

An Integrated Total Neutron Scattering - NMR Approach for the Study of Heterogeneous Catalysis

Markus Leutzsch^{a,‡}, Marta Falkowska^{b,‡}, Terri-Louise Hughes^{b,‡}, Andrew J. Sederman^a,
Lynn F. Gladden^a, Michael D. Mantle^{*,a}, Tristan G. A. Youngs^c, Daniel Bowron^c, Haresh
Myanar and Christopher Hardacre^{*,b}

^a Department of Chemical Engineering and Biotechnology, Philippa Fawcett Drive, University of Cambridge, Cambridge, CB3 0AS (UK), E-mail: mdm20@cam.ac.uk

^b School of Chemical Engineering and Analytical Science The University of Manchester, Manchester, M13 9PL (UK), E-mail:

c.hardacre@manchester.ac.uk

^c STFC ISIS Facility, Rutherford Appleton Laboratory Chilton, Didcot, Oxon, OX110QX (UK).

^d School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast, BT9 5AG (UK).

‡ These authors contributed equally to this work.

* Corresponding author

Supporting Information

Table of Contents

Table of Contents.....	S-1
1. Materials and Methods.....	S-2
2. Catalyst Synthesis and Characterisation	S-2
3. Experimental Procedures	S-3
4. NeuNMR – Setup	S-7
5. Temperature and Pressure Changes during the Reaction.....	S-8
6. References.....	S-9

1. Materials and Methods

All chemicals, unless otherwise stated, were purchased from Sigma Aldrich and used without further purification.

All presented NMR experiment were performed using an Oxford Instruments Pulsar 60 MHz benchtop NMR spectrometer equipped with a 5 mm $^1\text{H}/^{13}\text{C}$ probe with deuterium lock.

^2H -NMR chemical shifts are referenced to the chemical shift of C_6D_6 ($\delta_{2\text{H}} = 7.16$ ppm)¹

2. Catalyst Synthesis and Characterisation

3 wt.% Pt/MCM-41 was prepared by incipient wetness impregnation using platinum nitrate (Johnson-Matthey) as the platinum precursor. After impregnation, the material was dried in air at 393 K for 12 h followed by calcination in air at 773 K for 4 h.

Powder X-ray diffraction (XRD) data were collected on PANalytical X'Pert Pro diffractometer using $\text{Cu K}\alpha$ radiation. Four reflections are observed in the 2θ range 2 - 10° , indexed assuming a hexagonal cell as (100), (110), (200) and (210).

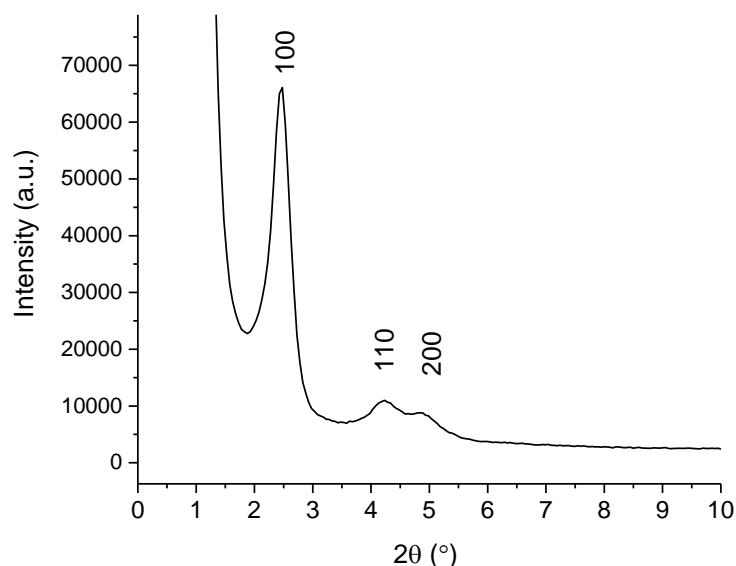


Figure S-1: XRD pattern at low diffraction angles for 3 wt.% Pt/MCM-41

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 can be identified as a type IV according to IUPAC classification, *i.e.* describing mesoporous solids.

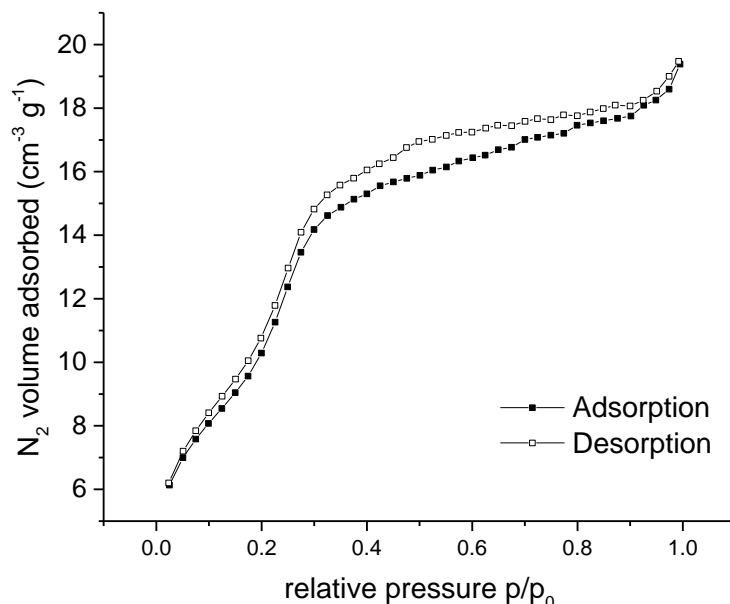


Figure S-2: N₂-Adsorption isotherm of 3 wt.% Pd/MCM-41

3. Experimental Procedures

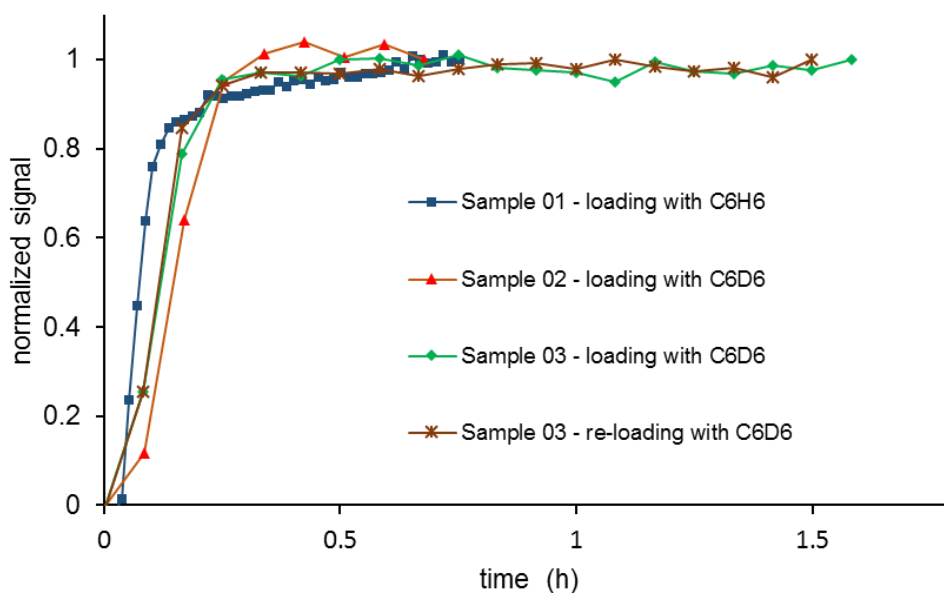
3.1. Sample Preparation

Prior to the experiment 3 wt.% Pt/MCM-41 was dried in a vacuum oven at 200 °C for 48 h. After cooling the catalyst was quickly transferred in an Argon filled glovebox for sample preparation and storage. For the experiments the vanadium tube and the NMR tube were filled to an approximate height of 4 cm. The catalyst amount used was approximately 0.34 g for the Neutron and 0.17 g for the NMR sample. The sample position of both samples was fixed by a silanized glass wool plug. Prior to the measurements samples were transferred from the glovebox to the NeuNMR setup and set under vacuum.

3.2. Deposition of Benzene in 3 wt.% Pt/MCM-41

The connected samples were kept in the setup under high vacuum ($<10^{-4}$ mbar) for at least an hour to ensure degassing of the sample. For benzene deposition the connection to the vacuum pump was closed and the one to a container of benzene under vapour pressure at 20 °C was opened. The process was monitored by NMR and Neutron Scattering (see Figure S-3 and Figure S-4). Generally, after approximately 15 min no further changes were observed.

Deposition of benzene in
different 3 wt.% Pt/MCM-41 samples



Monitoring of Benzene Loading

The vapour phase deposition of benzene into the pores of MCM-41 was monitored by NMR and neutron scattering. An equilibrium was reached after approx. 15 minutes.

Figure S-4: Deposition of benzene into different samples of 3 wt.% Pt/MCM-41 monitored by $^1\text{H}/^2\text{H}$ NMR

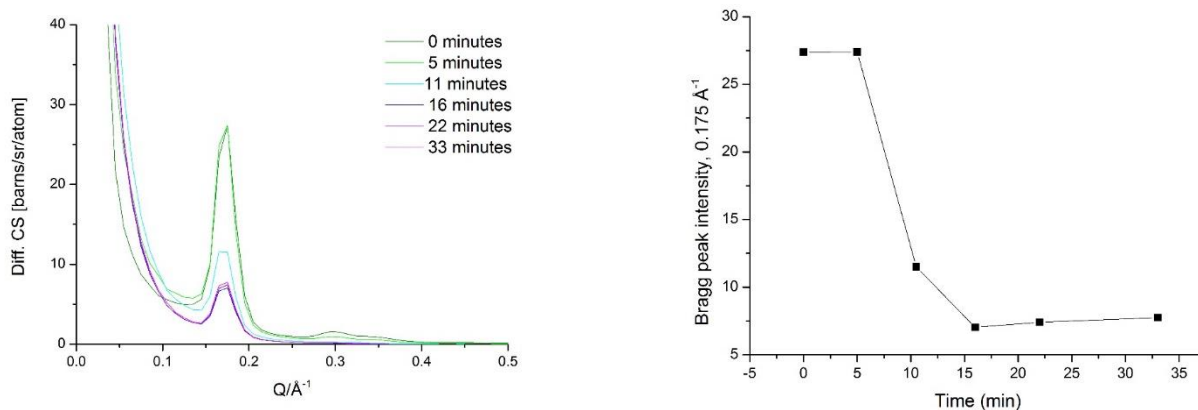


Figure S-3: Changes of Bragg peak intensity during the deposition of benzene- d_6 in 3 wt.% Pt/MCM-41 measured by neutron scattering at different time points.

3.3. Reaction Initiation

After deposition of benzene was completed the connection to the benzene reservoir was closed and the vapour phase benzene was removed from the line for approximately one minute ($<1\text{mbar}$) with a vacuum pump. The line was then opened to a reservoir containing 4 L of D_2 at 250 mbar allowing the reaction to proceed.

3.4. Data Acquisition

Neutron Data Acquisition

Neutron data were acquired using a minimised beam size of 8 mm x 30 mm on the Near and Intermediate Range Order Diffractometer. During the experiment, total neutron scattering spectra were acquired every 5 min. Post data collection, for increased signal-to-noise ratio, three data sets are merged to give an overall time resolution of 15 minutes.

NMR Data Acquisition

During the whole experiment ^2H NMR spectra were acquired every 5 min using the lock channel of the Pulsar by averaging 128 FIDs with an total individual acquisition time of 1 s over approximately 2.2 min. Each individual FID was acquired using a 150 μs $\pi/2$ excitation pulse with a dwell time of 10 μs and contained 4096 complex data points. The field strength of the magnet was determined after calibrating the overall temperature dependent field drift. The offset was readjusted to the highest signal prior to each data acquisition to correct for field drifts.

Prior to the data acquisition the T_1 relaxation time of benzene- d_6 and cyclohexane- d_{12} in 3 wt.% MCM-41 were determined by the inversion recovery sequence to ensure full relaxation prior to the individual scans (see Figure S-5). The T_1 times measured for C_6H_6 and C_6H_6 were 65.3 ± 5.3 ms and 135.1 ± 9.3 ms respectively. A relaxation delay of 1 s ($> 5 * T_1$ of the individual components) was chosen therefore for all the experiments.

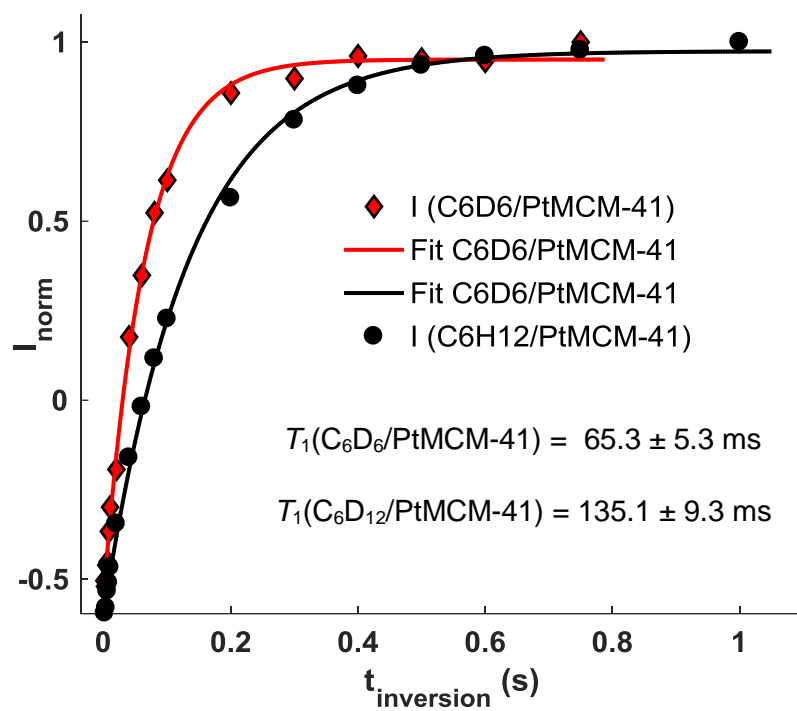


Figure S-5: Inversion recovery plots of in 3 wt.% MCM-41 and the corresponding T_1 relaxation times

4. NeuNMR – Setup

The NMR-spectrometer used in the studies was an Oxford Instruments Pulsar 60 MHz Benchtop NMR spectrometer, which was used with small modifications to fit into the NeuNMR setup. The electronics of the spectrometer had to be placed outside the vacuum chamber due to sample and magnet heating as there is no air available for cooling the electronics that reside within the vacuum chamber. The plastic casing of the magnet unit was removed so as to fit the magnet into the vacuum chamber. Furthermore, the temperature control of the magnet, which is responsible for the stabilisation of the magnetic field, has to be turned off. As a result of this, the magnetic field drifts between individual NMR data acquisitions, and a correction is therefore necessary before each individual NMR measurement. A simple frequency lock algorithm was established to correct for this behaviour.

The following figure shows some images from the inside of the NeuNMR setup:

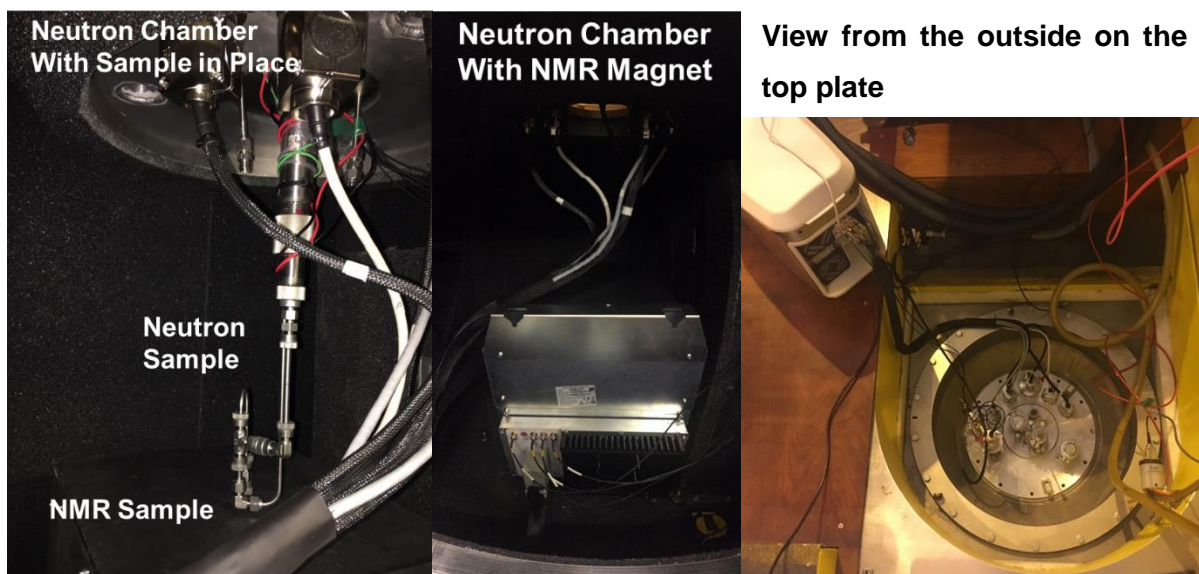


Figure S-6: Pictures of the setup installed at NIMROD.

5. Temperature and Pressure Changes during the Reaction

Pressure and temperature changes during the reaction are shown in Figure S-7 and Figure S-8:

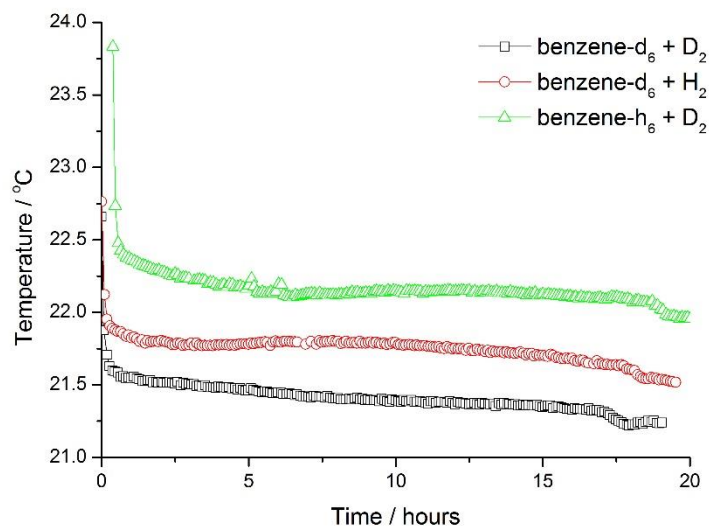


Figure S-7: Observed temperature changes during different reactions

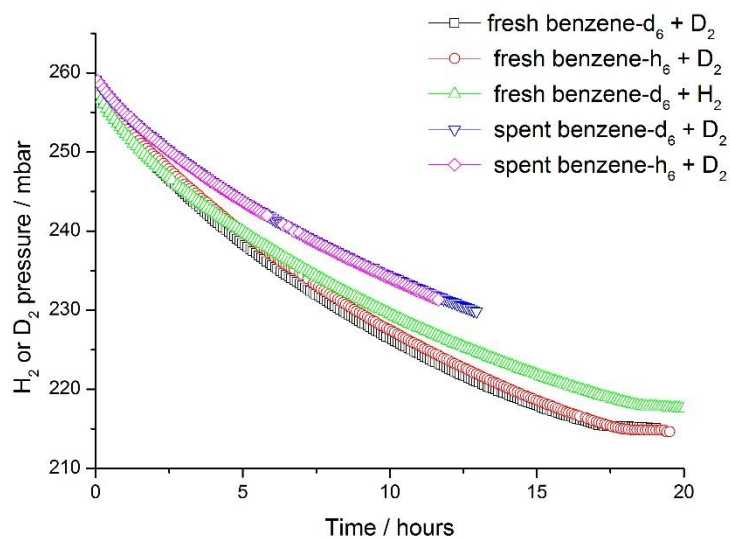


Figure S-8: Observed pressure changes during different reactions

The observed overall changes are in good agreement with changes observed in the NMR and total neutron scattering data.

6. References

- 1 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176.
- 2 T. G. A. Youngs, H. Manyar, D. T. Bowron, L. F. Gladden and C. Hardacre, *Chem. Sci.*, 2013, **4**, 3484.
- 3 M. Sulpizi, M.-P. Gaigeot and M. Sprik, *J. Chem. Theory Comput.*, 2012, **8**, 1037.
- 4 I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 1164.
- 5 O. B. Bogomolova, N. M. Ostrovskii, M. D. Smolikov, A. S. Belyi and V. K. Duplyakin, *React. Kinet. Catal. Lett.*, 1989, **40**, 131.
- 6 I. McManus, H. Daly, J. M. Thompson, E. Connor, C. Hardacre, S. K. Wilkinson, N. Sedaie Bonab, J. Ten Dam, M. J. H. Simmons, E. H. Stitt, C. D'Agostino, J. McGregor, L. F. Gladden and J. J. Delgado, *J. Catal.*, 2015, **330**, 344.
- 7 P. C. Aben, J. C. Platteuw and B. Stouthamer, *Recl. des Trav. Chim. des Pays-Bas*, 2010, **89**, 449.