diffusion-fundamentals

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Diffusion of Methanol in Zeolites: a Molecular Dynamics Study

David F. Plant[a b], Guillaume Maurin[b] and Robert G. Bell[a]

[a] The Davy Faraday Research Laboratory, Royal Institution of Great Britain, London W1S 4BS, United Kingdom.

[b] Laboratoire LPMC, UMR CNRS 5617, Université Montpellier II, Pl. E. Bataillon, 34095 Montpellier cedex 05, France.

1. Introduction

Methanol is an important feedstock in numerous catalytic processes. It can be produced via Fischer-Tropsch reaction from synthesis gas [1] and its further transformation to hydrocarbons up to C_{10} is the basis of several industrially important reactions as for instance the Methanol to Gasoline process [2]. Methanol can also be used as an alkylating agent for aromatic compounds in zeolite-catalysed reactions. This reaction takes place in a number of basic zeolites, including alkali metal-exchanged X and Y zeolites. The optimisation of such processes demands a sophisticated understanding of the interactions between the zeolite surfaces and the reactant methanol molecules, including the transport properties of the reagent within the catalyst micropores. Here we investigate the microscopic diffusion mechanism of this adsorbate in the zeolites NaY by means of molecular dynamics simulations. To achieve this, a new potential for reproducing the interaction between the extra-framework cations Na^+ and the oxygen of methanol was derived from our results of *ab initio* calculations [3]. The resultant forcefield was then used to carry out the NaY molecular dynamics calculations. These results were then compared with those obtained for the purely siliceous zeolite Y (DAY) in order to emphasise the difference in methanol diffusion in a “cation-free” zeolite.

2. Results and discussion

Mean Square Displacement (MSD) plots of methanol, for loadings of 8, 16, 32, 40, 48, 56, 64, and 96 molecules/u.c. for temperatures ranging from 300 to 700K were obtained in the NaY and DAY systems. For these loadings, the MSDs increase with temperature, appearing linear at the lowest loading and it was apparent that the diffusivity did not increase smoothly with the temperature. In the NaY system, for each methanol loading, two distinct regions may be discerned, a low-temperature regime where the slope of the plot (activation energy) is lower, and a high-temperature one where the Arrhenius plot is steeper. Furthermore, we can define two types of motion, “short-range” and “long-range”. Short-range motion is essentially intra-cage, i.e. within a single FAU supercage, whereas long-range is not so restricted, and involves diffusion throughout the pore structure combining both intra- and inter-supercage motion. For NaY the activation energies, characteristic of the two activated processes, (short-range and long-range), were derived by linear least-squares fits to the Arrhenius plots. The activation energies for the intra- and intercage motion decrease from 0.14 to 0.05 eV and from 0.25 to 0.18 eV when the loading increases from 8 to 48 methanol/u.c. In the DAY system we report that the MSD values of methanol are higher at all temperatures, when compared to NaY. Furthermore, we identify only one type of diffusion behaviour whatever the temperature, which shows that even at ambient temperature, the methanol molecules are mobile enough to cross the free energy barrier that allows them to travel through the 12-ring window separating the supercages. The corresponding activation energy slightly increases with loading, varying from 0.06 to 0.085 eV when we go from 8 to 48 methanol/u.c due to increasing steric effects.

Figure 1 reports the evolution of the diffusion coefficients for methanol for both NaY and DAY at each temperature as a function of the loading. The calculated values are of much higher magnitude for DAY than for NaY, which emphasizes that the extra-framework cations contribute to a restriction in the diffusivity of the methanol molecules. For NaY, it is clearly demonstrated that, for the majority of the temperatures sampled, the diffusion coefficient reaches a maximum for 32 methanol molecules per unit cell, which in turn corresponds to a loading of 1 methanol molecule per extra-framework cation within the supercages at the SII sites. Such behaviour has been already pointed out for similar zeolite system [4]. This behaviour is different to that observed for DAY where the diffusion coefficient decreases when the loading increases, due to steric effects.

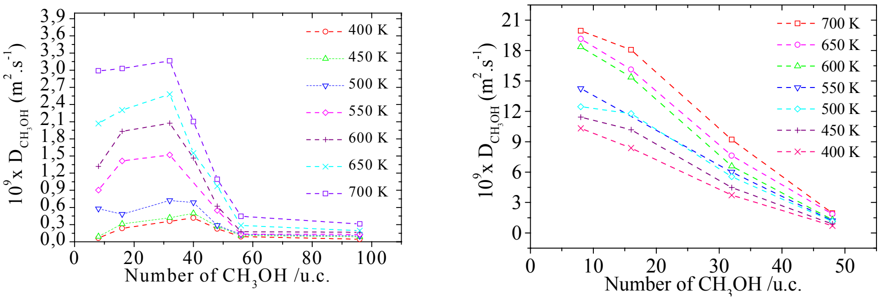

Figure 1 : Evolution of the diffusion coefficients in the NaY(a) and DAY (b) systems.

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