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Synthesis of aluminophosphate by the ionothermal method using factorial design

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ABSTRACT

This work addresses the ionothermal synthesis of aluminophosphates with magnesium incorporation in order to generate ion exchange sites. The deep eutectic mixture of urea and choline chloride acts as the solvent and template. A central composite design was used to systematically study the effects of some synthesis parameters on types of aluminophosphates and their ion exchange capacity. XRD analysis revealed that condensed AlPO-CJ2, AEL, AEN, and GIS topologies were formed. Mg incorporation was confirmed by thermogravimetric analysis and ion exchange experiments. The statistical analysis showed that the percentage of eutectic mixture in the gel was the main variable affecting the ion exchange capacity, followed by the crystallization time and the percentage of Mg in the gel. The percentage of choline chloride in the eutectic mixture did not have an influence on the ion exchange properties.

1. Introduction

The diversity of applications for molecular sieves, usually obtained via hydrothermal syntheses, indicates that the development of new routes and techniques to obtain new zeolitic and zeotype structures is imperative. In this context, the use of new solvents and templates has been intensively investigated [1].

Recently, ionothermal synthesis using ionic liquids and deep eutectic mixtures has been studied to prepare new zeotypes. These liquids and eutectic mixtures are formed by fused salts (generally formed using organic cations and inorganic anions) at close to ambient temperatures and they can act either as solvents or templates during the synthesis of molecular sieves [2,3]. Although ionothermal synthesis is a potential technique to prepare microporous materials, such as aluminophosphates (AlPOs) [4–13], the role of the several synthesis parameters in the structure and properties of the zeotype must be well understood.

Aluminophosphates have neutral charge which limits their application, hence other metals are generally incorporated into their framework in order to generate charges which will provide ionic exchange capacity and catalytic properties [14,15].

Some years ago, the new aluminophosphate SIZ-2 (St. Andrews Ionic liquid Zeotype 2) was prepared by using the eutectic mixture choline chloride/urea. Despite the neutral charge of the aluminophosphates, this zeotype showed an interesting ionic exchange property which was attributed to its interrupted structure whose defects were responsible for the cation exchange sites [2]. One strategy to enhance the ion exchange capacity would be the incorporation of a metal ion like magnesium into the framework of SIZ-2 aluminophosphate.

In a previous work published by our group it was shown that the ion exchange capacity of the interrupted structure of SIZ-2 could be optimized by varying the synthesis conditions. For the best synthesis conditions, the ion exchange capacity towards Cu^{2+} sorption was 0.0801 g Cu^{2+} per gram of AlPO. This ion exchange capacity is a bit lower than those obtained using polymeric resins (0.1188 g Cu^{2+} per gram of resin) [13].

The development of new methods for aluminophosphate synthesis involves a large number of variables, thus demanding a conscious experimental work. In this sense, the factorial experimental design is an important tool that can be used to minimize the experimental labor and to determine the optimum synthesis condition in order to obtain the material with the desired property [16,17].

Among the experimental designs, the central composite factorial design is a modified two-level factorial design with central and axial points that provide excellent predictability, requiring fewer experiments than other three-level designs with the same number of factors [18]. In central composite factorial designs, the low, center, and high levels of each variable are assigned as −1, 0, and +1, respectively. Additionally, two axial points also must be provided. For example, for four-factor designs, the axial points are −2 and +2 [18]. In all cases, each level of the independent variables is coded according to the equation:

$$X_i = \frac{\xi_i - \xi_o}{\xi_1 - \xi_o} \quad (1)$$

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where x_i is the dimensionless coded value of the independent variable i, ξ_i is the uncoded value of i, ξ_0 is the uncoded value of the variable at the center point, and ξ_1 is the uncoded value of the variable at its highest level.

Considering the aspects aforementioned, this work addresses the magnesium incorporation into the SIZ-2 framework using the ionothermal method as an attempt to generate new ion exchange sites. A central composite design was used for the systematic study of the effects of some selected synthesis parameters on the Mg–AlPO formation and its ion exchange capacity towards Cu^{2+} sorption. The parameters studied were choline chloride percentage in the eutectic mixture (%CCh), percentage of the eutectic mixture in the gel synthesis (%EU), magnesium percentage in the gel (%Mg), and crystallization time (t_c).

2. Experimental section

2.1. Ionothermal synthesis

Choline Chloride – CCh (Sigma–Aldrich) and urea (Synth) were used in different concentration ratios to prepare the eutectic mixture (EU). The mass of urea and CCh for each experimental condition was varied according to the molar percentage of CCh in the eutectic mixture: 10.0%, 21.5%, 33.0%, 44.5% and 56.0% [19]. Both of the solid components were mixed until becoming a liquid.

The typical synthesis procedure was as follows: a Teflon-lined autoclave (50 mL) was filled with choline chloride/urea eutectic mixture, phosphoric acid 85 wt.% (Mallinckrodt), aluminum isopropoxide (Sigma–Aldrich) and magnesium acetate tetrahydrate (Sigma–Aldrich). The gels were prepared with the following molar ratio:

$$\boldsymbol{x}MgO : (1 - \boldsymbol{x}/2)Al_2O_3 : 3P_2O_5 : \boldsymbol{y}EU : \boldsymbol{z}H_2O \quad (2)$$

$$\boldsymbol{x} = 0.05 - 0.250$$
$$\boldsymbol{y} = 14.7 - 40.0$$
$$\boldsymbol{z} = 2.9 - 3.9$$

The stainless steel autoclaves were heated in a stove at 180 °C. After crystallization, the solid product was separated by centrifugation, washed with deionized water and then dried at 110 °C.

The synthesis parameters %CCh, %EU, %Mg, and t_c were coded according to the statistical technique of central composite factorial design [18]. The coded values and the levels assumed for all the factors studied are shown in Table 1.

2.2. Characterization of the aluminophosphates

The samples were analyzed by powder X-ray diffraction (XRD) with CuKα radiation using a Rigaku MiniFlex X-ray diffractometer (40 kV, 40 mA, CuKα radiation with the Ni filter) at a rate of $2^\circ\,min^{-1}$ 2θ. Using the X-ray patterns, the relative crystallinity was calculated according to Eq. (3). The relative crystallinity (%crystallinity) was defined as the ratio between the area under the characteristics peaks of the synthesized samples of SIZ-2 or AlPO-CJ2 and that attributed to the standard samples [13].

Table 1
Values of the codified factors.

Factors	−2	−1	0	+1	+2
CCh (wt.%)	10.0	21.5	33.0	44.5	56.0
EU (wt.%)	35.0	50.0	65.0	80.0	95.0
Mg (mol%)	5.0	10.0	15.0	20.0	25.0
t_c (h)	72	84	96	108	120

$$\%\ Crystallinity = \frac{\text{area under peaks(sample)}}{\text{area under peaks(standard)}} \times 100 \quad (3)$$

Thermogravimetric analysis (TGA) was performed using equipment from TA Instruments, model SDT Simultaneous DSC-TGA. A 20 mg sample of aluminophosphate was heated at a constant rate of 10 °C min^{-1} under 100 mL min^{-1} oxygen flows.

2.3. Ion-exchange experiments

The ion exchange capacity ($\boldsymbol{q}$) of the prepared aluminophosphates was evaluated by testing Cu^{2+} sorption in a batch system. $CuSO_4{\cdot}5H_2O$ (Synth) was used as the source of copper ions. Deionized water was used to prepare all solutions.

The experiments to measure the ion-exchange capacity were done in Erlenmeyers containing 0.04 g of aluminophosphate and 10 mL of 3.610 mg L^{-1} Cu^{+2} solution. This initial concentration was chosen in order to guarantee that the maximum ion exchange capacity ($\boldsymbol{q}_{max}$) could be attained, as determined from previous experiments (not shown). The Erlenmeyers were left under agitation at 30 °C in a shaker for 72 h in order to ensure that the equilibrium condition would be reached. After that, the solids were separated from the liquid phase by vacuum filtration and dissolved in 0.5 mL of concentrated HF. The solution was diluted and the copper concentration was determined by colorimetric analysis using cuprizone (λ = 610 nm) [20].

The ion exchange capacity ($\boldsymbol{q}$) was determined using Eq. (4), which represents the ratio between the mass of Cu^{2+} retained in the solid and the mass of aluminophosphate used.

$$q = \frac{m_{Cu^{2+},solid}}{m_{AlPO}} \quad (4)$$

The values of $\boldsymbol{q}$ were statically analyzed and adjusted according to the polynomial model given by Eq. (5), in which x and y represent the factors and response variables, respectively. The β regression coefficients were determined by the least squares method.

$$y = \beta_0 + \sum_{j=1}^{k}\beta_j x_j + \sum_{j=1}^{k}\beta_{jj}x_j^2 + \sum_{j=1}^{k}\sum_{p=1}^{k}\beta_{jp}x_j x_p \quad (5)$$

The analysis of the variable effects on the responses was performed using the response surface methodology [18].

3. Results and discussion

3.1. X-ray diffraction (XRD)

The structures obtained as a function of the variables studied are shown in Table 2, together with their relative crystallinities and ion exchange capacities. Contrary to what has been reported in literature concerning ionothermal synthesis in the absence of magnesium, in which only SIZ-2 and AlPO-CJ2 are obtained [2,13], in this work the ionothermal synthesis only provided AlPO-CJ2 and other topologies such as AEL, AEN, and GIS [15,21,22]. The results indicate that the zeotypes obtained with shorter crystallization times (72 and 84 h), low %Mg, and high %EU are composed by a mixture of phases containing the AEL aluminophosphate. This topology has a medium pore diameter with 10-membered rings (5.0 Å $\leqslant d_p \leqslant$ 6.0 Å), that is, the Al–O–P bonds are more distorted, forming a topology less energetically favored [9]. Hence, a small variation of the synthesis conditions enables the formation of the dense structured AlPO-CJ2 (see Table 2) and/or zeolitic structures of small pores with 8-membered rings such as AEN and GIS topologies [21,22]. These results are in agreement with those observed by Cooper et al. in which the interrupted structure of SIZ-2 was easily converted into a dense structured