In Situ Characterization of AlPO-14 Using Synchrotron Powder Diffraction

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Introduction

The separation of propane/propylene mixtures is an important yet difficult industrial process [1,2,3] that can be accomplished by a pressure swing adsorption process using AlPO-14 as the adsorbent [4]. Although the AlPO-14 structure has been studied with different techniques, the detailed structure under conditions of the adsorption process has not been clarified. We have used synchrotron x-ray powder diffraction and an *in situ* reactor system to obtain detailed structural information of AlPO-14 with the Rietveld method. Molecular modeling using the structural data allowed determination of the diffusion path of propylene in AlPO-14.

Methods and Materials

The design of the *in situ* reactor system allows different chemicals to be loaded and the system to be heated and pressurized up to 90 psi with various gases or liquids [5]. For this work, AlPO-14 powder was loaded into a 1 mm capillary tube and attached to the cell. Diffraction scans were collected during treatments in nitrogen, propane and propylene at various temperatures up to 300°C and various pressures up to 90 psig.

Results

A selected region of the x-ray diffraction patterns under different experimental conditions is shown in Fig.1. The diffraction patterns for AlPO-14 in nitrogen and propane are very similar, whereas the pattern in propylene changes considerably suggesting structure changes caused by adsorption of propylene into the pores.

Discussion

The structures of AlPO-14 saturated with different gases were refined with Rietveld methods using the GSAS software package [6, 7] in order to clarify the structure changes. The lattice parameters (Fig.1) under propane were found to be the same as those under nitrogen, whereas the lattice parameters (a, b, and c) increased after adding propylene. The total volume of the unit cell increased by about 1%. In addition, the pore openings of AlPO-14 were found to be modified by propylene but not by propane. These observations are consistent with exclusion of propane and adsorption of propylene into the structure.

Rietveld refinements for the dried sample in nitrogen and for the samples in propane were completely satisfactory assuming only the presence of framework atoms. On the other hand, the refinement of the propylene saturated structure was not satisfactory until the adsorbed propylene was located by difference Fourier techniques and included in the refinements.

The refined structure data were used in theoretical modeling of diffusion of the gases and energy barriers were calculated along the four possible diffusion paths. The results showed that the energy barrier for propane was too high at any pore opening to diffuse into AlPO-14. Surprisingly, the barriers to diffusion of propylene were found to be too high in three of the possible diffusion paths. The only favorable diffusion pathway was found to be along the <11-1> direction (Fig.2).

The structure data also explained why experimentally it was found that the temperature had to be raised to 300ºC to completely remove propylene (as evidenced by lattice parameter shifts). It appears that the adsorption of propylene shrinks the pore opening enough to restrict its desorption.

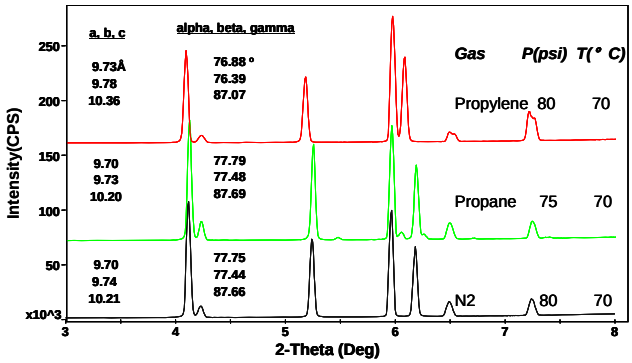

Fig.1 Selected region of the diffraction pattern under different gases and the lattice constants from the Rietveld refinement.

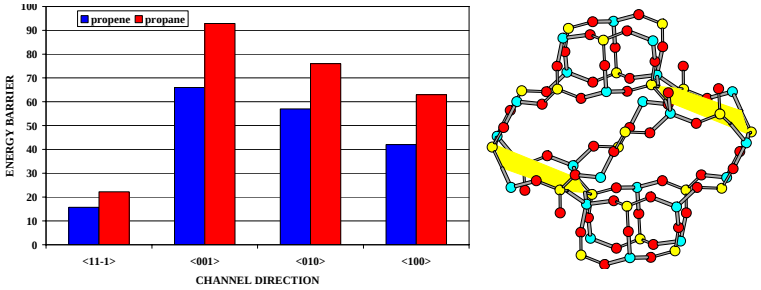

Fig.2 Left: Diffusion energy barriers of propane and propylene in four different directions. Right: Pore opening along the only favorable diffusion path are designated by gray areas.

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