

Dynamics of water within Cu-loaded zeolites: A quasielastic neutron scattering study

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ABSTRACT

Quasielastic Neutron Scattering (QENS) was employed in order to probe the dynamics of water confined within copper-loaded MOR, MFI and CHA zeolite frameworks in the temperature range 100–300 K. At 100 K, motion was outside the experimental time window and the adsorbate appeared static. Rotational quasielastic line broadenings were observed across all three Cu-zeolites at 200 K; and both rotation and translation were pronounced at 300 K. The findings indicate Cu content and the cavity size affect water mobility, which appears to represent diffusion within localised clusters.

1. Introduction

Zeolites are tectosilicates primarily composed of linked SiO₄ tetrahedra, that form a plethora of three-dimensional structures with various pores and cavities [1,2]. Framework Si⁴⁺ can be substituted with Al³⁺, yielding anionic sites due to a charge imbalance. This negative charge may be compensated for by either H⁺ or metal cations, giving rise to both Brønsted and Lewis acid sites (BAS/LAS) [3]. This renders zeolites to be exceptional heterogeneous catalysts for numerous processes including molecular sieving, NO_x remediation, ion capture and activation of unreactive hydrocarbons [4]. This latter application is of a particular interest in the pursuit to valorise methane from natural gas via its direct conversion to methanol [5]. This reaction is effected *in vivo* by iron and copper metalloenzymes called methane monooxygenases, or MMOs [6]; the framework topology and tunable acidity of zeolites can define well-controlled local coordination environments to these metals in a similar way [7]. Despite Fe-zeolites being active towards the partial oxidation of methane, Cu-loaded zeolites have been the subject of the majority of research due to their ability to activate the C–H bond using oxygen as the sole oxidant, and water as the methanol extraction solvent [8]; with mordenite (MOR), ZSM-5 (MFI) and SSZ-13 (CHA) frameworks currently the best performers in terms of methanol production per copper atom [9]. However, this requires separate process steps for

production and extraction of methanol whereas continuous flow would be both more efficient and industrially preferable. Currently the best descriptor of the active species responsible for partially oxidising methane within Cu-loaded zeolites comprises two Cu²⁺ ions bridged by a single oxygen. Independent evidence for this mono(μ-oxo)dicopper species has come from resonant Raman spectroscopy, EXAFS and DFT calculations [10–13]. However, other structures such as mono- and tri-copper species have also been proposed and the subject is still a matter of ongoing debate in both biological and chemical communities [9,14].

With a proliferating body of research on the active sites and mechanisms involved in this direct methane-to-methanol conversion, it is somewhat surprising that there is a paucity in literature documenting the dynamics of molecules within copper-loaded zeolites. Other studies investigating molecules such as ammonia [15], methanol [16], propene [17] and water [18] confined within other zeolite structures have been reported, but very little is available on Cu-based methane-to-methanol conversion catalysts. Water plays a key role in this reaction, among a variety of other biological, chemical and geophysical processes [18]; understanding how its dynamics are influenced by surface interactions and geometrical confinement is thus a fundamental step in optimum catalyst design for direct methane-to-methanol conversion and beyond.

Purely silicious zeolitic materials are hydrophobic and do not permit

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continuous sorption of H₂O molecules in an equivalent density of liquid water [19]. Increasing the aluminium and associated cation content within the framework leads to strong dipole-ion interactions subsequently increasing polarity and reducing the hydrophobicity [20]. Furthermore, a recent and comprehensive review by Mitra et al. [21] discusses a variety of features, from framework topology and cation content to guest molecule size, symmetry and amount, which collectively determine the nature of the dynamics of guest-host interaction. Zeolite composition therefore clearly affects the access and egress of reactants and products to and from active sites. Diffusion is the primary process by which guest molecules migrate between different regions of the framework, and mass transfer limitations can affect overall rates [22]. With the structure and chemistry of both the host and the guest influencing the dynamics, there is presently no consensus on the mechanisms directing diffusion in zeolites [23,24].

Quasielastic neutron scattering (QENS) allows measurement of diffusion on the molecular length and ps time scales, whereas most other measurement techniques average over much longer distances and times. QENS can therefore provide a fundamental understanding of the diffusion mechanisms and so is an ideal tool to investigate the diffusion of water within prototype Cu-loaded mordenite, SSZ-13 and ZSM-5 methanol synthesis catalysts.

2. Experimental

2.1. Preparation of zeolites

Commercial grade ammonium precursors of mordenite and ZSM-5 (Si/Al = 10 and 15, respectively) were purchased from Alfa Aesar; H-SSZ-13 (Si/Al = 12) was kindly supplied by Johnson Matthey. The ammonium precursors of mordenite and ZSM-5 were calcined at 823 K, in air, for 8 h to yield H-MOR and H-ZSM-5. The three protonic zeolites were then subjected to ion exchange by placing each zeolite into 0.1 M Cu(NO₃)₂ and stirring continuously for 24 h at 298 K. The zeolites were then washed with deionised water and placed in a fresh solution of 0.1 M Cu(NO₃)₂; the process was repeated three times to maximise Cu uptake. This yielded mordenite, ZSM-5 and SSZ-13 containing 3.31, 3.15 and 5.32% Cu (w/w), as determined via X-ray fluorescence analysis (Malvern Analytical Epsilon 3). The powder x-ray diffraction (PXRD) patterns of the catalysts before and after ion exchange were obtained on a Rigaku Miniflex, shown in Fig. 1. The PXRD patterns were compared to the zeolite structure database [25] to ensure matching structures. No change in the patterns pre- and post- Cu loading is visible, indicating successful incorporation of Cu and absence of any extra-framework CuO.

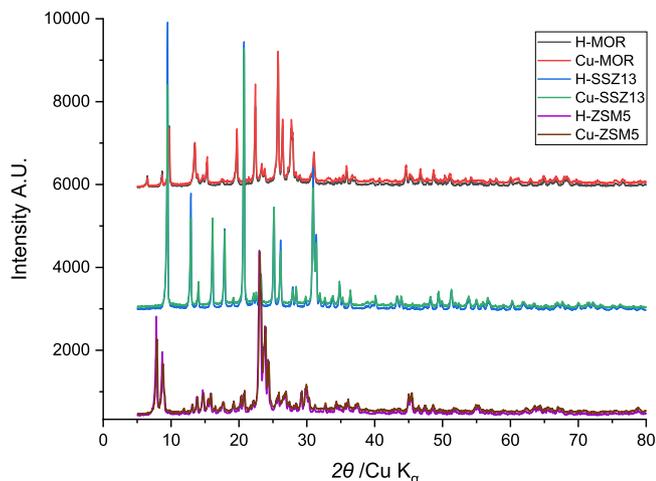


Fig. 1. XRD patterns of the protonic and Cu-loaded Zeolite catalysts.

2.2. Water dosing

Prior to water dosing, the samples were dried in a furnace, overnight, at 623 K using a sample holder which was attached to a vacuum system incorporating a turbopump. The samples were subsequently transferred to an argon-filled glovebox for further processing. A weighed portion of each sample was placed in a desiccator containing saturated KNO₃ solution – which provided 95% relative humidity – for 20 h to ensure equilibrium was reached. The samples were then reweighed prior to sealing in aluminium cans for QENS measurements. This yielded 3 samples comprising: 2.51 g Cu-MOR (37.8% H₂O w/w; ~97 molecules per unit cell); 2.20 g Cu-SSZ-13 (20.0% H₂O w/w; ~30 molecules per unit cell); and 2.16 g Cu-ZSM-5 (12.50% H₂O w/w; ~46 molecules per unit cell). It is worth noting that the calculated numbers of water molecules per unit cell are approximate since they are derived from expected unit cell compositions and corresponding weights; a more concrete determination of framework composition employing a technique such as atomic emission spectroscopy was not possible at this time.

2.3. QENS measurements

QENS measurements were carried out on the IRIS spectrometer [26] at the ISIS neutron and muon source. The (002) reflection from the graphite analyser was used, giving a resolution of 17.5 μeV and covering a Q range of 0.4–1.9 Å. Samples were initially cooled below 15 K to obtain the instrumental resolution function before spectra were collected at 100, 200 and 300 K. The quasielastic peaks of the experimental spectra were fitted with the resolution function convoluted with combinations of a delta function to represent the elastic scattering from immobile atoms and Lorentzian functions to represent the broadening in energy that occurs during scattering from moving particles. Data reduction and analysis were carried out using Mantid [27].

3. Results and discussion

The quasielastic peak for water sorbed on all catalysts at 100 K could be adequately fitted with a Delta function convoluted with the instrumental resolution. This indicates that all scattering is elastic, whether from the zeolite framework or the adsorbate. Elastic scattering occurs from atoms which are static. In this case the diffusive motions are slower than the experimental time window of the instrument, as defined by its resolution. At 200 K, the data was best represented by the resolution convoluted with a delta function and a single Lorentzian (e.g., Fig. 2).

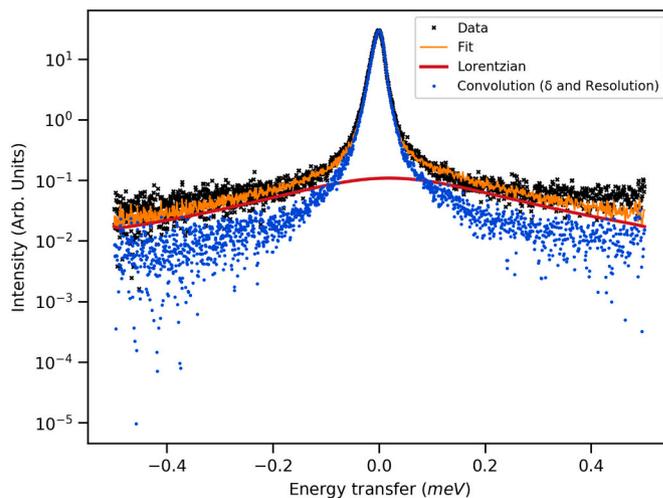


Fig. 2. Data obtained from Cu-Mordenite at 200 K and the subsequent fits applied.

The line widths (Γ) obtained from all three Cu zeolites were independent of Q , as shown in Fig. 3, and correspond to the time constant for the molecular rotation of water, with derived values presented in Table 1. Whilst the geometry of confined motion may be analysed through the elastic incoherent scattering function (EISF), the limited Q range coupled with the small size of water molecules prevented useful analysis in this case.

Spectra collected at 300 K had increased quasielastic line broadenings for all three samples, which were described using two Lorentzian components: one for rotational and one for translational motion (e.g., Fig. 4). The linewidths of the translational component were subsequently fitted using the Singwi & Sjölander (SS) jump diffusion model [28], (Fig. 5), which has a form:

$$\Gamma_Q = \frac{1}{\tau_0} \left[1 - \frac{\exp(-2W)}{1 + DQ^2\tau_0} \right]$$

$$2W = DQ^2\tau_0 \frac{\langle R^2 \rangle}{\langle l^2 \rangle}$$

This model hypothesises that a water molecule undergoes continuous, linear diffusive motion after oscillating for a mean time τ_0 . $\langle R^2 \rangle$ represents the mean square radius of a thermal cloud engendered by the oscillatory motions and $\langle l^2 \rangle$ the mean square jump length. The rotational and translational dynamics thus derived are presented in Table 1.

Both mordenite and ZSM-5 samples present a similar period of rotation at 3.52 and 3.69 ps, respectively, at 200 K; likely as a result of a similar cation content (3.31% in Cu-MOR and 3.15% in Cu-ZSM-5) which act as adsorption sites. The faster rotational time of 2.65 ps observed in Cu-SSZ-13 has a twofold explanation: it contains a higher cation content (5.32%) and a smaller cavity size ($3.8 \times 3.8 \text{ \AA}$) leading to more water-cation interactions, thus causing more frequent reorientation of the molecules. The increase to 300 K decreases the water rotation time within Cu-MOR and Cu-ZSM-5. A much smaller change was observed within Cu-SSZ-13 suggesting that the amount and distribution of copper, as well as the cavity size, have a stronger influence on rotation dynamics than the temperature range probed.

The diffusion constant for water within Cu-ZSM-5, calculated using a two-Lorentzian fit, may be considered questionable. Despite having a comparable residence time to the other samples, the diffusion constant derived ($3.89 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) is greater than that of bulk water at room temperature ($2.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) and the jump length (7.06 \AA) is greater than the pore cage size ($5.6 \times 5.6 \text{ \AA}$). An attempt to fit the data using a single Lorentzian and a flat background – the latter indicating motions

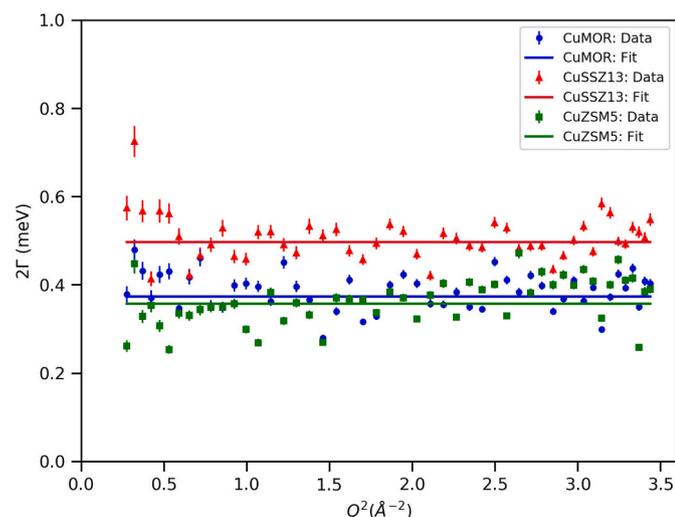


Fig. 3. Lorentzian linewidths from fits to spectra of water-dosed zeolites at 200 K.

Table 1

Rotational & Translational Dynamics of Water in three Cu-loaded zeolites at 200 and 300 K. τ_r and τ_t correspond to rotational and translational components, respectively.

Sample	T (K)	τ_r (ps)	$\sqrt{\langle r^2 \rangle}$ (Å)	τ_t (ps ⁻¹)	D_s (m ² s ⁻¹)
Cu-MOR	200	3.52	–	–	–
Cu-SSZ-13	200	2.65	–	–	–
Cu-ZSM-5	200	3.69	–	–	–
Cu-MOR	300	2.16	4.17	23.19	1.25×10^{-9}
Cu-SSZ-13	300	2.23	3.44	20.64	9.53×10^{-10}
Cu-ZSM-5	300	2.27	7.06	21.35	3.89×10^{-9}
Cu-ZSM-5*	300	n/a	3.65	7.99	2.77×10^{-9}

* Quasielastic line broadening fitted using a single Lorentzian and a background.

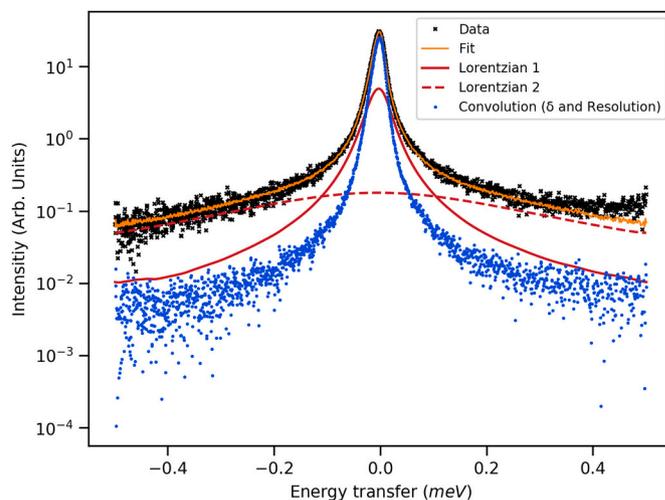


Fig. 4. Data obtained from Cu-SSZ13 at 300 K and the subsequent fits applied.

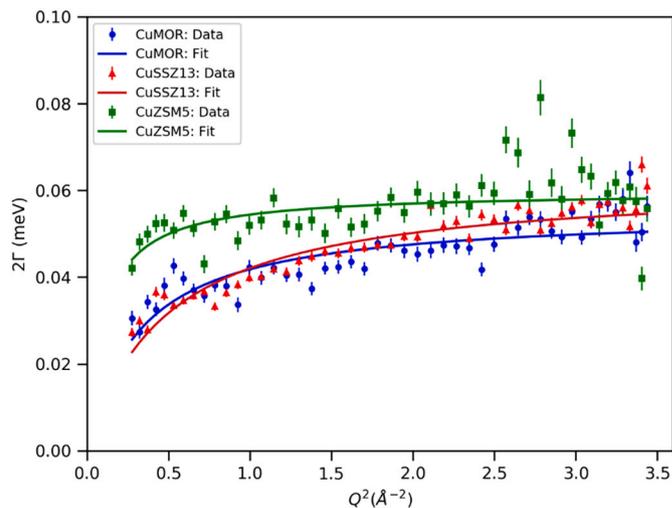


Fig. 5. Lorentzian linewidths from fits to spectra of water-dosed zeolites at 300 K.

which are too fast for the experimental time window probed – resulted in a decrease of the jump length to a more realistic and comparable 3.65 \AA . However, this resulted in a reduced residence time, and the diffusion constant still exceeding that of bulk water. Interestingly, each model provided either a jump length or a residence time parameter comparable to that of the other two zeolites. This indicates that the rotations and

translations may overlap too closely in rate within ZSM-5 to allow their resolution at 300 K. The model comprising a single Lorentzian and a flat background was applied to all samples for comparison purposes; in all three cases the SS model provided a good fit to the Lorentzian linewidths (Fig. 6), however the fits of the individual spectra contained considerably higher residuals indicating that further components are necessary to adequately fit the quasielastic line broadening. The model containing two Lorentzian components can therefore be considered a better representation of these systems, which is indicated by the diffusion constants ascertained for both mordenite and SSZ-13. For example, the D_s value obtained for Mordenite, at $1.25 \times 10^{-9} \text{ m}^2\text{s}^{-1}$, is commensurate to that found within Prussian blue ferrocyanide ($1.36 \times 10^{-9} \text{ m}^2\text{s}^{-1}$) [29] which contains pores of comparable size ($\sim 6 \text{ \AA}$). A fraction of the water is present in the hydration shells around the charge-balancing cations, which affects their mobility; Mitra et al. [30] documented that such water, at lower temperatures, is either rendered immobile (on the timescale of the instrument) or moves very slowly, thus reducing average diffusivity. An increase in temperature, however, reduces this fraction and increases the overall mobility. Sharma et al. [31] also reported this observation and attributed it to an increase in thermal energy, thus allowing water molecules to break the coordination from the cations within the system. Water content also contributes to the diffusivity, since a higher number of water molecules results in bigger clusters, with more molecules situated further away from the framework and the charge-balancing cations, consequently experiencing less hindrance. Hence, the slowest diffusivity found within SSZ-13, at $9.53 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, has a threefold explanation: it has a higher cation content, reduced pore size and a smaller amount of water.

4. Conclusions

QENS was employed to investigate the dynamics of water confined within three different Cu-loaded zeolites. No motions were observed at 100 K; rotational dynamics were deduced at 200 K; and both rotational and translational motions were pronounced at 300 K. Diffusion constants obtained for Mordenite and SSZ-13 are lower than that of bulk water due to the strong interaction between water molecules and the Cu ions present in the zeolites' pores, hindering their jumping between adjacent positions. Furthermore, this is reiterated by the slower diffusivity observed in zeolite SSZ-13, which contains the highest amount of Cu counterions and the lowest content of water. The calculated jump lengths within both of these zeolites are smaller than their pores indicating that the diffusive motions observed are intra- and not inter-crystalline. Indeed, the jump-lengths correspond reasonably closely to that seen in bulk water. Grifoni et al. [32] have recently reported that water does not diffuse between the zeolite's pores, instead concentrating in clusters of limited size at the BAS. The jump lengths observed in this study, therefore, may correspond to jumps within water clusters located at different cationic and BAS. Separately resolving the translational and rotational dynamics of water within Cu-ZSM-5 was not possible, which is likely due to motions overlapping too closely in rate.

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CRediT authorship contribution statement

Vainius Skuuskas: Methodology, Formal analysis, Investigation, Data curation, Writing – original draft, Visualization. **Ian P. Silverwood:** Methodology, Formal analysis, Investigation, Writing – review &

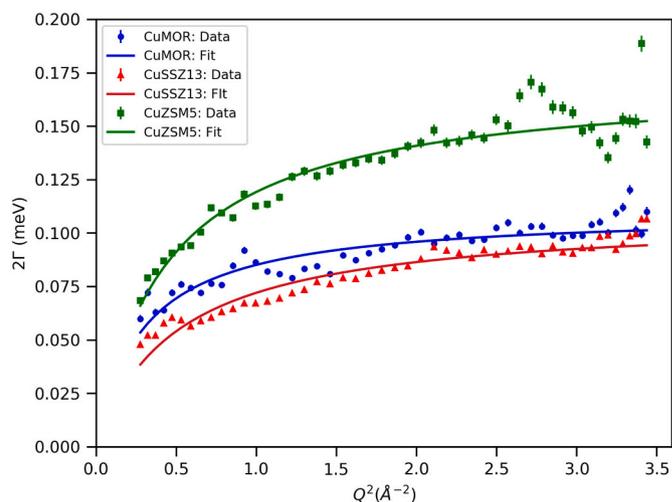


Fig. 6. Linewidths from spectra obtained at 300 K and fitted using a single Lorentzian and a flat background.

editing, Supervision, Project administration, Funding acquisition. **Emma K. Gibson:** Methodology, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

H-SSZ-13 was supplied without charge by Johnson Matthey.

There are no other relevant financial or non-financial competing interests to report.

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