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Inhibitory effect of oxygenated heterocyclic compounds in mesoporous catalytic materials: A pulsed-field gradient NMR diffusion study

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ABSTRACT

Oxygenated heterocyclic compounds are often used as solvents in liquid-phase catalytic reactions, such as hydrogenation and oxidation over porous oxide-based catalysts. It has often been reported that such compounds inhibit catalyst activity relative to the use of hydrocarbons as the solvent media. In this work we use ^{1}H pulsed-field gradient (PFG) NMR diffusion studies to study diffusion properties of binary mixtures 1,4-dioxane/cyclohexane in mesoporous TiO_2 over the whole composition range in order to understand the effect of the solid surface on molecular transport and molecular interactions within the pore space. The results reveal that whilst the diffusion of the hydrocarbon is only affected by geometrical restrictions, the diffusion profile of 1,4-dioxane is highly influenced by interactions within the catalyst pore, which is thought to be due to the presence of lone electron pairs on the oxygen atoms of 1,4-dioxane, allowing the molecule to act as a Lewis base when in contact with the solid surface. This agrees with findings on the inhibitory capacity of oxygenated heterocyclic compounds when used either as solvent in catalysis or present as impurities in some chemical feedstocks. The work shows that it is possible to use ^{1}H PFG NMR in order to characterise the effect of surfaces on molecular transport and hence understand catalytic behaviour in liquid-phase catalytic reactions.

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1. Introduction

Oxygenated organic compounds, such as linear and heterocyclic ethers, are common solvent media in heterogeneous catalysis and they have been used in several liquid-phase heterogeneously catalysed chemical reactions [1–4]. It has often been reported that relative to the use of hydrocarbons as solvents, these compounds tend to inhibit the catalyst activity. For example, the use of 1,4-dioxane as the solvent for the catalytic hydrogenation of cyclohexene on several SiO_2-supported catalysts gives turnover frequency (TOF) values that are significantly lower than those observed when hydrocarbons, such as cyclohexane, are used as the solvent medium or in many cases results in a total inhibition of the reaction [4]. Takagi et al. [1] also reported an inhibitory effect of 1,4-dioxane for the hydrogenation of several aromatic compounds on porous metal oxide-based catalysts when compared to hydrocarbons. Recent work on the oxidation of benzyl acetone on TiO_2-based catalysts has also shown that the use of heterocyclic ethers as the solvent medium leads to a complete deactivation of the catalyst [5]. Unlike hydrocarbons, oxygenated heterocyclic compounds are thought to adsorb more strongly onto the catalytic surface, hence blocking the reactive sites [5].

Understanding the physical chemistry of these solvents within porous solids is therefore of importance in order to elucidate and rationalise inhibitory effects of these compounds. It has previously been shown that the use of pulsed-field gradient (PFG) NMR techniques is able to elucidate the physico-chemical behaviour of single species in mesoporous catalytic materials, which can be related to the catalyst behaviour [6]. In this work we have performed a detailed PFG NMR study of binary mixtures of 1,4-dioxane (an oxygenated heterocyclic compound) and cyclohexane as bulk liquid mixtures and mixtures within mesoporous TiO_2 in order to probe the effect of composition and molecular interactions on the self-diffusion coefficients of both components as bulk liquid and as liquid within the pore space. The choice of this system is threefold: i) Mixtures of cyclohexane/1,4-dioxane are representative of typical hydrocarbon and oxygenated heterocyclic compounds used as solvent media in liquid-phase catalysis. In addition, TiO_2 is used in

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catalytic reactions as support [7,8] and catalysts [9,10]. The role of such materials in affecting adsorption and catalytic performances is often considered to be a key step [11,12]. ii) The geometrical features of these two molecules are similar but the nature of interactions is very different due to the ability of 1,4-dioxane to act as a Lewis base [13]. iii) The simple ^{1}H NMR spectral features of these compounds and their relatively well separated chemical shifts should be able to provide an unambiguous peak assignment of such mixtures imbibed in porous materials, where line broadening may become significant and, for some porous materials, make the spectral assignment unfeasible. In this way, the self-diffusivities of both species can be measured unambiguously. The behaviour of the weak-interacting species (i.e., cyclohexane) and that of 1,4-dioxane were assessed by measuring their PFG interaction parameter as a function of composition. According to our knowledge, this is the first study that uses PFG NMR to understand diffusion of binary liquid mixtures within porous materials as a function of composition.

2. Experimental

2.1. NMR set up

PFG NMR experiments were performed on a Bruker Biospin DMX 300 operating at a ^{1}H frequency of 300.13 MHz. The ^{1}H PFG NMR experiments were carried out using a Bruker Biospin Diff-30 diffusion probe capable of producing magnetic field gradient pulses up to a strength of 11.76 T m^{-1}. Diffusion measurements of pure bulk liquids were performed at room temperature using the pulsed gradient stimulated echo (PGSTE) pulse sequence [14], while the 13-interval alternating pulsed gradient stimulated echo (APGSTE) pulse sequence [15] was used when studying diffusion of liquids within catalyst pellets to minimise the effects of background magnetic field gradients. Values of self-diffusion coefficients, D, were calculated by fitting the experimental data using Equation (1) when the PGSTE sequence was used, and Equation (2) when the 13-interval APGSTE sequence was used.

$$\frac{E(g)}{E_0} = \exp\left[- D\gamma^2 g^2 \delta^2 (\Delta - \delta/3)\right] \quad (1)$$

$$\frac{E(g)}{E_0} = \exp\left[- D\gamma^2 g^2 \delta^2 (\Delta + 3\tau/2 - \delta/12)\right] \quad (2)$$

In Equations (1) and (2), E_0 is the NMR signal in the absence of gradient, γ is the gyromagnetic ratio of the nuclei being studied (i.e., ^{1}H in our case), g is the strength of the gradient pulse of duration δ, τ is the spacing between the first two $\pi/2$ pulses and Δ is the observation time (i.e., the time interval between the leading edges of the gradient pulses). The measurements were carried out holding the gradient pulse duration, δ, constant and varying the magnetic field gradient strength, g. The observation time, Δ, was set 100 ms. The gradient pulse duration, δ, was set to 1 ms and 64 to 256 scans were acquired for each experiment, with a recycle time of 5 s and a gradient stabilisation delay of 1 ms. It is noted that the chosen value for Δ is such that $\Delta >> \delta$ and τ, hence both Equations (1) and (2) are practically the same.

2.2. Materials and sample preparation

1,4-dioxane and cyclohexane were purchased from Sigma Aldrich and were of the highest purity available. TiO_2 anatase pellets were supplied by Evonik-Degussa. N_2 BET adsorption measurements show that the material has a specific surface area of 40 m^2 g^{-1}, with an average pore size of 22 nm. For the sample preparation, TiO_2 pellets were first dried for 2 h at 110 °C in order to remove moisture present within the pores. The pellets were then immersed in mixtures of 1,4-dioxane and cyclohexane at different compositions and left in the liquid for at least 24 h, in order to ensure saturation of the pores. The pellets were then removed from the liquid mixture and, after removal of the liquid present on the external surface, were placed in 5 mm NMR tube. In order to avoid evaporation of the liquid during the experiments, a little piece of adsorbent paper soaked with the liquid mixture was placed under the cap of the NMR tube and then the tube was sealed with parafilm. NMR spectra were acquired at the beginning and at the end of the PFG NMR experiments in order to check for any loss of signal due to evaporation of the liquid within the pores, which was negligible in all cases.

3. Results and discussion

3.1. Self-diffusion in bulk binary liquid mixtures

Fig. 1 shows self-diffusion coefficients of 1,4-dioxane and cyclohexane in pure liquid mixtures as a function of 1,4-dioxane mole fraction. The values are consistent with those measured by Merzliak et al. [16] for this mixture. The self-diffusivity profiles of both components within the mixture show maxima at a 1,4-dioxane mole fraction of approximately 0.4. The excess of molar Gibbs energy G^{ex} [17], and excess molar volume V^{ex} [18], profiles for this mixture also show maxima at approximately the same mole fraction. The positive values of the excess of molar volume may contribute to the observed increased mobility observed at intermediate mole fractions [19–21].

3.2. Self-diffusion of binary liquid mixtures in mesoporous TiO_2

In order to have unambiguous measurements of self-diffusivities of both components within a binary mixture, it is important to be able to clearly separate the NMR resonances of both components within the mixture. This is often straightforward for many pure liquid mixtures but it may be an issue when measuring

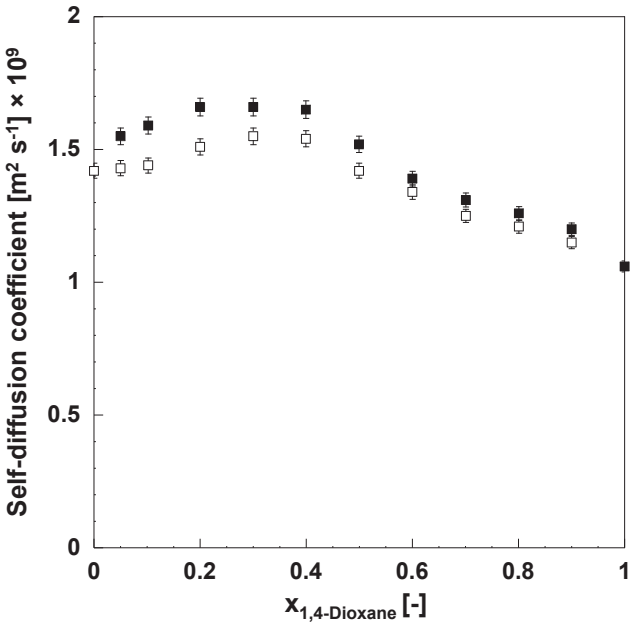

Fig. 1. Pure liquid self-diffusion coefficients of 1,4-dioxane (■) and cyclohexane (□) as a function of 1,4-dioxane mole fraction.

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