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Propane diffusion in ZSM-5 pores measured by quasielastic neutron scattering under macroscopic flow

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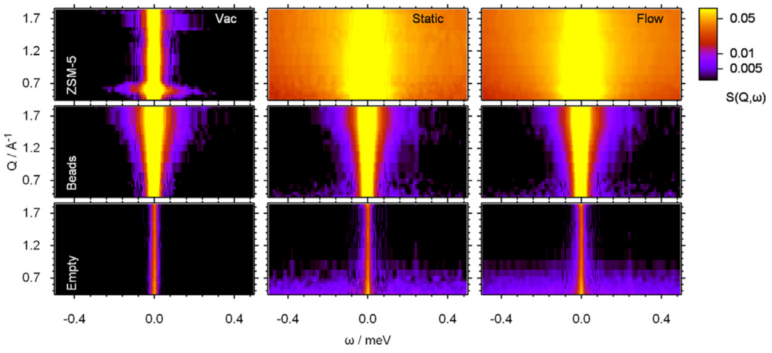
HIGHLIGHTS

- Increase in pore diffusion rate under gas flow.
- Selective measurement from condensed phase, not gas.
- Insight into diffusion under dynamic conditions.

GRAPHICAL ABSTRACT



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ABSTRACT

Quasielastic neutron scattering (QENS) was used to investigate the diffusion of propane in zeolite ZSM-5 under static and macroscopic flow conditions. The rate of self-diffusion in the adsorbed phase was slightly faster under the flow conditions studied. Control measurements showed that the broadening seen in the quasielastic signal must result from propane condensed in the zeolitic pore and not from gas, either in the bulk or inter-particle voids.

1. Introduction

Microporous materials have a range of uses that are important to society. Recently, there has been an explosive expansion in microporous materials with the advent of metal organic frameworks (MOFs) that allow remarkable synthetic possibilities and new reactive capabilities (Li et al., 2014). However, their practical applications are limited and zeolites remain the pore frameworks most widely used in roles where adsorption and desorption of hosts are beneficial. This includes ion-exchange effects used in water softening formulations for washing powders (Smoot and Lindquist, 1997) or the size selectivity of cracking catalysts in the petrochemical industry (Smit and Maesen, 2008). Gas separation (Cheung and Hedin, 2014) and storage (Dong et al., 2007) are also of great interest with both reversible (gas storage) and irreversible (CO_2 sequestration and waste management) applications.

Access to the internal structure of microporous materials is controlled by factors such as the particle size, ratio of macro- and mesopores, and crystallite dimensions. Measurement of diffusion

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rates is of key importance as poor diffusion can limit the reaction rate in a catalyst or the practicality of a storage medium. The results obtained can be problematic, with techniques proving contradictory, as each operates over a limited time/distance scale. Macroscopic limitations, such as particle size effects, may dominate and prevent an assessment of the true movement within a pore. As a result, a variety of techniques are used, such as microscopic tracer studies (Kärger et al., 2006), zero-length column chromatography (Gunadi and Brandani, 2006), frequency modulation (Song et al., 2002), and pulse-field gradient NMR (Arzumanov et al., 2015). Each of these methods has drawbacks but in general provide a measure of the diffusion coefficient over length scales greater than the size of adsorbent crystallites.

Quasielastic neutron scattering (QENS) measures the Doppler broadening of a neutron beam after scattering from atoms in motion. This provides information on motions occurring over the time scale of picoseconds to nanoseconds and Angstrom lengths. It has been used to probe self-diffusion of sorbates in zeolites for a few decades (Wright and Riekel, 1978, Stockmeyer, 1997, Gergidis et al., 2000, Sharma et al., 2008, O'Malley et al., 2016a, 2016b) and provides the most accurate measure of microporous transport. Obtaining a greater appreciation of the diffusion process on the molecular scale, may allow rational design to generate materials with improved properties.

The signal obtained from a QENS experiment on a sample containing hydrogen, is dominated by the incoherent scattering of the hydrogen atoms, since its neutron incoherent cross-section is the largest of all elements. The measured incoherent scattering function $S(Q, \omega)$, describes the intensity of the incoherently scattered neutrons as a function of Q, the momentum transfer and $\hbar\omega$, the energy change resulting from the scattering event. This scattering function, also referred to as the dynamic structure factor, contains all the information on the dynamics of the atoms, and is the time and space Fourier transform of the van Hove function $G(r, t)$. QENS typically probes processes where the energy transfer $\hbar\omega$ is small (quasi- or near zero) which corresponds to molecular motions such as rotational and translational modes. These are typically treated as independent motions such that the dynamic structure factor can be mathematically written as the convolution of two components:

$$S_{quasi}(Q,\omega) = S_{trans}(Q,\omega) \otimes S_{rot}(Q,\omega) \tag{1}$$

The simplest case for translational diffusion is that of isotropic continuous diffusion according to Fick's law. On the microscopic scale the diffusion gradient is sufficiently small that this corresponds to Brownian motion and gives a Lorentzian scattering function. The broadening of the Lorentzian, the full- width at half maximum (2Γ), varies as DQ^2, where D is the self-diffusion coefficient i.e. the diffusion coefficient with the chemical potential gradient equal to zero. An alternative model is that of jump diffusion on a lattice, which can be described by the Singwi-Sjölander model (Singwi and Sjölander, 1960). This specifies periodic jumps occurring between energy minima where the scatterers perform oscillatory motion. The peak broadening is also described by a Lorentzian in this model, with width variation in Q given by

$$2\Gamma(Q) = \frac{1}{6\tau} \times \frac{Q^2\langle r^2\rangle}{1 + Q^2\langle r^2\rangle/6} \tag{2}$$

The diffusion constant is given by $D = \langle r^2\rangle/6\tau$ for this model, where $\langle r^2\rangle$ is the mean square jump length and τ is the time between instantaneous jumps. The diffusion constant is then calculated from the extracted fitting parameters. Obtaining the diffusion constant at a number of temperatures therefore easily allows calculation of the activation energy of diffusion using an Arrhenius plot.

In this experiment the IRIS neutron backscattering spectrometer at the ISIS Pulsed Neutron and Muon Source, Didcot, UK was run using the (0 0 2) reflection from a pyrolytic graphite analyser which provides coverage in Q of 0.42–185 $Å^{-1}$, a dynamic range of −0.4 to +0.4 meV and an energy resolution of 17.5 μeV (Campbell et al., 2000, Carlile and Adams, 1992). The resolution of the instrument provides a limit to the broadening that can be measured and therefore slowest motion that may be detected. For observable motions, the peak structure is modified by the resolution, and must be convoluted with the fit function. The resolution function is experimentally measured using a sample that displays no motion on the timescale of the instrument. Individual fitting for each value of Q can thus be described as

$$S(\omega) = f\left[A_0\delta(\omega) + A_1\frac{1}{\pi}\frac{\Gamma}{\omega^2\Gamma^2}\right] \otimes R(\omega) + B(\omega) \tag{3}$$

where f, A_0 and A_1 are scaling functions, $R(\omega)$ is the instrumental resolution function and $B(\omega)$ is a linear background.

In the field of catalysis there is an increasing drive towards operando measurements. The ultimate goal is to measure the reacting system whilst operating under realistic industrial conditions. For this methodology it is important to minimise the interference from the reactor in making a measurement. As this is impractical in many cases, practitioners seek to minimise the changes in reactor design and conditions necessary to obtain the required measurement at realistic operating conditions. It is unrealistic for a university researcher to build a multi-tonne reactor for their investigation, but the conditions of pressure, flow and mixing, etc. can be replicated on a lab scale through careful design. Development of new techniques and sample environment is key to this field, allowing simultaneous measurement under increasingly extreme conditions.

Prior diffusion measurements using QENS have predominantly been made under static gas loading conditions. However, many catalytic processes operate under a flowing gas stream. Whilst QENS has previously been used to measure liquid flows (Wolff et al., 2005), the measurements reported here demonstrate the use of the technique to measure an adsorbed phase in equilibrium with a flowing gas. This is the first demonstration of QENS measurement of an adsorbed phase in equilibrium with a flowing gas to the best of the authors knowledge. In this article we report the measurement of propane in ZSM-5 under both static (batch) and flow conditions, in a newly built niobium cell of annular geometry optimised for the QENS technique. ZSM-5 is a synthetic aluminosilicate zeolite widely used in the petrochemical industry as a solid acid catalyst. The framework structure is well characterised and measurement of propane diffusion with QENS in ZSM-5 has been previously reported by Jobic et al. (1992)

2. Experimental

The ammonium form of ZSM-5 was obtained from Johnson Matthey (Intercat IC16926, Si:Al ratio 30) and calcined in air at 773 K for 5 h to remove any residual template. The zeolite was loaded into the annulus of a custom-made niobium sample holder that allowed sample preparation to be carried in place. The design was adapted from the standard aluminium cells used on the quasielastic instruments at ISIS. Annular geometry allows the sample to fill the beam without shadowing of the detectors and decreases the chance of multiple scattering from the sample. The outer diameter of the annulus was 20 mm, which matches the beam width on the IRIS instrument used (Campbell et al., 2000, Carlile and Adams, 1992), and an annular spacing of 2 mm was chosen, as it is well suited for gas adsorption experiments. Niobium was chosen due to its chemical inertness, neutron compati-