Experimental report

12/12/2023

Proposal: **7-05-582** **Council:** 4/2023

Title: Probing the dynamics of lignin derivatives within different zeolite catalysts for biomass conversion

Research area: Chemistry

This proposal is a new proposal

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Samples: m-cresol in zeolites (HY, HBeta, HZSM5)
p-cresol in zeolites (HY, HBeta, HZSM5)
Anisole (C_7H_8O) and guaiacol ($C_7H_8O_2$) in zeolites

Instrument	Requested days	Allocated days	From	To
WASP	6	0		
IN16B Si 111 BATS	5	4	18/06/2023	22/06/2023

Abstract:

Lignin is an abundant component of biomass that can be catalytically upgraded into fuels and value-added chemicals. Due to the importance of developing lignin conversion processes, we wish to study the dynamics of model lignin monomers (cresol isomers) within promising acidic zeolite catalysts of varying pore sizes (HY, HBEA, HZSM5). Together, the sub-¿eV-energy resolution of the BATS configuration on IN16B in combination with NSE on WASP should capture the long-range diffusion and rare pore-to-pore or catalytic site-to-site jumping of cresol molecules, which is significant to its overall rate of catalysis. Fundamental studies into cresol mobility upon confinement in shape-selective zeolites will contribute greatly to catalyst development for lignin depolymerisation. Experimental mobility data such as diffusion coefficients and activation energies will help validate and parametrise classical computational force-fields for running simulations, which can then be used to study the effect of further catalytic adaptations and explain the slow rate of cresol diffusion on an atomistic scale.

Experiment Objectives

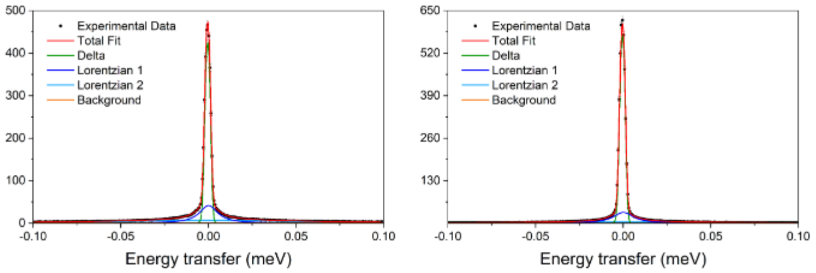
Lignin is a widely available, renewable, and inexpensive resource, with the potential for its transformation into value-added fuels and chemicals hindered by its highly variable and oxygenated structure. Zeolite catalysts show promise in transforming lignin, but for their optimisation the fundamental interactions of the zeolite framework/acid sites with lignin pyrolysis products must first be understood. Hence, we proposed this experiment to investigate the dynamics of the lignin derivatives adsorbed within the commercially available zeolites H-Y (Si/Al = 15) and H-beta (Si/Al = 12.5). With approval, the proposed adsorbates (cresol isomers) were exchanged for anisole and guaiacol. Data gathered will illustrate the influence of zeolite pore size (~12 Å and ~6.7 Å in diameter for H-Y and H-Beta respectively), and molecular shape/functionality on both local and long-range diffusion. IN16b was vital for accessing timescales for translation, which is important to the rate of catalysis. Alongside the QENS data we will run classical MD simulations to help explain our results.

Experiment Set-up

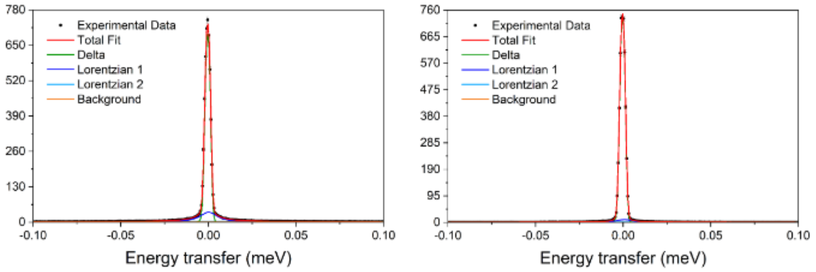
Approximately 2 g of the Brønsted acidic zeolite (H-Y and H-beta) samples were loaded with 10% of guaiacol and anisole, measured at 310, 340 and 370 K. Empty zeolite measurements were taken at 340 K and subtracted from the loaded spectra, scaled as required. A measurement on a vanadium standard was used for calibration, and measurements of the empty cryofurnace and empty cell were subtracted from each measurement. Base temperature measurements (~2 K) were taken on anisole in H-Y and guaiacol in H-beta to use as the delta resolution function. Elastic window scans were also run on a sample of *p*-cresol in H-Y and H-beta from 10-500 K due to spare time.

Experiment Results

QENS spectra taken at Q = 0.95 Å and at 340 K (Figure 1) show more quasielastic broadening with the H-Y versus H-beta samples, due to more mobile molecules/faster dynamics within the larger pores of H-Y. The anisole samples also showed more broadening than guaiacol potentially due its lower melting point/inability to form hydrogen bonds with the zeolite acid sites due to lack of a hydroxyl group/smaller kinetic diameter. A delta function, two Lorentzian functions and a background was convoluted to give a good fit to the QENS spectra.



(a) anisole in H-Y (b) anisole in H-beta



(c) guaiacol in H-Y (d) guaiacol in H-beta

Figure 1. *QENS spectra at Q = 0.95 and 340 K for each sample, fit with a delta and two Lorentzian functions.*

By calculating the elastic incoherent structure factor (EISF) as it varies with Q, we could calculate the mobility of the sample and characterise the possible types of motions occurring, shown in Figure 2.

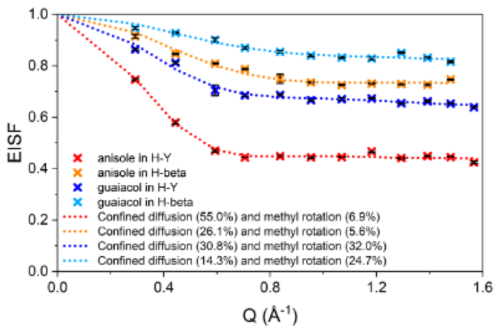


Figure 2. *EISF varying with Q for each sample at 340 K, fit with a combined model of confined diffusion and methyl rotation with their relative percentages shown in brackets.*

The best fit to all of the data sets was a model of confined jump diffusion and methyl rotation in varying percentages. Table 1 shows that generally, with temperature, the percentage of molecules undergoing confined diffusion always increases, with the radius of confinement also increasing but at a size similar to that of the radius of the largest pores/ channel intersections present in the zeolite samples. The fraction of methyl rotation decreases with temperature. This dynamical mode could become hindered as more molecules translate, however it could also be masked by the increase in the diffusive motion. Mostly, the same trends are observed going from H-Y to H-beta, and from anisole to guaiacol in the same zeolite.

System	Temperature (K)	Confined diffusion (%)	Confining radius (Å)	Methyl rotation (%)	Static (%)
anisole in H-Y	310	49.5	5.4	9.7	40.8
	340	55.0	5.8	6.9	38.1
	370	57.5	6.5	5.8	36.7
anisole in H-beta	310	23.6	4.2	5.5	70.9
	340	31.7	4.2	5.6	68.3
	370	27.0	4.7	8.1	64.9
guaiacol in H-Y	310	22.8	4.6	38.8	38.4
	340	30.8	5.1	32.0	37.2
	370	38.0	5.2	26.0	36.0
guaiacol in H-beta	310	6.9	5.6	53.8	39.3
	340	14.3	4.0	24.7	61.0
	370	17.1	4.0	24.2	58.7

Table 1. *The percentages of molecules undergoing confined diffusion (and the radii of such confinement) and methyl rotation contributing to the total mobile fraction.*

The half-width half-maxima (HWHM) varying with Q of the narrower Lorentzian 1 and broader Lorentzian 2 are shown in figure 3(a) and (b), with the associated parameters listed in tables 2 and 3 respectively. Lorentzian 1 corresponds to a model of confined diffusion, with the diffusive region at higher Q fit by a model of jump diffusion (Hall-Ross). Lorentzian 2 must is the methyl rotation.

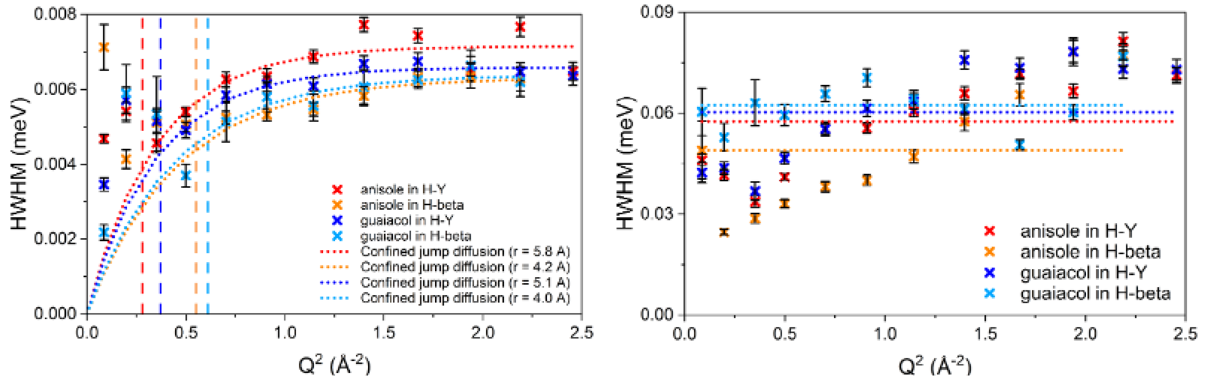
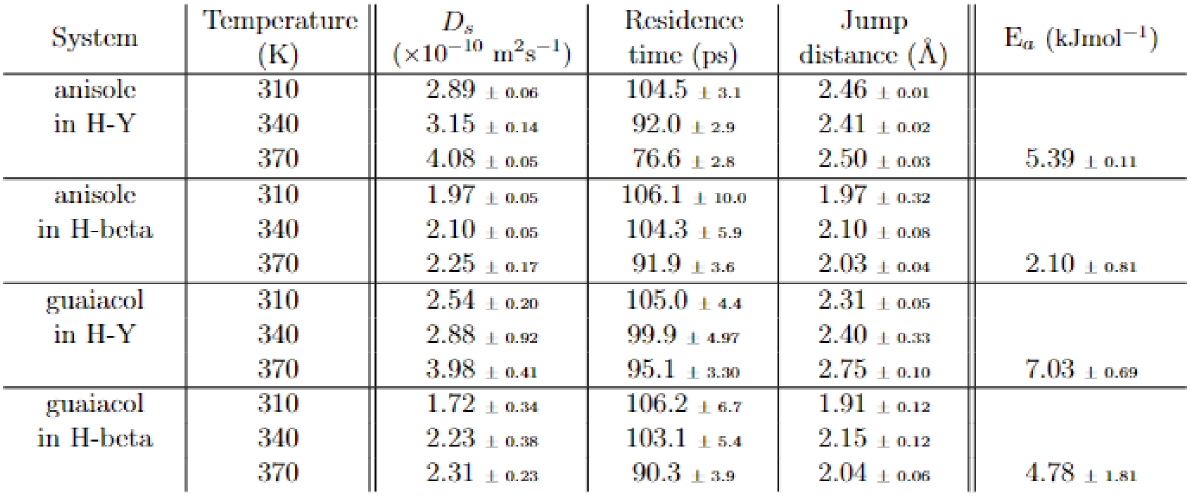


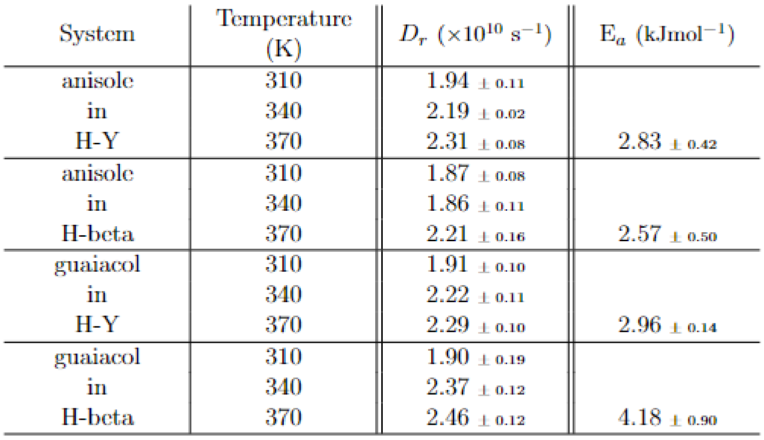
Figure 3. *HWHM obtained from QENS for each sample at 340 K. (a) Lorentzian 1 fit by a model of jump diffusion, but expressing confined diffusion at low Q. (b) Lorentizan 2 fit by a model of rotation.*



System	Temperature (K)	D_s ($\times10^{-10}$ m^{2}s^{-1})	Residence time (ps)	Jump distance (Å)	E$_a$ (kJmol^{-1})
anisole in H-Y	310	2.89 $\pm$ 0.06	104.5 $\pm$ 3.1	2.46 $\pm$ 0.01	
	340	3.15 $\pm$ 0.14	92.0 $\pm$ 2.9	2.41 $\pm$ 0.02	
	370	4.08 $\pm$ 0.05	76.6 $\pm$ 2.8	2.50 $\pm$ 0.03	5.39 $\pm$ 0.11
anisole in H-beta	310	1.97 $\pm$ 0.05	106.1 $\pm$ 10.0	1.97 $\pm$ 0.32	
	340	2.10 $\pm$ 0.05	104.3 $\pm$ 5.9	2.10 $\pm$ 0.08	
	370	2.25 $\pm$ 0.17	91.9 $\pm$ 3.6	2.03 $\pm$ 0.04	2.10 $\pm$ 0.81
guaiacol in H-Y	310	2.54 $\pm$ 0.20	105.0 $\pm$ 4.4	2.31 $\pm$ 0.05	
	340	2.88 $\pm$ 0.92	99.9 $\pm$ 4.97	2.40 $\pm$ 0.33	
	370	3.98 $\pm$ 0.41	95.1 $\pm$ 3.30	2.75 $\pm$ 0.10	7.03 $\pm$ 0.69
guaiacol in H-beta	310	1.72 $\pm$ 0.34	106.2 $\pm$ 6.7	1.91 $\pm$ 0.12	
	340	2.23 $\pm$ 0.38	103.1 $\pm$ 5.4	2.15 $\pm$ 0.12	
	370	2.31 $\pm$ 0.23	90.3 $\pm$ 3.9	2.04 $\pm$ 0.06	4.78 $\pm$ 1.81

Table 2. *The average rates of jump diffusion (D_s) calculated from Lorentzian 1 HWHM.*

Largely, as a function of increasing temperature and zeolite pore size (H-beta to H-Y) and of decreasing molecular size (guaiacol to anisole), an increase in the jump diffusion coefficient is observed. The average residence times decrease and the jump distances increase. The activation energies are close within error.



System	Temperature (K)	D_r ($\times10^{10}$ s^{-1})	E$_a$ (kJmol^{-1})
anisole in H-Y	310	1.94 $\pm$ 0.11	
	340	2.19 $\pm$ 0.02	
	370	2.31 $\pm$ 0.08	2.83 $\pm$ 0.42
anisole in H-beta	310	1.87 $\pm$ 0.08	
	340	1.86 $\pm$ 0.11	
	370	2.21 $\pm$ 0.16	2.57 $\pm$ 0.50
guaiacol in H-Y	310	1.91 $\pm$ 0.10	
	340	2.22 $\pm$ 0.11	
	370	2.29 $\pm$ 0.10	2.96 $\pm$ 0.14
guaiacol in H-beta	310	1.90 $\pm$ 0.19	
	340	2.37 $\pm$ 0.12	
	370	2.46 $\pm$ 0.12	4.18 $\pm$ 0.90

Table 3. *The average rates of methyl rotation (D_r) calculated from Lorentzian 2 HWHM.*

For the rates of methyl rotations, an increase is observed with temperature but with changes in zeolite and molecule type the rate of methyl rotation is largely unaffected, within error. The activation energies are similar within error and lower than that of confined diffusion, except for anisole in H-beta.

The results above will be analysed in depth and compared to molecular dynamic simulations of the same systems run at the same temperatures.