

Potential Parameters

Table 2 Interatomic Potentials used for MCM-41

Charge				
Si		+4		
O		-2		
Oh		-1.4		
H		+0.4		
Buckingham Potential				
		A (eV)	ρ (Å)	C (eV Å ⁶)
Si	O	1283.91	0.32052	10.66158
Si	Oh	983.56	0.32052	10.66158
O	O	22764	0.149	27.88
O	H	396.97	0.25	0
O	Oh	22764	0.149	13.94
Oh	Oh	22764	0.149	6.97
Oh	H	312	0.25	0
Morse Potential				
		D (eV)	α (Å ⁻¹)	R ₀ (Å)
Oh	H	7.0525	3.1749	0.9258
Three-Body Potential				
		K (eV rad ⁻²)	θ_0	
O-Si-O		2.09724	109.47	

Table 3 Internal Parameters for benzene

Charge				
C		-0.153		
Hb		0.153		
Bonds		K (eV)	R ⁰ (Å)	
C-C		48.94	1.385	
C-Hb		31.25	1.085	
Angles		K (eV)	Θ^0 (deg)	
C-C-C		3.44	120	
C-C-Hb		3.44	120	
Dihedrals		A (eV)	n	Δ (deg)
C-C-C-C		0.2166	2	180
C-C-C-Hb		0.0867	2	180
Hb-C-C-Hb		0.0867	2	180

Table 3 Benzene - Benzene and Benzene - MCM-41 potentials

Lennard- Jones Parameters	A (eV Å ¹²)	B (eV Å ⁶)
C-C	32475	39.838
C-Hb	3721.2	7.6182
Hb-Hb	384.84	1.9867
C-O	25022.1	22.99
Hb-O	1563.1	3.20
C-Oh	18331.7	18.63
Hb-Oh	1045.9	2.403
C-H	1299.3	2.588
Hb-H	88.1	0.455

In tables 1, 2 and 3 the symbol Oh refers to an oxygen of a hydroxyl group and Hb to a hydrogen of a benzene molecule.

Experimental - QENS

All measurements were performed using the IRIS time-of-flight inverted-geometry spectrometer at the ISIS Pulsed Neutron and Muon Source, Rutherford Appleton Laboratory, Oxfordshire. Pyrolytic graphite 002 analyser crystals were used giving an energy resolution of 17.5 μeV with energy transfers measured in a window of ± 0.55 meV.

The bulk liquid samples were loaded into 0.1 mm annular aluminium cans with no further preparation. The catalyst samples were first dehydrated under flowing helium gas at 120°C for 2 hours, the complete dehydrated weight of the catalyst was checked by periodically weighing until no further weight loss was observed. After cooling to room temperature the catalyst samples were loaded with each sorbate using a bubbler with helium as a carrier gas until 40 % by weight was achieved. The loaded samples were then transferred to 2 mm annular aluminium cans inside a glove box under an argon atmosphere. Measurements were taken of the unconfined liquids and confined in Pt/MCM-41 along with an empty Pt/MCM-41 sample at 300, 325 and 350 K. The empty measurement was subtracted from the loaded catalyst samples giving just the scattering from the confined sorbates. Resolution measurements were taken at 2 K. All QENS data was reduced using Mantid¹ and analysed using DAVE².

QENS spectra were recorded on the 51 detectors available on the IRIS spectrometer covering a range of Q from 0.42 Å⁻¹ to 1.85 Å⁻¹. These 51 detectors were grouped into groups of 3 to improve the statistics. Only the first 13 groups are used due to the data at high Q (beyond 1.67 Å⁻¹) being of poor quality. Each of the 13 groups was then an average of the spectra recorded on three individual detectors. The data was reduced from TOF to change of energy using the Mantid suite of programs. For the unconfined liquids no further treatment of the data was necessary and analysis of the QENS spectra was undertaken. For the confined liquids the spectra of empty Pt/MCM-41 at each temperature was subtracted from each of the filled catalyst samples leaving only the contribution to the QENS spectra of the motion of the confined liquid.

All of the spectra were convoluted with the resolution function measurement taken at < 10 K which shows no elastic broadening on the instrument timescale. For all of the measurements the data is fit with a delta peak corresponding to the elastic peak convoluted with the resolution function, and two Lorentzians that describe the diffusive motions. The need for two Lorentzians to fit the data suggests that there are two types of motion present in the system. The two Lorentzians are defined as a narrow (HWHM < 0.4 meV) and a broad (HWHM > 0.4 meV). The broad motion shows a linear dependence on Q^2 and so has been ascribed to normal translational diffusion. The narrow Lorentzian corresponds to a jump diffusion motion.

The diffusion coefficient can be obtained from the variation of quasielastic widths with Q . For a linear relationship between Lorentzian HWHM and Q^2 the diffusion coefficient can be obtained through the relationship:

$$\Gamma = D_s Q^2$$

For non-linear relationships the Chudley-Elliott jump diffusion model is used with the form:

$$\Gamma = \frac{1}{t} \left(1 - \frac{\sin Qd}{Qd} \right)$$

And the diffusion coefficient calculated by:

$$D = \frac{d^2}{6t}$$

Unconfined Benzene

MD

Table 8 Diffusion coefficients of benzene

System Size (Å)	Number mol.	Diffusion Coefficient ($\text{m}^2 \text{s}^{-1}$) $\times 10^{-9}$		
		300 (K)	325 (K)	350 (K)
20³	54	1.50	1.71	1.81
25³	106	1.54	1.69	1.84
30³	183	1.56	1.82	1.89
Corrected Diffusion Coefficient		1.68	1.98	2.04

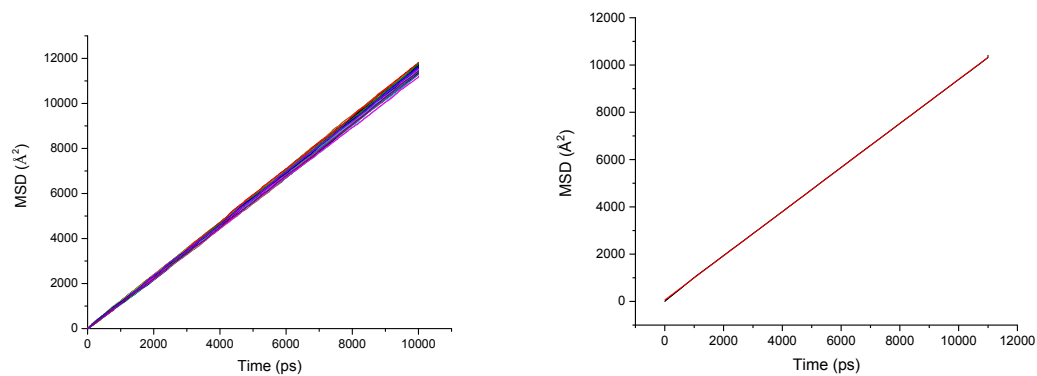


Figure S1 Mean Square Displacement of all 183 individual benzene molecules in the 30 \AA^3 system (left) and average MSD of all benzene molecules (right)

The diffusion coefficient of benzene is calculated from the average MSD of all benzene molecules in each system.

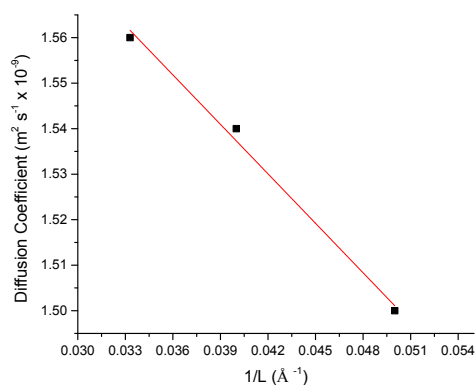


Figure S2 System size dependence of benzene at 300 K

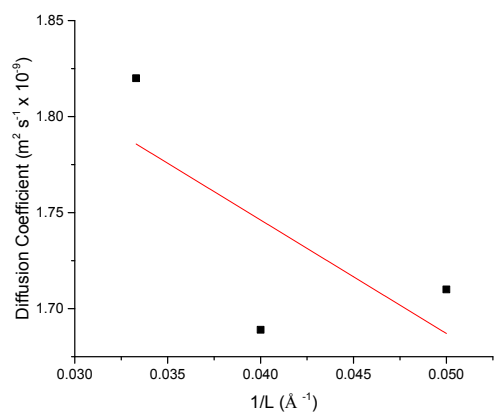


Figure S3 System size dependence of benzene at 325 K

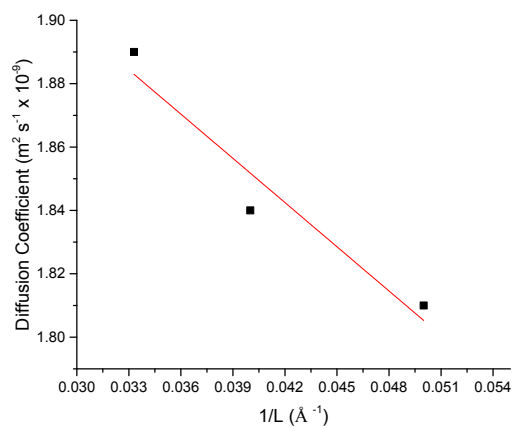


Figure S4 System size dependence of benzene at 350 K

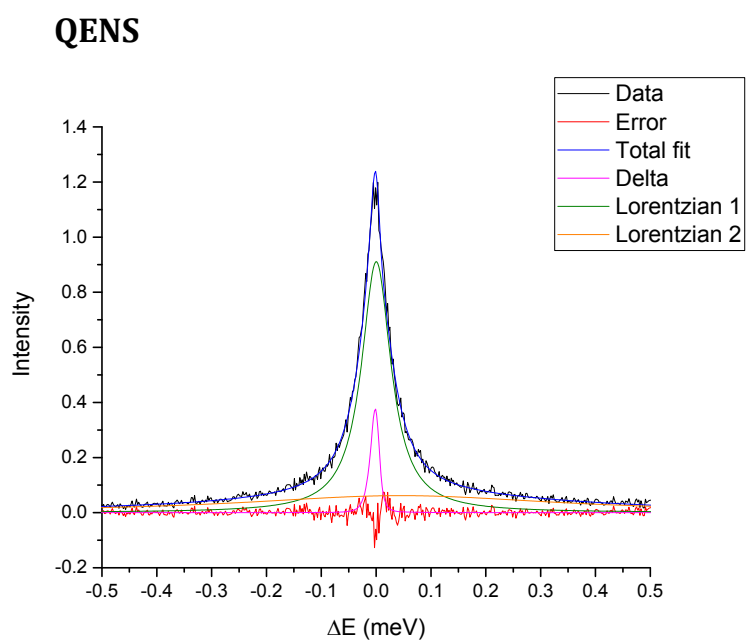


Figure S5 QENS spectra of unconfined benzene - Group 1, $Q = 0.483 \text{ \AA}^{-1}$

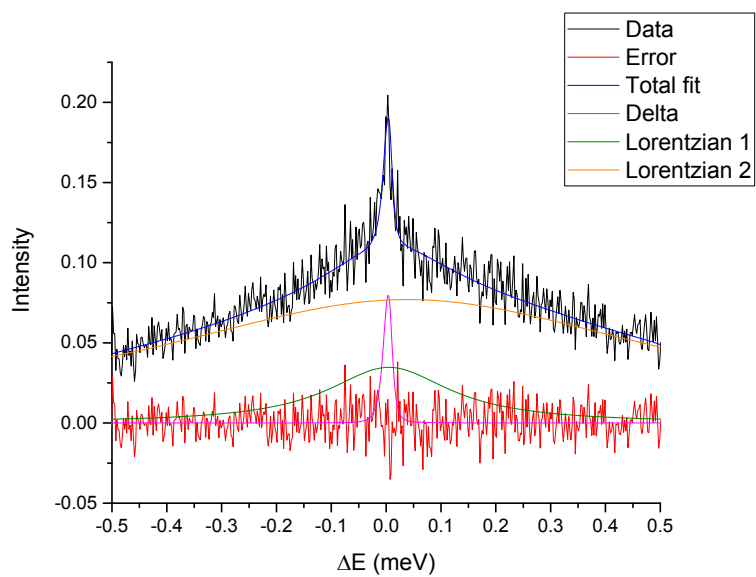


Figure S6 QENS spectra of unconfined benzene - Group 7, $Q = 1.174 \text{ \AA}^{-1}$

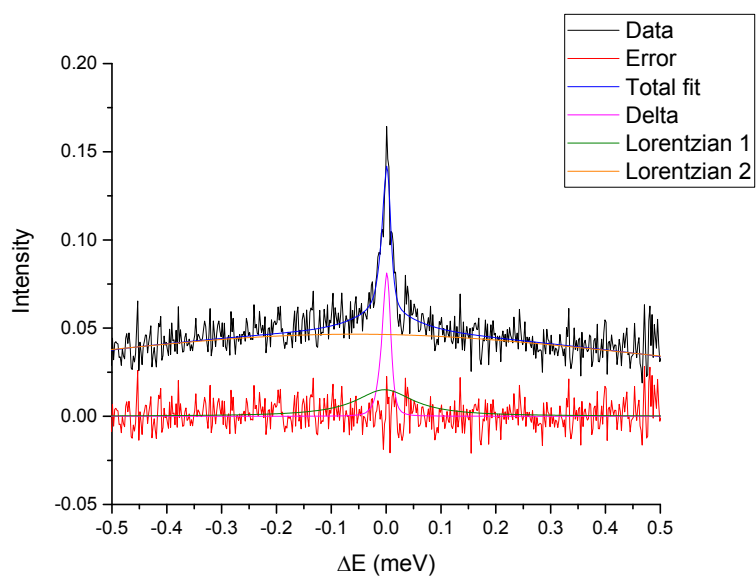


Figure S7 QENS spectra of unconfined benzene - Group 13, $Q = 1.668 \text{ \AA}^{-1}$

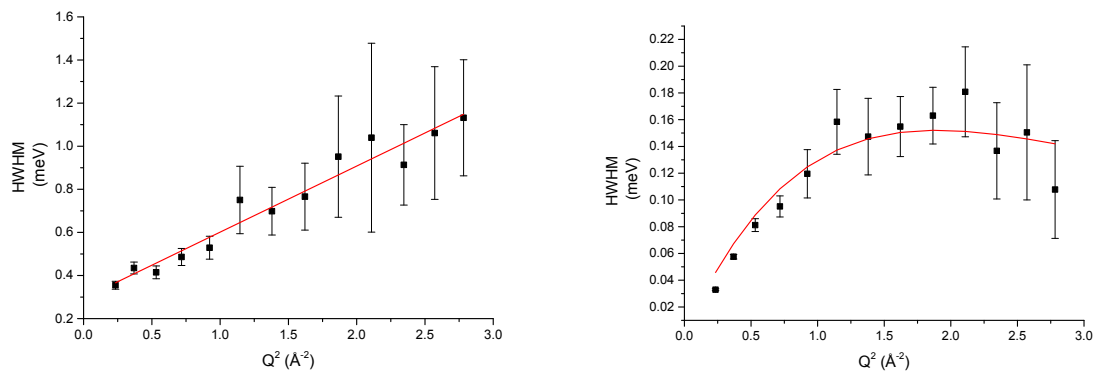


Figure S8 Lorentzian broadenings of the broad (left) and narrow (right) of unconfined benzene at 300 K

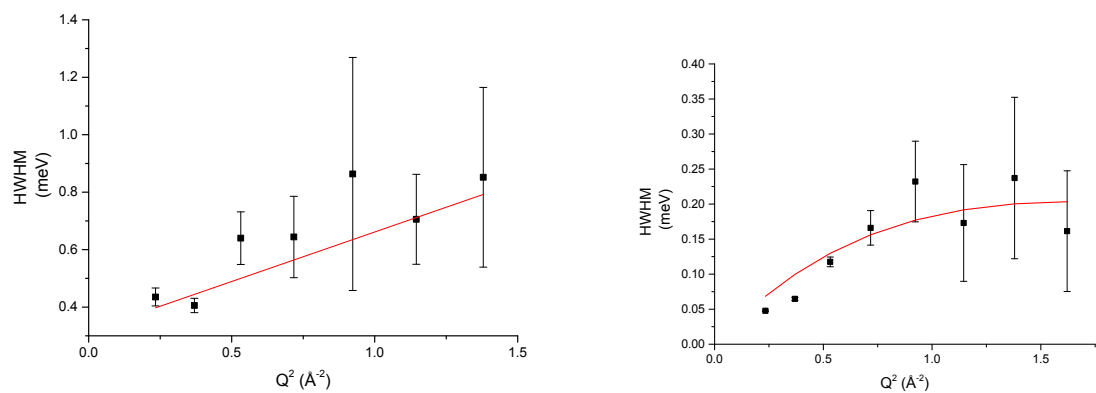


Figure S9 Lorentzian broadenings of the broad (left) and narrow (right) of unconfined benzene at 325 K

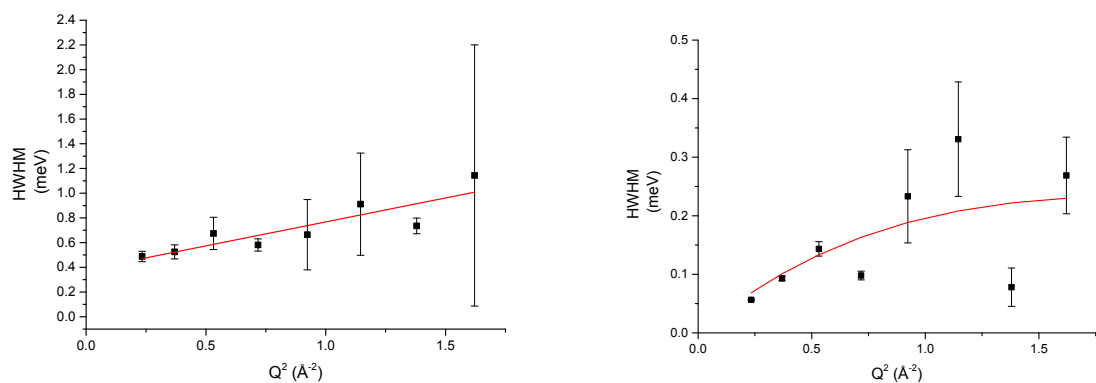


Figure S10 Lorentzian broadenings of the broad (left) and narrow (right) of unconfined benzene at 350 K

Table S10 Dynamical parameters as measured by QENS of unconfined benzene

Temperature (K)	Jump distance (Å)	Residence (ps)	time	Ds L1 $\text{m}^2 \text{s}^{-1} (\times 10^{-9})$	Ds L2 $\text{m}^2 \text{s}^{-1} (\times 10^{-9})$
300	3.26	5.27		3.37	2.02
325	3.48	3.94		5.13	2.48
350	3.22	3.43		5.02	2.58

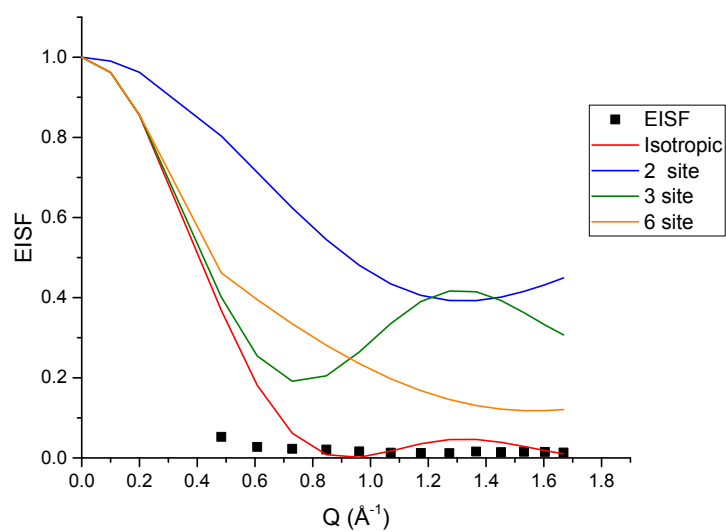


Figure S11 EISF of bulk benzene at 300 K

In each of the models the radius is set to the jump length 3.26 Å.

Confined Benzene

QENS

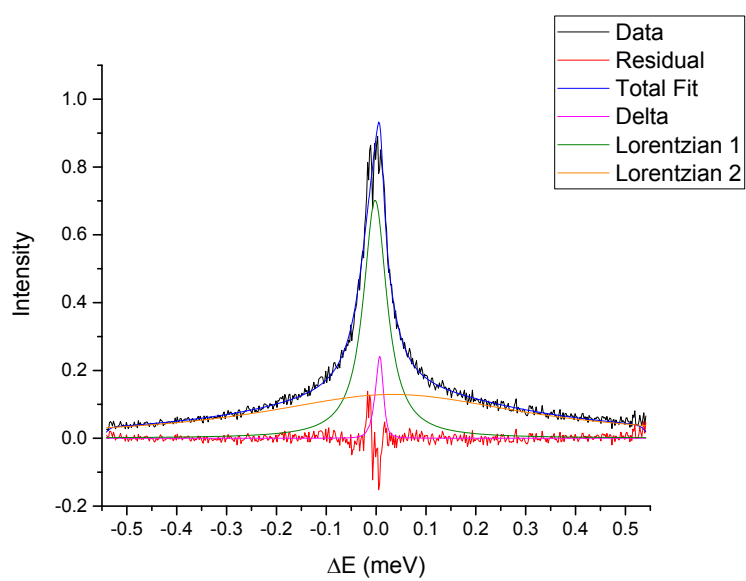


Figure S12 QENS spectra of benzene in Pt/MCM-41 at 300 K - Group 2, $Q = 0.608 \text{ \AA}^{-1}$

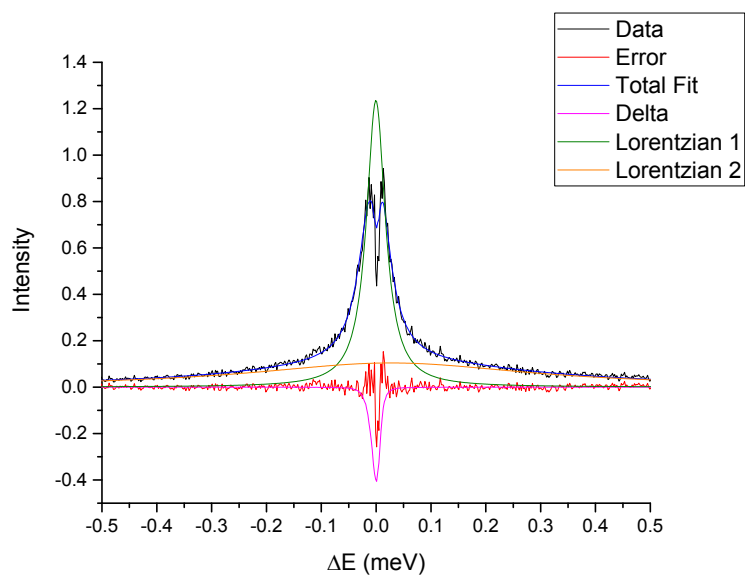


Figure S13 QENS spectra of benzene in Pt/MCM-41 at 300 K - Group 1, $Q = 0.483 \text{ \AA}^{-1}$

A negative peak is present in the first group only and is due to the subtraction of the spectra of empty Pt/MCM-41 from that of benzene and Pt/MCM-41.

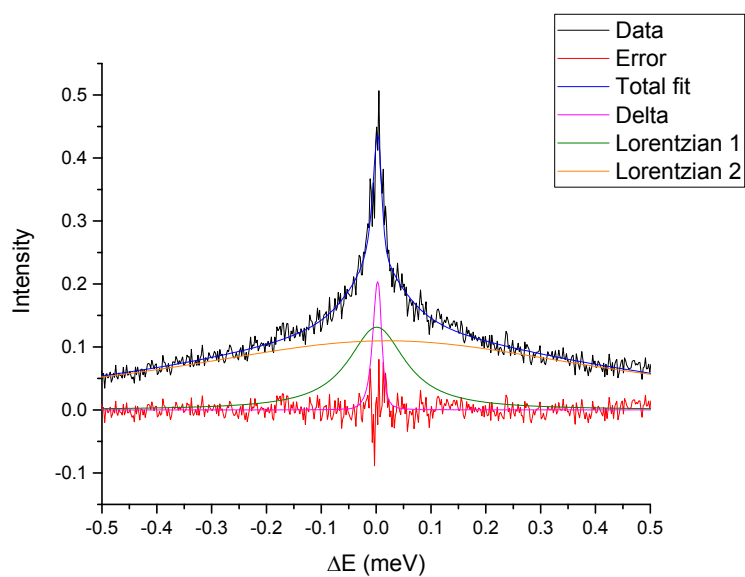


Figure 14 QENS spectra of benzene in Pt/MCM-41 at 300 K - Group 7, $Q = 1.174 \text{ \AA}^{-1}$

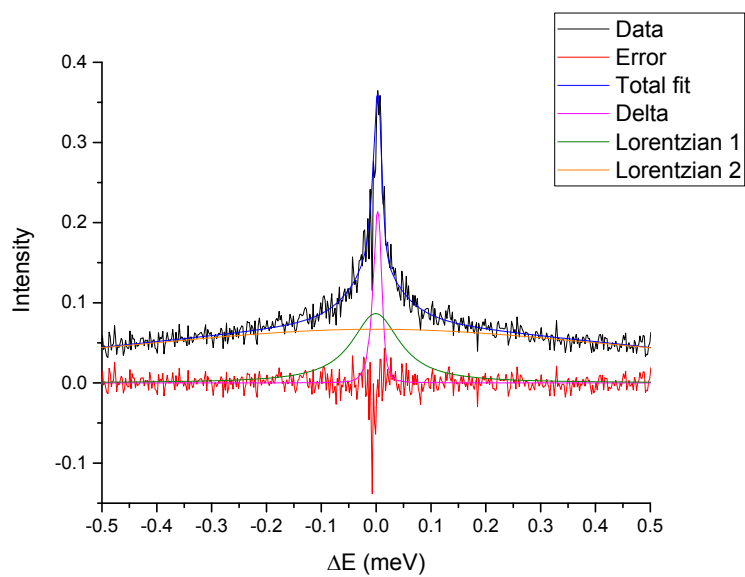


Figure 15 QENS spectra of benzene in Pt/MCM-41 at 300 K - Group 13, $Q = 1.668 \text{ \AA}^{-1}$

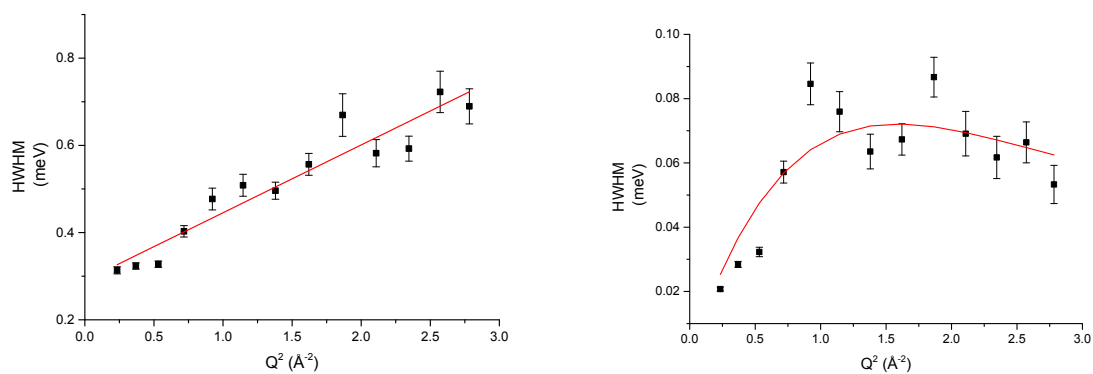


Figure S16 Lorentzian broadenings of benzene in Pt/MCM-41 at 300 K, broad (left) and narrow (right)

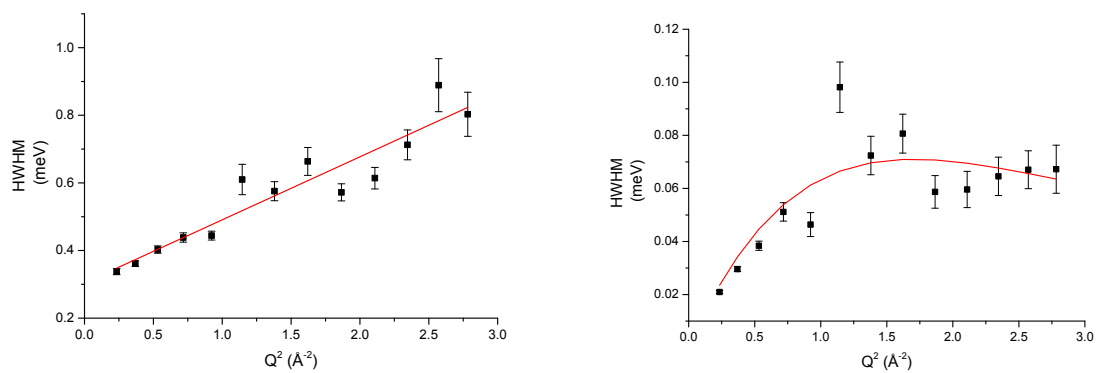


Figure S17 Lorentzian broadenings of benzene in Pt/MCM-41 at 325 K, broad (left) and narrow (right)

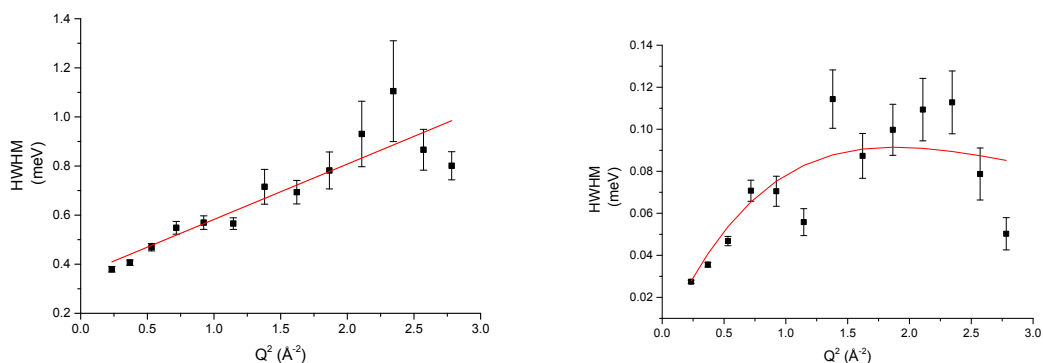


Figure S18 Lorentzian broadenings of benzene in Pt/MCM-41 at 350 K, broad (left) and narrow (right)

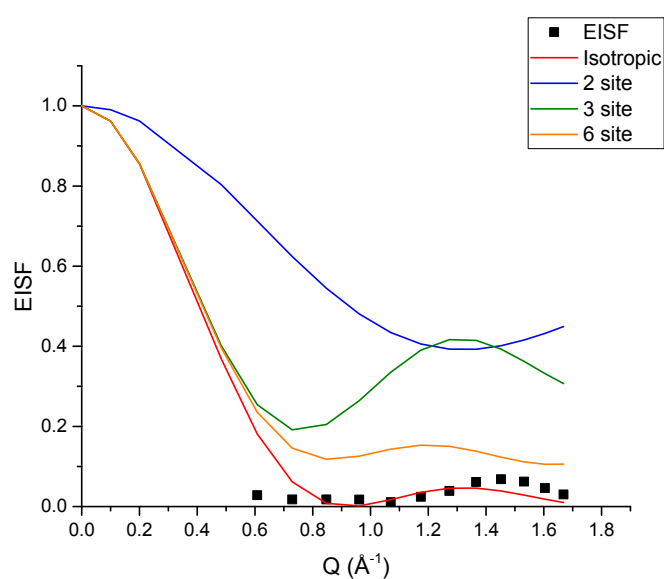


Figure S19 EISF of benzene in Pt/MCM-41 at 300 K

Table S11 Dynamical parameters as measured by QENS of benzene in Pt/MCM-41

Temperature (K)	Jump distance (Å)	Residence time (ps)	Ds L1 $\text{m}^2 \text{s}^{-1} (\times 10^{-9})$	Ds L2 $\text{m}^2 \text{s}^{-1} (\times 10^{-9})$
300	3.57	11.11	1.91	1.03
325	3.45	11.28	1.75	1.24
350	3.28	8.76	2.04	1.50

Catalyst characterisation

3 wt% Pt/MCM-41 was used as the catalyst, which was prepared by an incipient wetness technique using MCM-41 support (Sigma Aldrich) and 15 % w/w $\text{Pt}(\text{NO}_3)_2$ aqueous solution (Johnson-Matthey)

as the precursor. The catalyst was dried in air for 12 h at 393 K followed by calcination in air for 4 h at 773 K.

Powder X-ray diffraction (XRD) data were collected on Rigaku's MiniFlex diffractometer using Cu K α radiation filtered by Ni. Four reflections seen in Figure S16 are observed in the 2θ range 2-10°, indexed assuming a hexagonal cell as (100), (110), (200) and (210).

Nitrogen adsorption-desorption isotherms on 3 wt% Pt/MCM-41 were measured at 77.35 K using a Quantachrome Autosorb iQ Any Gas (AG) Sorption porosimeter. The outgassing temperature was slowly (3 K min⁻¹) raised from room temperature to 573.15 K and maintained at that temperature overnight with a residual pressure of ca. 10⁻⁴ mbar before being cooled to 77.35 K. The isotherm in Figure S17 can be identified as a type IV according to IUPAC classification, i.e. describing mesoporous solids.

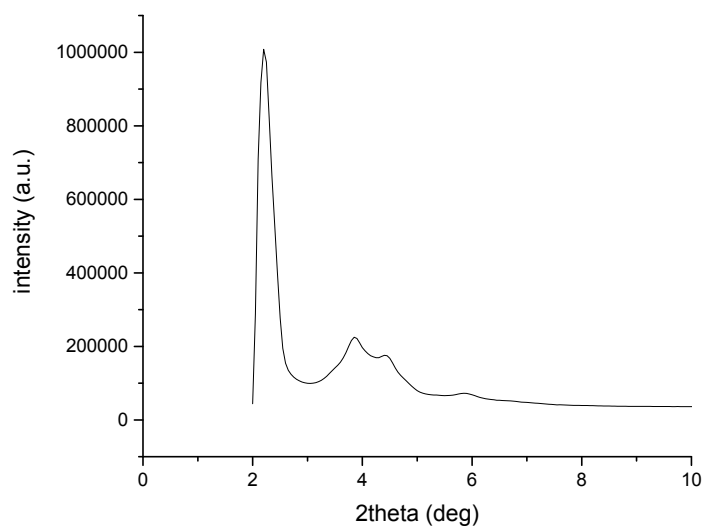


Figure S20 XRD of Pt/MCM-41

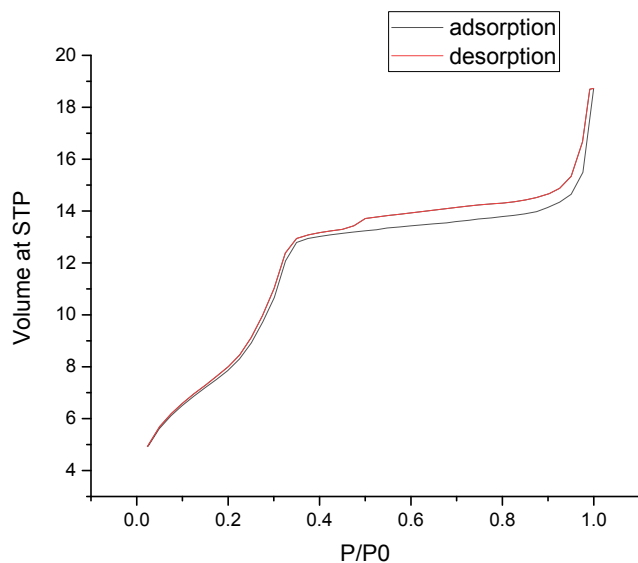


Figure S21 Isotherm of Pt/MCM-41

References

- 1 J. Taylor, O. Arnold, J. Bilheaux, A. Buts, S. Campbell, M. Doucet, N. Draper, R. Fowler, M. Gigg and V. Lynch, in *APS Meeting Abstracts*, 2012.
- 2 R. T. Azuah, L. R. Kneller, Y. Qiu, P. L. W. Tregenna-Piggott, C. M. Brown, J. R. D. Copley and R. M. Dimeo, *J. Res. Natl. Inst. Stand. Technol.*, 2009, **114**, 341.