Toluene disproportionation activity in mole % (H_2/toluene = 2·5/1)	
		after 0·5 h	after 2 h
SP 1·1	TPA	4	4
SP 1·2	TEA	35	15
SP 1·3	TPAOH	16·7	9·3
SP 1·4	DEAE	18	10·3

determined silicon content of the samples (Table I), no correlation is found. We have, therefore, to conclude that (i) not all of the silicon atoms incorporated in the $AlPO_4$-5 framework exist in a monomeric form and (ii) that the TPD results represent not only the strong Brønsted sites but also weaker acidic centers which do not contribute to SAPO activity in toluene disproportionation. In the second part of Table IV the results of the toluene disproportionation on the SAPO-5 samples SP 1·1 and SP 1·2 (synthesized with different template agents) are listed. As can be seen from Table I, the nature of the template has only a small influence on the total Si content in the molecular sieve crystals. However, the catalytic activity of the sample SP 1·2 is much higher than that of SP 1·1. This is in agreement with the concentration of the strong acid sites of the sample SP 1·2 (derived from TPD and IR spectroscopic measurements).

Further results of toluene disproportionation on SP 1·3 and SP 1·4 confirm the outstanding activity of SAPO-5 synthesized with triethylamine, as follows from Table V. The sample SP 1·1 has the lowest activity (but it is constant over the time on stream), sample SP 1·2 has the highest activity and the catalysts SP 1·3 and 1·4 are of medium activity. However, for the sample with the highest activity, the highest deactivation rate is found.

Summarizing the results of the chemical analysis, the acidic properties and the catalytic behaviour of the two series of molecular sieves, some conclusions about the mechanism of the silicon substitution in a $AlPO_4$-5 lattice can be suggested. Silicon replaces mainly P in the presence of TEA molecules which accounts for the highest acidity of the samples and consequently for the highest catalytic activity. The synthesis using TPA molecules results in samples where silicon mainly replaces Al and P. Obviously, the conditions of the synthesis and especially the nature of the template molecule influence the equilibrium between the substitution mechanism under discussion in a complex way.

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