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Effect of Ionic Conductivity in Aluminophosphates with Different Organic Structure Directing Templates

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The ionic conductivity has been measured for different organic templates in aluminophosphate gels. After crystallization of aluminophosphates under hydrothermal conditions, the conductivity exhibited by these materials arises from the migration of cations through the anion framework cages. The thermodynamic parameters have been evaluated.

Key Words: Ionic conductivity, Templates, Aluminophosphate gel.

INTRODUCTION

Organic amines play an important role in zeolite synthesis. Initially a templating theory[1] was developed to explain the structure-directing effect of these molecules, but it has recently been accepted that the gel chemistry is also important[2]. When such organic amines were added to aluminophosphate gels, that have chemical properties different from high pH aluminosilicate system required for zeolite synthesis, a series of crystalline microporous aluminophosphate structures were developed[3] after removal of organic amines. Wilson *et al.*[4] concluded that the organic amines had both steric and electronic effects. The electronic effects are exemplified by the fact that different amines differ only in the relative position of the amine groups resulting in the productionof quite different products.

EXPERIMENTAL

In the present work, the microporous aluminophosphates have been crystallized by hydrothermal method. The conditions used in the crystallization process are:

(1) Neutralization of the pseudobohemit (AlOOH) suspended in water with equimolar amount of dilute orthophosphoric acid (H_3PO_4) to obtain the reactive aluminophosphate gel.
(2) Aging of the reactive aluminophosphate gel.
(3) Addition of organic amines to the reactive aluminophosphate gel. This is

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referred to as precursor gel. The conductivity has been measured for different organic template (propylamine, butylamine, hexylamine, diethylamine, dipropylamine, dibutylamine, trimethylamine, triethylamine and tributylamine) in this precursor gel using conductivity cell as illustrated in Figure 1.

(4) Aging of the precursor gel, if necessary and finally.

(5) Closed hydrothermal treatment of the precursor gel.

The time required for crystallization is 24 h at 150°C. After the experimental run, the autoclaves were quenched initially using an air jet followed by water. The products were washed thoroughly using double distilled water and ultrasonicated to remove all the excess organic templates.

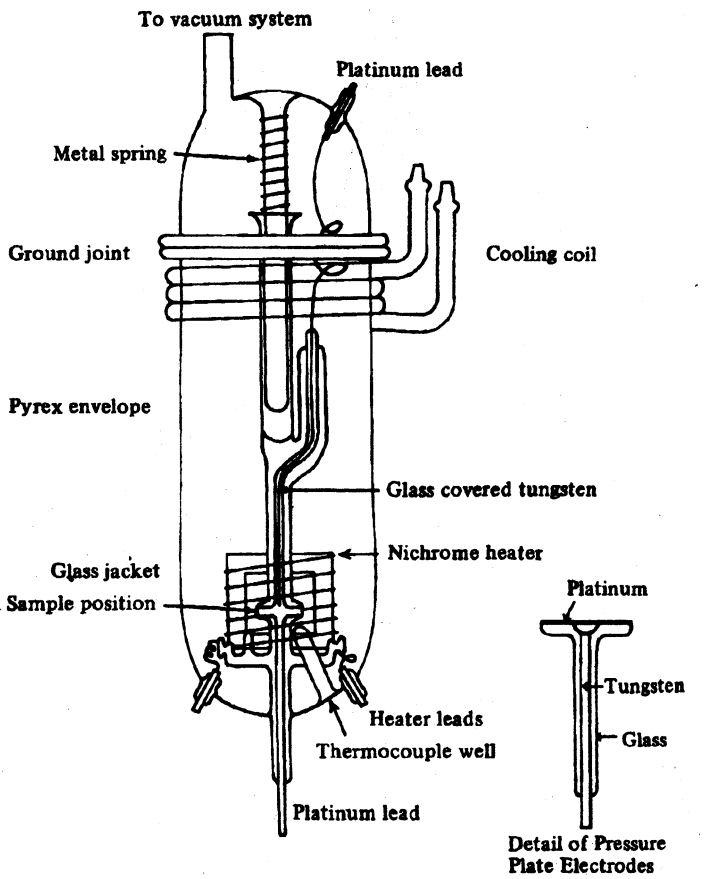

Fig. 1. Cell for measuring conductivity of compacted, zeolite powder specimens

The conductivity data were obtained for crystalline microporous aluminophosphates as a function of temperature at different concentration of organic templates. Typical conductivity data for crystalline aluminophosphates are given in Fig. 2 as Arrhenius plots, conductivity (σ) *vs.* 1/T. Conductivity of al-

uminophosphates as a function of Na^+ ion concentration for different amin groups is shown in Fig. 3. The typical conductivity data for different concentrations of aluminophosphate zeolite as a function of temperature at constant number of Na^+ ions were determined and activation energy ΔH is obtained from Arrhenius plots shown in Fig. 4(a–c) and the Table 1.

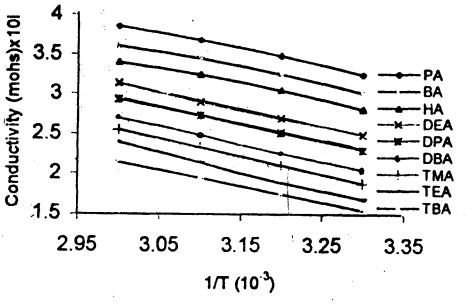

Fig. 2. Arrhenius plots for electrical conductivity of crystalline aluminophosphate

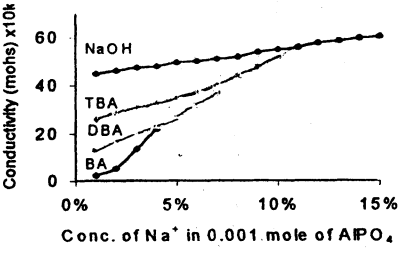

Fig. 3. Conductivity of crystalline aluminophosphate *vs.* concentration of different amine groups

TABLE-1
ACTIVATION ENERGY OF ALUMINOPHOSPHATE WITH PRIMARY (BUTYL AMINE), SECONDARY (DIBUTYL AMINE) AND TERTIARY (TRIBUTYL AMINE) AMINO GROUPS

Conc. of $AlPO_4$	ΔH-BA	ΔH-DBA	ΔH-TBA
0.05	45.1585	52.0226	182.4419
0.10	45.1772	52.2096	182.4485
0.15	45.2215	52.6526	182.4658
0.20	45.2798	53.1452	182.4801
0.25	45.3325	53.3621	182.4856
0.30	45.3478	53.3715	182.4878

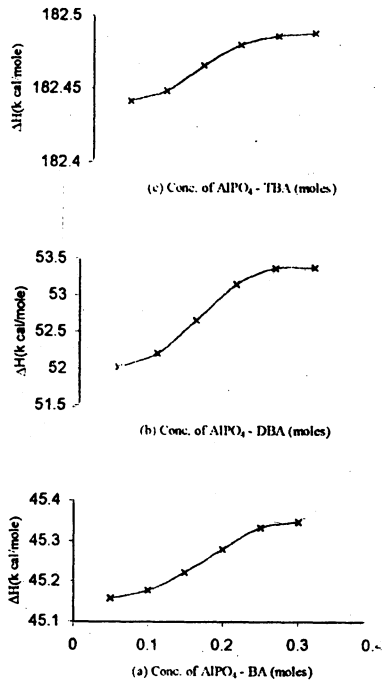

Fig. 4. (a-c). Variation of the activation energy of aluminophosphate with primary, secondary and tertiary amino groups

RESULTS AND DISCUSSION

The ionic conductivity of aluminophosphate gels with different organic templates shows decrease in conductivity in the order of tertiary amine < secondary amine < primary amines. Further, hydrothermal treatment of aluminophosphate at 150°C for the duration of 24 h, the conductivity of crystalline aluminophosphate zeolites shows the same trend as in gels. The change in conductivity is due to the occlusion of different amines in the pores of aluminophosphate structures, and it is observed that lower conductance for tertiary amines, compared to secondary and primary amines, is because of larger size of tertiary amines which experience more hindrance for their movements. This may indicate that the pore size of aluminophosphates with tertiary amines is larger than secondary and primary amines.

The elimination of the amines from the pores of aluminophosphate structures by calcinations at about 400°C results in microporous aluminophosphates with different pore sizes. The conductivity of microporous aluminophosphates that was obtained from tertiary amines, at different concentrations of Na^+, shows high conductance as compared to the microporous aluminophosphates that was obtained from secondary and primary amines. This gives the evidence for obtaining large pore sizes in aluminophosphate structures by using tertiary amines

as templates or structure directing agents. Also, the increase of concentration of Na^+ ions increases the conductance and it reaches a constant value as the pores in the aluminophosphate structures are completely occupied by na^+ ions.

The ionic conductivity at different temperatures for microporous aluminophosphates increases the conductance. From this activation energy, ΔH is calculated. The value of energy of activation, ΔH indicates that the microporous aluminophosphate structures obtained from primary amines is less than the secondary amines which is also less than the tertiary amines. This shows that, the latter one, *i.e.*, tertiary amine is larger and more bulky as compared to the former amines (secondary and primary amines). This is the clear evidence for the fact that the formation of larger pores in aluminophosphate structures is due to tertiary amines which were used as structure building units; and hence, greater the energy of activation.

The energy of activation ΔH increases rapidly for microporous aluminophosphates obtained from different amino groups (primary, secondary and tertiary amino groups). Further, the increase of concentration of microporous aluminophosphates increases the number of pores, resulting in the decrease of cation density, which is a characteristic of more strongly bonded cation.

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