Experimental report

08/09/2021

Proposal: 7-05-530 **Council:** 10/2020

Title: The diffusion of methanol in ZSM-5

Research area: Chemistry

This proposal is a new proposal

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Samples: Zeolite HZSM-5
Methanol / CH3OH

Instrument	Requested days	Allocated days	From	To
WASP	4	4	26/05/2021	30/05/2021

Abstract:

The reaction of methanol over a ZSM-5 catalysts to light olefins and gasoline (methanol-to-hydrocarbons, MTH) is a process that is attracting increasing interest, both academically and industrially. Absolutely crucial to the process is the diffusion of methanol into the catalyst. QENS measurements using the backscattering spectrometer OSIRIS at ISIS, show no translational diffusion in the time window. This is consistent with a 1986 measurement by Jobic et al using IN10 that found a translational diffusion constant "on the order of 10-11 m2 s-1 at 300 K". This measurement was at the limit of IN10, thus an instrument with better resolution so that it can access slower motions is required. This appears ideally suited to spin echo spectroscopy on WASP. We propose to measure the translational diffusion of methanol in an industrial ZSM-5 sample in the empty state and after adsorption of methanol. Three temperatures will be measured to obtain both the diffusion constants and the activation energy. This pilot study will use fresh ZSM-5; if this is successful, then future work will use steam dealuminated ZSM-5, which is more representative of the catalyst as used industrially.

Experimental Report for 7-05-530: Methanol diffusion in a commercial ZSM-5 catalyst

The diffusion of methanol in fresh and steam dealuminated HZSM-5 was investigated by neutron spin echo spectroscopy on WASP. Four measurements were made: (i) an empty can, (ii) a dried, fresh sample of HZSM-5, (iii) fresh sample + methanol and (iv) a steam dealuminated sample + methanol. The empty can (i) provides a background for all the measurements. The dried, fresh sample of HZSM-5 (ii) was to investigate if the zeolite, more specifically the protons of the Brønsted acid sites, showed any dynamics on the WASP time scale, if so, these would need to be accounted for in the analysis of the methanol loaded samples. Figure 1 shows the results at 325 K for sample (ii), it can be seen that, fortunately, there is no movement on the WASP timescale (all traces flat, no Q-dependence). As this sample contains approximately three times as many protons as the sample after steam dealumination, it was decided not to run a blank for the steam dealuminated sample in order to save time for more interesting measurements.

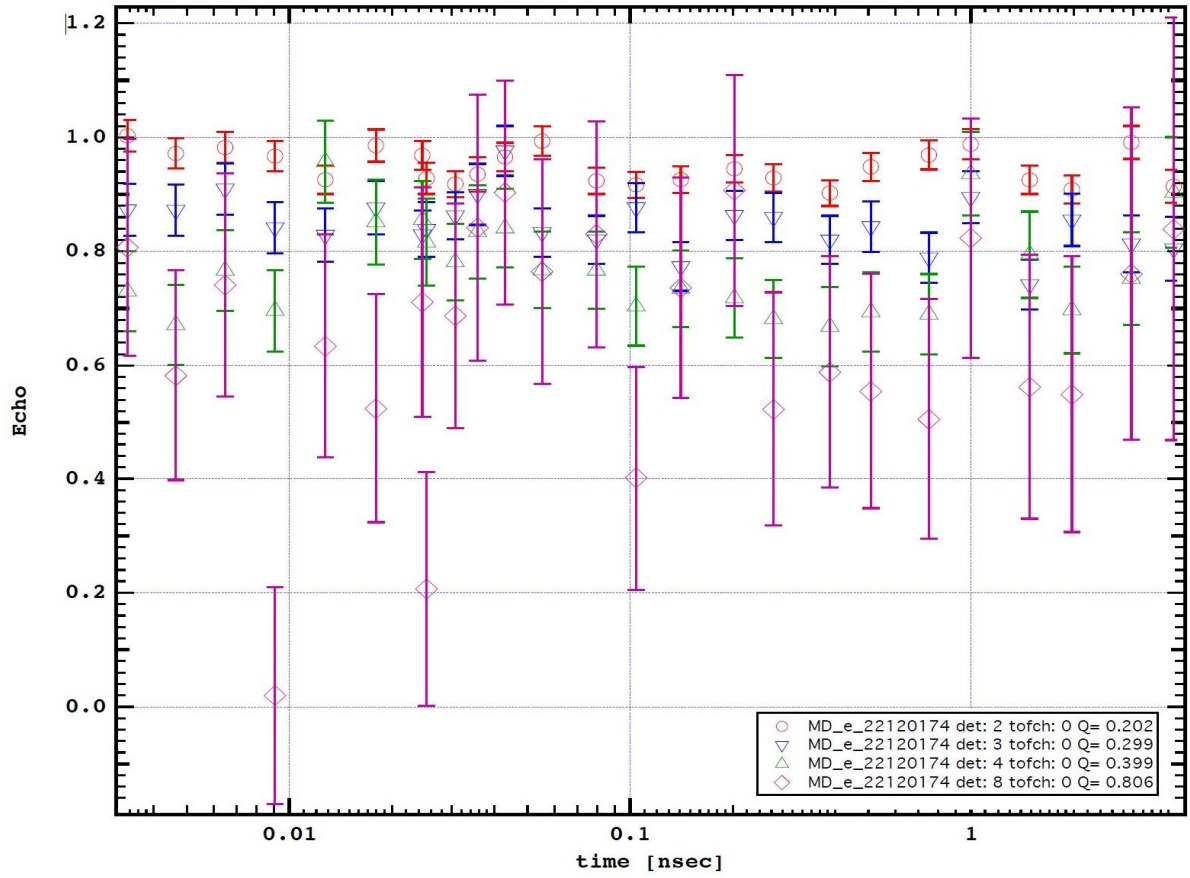

Figure 1: Data for the dried, fresh sample of HZSM-5 at 325 K with an incident wavelength of 6 Å. No movement on the WASP timescale is present.

The fresh HZSM-5 + methanol sample, (iii), shows motion at 275 and 325 K, at 225 K the methanol is static on the WASP timescale, see Figure 2. From the absence of any *Q*-dependence, see Figure 3, the motion appears to be rotational rather than translational and is consistent with rotation within a zeolite pore.

Measurements on the steamed HZSM-5 sample + methanol were also made, but were hampered by an apparent leak in the can. Further analysis of all the data is on-going and is expected to result in a publication.

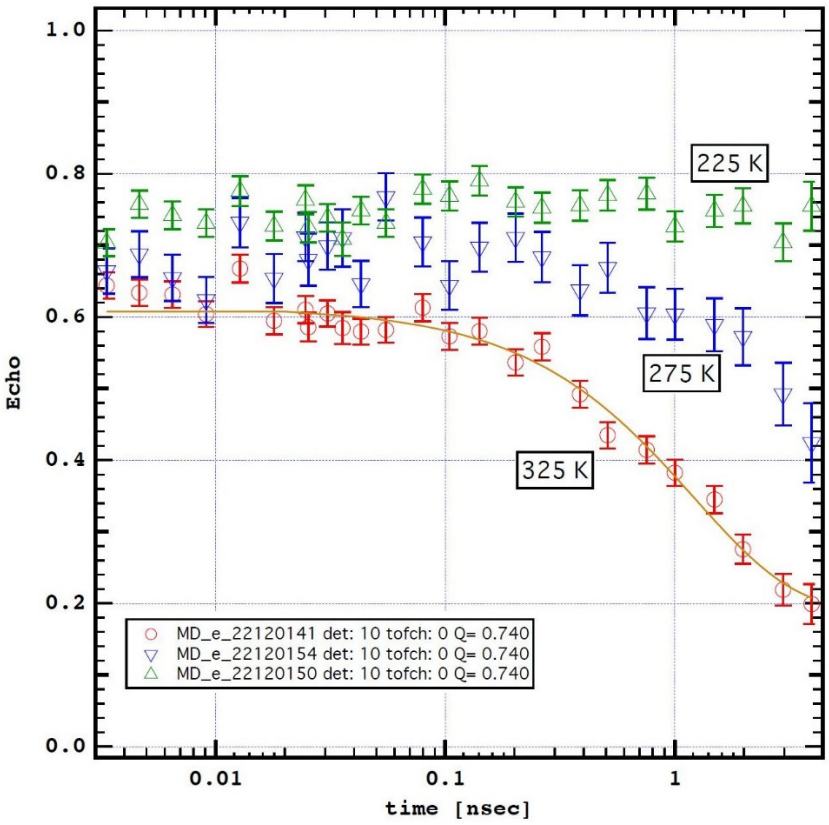

Figure 2: Data for the fresh sample of HZSM-5 + methanol as a function of temperature with an incident wavelength of 6 Å. Motion is apparent at 275 and 325 K but not at 225 K.

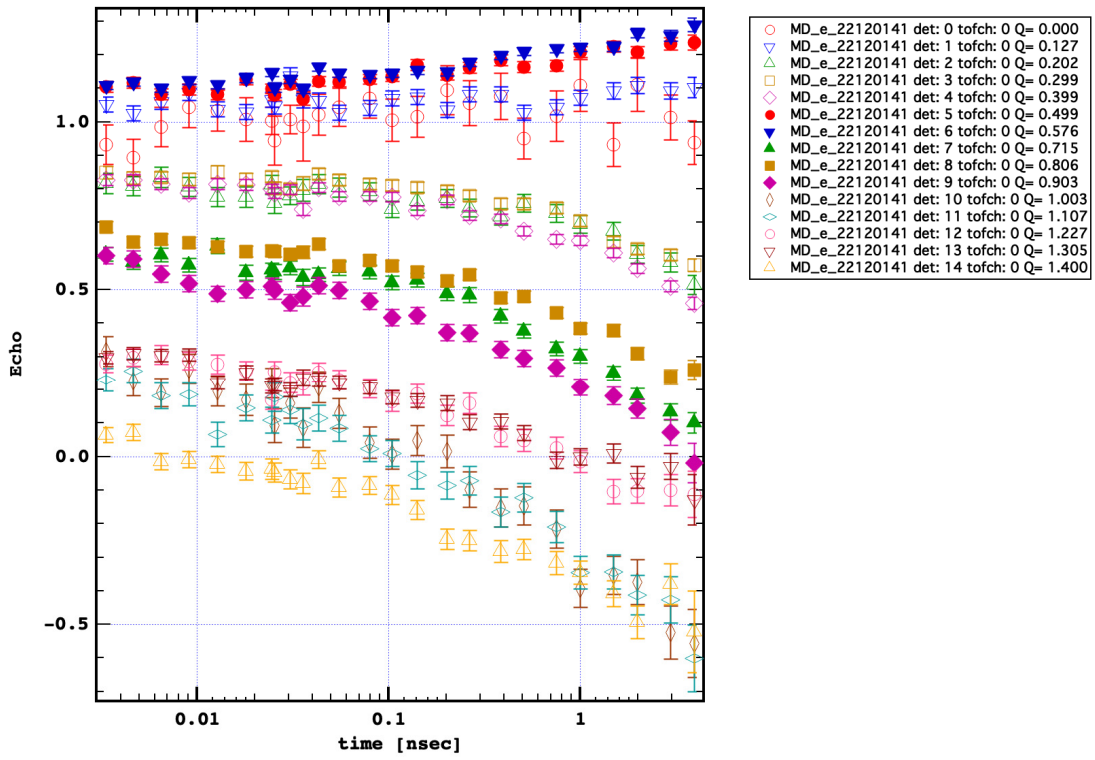

Figure 3: Data for the fresh sample of HZSM-5 + methanol at 325 K as a function of Q with an incident wavelength of 6 Å. The motion is Q-independent, demonstrating that it is rotational in origin.