Sorption and Diffusion of \textit{p}-Xylene and \textit{o}-Xylene in Aluminophosphate Molecular Sieve AlPO\textsubscript{4}-11

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Abstract. This paper presents experimental results for equilibrium and diffusion of C\textsubscript{8} aromatics in laboratory synthesised crystals of AlPO\textsubscript{4}-11. The samples were prepared by the hydrothermal method, starting from pseudoboehmite (CONDEA), 85% phosphoric acid, water and di-isopropilamine as organic template. Adsorption and diffusion data were obtained mainly by gravimetry at temperatures between 60–100°C. Saturation capacities were found in the range of 4 wt%. Equilibrium constants were estimated using virial plots yielding heats of adsorption between 10–12 Kcal/mol at low coverage. Intracrystalline diffusivities at higher temperatures (150–180°C) were also measured, using the Zero-Length-Column (ZLC) method. Diffusivities from both methods (gravimetric and ZLC) agreed reasonably well and followed a typical Arrhenius behaviour, with low activation energy (ca. 7 Kcal/mol).

Keywords: equilibrium, diffusion and kinetics, AlPO\textsubscript{4}-11 molecular sieve

Introduction

The aluminophosphate molecular sieves (AlPO\textsubscript{4}-\textit{n}), first reported by Wilson et al. (1982), represent the first class of oxide materials free of silica. Most of these materials exhibit properties similar to those of zeolites, indicating that they can be used as adsorbents, catalysts or catalyst supports in several chemical processes (Rabo et al., 1989; Davis, 1991; Sierra et al., 1994). The main advantages of the aluminophosphate molecular sieves, as compared to other supports, are related to the possibility of varying the following physicochemical properties: pore size, pore shape, dimensions of the pore system, presence or absence of cages, acid sites properties, surface properties, void volume and framework compositions (Araujo et al., 1997).

Microporous crystalline AlPO\textsubscript{4}-11 has an AEL topology and is a member of the aluminophosphate molecular sieves family, which exhibits unidimensional 10-membered ring channels. The pore opening is elliptical with about 3.9 × 6.3 Å. The symmetry of AlPO\textsubscript{4}-11 is orthorhombic with the following unit cell dimensions: \(a = 13.5336\) Å, \(b = 8.4821\) Å and \(c = 8.3703\) Å (Treacy et al., 1996).
C₈ aromatics are the starting material for the production of dimethylteraphtalate (DMT), teraphtalic acid (TPA), poliethylene teraphtalate (PTA), largely used in the modern plastics industry. C₈ aromatics separation processes using selective adsorption on aluminosilicate molecular sieves, mainly zeolites X or Y, are currently among the most important industrial large-scale processes (e.g. Sorbex™). There have been attempts to synthesize aluminophosphate molecular sieves to replace zeolites as adsorbents for xylene separations. For instance, AlPO₄-5 and AlPO₄-11 have been reported as ortho-selective (Barthomeuf and Mallmann, 1990; Chiang et al., 1991).

In this paper, we report experimental data for equilibrium and diffusion of p-xylene and o-xylene in crystals of AlPO₄-11, at temperatures between 60–180°C. Equilibrium data are correlated using Langmuir, virial and Dubinin plots, in order to estimate equilibrium constants, saturation capacities and heats of adsorption at low coverage. Intracrystalline diffusivities are reported from two different experimental methods (gravimetric and ZLC) with reasonable agreement among them.

Experimental

Synthesis and Characterisation

The AlPO₄-11 crystals were synthesised by the hydrothermal method, starting from pseudobohemite (CONDEA), 85% orthophosphoric acid (MERCK), water and di-isopropilamine (RIEDEL) as organic template. The reactants were mixed in the following stoichiometric molar composition:

\[ \text{1.0 iso-} (\text{C}_3\text{H}_7)\text{H}_{12} \text{NH} : 1.0\text{Al}_2\text{O}_3 : 1.0\text{P}_2\text{O}_5 : 80\text{H}_2\text{O} \]

The synthesis procedure involved the following steps: (i) pseudobohemite was slurried in half of total volume of water; (ii) orthophosphoric acid was diluted to the rest of water and; (iii) the orthophosphoric acid solution was added to the aluminium hydroxide slurry. The mixture thus obtained was aged for two hours at room temperature under continuous stirring until pH stabilisation. At last di-isopropilamine was added to the mixture to form a reactive hydrogel, which was charged into a PTFE vessel and autoclaved at 170°C for three days, under autogenic pressure. The resulting material was then washed with deionized water and dried at 100°C for one day. Finally, the sample was calcined at 500°C under 60 mL-min⁻¹ oxygen flow, until complete removal of the organic template.

A full detailed characterisation of these samples has been reported by Araujo et al. (1999). X-ray diffraction pattern of the sample was recorded on a Rigaku diffractometer using Cu-Kα radiation, and the diffractions angle ranging from 5 to 40° (Fig. 1). The morphology and size of the crystals were determined by scanning electron microscopy, in a Zeiss DSM microscope, at 10 Kv and 77 μA (Fig. 2). Adsorption isotherms of nitrogen on the aluminophosphate crystals were measured with an Accusorb 2100E (Micrometrics) at room temperature. Table 1 summarises the main characteristics of the sample.