

Research Note

PFG NMR observation of an extremely strong dependence of the ammonia self-diffusivity on its loading in H-ZSM-5

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Abstract

Ammonia diffusion in H-ZSM-5 (Si/Al = 20) has been studied by the PFG NMR method for different ammonia loadings at 298 K. The results obtained indicate that the self-diffusion coefficient of ammonia changes by up to two orders of magnitude if ammonia loading is varied by a factor of only 2 between 1.6 and 0.8 mmol/g. This unusually strong loading dependence is attributed to the strong interaction of ammonia molecules with the limited number of acid sites of the H-ZSM-5 framework.

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1. Introduction

Framework acidity is of crucial importance for many catalytic applications of microporous materials. Although the mechanism of chemical transformations on acid sites in zeolites is sufficiently well understood for many industrially important reactions, studies of the influence of these sites on the intracrystalline molecular transport still remain one of the challenging subjects in zeolite research [1,2]. Such studies are particularly important in view of recent data suggesting that the rates of some important chemical reactions may be limited by the rates of intracrystalline molecular transport [3].

NH₃ is routinely used as a probe molecule for acid sites. Hence, intracrystalline diffusion of ammonia can be expected to depend significantly on the presence of such sites. This makes ammonia an ideal probe for the investigation of the influence of acid sites on intracrystalline transport. Understanding of the mechanism of ammonia transport in acidic zeolites is also important because the temperature-programmed desorption (TPD) of ammonia has become a standard method for probing acid sites [4]. The competition between ammonia desorption from acid sites and the intracrystalline diffusion of these molecules during TPD was a subject of very recent studies [2].

In this note we report for the first time the coefficients of intracrystalline self-diffusion of ammonia in H-ZSM-5 at different loadings. The diffusion measurements were performed using the pulsed field gradient (PFG) NMR technique [5]. The observed strong loading dependence of ammonia diffusivity is quantitatively correlated with the interaction between ammonia and the limited number of acid sites present in the H-ZSM-5 framework.

2. Experimental

The measurements were carried out using the homebuilt PFG NMR spectrometer FEGRIS 400 NT operating at a ¹H resonance frequency of 400 MHz [6]. For all measurements the 13-interval pulse sequence [7] was employed. This sequence suppresses distortions of PFG NMR diffusion results by internal magnetic field inhomogeneities induced by susceptibility variations in a sample.

To obtain the diffusivity, the attenuation of the PFG NMR spin echo signal (Ψ) was measured as a function of the amplitude of the applied field gradient (g). This amplitude was varied from 0.05 T/m to a maximum value of 20 T/m for samples with different ammonia loadings. Under our measurement conditions the molecular displacements were in all cases sufficiently small in comparison with the smallest dimension of the crystals to ensure that the measured diffusivities represent intracrystalline diffusion coefficients.

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The sample of calcined H-ZSM-5 zeolite (Si/Al = 20) was kindly provided by Professor Weitkamp (Stuttgart, Germany). The calcination was performed at 973 K for 40 h under atmospheric pressure of air. The mean dimensions of the zeolite crystals were $(80 \times 20 \times 20) \mu\text{m}^3$. The zeolite was used as received.

The samples for the PFG NMR measurements were prepared as follows. Around 300 mg of H-ZSM-5 was introduced into the NMR tube. Then the tube was connected to the vacuum system and the zeolite sample was activated by keeping the sample under high vacuum at 673 K for 20 h. Subsequently, the zeolite sample was loaded with ammonia by freezing it from a fixed volume of the vacuum system. Upon loading, the NMR tube was sealed and separated from the vacuum system.

3. Results and discussion

Figure 1 shows the loading dependence of the self-diffusion coefficient of ammonia in the H-ZSM-5 zeolite at 298 K. It is seen that the diffusivity increases strongly with increasing loading of ammonia, starting from 0.8 mmol/g. The latter loading represents the smallest ammonia loading where PFG NMR measurements were still possible. Small NMR relaxation times prevented the measurements for still lower loadings. With increasing loading the dependence of the diffusivity on the loading in Fig. 1 becomes progressively less pronounced. The observed loading dependence can be qualitatively understood by assuming the existence of a limited number of strong adsorption sites in the zeolite. The mean residence time of ammonia on such sites is expected to be significantly larger than that on the other lattice sites (i.e., mobile sites). In this model we assume fast molecular exchange between different sites on the time scale of diffusion measurements (several milliseconds). At ammonia concentrations smaller than that of the strong adsorption sites the diffusion rate will be primarily governed

by the hopping rate between these sites. At the same time, for sufficiently large ammonia concentrations only a small fraction of ammonia will reside in the strong adsorption sites, while the overall diffusion rate will be mostly determined by the hopping between mobile sites. The latter case is consistent with the weak loading dependence observed at large ammonia loadings (Fig. 1). The diffusivity, rapidly decreasing with the decreasing ammonia loading observed at lower loadings in Fig. 1, marks the onset of the transition between the two regimes discussed above. A similar model was previously used to describe ammonia diffusion in silicalite where the role of the strong adsorption sites was played by silanol groups [8]. Using this model the effective self-diffusion coefficient of ammonia in H-ZSM-5 can be presented as

$$D_{\text{eff}} = p_s D_s + p_m D_m \approx p_m D_m = \frac{N - N_s}{N} D_m, \quad (1)$$

where p_s , D_s , p_m , and D_m are the relative fractions and the diffusivities of the molecules residing on the strong adsorption sites and those residing on the mobile sites of the lattice, respectively. N and N_s in Eq. (1) denote the number of ammonia molecules and the number of strong adsorption sites in the lattice. The right-hand side of Eq. (1) was written assuming that the value of D_s is sufficiently small so that the first term on the left-hand side of the equation may be neglected under our experimental conditions.

The full line in Fig. 1 shows the result of the best fit of the experimental data by Eq. (1), where both N_s and D_m were treated as variables. The best-fit values were determined to be $N_s = 0.829 \pm 0.037$ mmol/g and $D_m = (2.3 \pm 0.19) \times 10^{-9} \text{ m}^2/\text{s}$.

In our opinion, the best candidates for the strong adsorption sites are the acid sites present in H-ZSM-5 zeolites. The concentration of the acid sites may be directly correlated with the Al content of the zeolite framework. Assuming that there is a one-to-one correlation between the number of Al atoms and that of acid sites, the concentration of the acid sites in our sample was estimated at 0.83 mmol/g. This value is apparently in excellent agreement with the best fit value of N_s . It is also interesting to note that the best fit value of D_m is in good agreement with the diffusivity of the ammonia molecules in the silicalite free of defect (silanol) sites ($10^{-9} \text{ m}^2/\text{s}$) [8].

The procedure for activation the zeolite samples used in this work ensures that most of the acid sites in the samples are Brønsted acid sites [9]. It was shown by ^1H MAS NMR spectroscopy that the mean residence time of ammonia on these sites in H-ZSM-5 is orders of magnitude smaller than the characteristic diffusion times (milliseconds) used in the present study [10]. This justifies our assumption about fast molecular exchange between different adsorption sites on the time scale of the diffusion measurements. The discussed above supports our conclusion that the observed strong loading dependence of ammonia diffusivity in H-ZSM-5 is due to interaction between NH_3 molecules and the limited number of acid sites of the zeolite framework.

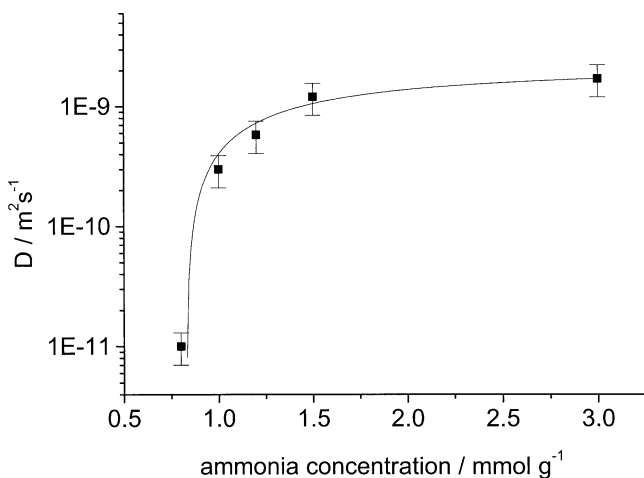


Fig. 1. Loading dependence of the self-diffusion coefficient of ammonia in H-ZSM-5 at $T = 298$ K. The full line is the best fit using Eq. (1).

At the highest ammonia concentration used in this work (3 mmol/g, which corresponds to around four molecules per channel intersection), the alternative mechanism of proton diffusion in the zeolite channels may be considered, i.e., H^+ diffusion in the NH_3 phase via NH_4^+ . In our opinion, this mechanism does not contribute significantly to the measured diffusivities because strong dependence of the diffusivity on the NH_3 concentration, which can be expected in this case, was not observed. Indeed, the diffusion coefficient remained practically unchanged in the concentration range between 3 and 1.5 mmol/g (Fig. 1).

4. Conclusions

Self-diffusion measurements of ammonia in H-ZSM-5 have been performed by PFG NMR for different ammonia loadings at $T = 298$ K. The measurements were carried out using the 13-interval bipolar PFG NMR pulse sequence, which prevents systematic errors caused by unwanted internal magnetic field gradients. The observed strong loading dependence of the ammonia self-diffusion coefficient in H-ZSM-5 was quantitatively described, assuming strong interaction between NH_3 and the zeolite acid sites as well as fast molecular exchange between different adsorption sites on the time scale of the diffusion measurements.

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