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Dynamic properties of water in silicalite-1 powder

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Abstract

Self-diffusion of D₂O in partially filled silicalite-1 crystals was studied at 25°C by ²H nuclear magnetic resonance (NMR) with bipolar field gradient pulses and longitudinal Eddy-current-delay. For the first time, reliable experimental diffusion data for this system were obtained. Analysis of NMR diffusion decays revealed the presence of a continuous distribution of apparent self-diffusion coefficients (SDCs) of water, ranging from 10⁻⁷ to ~10⁻¹⁰ m²/s, which include values much higher and lower than that of bulk water (~10⁻⁹ m²/s) in liquid phase. The observed distribution of SDC changes with variation of the diffusion time in the range of 10–200 ms. A two-site Kärger exchange model was successfully fitted to the data. Finally, the water distribution and exchange in silicalite-1 pores were described by taking into account (a) a gas-like phase in the zeolite pores, a gas-like phase in mesopores and an intercrystalline gas-like phase and (b) intercrystalline liquid droplets with intermediate exchange rate with the other phases. The other phases experience fast exchange on the NMR diffusion time scale. Diffusion coefficients and mean residence times of water in some of these states were estimated.

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1. Introduction

Zeolites are crystalline microporous aluminosilicates, which due to their unique properties are frequently used in the chemical industry as catalysts and adsorbents and also in petroleum in petrochemical industries. In many of these processes, zeolites are loaded with one or several condensing fluids. Thus, the state and behavior of the fluid molecules in zeolites are of both practical and scientific interest. Today, more than 190 different zeolite structures are known, and new structures are frequently reported. However, only a few of these structures have so far found applications in industry, and one example is the mordenite framework inverted (MFI) structure [1]. MFI-zeolites have a three-dimensional pore system with straight channels of a diameter of 5.3×5.6 Å propagating along the crystallographic *b*-direction and

intersecting zigzag channels of a diameter of 5.1×5.5 Å propagating along the *a*-direction of the crystallographic unit cell. Zeolite crystals may also contain mesopores, and the amount of such pores can, to some extent, be controlled by the synthesis procedure and postsynthesis treatment [2,3]. The polarity of the zeolite framework may be controlled during synthesis by varying the aluminum content, and more aluminum in the structure results in a more polar zeolite [4,5]. MFI zeolite can be prepared without aluminum, resulting in a zeolite known as silicalite-1 [4].

Although most applications of MFI zeolites so far have been as adsorbent/catalyst for hydrocarbon separations or reactions, MFI zeolite has shown great potential for recovering biobutanol from fermentation broths, and other applications for separating organics from water solutions will most likely emerge [6]. Therefore, a thorough understanding of the behavior of water in MFI zeolite is important.

Earlier theoretical and experimental studies revealed certain complexities concerning the state and properties of water in silicalite-1 powder samples. Two types of attractive

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