

**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 ^1H 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 ~~the~~ 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 ^1H PFG NMR in order to characterise the effect of surfaces on molecular transport and hence understand catalytic behaviour in liquid-phase catalytic reactions.

Keywords: Mesoporous titania, PFG NMR, diffusion, catalysis

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 SiO₂-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 TiO₂-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 TiO₂ 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, TiO₂ is used in 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

¹H 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 ¹H frequency of 300.13 MHz. The ¹H 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.

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

$$\frac{E(g)}{E_0} = \exp\left[-D\gamma^2 g^2 \delta^2 (\Delta + 3\tau/2 - \delta/6)\right] \quad (2)$$

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~~to the experimental data.~~ 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., ^1H 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 $\Delta \gg \delta$ and τ , hence both equations (1) and (2) are practically the same.

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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 $40 \text{ m}^2 \text{ g}^{-1}$, with an average pore size of 22 nm. For the sample preparation, TiO_2 pellets were first dried for two hours at $110 \text{ }^\circ\text{C}$ in order to remove moisture present within the pores. The pellets were then imbibed in mixtures of 1,4-dioxane and cyclohexane mixtures at different compositions and left in the liquid for at least 24 hours, in order to ensure saturation of the pores. The pellets were then removed from the liquid mixture and, after removal of the liquid present of 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 mixtures was placed under the cap of the NMR tube and then the tube was ~~then~~ 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

Figure 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] profile 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].

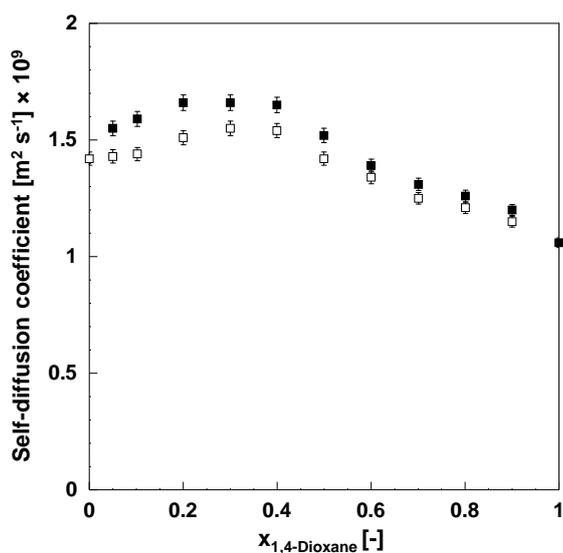


Figure 1. Pure liquid self-diffusion coefficients of 1,4-dioxane (■) and cyclohexane (□) as a function of 1,4-dioxane mole fraction.

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 multicomponent diffusion in porous media due to NMR line broadening. Cyclohexane and 1,4-dioxane

have NMR resonances which are well separated from each other, hence, if the broadening due to the presence of the porous material is not significantly large, it should be still possible to clearly separate the two species. Figure 2 shows the NMR spectrum of a 60% 1,4-dioxane mole fraction mixture of 1,4-dioxane/cyclohexane in mesoporous TiO₂. Despite the broadness of the NMR lineshapes, the resonances of both 1,4-dioxane (~ 3.8 ppm) and cyclohexane (~ 1.7 ppm) are clearly distinguishable and no overlap occurs. This makes it possible to measure accurately and unambiguously their diffusion coefficients with the mixture imbibed in TiO₂.

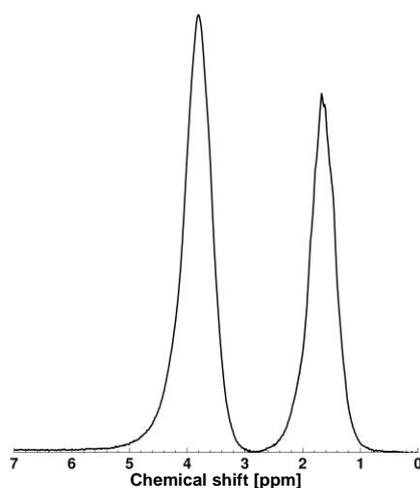


Figure 2. ¹H NMR spectrum of a 60% mole fraction mixtures of 1,4-dioxane (3.8 ppm) and cyclohexane (1.7 ppm) in mesoporous TiO₂. TMS used as the chemical shift reference.

Typical PFG NMR log attenuation plots are shown in Figure 3 for two mixtures within TiO₂, 5% (Figure 3a) and 50% (Figure 3b) mole fraction of 1,4-dioxane in cyclohexane. The Stejskal-Tanner plots in Figure 3 are approximately linear, which is consistent with previous studies on similar materials and is described as *quasi-homogeneous* behaviour [22, 23].

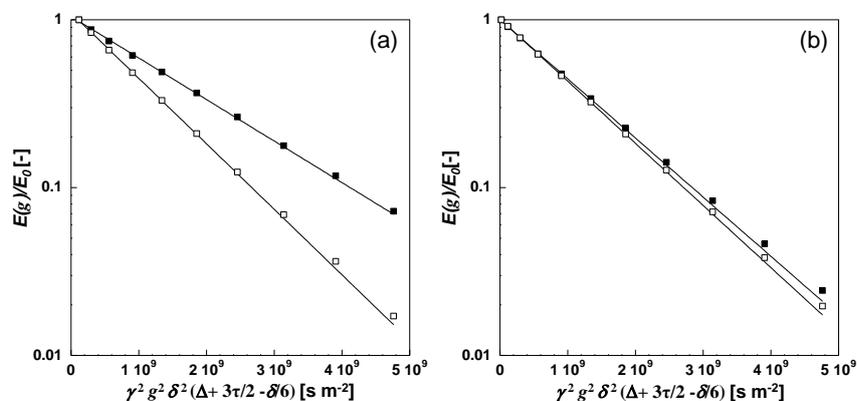


Figure 3. ^1H PFG NMR plots of: (a) 5% and (b) 50% 1,4-dioxane (■) in cyclohexane (□) binary mixtures within TiO_2 . Solid lines are fitting of equation (24) to the experimental data points.

For the 5% mole fraction (Figure 3a) the difference in the slope of the log attenuation plots of 1,4-dioxane and cyclohexane can be clearly seen in the graph, which indicates two very distinct self-diffusion coefficient values, a much faster self-diffusivity for cyclohexane, $9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, compared to the value for 1,4-dioxane of $5.7 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. Conversely, for the 50% mole fraction (Figure 3b), the PFG NMR log attenuation plots exhibits similar slopes, indicating that both components within the mixture diffuse at a similar rate.

The values of self-diffusivity for 1,4-dioxane and cyclohexane in TiO_2 over the whole composition range are reported in Figure 4. It is noted that in Figure 4 we report the actual values of 1,4-dioxane mole fraction, that is, measured inside TiO_2 using ^1H NMR spectra. These values are noticeably different from those of the bulk mixtures used to load the TiO_2 ; in particular we have found that such values are greater, suggesting a preferential attractive interaction between 1,4-dioxane and the pore walls. The values of self-diffusivity are clearly lower compared to the case of bulk liquid, due to the confinement of the mixture within the pore space and consequent decrease of the root mean square displacement (RMSD) of guest molecules. Several important observations can be made on Figure 4. Firstly, over the whole composition range, for the mixtures in TiO_2 the diffusion of 1,4-dioxane is slower than that of cyclohexane, as opposed to the case of bulk liquid mixtures, where 1,4-dioxane exhibits a faster diffusion. Another major difference between 1,4-dioxane and cyclohexane can be observed: the diffusion profile of cyclohexane in TiO_2 is

qualitatively very similar to that observed for the bulk but shifted towards lower values of self-diffusivity. The profile for 1,4-dioxane shows a clear qualitative difference; in particular, the presence of the porous materials seems to affect significantly the self-diffusivity profile at low 1,4-dioxane mole fractions.

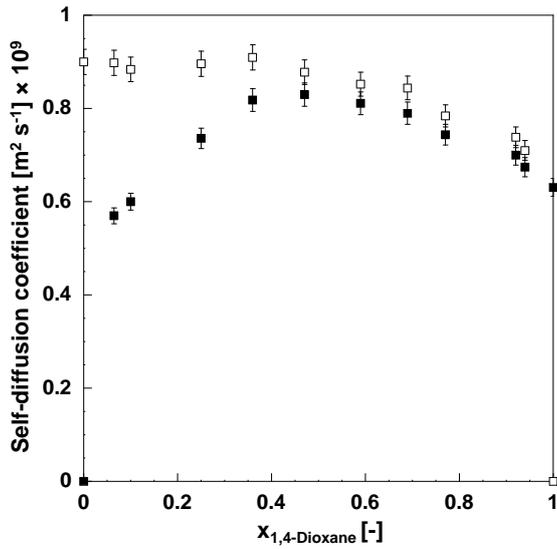


Figure 4. Self-diffusion coefficients within TiO₂ of 1,4-dioxane (■) and cyclohexane (□) as a function of 1,4-dioxane mole fraction measured inside the TiO₂ pore space from ¹H NMR spectra.

In order to assess in more detail the diffusive behaviour of this mixture in TiO₂, it is useful to calculate the PFG interaction parameter defined as [23]:

$$\xi = \frac{D_{0,i}}{D_{\text{eff},i}} \quad (23)$$

where $D_{0,i}$ is the self-diffusivity of component i in the bulk liquid mixture and $D_{\text{eff},i}$ is the self-diffusivity of the same component within the pore space. A plot of the PFG interaction parameter, ξ , as a function of mole fraction is reported in Figure 5. Such a ratio can be considered to be equal to the tortuosity, τ , of the porous material, if weakly-interacting molecules such as alkanes, are used as probing species [24]. However, for other molecules, this is generally not the case, as previously demonstrated [6, 24].

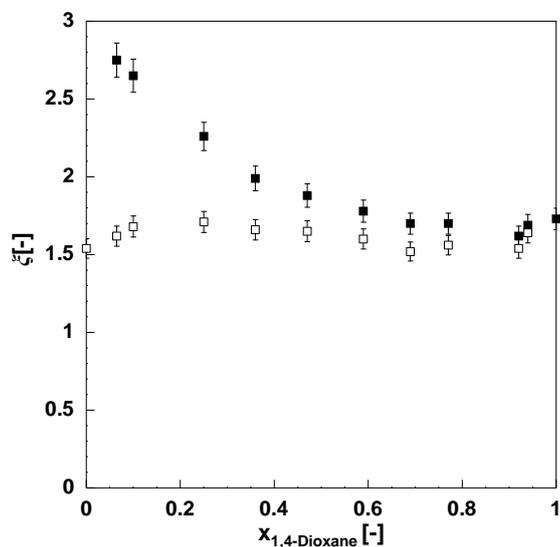


Figure 5. Plot of the PFG interaction parameter, ξ , in TiO_2 for mixtures of 1,4-dioxane (■) and cyclohexane (□) as a function of 1,4-dioxane mole fraction [measured inside the \$\text{TiO}_2\$ pore space from \$^1\text{H}\$ NMR spectra.](#)

Tortuosity is an intrinsic characteristic of the porous matrix, such as porosity, and therefore its value should be independent of the probe molecule used as well as composition. The use of alkanes as suitable molecules to probe tortuosity of porous materials with PFG NMR is justified by the observation that these are weakly-interacting species [25] and therefore any reduction in diffusivity will mainly be due to geometric characteristics of the pore structure, in particular, pore network connectivity [24]. It is clear from Figure 5 that the ξ values for cyclohexane are similar, within the experimental error, over the whole composition range, with a value of 1.60 ± 0.06 . This value can be taken as a good estimate of tortuosity of the mesoporous TiO_2 and indeed it is consistent with tortuosity measurements previously estimated for the same material using a series of pure alkanes [24]. This new result also suggests that even within mixtures, alkanes seem to behave ideally in terms of diffusion within mesoporous materials, that is, the self-diffusivity is reduced by the geometrical factor τ and the composition has no significant effect on the extent of such a reduction.

The behaviour of 1,4-dioxane is rather different. At low mole fractions, this molecule shows much larger values of ξ relative to cyclohexane (i.e., much larger decrease in self-diffusivity relative to the bulk liquid) compared to high mole fraction. The ξ values of 1,4-dioxane decrease as its mole fraction increases, reaching a plateau above 40% mole fraction, with values slightly above those obtained for cyclohexane. It is clear that despite the similar molecular weight and size these two species behave quite differently when they are confined in the TiO_2 pore space.

In order to understand this different behaviour, one has to consider the molecular structure of the two species. Cyclohexane is a cyclic alkane, it is non-polar with a bulk dielectric constant of $\epsilon = 2.02$ and the only interactions involved are van der Waals forces; 1,4-dioxane is a cyclic ether with a bulk dielectric constant almost identical to that of cyclohexane, $\epsilon = 2.25$. Similarly to alkanes, ether molecules, such as 1,4-dioxane, cannot form hydrogen bonds with themselves nor with alkanes. Therefore, within bulk binary mixtures, van der Waals forces will be the dominant inter-molecular interaction and this may well explain why 1,4-dioxane behaves very similarly to cyclohexane when both species are diffusing in bulk liquid mixtures (see Figure 1).

However, it is important to note that 1,4-dioxane can act as a Lewis base through the two oxygen atoms with lone electron pairs [26]. Indeed, this is thought to be responsible for the inhibitory effects of 1,4-dioxane when used as solvent in several liquid-phase catalytic reactions in porous solids [5, 27]. Therefore, when liquid mixtures of 1,4-dioxane and cyclohexane are confined within the mesopores of TiO_2 , 1,4-dioxane can interact with the Lewis acid sites in TiO_2 , which can accommodate the unshared pairs of electrons of the oxygen atoms in 1,4-dioxane, the latter acting as a Lewis base. Indeed, Lewis acid-Lewis base pairs are formed when oxygenated compounds are adsorbed onto metal oxides [28]. Conversely, cyclohexane interactions within the pore space will still be dominated by weaker van der Waals forces. Indeed, in general, the use of saturated hydrocarbons as solvent media for catalytic reactions over porous oxide-based catalysts does not lead to any significant inhibition relative to heterocyclic oxygenated compounds [1, 4]. The high values of the PFG interaction parameter, ξ , of 1,4-dioxane at low 1,4-dioxane mole fraction can therefore be rationalised by considering the formation of Lewis base-Lewis acid pairs. When 1,4-dioxane is very dilute in cyclohexane, it is reasonable to expect that most of

the population of 1,4-dioxane molecules will have preferential interactions with the TiO₂ surface relative to cyclohexane, which may affect significantly the diffusion pathway within the pores, in addition to geometrical restrictions [24]. These findings are also in agreement with the increased mole fraction of 1,4-dioxane measured inside TiO₂ relative to the bulk mole fraction, which is indicative of preferential interaction of 1,4-dioxane with the pore walls of TiO₂. It is worth noting that it has been reported that trace amounts of 1,4-dioxane in benzene can seriously deactivate and spoil catalysts used for the production of linear alkyl benzenes [29]. As the mole fraction of 1,4-dioxane increases, 1,4-dioxane molecules will tend to cover a higher portion of the solid surface, forming multilayers. At this point the average self-diffusion of 1,4-dioxane will start to be dominated by the bulk phase within the pores, approaching a “bulk-like” behaviour, similar to that observed for cyclohexane. That is, the weighting of the self-diffusivity value of 1,4-dioxane moves from a more “surface-dominated” behaviour, at low mole fractions, to a more “bulk-dominated” diffusion mechanism as the mole fraction increases. As for cyclohexane, because this molecule can only form weak van der Waals interactions, it is expected that the surface will have a weak or negligible effect, which explains why the PFG interaction parameter is essentially not affected by mole fraction.

In summary, we have shown that it is possible to use PFG NMR to unambiguously probe diffusion of mixtures within mesoporous materials and that important information on the diffusion mechanisms and molecular interactions within the pores can be gained by the collected data. Weakly-interacting molecules, such as alkanes, show changes in their diffusion behaviour within TiO₂ pores due to the presence of geometrical constraints only; conversely, the diffusion behaviour of 1,4-dioxane will also be affected by interactions within the pore space, which are likely to be Lewis base-Lewis pair formation between 1,4-dioxane and TiO₂, respectively. This type of study may be of high significance when studying, for example, catalytic reactions within porous catalysts and may help to understand catalytic performances and its relation to the diffusion properties of molecules.

Conclusions

PFG NMR has been used for the first time to understand the diffusive behaviour of liquid binary mixtures within mesoporous materials. The effect of composition on self-diffusivities in mixtures of 1,4-dioxane and cyclohexane, common solvents used

in liquid-phase heterogeneous catalysis, has been assessed both in the bulk liquid and liquid within the porous matrix of TiO₂. For bulk liquid mixtures, diffusion profiles of both species as a function of composition show maxima, which can be related to an increase of excess molar volume. The confinement of the liquid mixtures within the TiO₂ porous matrix has a significant effect on the self-diffusivity of 1,4-dioxane, which is influenced by a change in molecular interactions within the pores and are likely to be caused by Lewis base-Lewis acid pairs between 1,4-dioxane and TiO₂, respectively, which is reflected in the inhibitory effects observed when this species is used as solvent in catalytic reactions on porous oxide-based catalysts. Conversely, the self-diffusivity of cyclohexane is only affected by geometric features of the porous matrix, hence scaled down by the tortuosity factor, in agreement with previous studies. This work shows that it is possible to use PFG NMR to study diffusion processes in rather complex environments, such as multi-component mixtures within porous catalytic materials. The technique is able to probe changes in both geometric characteristics of the porous structure and molecular interactions due to the presence of the pores, and the knowledge gained may be used to understand and model various processes, including separation and catalytic reactions.

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