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Diffusion of water and ethanol in silicalite crystals synthesized in fluoride media

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ABSTRACT

Diffusion of water and ethanol in silicalite has been studied in large crystals (70 μm × 30 μm × 15 μm) synthesized via a fluoride mediated route. The near-perfect hydrophobic silicalite (F^-) crystals have very few internal silanol defects and, as a result, display water and ethanol transport behavior that is uncontaminated by these defects. The transport diffusivity (D_t) of ethanol is higher than that of water at the same sorbate activity. However, this difference is due to the difference in the shape of the isotherms. The thermodynamically corrected diffusivity (D_o) of water is almost an order of magnitude higher than that of ethanol reflecting the difference in molecular size. Estimates of the permeability/permselectivity/separation factors for ethanol/water separation based on the present kinetic and equilibrium data for the fluoride synthesized crystals are compared with the values observed for traditional silicalite membranes. The present diffusivity values for fluoride synthesized silicalite are similar to the values for regular silicalite (OH^-) derived from uptake rate measurements but much smaller (by more than four orders of magnitude) than the self-diffusivities derived from PFG-NMR measurements. This result is consistent with the results of other measurements of the diffusion of small molecules in silicalite which suggest that, in macroscopic measurements, the rate of intra-crystalline transport is controlled by the sub-structure (extensive twinning), rather than by diffusion in the ideal MFI micropores. In this situation micro-scale measurements such as PFG-NMR will lead to erroneously high estimates of transport rates and therefore of permeability and permselectivity.

1. Introduction

Zeolites are crystalline porous materials that can be used in catalysis, ion exchange and separation applications [1]. MFI-type zeolites in particular have a three-dimensional interconnected framework with a pore structure consisting of two channels: a straight channel with circular openings (0.54 × 0.56 nm) and a sinusoidal channel with elliptical openings (0.51 × 0.55 nm) [2–4]. MFI structures include both high-silica MFI (Al-free), commonly referred to as silicalite, and ZSM-5 (containing Al). Due to the absence of Al sites, silicalite shows unique hydrophobic and organophilic characteristics making it potentially useful for extraction of ethanol from low concentration aqueous solutions in which ethanol is the minor component. There has been significant research progress focusing on pervaporation membranes using silicalite for ethanol removal from water [5–17].

Silicalite is typically synthesized in alkaline conditions with OH^- as the mineralizing agent. In this synthetic method, a considerable number of internal silanol sites can be created on removal of the charge balancing centers for the template tetrapropylammonium [18]. MASNMR (magic angle spinning NMR) studies have shown that about 5% of the Si atoms are typically hydroxylated [19]. These silanol defects are hydrophilic and therefore unfavorable for ethanol extraction from water. A near-perfect hydrophobic silicalite crystal can be obtained with an extremely low density of internal defects by using fluoride as the mineralizing agent at near neutral conditions [20,21]. In the fluoride route, the fluoride ion (F^-) can offset the template ions in a way that generates few internal defects [22–25]. In a recent publication, we discussed the equilibrium adsorption of water and ethanol in a variety of MFI-type zeolites [26]. We found that the effective elimination of internal silanol defects dramatically reduces the water uptake, especially at higher water activities. For example, the total water uptake by silicalite (F^-) is almost an order of magnitude lower than the capacity for silicalite (OH^-) at a water activity level of 0.95 (35 °C). As a result, the ideal ethanol/water sorption selectivity of silicalite (F^-) is an order of magnitude higher than that of silicalite (OH^-) zeolites. The present paper reports the results of a parallel study of the diffusion phenomena of water and ethanol in silicalite (F^-). These results enhance our understanding of the transport

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behavior of water and ethanol in essentially hydroxyl-free silicalite (F^-) crystals and provide useful insight concerning the potential of such materials for the extraction of ethanol from dilute aqueous solutions.

2. Experimental

Silicalite (F^-) was prepared in a fluoride-mediated route by hydrothermal synthesis adapted from literature procedures [20,21,27]. Tetrapropylammonium bromide (TPABr, 1.62 g, 99% Sigma Aldrich) and ammonium fluoride (NH_4F, 0.116 g, >99.99% Sigma Aldrich, stored in a desiccator) were first dissolved in 26.88 g of DI water. The $TPABr–NH_4F–H_2O$ mixture was then transferred to a 40 mL Teflon sleeve and 4.48 g of Cab–O–Sil M-5 (Cabot Corporation) was slowly added to the mixture, stirring manually for 10 min to form a homogenous gel. The Teflon sleeve was then placed in a tightly sealed stainless steel reactor and heated at 180 °C for 14 days. The resulting solids were then vacuum filtered and washed with 200 mL of water. To remove any un-reacted silica, 30 mL of DI water was added to the solids and sonicated for 90 s. The slurry was then centrifuged and the water was decanted off. This sonication-centrifugation cycle was repeated a minimum of two more times. The crystals were then dried and calcined using the following profile: ramp 5 °C/min, 120 °C for 2 h, ramp 5 °C/min, 550 °C for 12 h. The reaction yielded 3.4 g, a 76% yield (based on silica) achieved with an average crystal size of 70 μm × 30 μm × 15 μm (Fig. 1). The BET surface area of silicalite (F^-) is 381 m^2/g and the pore volume is 0.196 cm^3/g.

As revealed by SEM microscopy (Fig. 1), the silicalite (F^-) crystals used herein have an average crystal size of 70 × 30 × 15 μm, which is large enough to allow reliable estimation of intra-crystalline diffusivities from measurements of the uptake rate. Note that the synthesis of large zeolite single crystals is also one of the major features of the fluoride mediated method [28].

The vapor adsorption rate experiments were performed on a VTI-SA vapor sorption analyzer from TA Instruments (New Castle, DE, United States) at temperatures of 25–45 °C. The vapor activity was controlled automatically by mixing the wet vapor feed with a dry N_2 line. As such, N_2 serves as a carrier gas for the vapors. The zeolite samples were dried in a vacuum oven at 110 °C for 48 h before being transferred to the sorption apparatus and dried under flowing N_2 for 18 h at 110 °C. The samples "dry mass" was measured under N_2 and were at equilibrium with N_2 before introduction of the vapors to the sample chamber. A large N_2 purge flow rate is used to minimize extraneous heat and mass transfer effects.

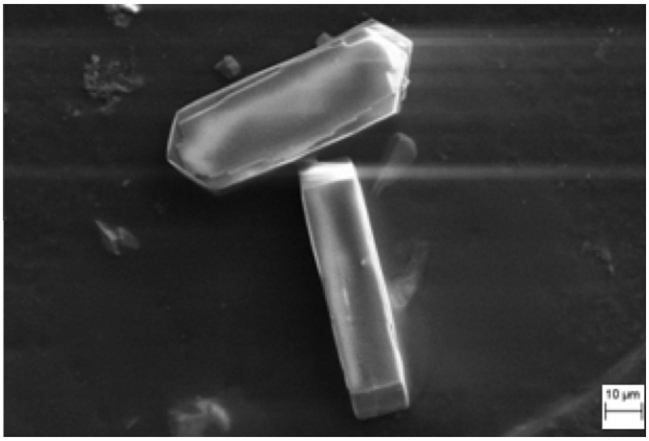

Fig. 1. Silicalite (F^-) crystals used in this study.

3. Results and discussion

3.1. Equilibrium isotherms

As discussed previously [26], the sorption isotherms for silcialite-1 (F^-) strongly favor ethanol, especially at low water activities (Fig. 2). The distinctly different forms of the isotherms observed for water and ethanol result from both the organophilic and hydrophobic characteristics of silicalite (F^-). A detailed discussion of water and ethanol adsorption phenomena in silicalite (F^-) can be found elsewhere [26].

3.2. Uptake rate curves

Fig. 3 shows typical transient uptake curves for water and ethanol adsorption as observed gravimetrically in this study. The curves have the expected form for a diffusion controlled process (linear with $\sqrt{t}$ in the initial region) and they have been interpreted in terms of the usual diffusion model. Although we cannot explicitly exclude the possibility of additional mass transfer resistance at the crystal surface, it seems clear that the mass transfer rate must be controlled mainly by intra-crystalline diffusion. It is worth noting that conformity with the diffusion model does not necessarily imply a true Fickian diffusion mechanism. However, alternative mechanisms such as the diffusion-immobilization model suggested by Weisz [29], require a clear distinction between mobile and immobile molecules and their applicability to intra-crystalline diffusion is therefore limited to meso-porous crystals (see for example Meunier et at. [30]). Weisz [29] also suggested that the site desorption could limit the overall diffusivity (rather than transport within the channels) when sorbate sorption energy is high enough. According to the characteristic desorption time constants and the time scale of sorption process, the sorption heats should be below 84 kJ/mol at room temperature range to validate the assumption that desorption does not limit the overall diffusion. The sorption heats of ethanol and water in silicalite (F^-) [26] are in the range of 35–45 kJ/mol, and therefore both sorption enthalpies of ethanol and water are sufficiently low that the desorption indeed is not a limiting step.

In an ideal silicalite crystal the straight and sinusoidal channels are oriented perpendicularly in the *x* and *y* directions (the shorter

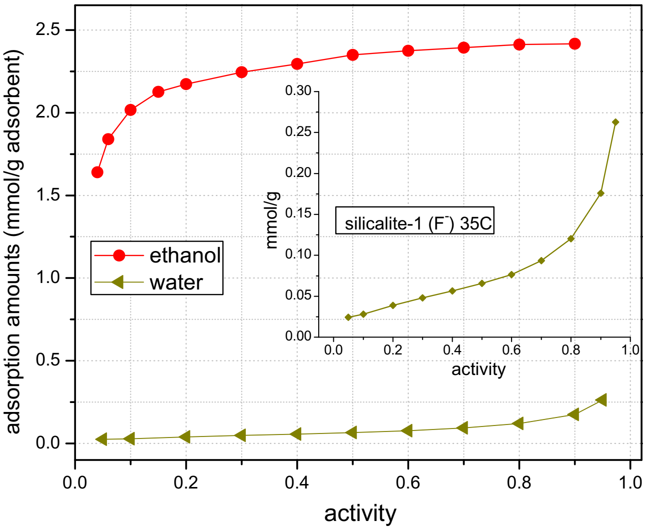

Fig. 2. Water and ethanol adsorption isotherms in silicalite(F^-) at 35 °C; inset figure depicts a detailed water adsorption isotherm for silicalite (F^-); water and ethanol isotherms at 25 and 45 °C are similar in shape [26].