THE TEMPLATING ROLE OF CYCLOHEXYLAMINE IN THE SYNTHESIS OF MICROPOROUS ALUMINOPHOSPHATES*

Heide-Lore ZUBOWA, Rolf FRICKE, Hendrik KOSSLICK, F. NEISSENDORFER
and E. SCHREIER

Central Institute of Physical Chemistry, D(0)-1199 Berlin-Adlershof, Germany

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The investigation of the synthesis of $AlPO_4$ molecular sieves from orthophosphoric acid and pseudoboehmite in the presence of cyclohexylamine shows that in this case the amine plays the role of a template in the sense of "Template theory". The geometric shape of the template determines the dimensions of the channels within the $AlPO_4$-lattices. The amount of template in the gel influences the void volumes, leading to different structures, however, with similar dimensions. The product composition is largely determined by the ratio amine/(Al, P)O_2. The molecular sieves have been characterized by IR, X-ray, TG and DTA measurements.

The aluminophosphate molecular sieves represent a new class of microporous solids with an unusual structural diversity. Hopeful expectations are pinned on their application in new type catalysts and adsorbents. The formation of these structures requires the addition of organic substances, the so-called templates, to the synthesis gel. For roughly 23 years organic quaternary ammonium species and amines have been employed as templating additives in both aluminosilicate and aluminophosphate molecular sieve synthesis. Two theories have been considered on the role of organic components in the synthesis.

The "template theory" explains the structure-directing effect of these organic species. It is supposed that the charge distribution on the template molecule depending on its size and geometric shape are the reason for structure-directing[1]. The crystalline aluminosilicate or aluminophosphate framework grows around the organic compound[1-6]. In a further theory the chemical effect of the organic compound on the starting solution (stabilizing, solubilizing, and clathrating properties) is assumed to be the crucial one for the crystallization of microporous molecular sieves[7-11]. The temperature and the SiO_2/Al_2O_3 ratio in the gel are of the same importance[1]. According to ref.[12], besides the structure-directing effect the organic compounds play an important role in the gel chemistry. So the pH value of the gel

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increased to the desirable range of 3·5 – 6·0 with the addition of organic bases. For microporous AlPO's only in this pH range successful crystallization is possible while the formation of aluminium phosphate dense phases is eliminated. Lok and others[1] propose that during the hydrothermal synthesis of molecular sieves, gel chemistry as well as template are important. The template becomes active only in the environment of the right gel.

In this study the influence of cyclohexylamine and of its concentration is investigated to further elucidate the role of the template. The use of cyclohexylamine should be a suitable choice, because it fits well into the channels or cavities of a great number of $AlPO_4$ lattices.

EXPERIMENTAL

Materials

The synthesis was carried out using the following composition of the gel: 11·5 g orthophosphoric acid (85 wt. %, R.G.) was diluted with 21·3 g distilled water, then 8·14 g pseudoboehmite (75 wt. % Al_2O_3) was added and the mixture was vigorously stirred until becoming homogeneous. Then, 14·6 g distilled water and cyclohexylamine (99 wt. %, Merck) were added and again stirred to obtain homogeneity. The amount of cyclohexylamine was varied from 2·48 g to 24·75 g. The resulting gel with the composition $x\,C_8H_{11}NH_2 : 1{\cdot}2\,Al_2O_3 : 1{\cdot}0\,P_2O_5 : 40\,H_2O$, where $x = 0{\cdot}5 - 5{\cdot}0$, was sealed in a teflon-lined stainless-steel autoclave and heated in an oven at 200 ± 2°C under autogeneous pressure for 24 h. After hydrothermal treatment the solid product was separated from the liquid phase, washed till neutral pH and dried in air at 130°C. The product was calcined in air at 600°C for 7 h in order to release the template.

Techniques

X-Ray powder diffraction patterns were made by the Bragg–Brentano diffractometer method using CuK_α radiation. The XRD patterns were recorded in the range $2{\cdot}2 \leqq \theta \leqq 20$. The IR spectra were obtained on a Specord M 85, Carl Zeiss, Jena. For structural investigations the samples were examined in the form of KBr discs with 0·7 mg sample in 800 mg KBr. For investigation of the OH-vibration spectra the samples were pressed in thin wafers (ca 7 mg/cm^2), placed in a vacuum IR cell and heated 1 h at 400°C. The thermogravimetric analysis (TG) and the differential thermal analysis (DTA) were carried out with a MOM Derivatograph (Budapest) in air and nitrogen using alumina sample holders. The heating rate was 5 K/min, sample weight of 100 mg, α-Al_2O_3 was taken as reference sample.

RESULTS

Three distinct phases crystallize in the system under consideration each at a certain template/(Al, P)O_2 ratio, although only the concentration of the template is changed (Table I). Remarkably, the composition of the synthesis product changes not continously with the template content but stepwise. With respect to the crystallinity of the products there exist three optimum template (Al, P)O_2 ratios. Deviations from these optima lead to a decrease in the crystallinity of the main product and sometimes to the occurrence of by-products. With increasing template content of the gel more open structures $AlPO_4$-17, $AlPO_4$-5 and AlPO-hydrate (SAPO-34) crystallize.

Characterization of Synthesis Products

$AlPO_4$-17

$AlPO_4$-17 crystallizes in the form of well shaped needles. The dimensions of these crystals are 0·3 × 4 – 5 μm. The sample is extremely uniform in size and shape of crystals. In the XRD diagram (Fig. 1) only the reflexes of $AlPO_4$-17 appear. The sample exhibits a high crystallinity. The reflexes are narrow and a comparatively low background is observed.

These findings are reflected in the IR lattice vibration spectrum of $AlPO_4$-17 in the range between 400 and 1 300 cm^{-1}. The absorption bands are intensive, well resolved and narrow (Fig. 2). The structure-sensitive double-ring vibration band appearing between 500 and 630 cm^{-1} is splitted into separate bands arising at 520 and 580 cm^{-1} in the dehydrated state. Between 400 – 500 cm^{-1} the band of the TO_4 deformation vibration and between 1 050 – 1 300 cm^{-1} that of the asymmetric T–O–T stretching vibrations appear. In the lattice vibration spectra of common alumosilicate zeolites these absorption bands usually are broad and often unresolved. However, in the case of $AlPO_4$-17 under consideration both types of absorption bands are narrow and splitted into several well resolved components with distinct maxima. In addition, the intensity of the band of POH-vibration at 3 676 cm^{-1} is low (Fig. 3). This shows that only a low number of internal POH-groups is present.

The combined TG-DTA measurements (Fig. 4) show two weight losses at 285°C (endothermic) and above 385°C (exothermic) with a broad DTA peak (T_{max} = = 520°C). The first weight loss is assigned to the desorption of water from the gmelinite cage. The second is assigned to the template decomposition in the crystals followed by the successive release of oxidation products.

TABLE I
Effect of template concentration on product composition

Template content, %		Template/(Al, P)O_2 ratio	Molecular sieve
gel	mol. sieve		
27	18	0·45	$AlPO_4$-17 (erionite)
35	32	0·64	$AlPO_4$-5
40	45	0·82	SAPO-34 (chabazite)

$AlPO_4$-5

$AlPO_4$-5 crystallites have a size of about 5 – 6 μm, which build up ball-like agglomerates. The XRD diagram is identical with the structure type of $AlPO_4$-5. In comparison with the XRD diagram of $AlPO_4$-17, the background is twice as high, which refers to a lower crystallinity of the synthesized $AlPO_4$-5 molecular sieve (Fig. 1*b*). This finding is supported by the IR lattice vibration spectrum (Fig. 2). The absorption bands are broader and not structured. In the range of the structure-sensitive double-ring absorptions a single absorption at 564 cm^{-1} of medium-

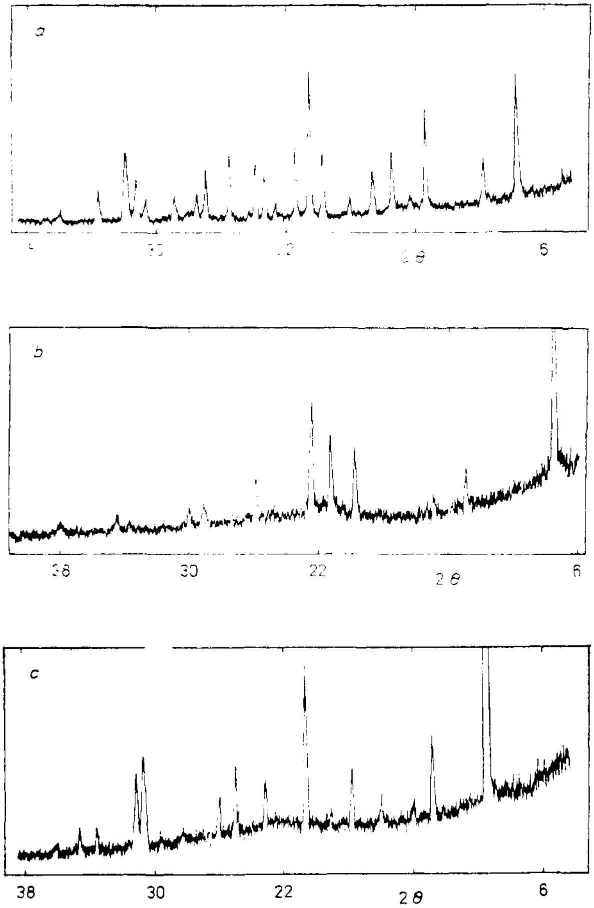

FIG. 1
XRD pattern of *a* $AlPO_4$-17, *b* $AlPO_4$-5, *c* $AlPO_4$-34

intensity is observed. The combined TG-DTA measurements show the desorption of water and template to occur together at T_{max} = 120°C. First, starting at 60°C water is desorbed very rapidly, followed by the desorption of the template with increasing temperature, starting at about 120°C. Both water and the template are loosely bonded so that the final desorption of water and the onset of template desorption could not be resolved in the TG curve. However, the DTA curve shows an endothermic peak with a maximum temperature of 120°C. Then, with further increase in temperature the desorption process becomes less endothermic due to desorption of template.

SAPO-34

At very high template content in the gel the crystallization of an $AlPO_4$/SAPO-hydrate of unknown structure is observed. This hydrate form is transformed into SAPO-34 in the presence of silicon after thermal treatment above 300°C. This is evidenced by the XRD diagram (Fig. 1c). The obtained cubic crystals are twinned and have a uniform size of 60 – 70 μm. Although the obtained SAPO-34 crystals

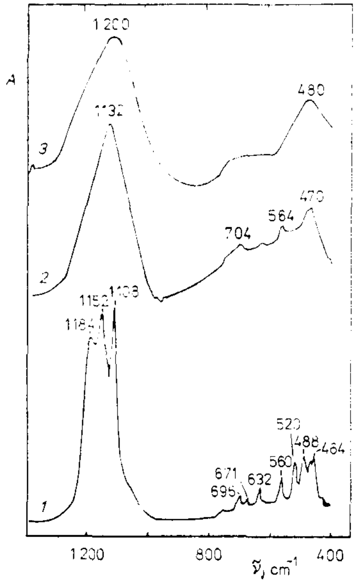

FIG. 2

Infrared lattice vibration spectra of $AlPO_4$ molecular sieves activated for 7 h at 600°C: *1* $AlPO_4$-17, *2* $AlPO_4$-5, *3* SAPO-34

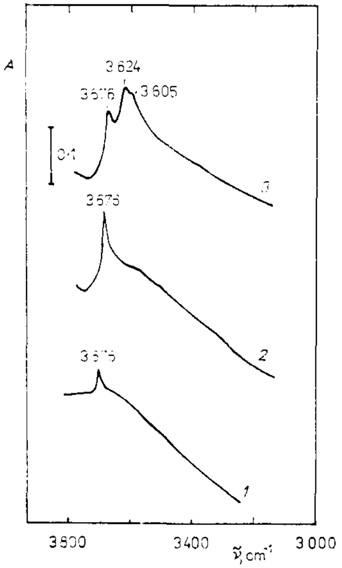

FIG. 3

Infrared spectra of the hydroxyl region of $AlPO_4$ molecular sieves activated for 7 h at 600°C: *1* $AlPO_4$-17, *2* $AlPO_4$-5, *3* SAPO-34 are well-shaped and very large, only very broad unresolved absorption bands are observed in the IR lattice vibration spectrum which refers to a high degree of lattice disorder.

The double-ring vibration band is not resolved, however, a broad absorption covering this spectral range is present. The disorder of the structure is reflected in the XRD diagram as an increased background. In the OH-vibration spectrum (Fig. 3) besides absorption bands of bridging hydroxyl groups at 3 624 and 3 605 cm^{-1} a strong absorption at 3 670 cm^{-1} is observed. The latter is assigned to terminal POH-groups. In comparison to the intensities of the absorption bands of bridging hydroxyls, the intensity of POH vibration bands is very high. Apparently, the SAPO-34 crystals contain a great amount of internal POH-groups. That means that this type of SAPO-34 contains a lot of lattice defects. This supports the above drawn conclusion on the high degree of disorder in the sample.

DISCUSSION

Although the structures of crystallized $AlPO_4$ types differ considerably, there are close similarities among the diameters of their channels and cavities as well as with the kinetic diameter of cyclohexylamine (ca 6 Å). Therefore, in this case a templating role of cyclohexylamine is concluded. The observed templating effect is assumed to be achieved by a dense stacking of the molecules along the 6-fold axis. Such a packing reduces the active hydrophobic surface of the template and allows the crystallization of $AlPO_4$ around the formed "cylindrical" template units. This

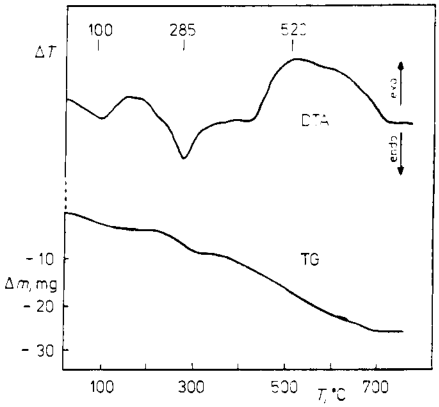

FIG. 4

DTA (top) and TG pattern of as-synthesized AlPO-17 in air (sample weight; 100 mg) hypothesis is confirmed by the observed dense packing of cyclohexylamine in the synthesized $AlPO_4$-17.

In our case the type of structure that crystallizes, i.e. erionite, chabazite, $AlPO_4$-5, depends only on the template/$(Al,P)O_2$ ratio of the gel. The latter corresponds close to the composition of the as-synthesized molecular sieve. With increasing amount of template in the gel structures containing greater void volumes build up (Table II).

If the template fits well into the channels or cavities, the crystallinity of the synthesis product is increased considerably. Obviously this is the case of $AlPO_4$-17. The dense stacking of cyclohexylamine molecules results in an increased density of the template in the molecular sieve with respect to the liquid state: e.g. 1·5 g/cm^3 for $AlPO_4$-17 in comparison to 0·87 g/cm^3 in the liquid state. If the fit is less established, the crystallinity of the synthesis product is decreased. So $AlPO_4$-5 contains pores of about 7 – 8 Å diameter, i.e. they are distinctly larger than the diameter of the cyclohexylamine molecule. The gap between the template volume and the pore volume is filled with water, which is present in a great amount. The water to template ratio is about 1 : 1. This value is in good agreement with the ratio of the template volume to the remaining free volume of $AlPO_4$-5 channels.

In our opinion these results support the idea of a steric templating role of organics in the synthesis of new type molecular sieves. However, the templating role cannot be reduced to a correspondence of the shape of the template molecules and the pores and channels of the molecular sieve. Even the amount of template in the gel determines the obtained structure type: high template content leads to structures with great void volumes. The templating role is also supported by the observed influence of the fit of molecules to the channels/pores on the crystallinity of the synthesis product.

It is surprising that the crystallinity of the prepared SAPO-34 is low although the obtained crystals are well-shaped and relatively large (60 – 70 μm). This may be caused by the fact that SAPO-34 is not crystallized from the synthesis gel. This

TABLE II
Properties of the molecular sieves

Molecular sieve	Windows (dimension) Å	Diameter of the cavity Å	Void volume per unit cell %
$AlPO_4$-17	08R/3·5 × 5·2	6·3 × 6·6	21·5
$AlPO_4$-5	012R/7 – 8	7 – 8	33·0
$AlPO_4$-34	08R/4·89 × 5·58	6·5	44·2

SAPO-34 is the product of a solid state transformation after thermal treatment of an $AlPO_4$ hydrate obtained after hydrothermal synthesis. From this point of view the high degree of disorder may be understood. The high intensity of the POH--vibration band shows the existence of a great amount of internal POH-groups, resulting from interrupted P—O—Al bridges in the framework.

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