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Surface Diffusion in Catalysts Probed by APGSTE NMR

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Abstract

In this work we report the application of a recently developed experimental protocol using Pulsed Field Gradient (PFG) Nuclear Magnetic Resonance (NMR) techniques to simultaneously assess bulk pore and surface diffusion coefficients in liquid saturated porous catalysts. This method has been developed to study solvent effects on the diffusion of methyl ethyl ketone (MEK) in mesoporous 1 wt% Pd/Al_2O_3 catalyst trilobes. The selection of solvents used in this work is known to have a complex effect on reaction rates and hence catalyst performance in heterogeneous liquid phase catalysis. Here, we report the bulk pore and surface diffusion characteristics of MEK, water and isopropyl alcohol (IPA) in 1 wt% Pd/Al_2O_3 catalyst trilobes. The results show that the physicochemical interactions of molecules in the porous catalyst matrix are very different for the different molecules. We also find that the mobility of water appears to be affected strongest by the catalyst surface.

Keywords

Surface diffusion; Catalysts; Pulsed Field Gradient; Nuclear Magnetic Resonance; Surface interactions

1. Introduction

The ability to measure surface diffusion in porous catalysts is of prime importance to further our understanding of liquid phase heterogeneous catalysis. In porous catalysts (typically in the form of extruded pellets), the reactant diffuses along its chemical potential gradient through the pore space until it reacts at an active surface site. Being able to distinguish between the diffusion coefficient of the reactant in the bulk pore space and on the surface allows for the assessment of the molecule’s interaction with the surface, its distribution within the pore space, and the effect of solvents on its mobility. This information can be used to further our understanding of the molecular dynamics that govern liquid phase catalysis in porous media on the pore scale of catalyst pellets. PFG NMR techniques allow the study of molecular self diffusion of molecules in porous media and are nowadays part of the standard NMR toolbox. In this work we use the 13-interval Alternating Pulsed Gradient Stimulated Echo (APGSTE) pulse sequence [1] and the experimental protocol described elsewhere [2] to distinguish between the bulk pore and surface diffusion coefficients of water, IPA, and MEK in porous catalyst trilobes. We also briefly discuss the diffusion of MEK in mixtures of the two solvents.

2. Methods and Materials

Samples for PFG NMR experiments were prepared in the following way. 1 wt% Pd/Al_2O_3 catalyst trilobes (~0.15 g; Johnson Matthey plc, 20 nm median pore diameter) were soaked in the respective liquid for at least 6 hours under ambient conditions. The trilobes were then transferred onto pre-soaked filter paper (Whatman No. 1) to remove any excess liquid. The liquid saturated trilobes were then transferred to a 10 mm NMR tube for the PFG NMR diffusion experiments. MEK and IPA were procured from Sigma Aldrich (> 99 %). Deionised (> 15 MΩ) water was used where necessary. All NMR experiments were performed on a Bruker Biospin DMX 300 spectrometer operating at a ^1H resonance frequency of 300.13 MHz. A Bruker Biospin DIFF-30 Diffusion Probe with a 10 mm diameter ^1H radio-frequency coil was used to excite and detect the NMR signal.

3. Results and Discussion

The signal attenuation plots of the PFG NMR diffusion experiments for the pure chemicals are shown in Fig. 1. The signal attenuation I/I_0 is plotted against b, which is defined as

$$b = g^2\gamma^2\delta^2 (\Delta - \delta/3) \qquad (1)$$

where g is the gradient strength, γ is the gyromagnetic ratio of the nucleus, δ is the gradient pulse duration and Δ is the observation time of the experiment. The gradient of such a plot yields an estimate of the molecular diffusion coefficient. In Fig. 1, the data are characterised by two limiting gradients. At small values of b, the experiments probe the bulk pore liquid diffusion coefficient. At large b-values, surface diffusion is sampled. The diffusion coefficients are summarised in Table 1. In addition, the free bulk liquid diffusivities are given. It is found that the effective tortuosities, as defined by

$$\tau = D_{free} / D_{pore} \qquad (2)$$

where D_{free} is the free bulk liquid diffusion coefficient and D_{pore} is the bulk pore diffusion coefficient, depend on the molecule.

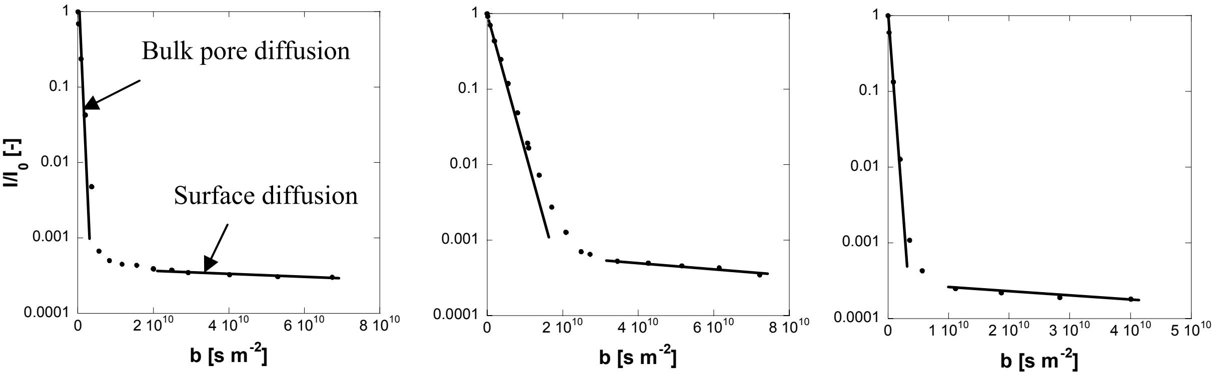

Figure 1: Signal attenuation plots of water (left), IPA (middle), and MEK (right) in mesoporous 1 wt % Pd/Al_2O_3 catalyst pellets. The diffusion coefficients are summarised in Table 1. Lines are shown to guide the eye.

MEK experiences an effective tortuosity of ~1.7, while for water and IPA the effective tortuosities are ~1.3 and ~1.4 respectively. These values indicate a different physicochemical interaction of each molecule in the porous space. These findings are supported by comparing the surface diffusion coefficients. The slowest diffusion coefficient is for water ($D = 0.53 \times 10^{-11}$ m^2 s^{-1}) with the diffusion coefficients of IPA and MEK being 0.99×10^{-11} and 1.18×10^{-11} m^2 s^{-1}, respectively. These data are consistent with water interacting most strongly with the surface. A complex effect of water on the reaction rates of hydrogenation reactions has been discussed in the literature [3-6]. While water is seen to enhance the reaction rate on Ru/SiO_2 catalysts, it appears to poison hydrogenation reactions on Pd/Al_2O_3 catalysts. The strong surface interaction of water seen here suggests that the surface access of MEK is limited in this solvent. While there will be many phenomena influencing the catalytic performance in such systems, it is apparent that surface diffusion measurements contribute to a better understanding of solvent effects.

Table 1: Bulk liquid (signal attenuation plots not shown in Fig.1), pore, and surface diffusion coefficients of water, IPA, and MEK.

	Bulk liquid	Bulk pore	Surface	τ (=$D_{\mathrm{bulk}}/D_{\mathrm{pore}}$)
Water (m^2 s^{-1})	2.2×10^{-09}	1.6×10^{-09}	0.53×10^{-11}	1.38
IPA (m^2 s^{-1})	0.5×10^{-09}	0.4×10^{-09}	0.99×10^{-11}	1.28
MEK (m^2 s^{-1})	3.3×10^{-09}	1.9×10^{-09}	1.18×10^{-11}	1.74

Bulk pore and surface diffusivities of MEK in binary mixtures of water and IPA over the entire range of mole fractions have also been investigated. The results show that the thermodynamic non-ideality of the bulk liquid mixture, indicated by a curvature of the diffusion values when plotted as a function of mole fraction, is also apparent for the liquid within the pore space (signal attenuation plots not shown here). This has implications for the refinement of theoretical models to predict diffusion coefficients in porous catalysts.

4. Conclusions

A novel experimental protocol using advanced PFG NMR techniques has been used to study the pore and surface diffusion coefficients of reactants and solvents in porous catalyst pellets. We find that water interacts strongest with the catalyst surface, followed by IPA, and MEK interacting weakest with the surface. Values of effective tortuosities are consistent with the physicochemical interactions of the molecules studied with the surrounding porous matrix being different for each molecular species.

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