$AlPO_4$ MOLECULAR SIEVES MODIFIED WITH METAL CHELATE COMPLEXES*

Stanisław KOWALAK[a] and Kenneth J. BALKUS, jr.[b]

[a] *A, Mickiewicz University, Faculty of Chemistry, 60-780 Poznań, Poland*
[b] *University of Texas at Dallas,*
Dept. of Chemistry, Richardson, Texas 75083-0688, U.S.A.

Received September 13, 1991
Accepted October 22, 1991

A new method for modification $AlPO_4$ molecular sieves has been presented. Lack of ion-exchange properties makes the modification of aluminium phosphates for catalytic applications difficult. We have developed a method that involves the crystallization of $AlPO_4$ moledular sieves around metal complexes. This results in encapsulation of the complexes within the intracrystalline pore system. Several metallophthalocyanines have been successfully encapsulated into $AlPO_4$-5 and subsequently tested as catalysts for cyclohexene oxidation. Significant differences in activity result from the presence of different metallophthalocyanines.

Despite a practically invariant chemical composition, the $AlPO_4$ family of molecular sieves is presently represented by several dozen crystalline structures. The intracrystalline pore systems of many $AlPO_4$ molecular sieves are expected to be shape selective. The lack of ion-exchange properties, however, makes the modification of $AlPO_4$ difficult, and therefore their application in catalysis is limited.

We have developed a new method for the encapsulation of metal complexes into molecular sieves[1]. This involves the crystallization of a molecular sieve structure around complex molecules. Using this technique we can introduce relatively large molecules (e.g. metallophthalocyanines) into the intracrystalline pore system. Otherwise, such molecules would not be able to diffuse inside the crystallites.

Encapsulation of metal complexes into aluminosilicate molecular sieves (zeolites) is an interesting and promising method of modification[2,3]. In the case of $AlPO_4$ molecular sieves, where modification is much more complicated (e.g. substitution of the framework atoms) the encapsulation of metal complexes can be very competitive and may provide many new catalytic materials. The metal complex must be within the channel system in such a way that it can play the role of active site without a substantial reduction in diffusivity (Fig. 1).

---

* Presented as a poster at the *International Symposium "Zeolite Chemistry and Catalysis", Prague, September 8—13, 1991.*

The following study focuses on $AlPO_4$-5 molecular sieves modified with metallophthalocyanines (MPc). The well known catalytic activity and stability of MPc complexes makes them attractive candidates for encapsulation. Organic templates are generally employed in the crystallization process and their thermal removal can be harmful to less temperature resistant complexes. The MPc molecular diameter (ca 1·3 nm) is larger than the pore size of $AlPO_4$-5 (ca 0·7 nm) and these complexes cannot be adsorbed inside the crystallites. It is known, on the other hand, that the diameters of template molecules are sometimes larger than the size of the pore system in resulting molecular sieves[4]. Furthermore, the phthalocyanines may distort, reducing their effective diameter as is proposed for X and Y zeolite encapsulated complexes.

EXPERIMENTAL

Equimolar portions of diluted H_3PO_4 and fresh $Al(OH)_3$ prepared by hydrolysis of aluminum sopropoxide (Aldrich) were the principal substrates. Tripropylamine (TPA) and dipropylamine (DPA) both from Aldrich were used as templates for crystallization of $AlPO_4$-5 and $AlPO_4$-11, respectively. Metallophthalocyanines Li(I), Cu(II), Fe(II), Co(II), Ni(II), Mn(II) were purchased from Strem Chemicals. The molar proportions of the crystallization mixture was following: $Al_2PO_3 : P_2O_5 : \text{amine} : H_2O = 1 : 1 : 1 : 40$. The amount of MPc made ca 3 wt. % of $AlPO_4$.

H_3PO_4 was slurried with $Al(OH)_3$ and the mixture was aged at ambient conditions for one hour. During this time an amorphous $AlPO_4$ precursor was formed. The value of pH rose from ca 1 to 2·5. Then template and MPc were added and stirred at room temperature for an additional hour. After addition of the amine the pH increased to ca 4·5. Afterwards the gel was transferred to an autoclave and crystallized at 150°C for 24 h. The pH of the post-reaction mixture was ca 7. The product was washed with water, centrifuged and dried at 100°C. Some samples were Soxhlet-extracted with pyridine for several days in order to remove the excess of MPc which was not encapsulated. The extraction was only partially effective at removing surface species while better results were achieved by thermal evacuation in a sublimation apparatus (530°C, vacuum ca 10 Pa, 24 h) during which the template decomposed. The prepared samples have been characterized by means of XRD (Scintag XDS 2000), FT-IR (Nicolet 5DX), UV-VIS (Varian Cary). Elemental analysis was provided by Galbraith Laboratories. Selected samples were examined by thermogravimetric analysis (MON OD 102).

The $AlPO_4$ samples were screened as catalysts for the partial oxidation of cyclohexene with O_2. The reaction was carried out in a glass pressure reactor. Cyclohexene was purified on an

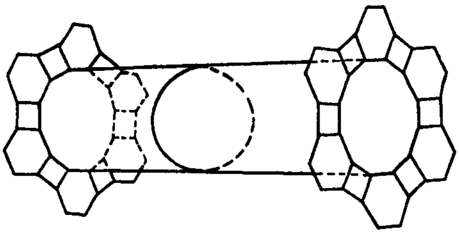

FIG. 1

Model of encapsulated metallophthalocyanine in the channel system of $AlPO_4$-5 alumina column to remove peroxides. Powder catalyst (50 mg) and 2 ml of cyclohexene were placed into the reactor, which was pressurized with oxygen (214 kPa). The reactants were stirred at 55°C for 24 h. The liquid products were analyzed by gas chromatography, using 2 m Carbowax column at 100°C.

RESULTS AND DISCUSSION

The procedure described above produced molecular sieves with the $AlPO_4$-5 structure. Depending on the amine applied as a template different structures can be obtained.

As follows from Fig. 2 the mid-IR spectra of the molecular sieves show bands around 1 120, 700 and 600 cm^{-1} characteristic for aluminum phosphate molecular sieve structures[4]. The TPA template directs the crystallization towards $AlPO_4$-5 (spectra *a*, *b*) whereas DPA results in the structure of $AlPO_4$-11 (spectrum *c*). Such structures were identified by X-ray powder diffraction[5]. The XRD patterns are presented in Figs 3*A* and 3*B*.

$AlPO_4$-5 containing encapsulated metallophthalocyanines display the same band in the IR spectra as are observed for neat molecular sieve crystals. However, XRD patterns for such samples show additional peaks indicating the presence of tridymite

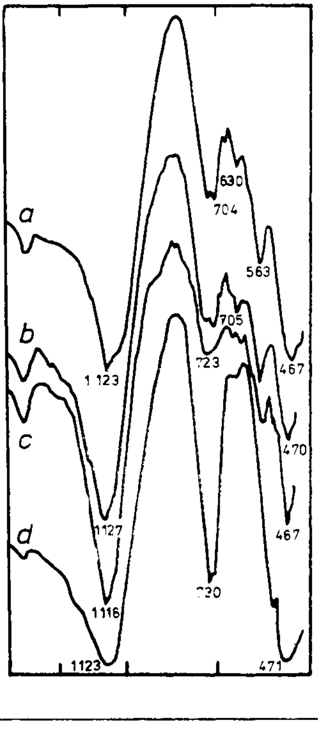

FIG. 2

IR spectra of the same samples as those in Fig. 3

(spectrum *a*). Tridymite is formed as the main product if MPc is added into the precursor gel as a pyridine solution (Fig. 2, spectrum *d*; Fig. 3*B*, spectrum *d*).

These facts suggest that MPc and its solvent affect the gel chemistry leading to the formation of condensed phase of $AlPO_4$. The nature of this interaction is not yet specified. The influence of various factors such as a type of metal, solvent, amount of water, aging procedure on crystallization of molecular sieve will be reported elsewhere[6].

In further experiments the MPc was not dissolved in a solvent prior to addition to the gel. We observed that some of MPc appears to dissolve in the amine (TPA) (e.g. FePc, MnPc) while others (e.g. LiPc) are only dispersed in the precursor gel by stirring. The solubility of complex does not seem to be an important consideration for encapsulation. However, the amount of MPc incorporated is higher in case of more amine-soluble complexes (Table I).

In all cases including CuPc–$AlPO_4$-11 a blue or blue-grey color did not change despite several days extraction with pyridine. It is rather unlikely that a molecule as large as CuPc could be encapsulated in 10-membered ring channel (0·65 × 0·35 nm size) of $AlPO_4$-11. This indicates that Soxhlet extraction was not satisfactory for removal of surface and extrachannel complexes. Therefore, samples were heated under a vacuum to sublime the complexes. Indeed, the CuPc–$AlPO_4$-11 sample after several hours treatment turned colourless. The sublimed MPc modified $AlPO_4$-5 samples are colored various shades of green. There is no indication of MPc com-

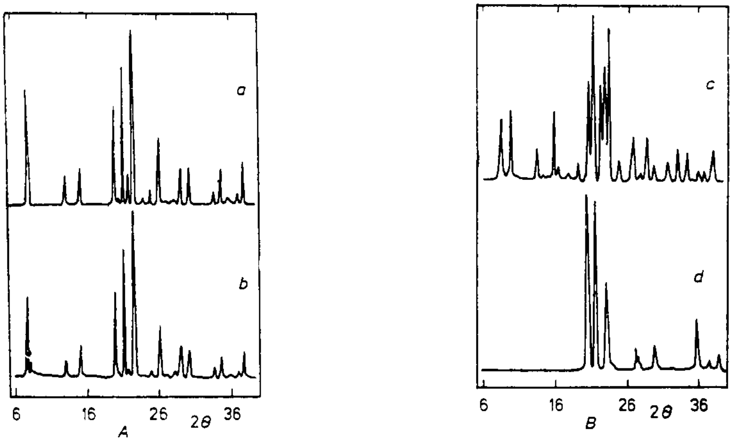

FIG. 3

XRD Patterns of selected samples. *A*: Sample NiPc–$AlPO_4$-5 (*a*); complex-free $AlPO_4$-5 (*b*). *B*: Sample CuPc–$AlPO_4$-11 (*c*); tridymite obtained by crystallization of mixture containing CuPc dissolved in pyridine (*d*) plexes decomposition during the crystallization or vacuum treatment. The intact metal complex can be recovered during extraction or sublimation. These changes can be consistent with a distortion of the phthalocyanine ring. The bathochromic effect associated with ring distortion was also observed in UV-VIS spectra of the solids.

The vacuum sublimation is accompanied by thermal decomposition of the template. This process is, however, less effective than the air calcination and some carbonaceous deposit remain in samples. Therefore, as seen in Table I, the carbon content is not quite consistent with the metal concentration to match the molar composition of the MPc. On the other hand, an air calcination cannot be applied to remove the template due to decomposition of MPc at lower temperatures than the amine. DTA curves in Fig. 4 show the exothermic effect at 580°C reflecting oxidation of the template and the next peak below 500°C resulting from the decomposition and oxidation of the MPc.

Since severe thermal treatment under a vacuum cannot remove all MPc molecules from $AlPO_4$-5 it is reasonable to assume that the location of the complex is inside the intracrystalline channel system. Considering the difference in size of the MPc (ca 1·3 nm) and the diameter (0·73 nm) of 12-membered ring channel, the molecules of encapsulated complex have to be severely distorted. It is likely that such distortion can affect stability of the complex itself or even that of molecular sieve structure. We have observed changes in the XRD pattern in period of several months after its preparation (unpublished results). If the size of complex molecule drastically exceeds

TABLE I

Samples of $AlPO_4$ molecular sieves modified with metallophthalocyanines

Sample	MPc (mg) per 1 g of $AlPO_4$	Wt. % after sublimation		Color	
		metal	carbon	before sublimation	after sublimation
$AlPO_4$-5	0·0	–	–	white	–
LiPc–$AlPO_4$-5	28·9	0·06	0·30	blue	dark green
CuPc-1–$AlPO_4$-5	10·0			blue	grey blue
CuPc-2–$AlPO_4$-5	33·0	0·08	0·94	blue	dark green
FePc–$AlPO_4$-5	33·0	0·25	1·97	grey blue	grey green
CoPc–$AlPO_4$-5	31·0	0·07	0·07	grey blue	green
NiPc–$AlPO_4$-5	22·5	0·05	0·60	grey blue	khaki
MnPc–$AlPO_4$-5	32·0	0·29	1·45	blue	grey green
CuPc–$AlPO_4$-11	23·0	0·0	–	blue	white

the pore diameter (i.e. $AlPO_4$-11) the MPc cannot be encapsulated into the channel structure.

The best evidence for encapsulation of a metal complex is modification of reactivity. The results of our preliminary catalytic tests are summarized in Table II.

The main products in the oxidation of cyclohexene were cyclohexenol, cyclohexenone and cyclohexene oxide.

Complex free $AlPO_4$-5 is practically inactive in this reaction. Taking into consideration the formula of a unit cell of $AlPO_4$-5 as $Al_{12}P_{12}O_{48}$ and the metal content from Table I, the highest and lowest loading is one complex per 130 and 780 unit

TABLE II
Results of catalytic cyclohexene oxidation

Catalyst	Cyclohexene conversion, %	Molar ratio of the products		
		cyclohexene oxide	cyclohexenone	cyclohexenol
CoPc	64	0·06	1·0	0·5
CoPc–$AlPO_4$-5	65	0·1	1·0	1·4
MnPc–$AlPO_4$-5	60	0·2	1·0	1·5
CuPc-2-$AlPO_4$-5	52	0·0	1·0	2·3
CuPc-1–$AlPO_4$-5	19	0·3	1·0	1·3
FePc–$AlPO_4$-5	16	0·3	1·0	1·0
NiPc–$AlPO_4$-5	5	0·3	1·0	1·2
LiPc–$AlPO_4$-5	4	0·2	1·0	1·2
$AlPO_4$-5	0·5	0·5	1·0	2·7

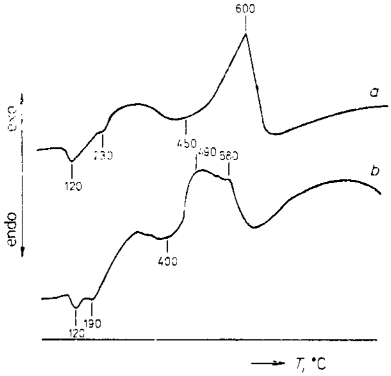

FIG. 4
Thermogravimetric curves (DTA) recorded in air for the complex-free $AlPO_4$-5 (*a*) and for sample CuPc-2–$AlPO_4$-5 (*b*)

cells, respectively. Even with such low loading the catalytic results clearly show the influence of encapsulated MPc on activity of modified molecular sieves. The CoPc containing $AlPO_4$-5 exhibits the highest activity among the samples studied. Eventhough the molecular sieve contains much less complex its activity is comparable with the free CoPc. Additionally the CoPc–$AlPO_4$-5 produces more epoxide and cyclohexenol compared to the free complex catalyzed reaction. Conversion and selectivity depends also on complex loading. The sample CuPc-2–$AlPO_4$-5 (of relatively high CuPc content) is more than twice as active as CuPc-1–$AlPO_4$-5 (of low CuPc loading).

In conclusion we want to emphasize that we have successfully modified $AlPO_4$-5 with metallophthalocyanines by encapsulation of metal complex during synthesis. Selective location of complex molecules can be attained by crystallization of the molecular sieve around the complex molecule. Various MPc complexes encapsulated into aluminum phosphates molecular sieves can act as catalysts, where activity of the modified samples depends on the type of metal. The thermal stability of MPc complexes allows removal of templates from prepared samples under a vacuum without decomposition of the complex. Air calcination of modified molecular sieves decomposes the metal complex and may result in well dispersed metal oxides within the channel system.

REFERENCES

1. Balkus K. J., Kowalak S.: U.S. UTSF; 030 (1990).
2. Tolman C. H., Herron N.: Catal. Today *3*, 235 (1988).
3. Kowalak S., Weiss R. C., Balkus K. J.: J. Chem. Soc., Chem. Commun. *1991*, 57.
4. Szostak R.: *Molecular Sieves, Principles of Synthesis and Identification*, p. 262. Van Nostrand, Reinhold, New York 1988.
5. Meier W. M., Olson D. H.: *Atlas of Zeolite Structure Types.* Butterworth, London 1987.
6. Balkus K. J., Bresinska I., Kowalak S.: Unpublished results.