Electronic Supplementary Information for Dalton Transactions

Parahydrogen-Induced Polarization effects in liquid-phase hydrogenations catalysed by Supported Metal nanoparticles

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Supporting information

Experimental section

NMR investigations

All ^{1}H NMR spectra were recorded at room temperature on Bruker DRX-400 and 500MHz Spectrometers. Some of the spectra were also recorded at 305K. ^{1}H NMR chemical shifts (ppm) are reported as related to the residual ^{1}H signals in the deuterated solvents (e.g. methanol-d4, 3.31 ppm; chloroform-d, 7.27ppm)

NMR experiments (one single scan) were acquired using 45^o rf pulses to maximize the PHIP signal. Under the multizg mode, the tube containing the solution with the catalyst, substrate, solvent and *para*-hydrogen was shaken for a few seconds and then 5 or 10 experiments were run until the enhancement decayed. Then, the tube was taken out and repeatedly shaken until the peaks of hydrogenation products reappeared.

Sample preparation

In the PASADENA experiments, 2-3 mg catalyst were placed at the bottom of a 5mm NMR tube with Young tap. The substrate (e.g. methyl propiolate, ethyl vinyl ether, 50µL) and the deuterated solvent (e.g. MeOD, $CDCl_3$, 0.55 mL) were added and the tube was subsequently degassed in a Schlenk line (three times using dry ice in acetone) until all air was removed. *Para*-hydrogen at 2-3 bar was then added. All experiments were performend in the same way to quantify and compare the enhancements observed.

Materials synthesis and methods

Preparation of Pt/Al-MCM-48 material

The preparation of the Pt/Al-MCM-48 was carried out following the protocol reported by Campelo *et al.* [1].

Preparation of metals supported on carbon

The commercial carbonaceous support (DARCO®) was used as purchased. The preparation of the metal supported materials (Pt, Rh and Ru) was performed, according to a previously reported protocol [2], as follows: 0.4 g DARCO® and 2 mL of a solution of the metal precursor [e.g. tetraamine platinum (II) nitrate, ruthenium (III) or rhodium (III) chlorides] in ethanol:water 1:1 v/v were microwaved on a CEM-DISCOVER for the desired period of time (usually 2 min) at 300W (maximum power output, 100-140^{o}C temperature reached). The mixture was filtered off and the recovered solid was thoroughly washed with ethanol and acetone and oven dried overnight at 100^{o}C prior its utilization in the reaction.

Preparation of Pt and Pd on silica, beta-zeolite and Al-SBA-15 supports

The mesoporous silica support was prepared following the protocol reported by Macquarrie *et al.* [3]. The Al-SBA-15 material was prepared according to the methodology reported by Bonardet *et al.* [4].

Pt and Pd metallic nanoparticles supported on silica were prepared following a the reported protocol by Campelo *et al.* [5]. 0.4 g silica and 2 mL of a solution of tetraamine platinum (II) chloride (Aldrich, 99.9%) or palladium acetate (Sigma–Aldrich, 99.9+%) in ethanol:acetone 1:1 v/v were microwaved for the desired period of time (usually 2 min) at 300–450W. The mixture was filtered off and the recovered solid was thoroughly washed with ethanol and acetone and oven dried overnight at 100°C.

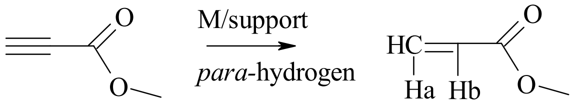
Other catalysts employed

Pd/Starch was prepared following the experimental reported by Budarin *et. al.* [6]. Au/Si-SBA-15 was prepared using the procedure reported by Barau *et al.* [7] and used as prepared. Fe/MCM-41 was prepared according to a recently reported protocol [8].

Generation of para-hydrogen

For the PHIP experiments, hydrogen enriched in *para-* spin state was prepared by cooling H_2 to 77 K over a paramagnetic catalyst using two systems described in literature [9].

Heterogeneous hydrogenation of methyl propiolate (MePr) using 0.5%Pt/silica



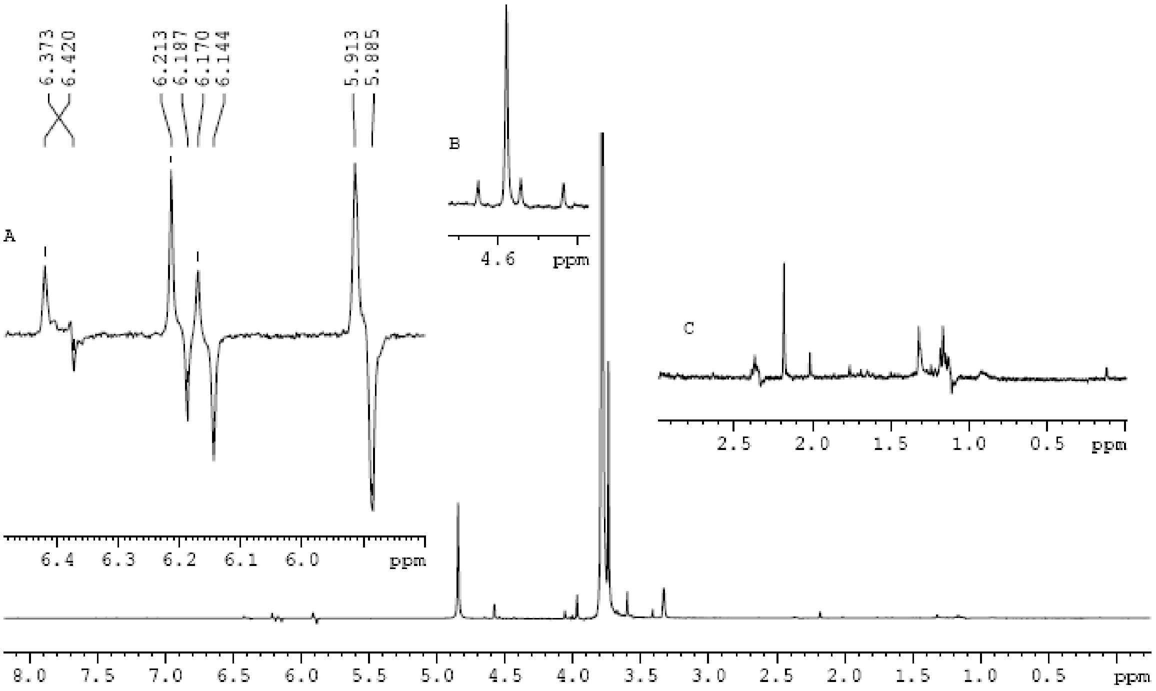


Figure S1. ^{1}H NMR spectra (1 scan) recorded in the heterogeneous hydrogenation of methyl propiolate (MePr) in methanol-d4 using a 0.5%Pt/silica catalyst. (A) PHIP enhancement clearly observed at 5.90, 6.18 and 6.39 ppm in the first step of hydrogenation from triple to double bond, when the hydrogenation is carried out in situ in the NMR probe (B) H_2 peak at 4.57 ppm, observed isotope shifted peak at 5.54 ppm, split due to deutherium coupling ($J_{H\text{-}D}$ approx. 43 Hz); (C) PHIP enhancement observed for the second step of hydrogenation at 1.13 and 2.35 ppm. The two hydrogens in the product coming from the parahydrogen molecule have been labelled as Ha and Hb.

Heterogeneous hydrogenation of MePr using 0.5%Pd/silica

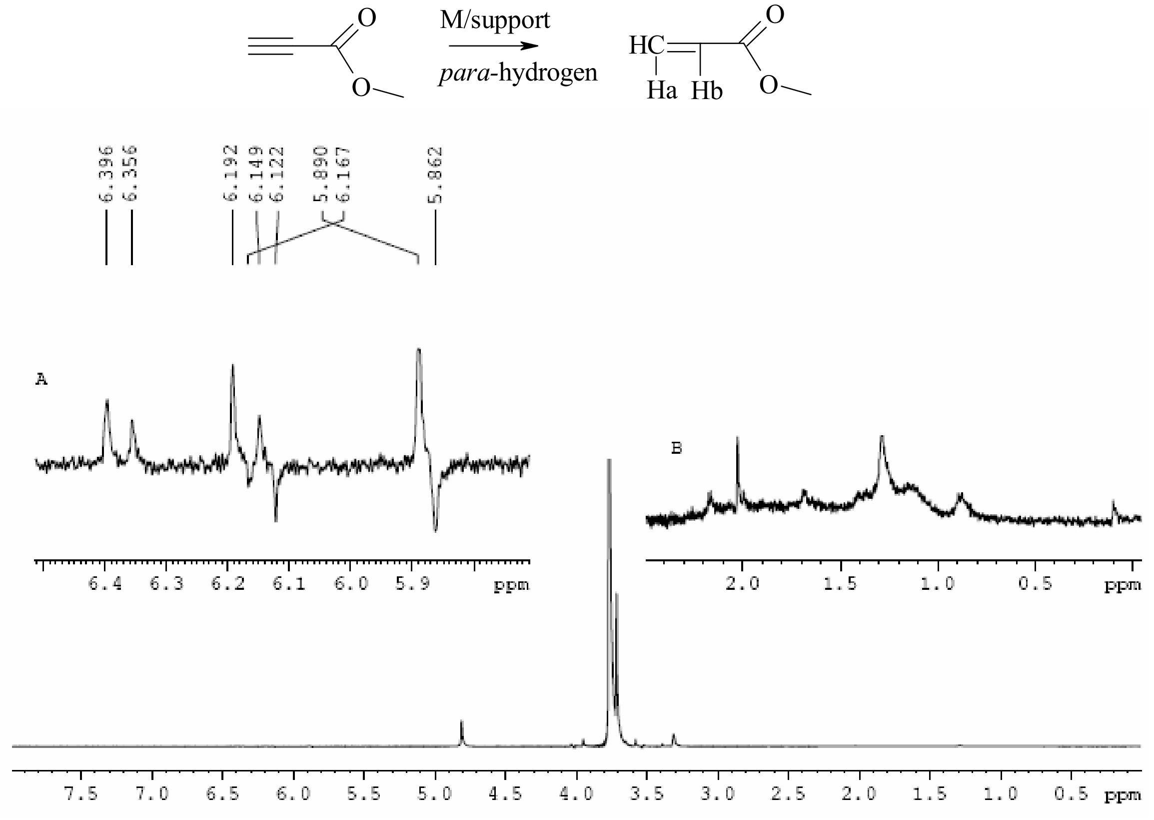
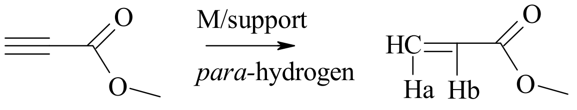


Figure S2. ^{1}H NMR spectra (1 scan) recorded in the heterogeneous hydrogenation of MePr in methanol-d4 using a 0.5%Pd/silica catalyst. (A) PHIP enhancement observed at 5.87 and 6.15 ppm in the first step of hydrogenation from triple to double bond, when the hydrogenation is carried out in situ in the NMR probe; (B) No PHIP enhancement observed in the second step of hydrogenation. The two hydrogens in the product coming from the parahydrogen molecule have been labelled as Ha and Hb.

Heterogeneous hydrogenation of MePr using 0.5%Pt/MCM-48



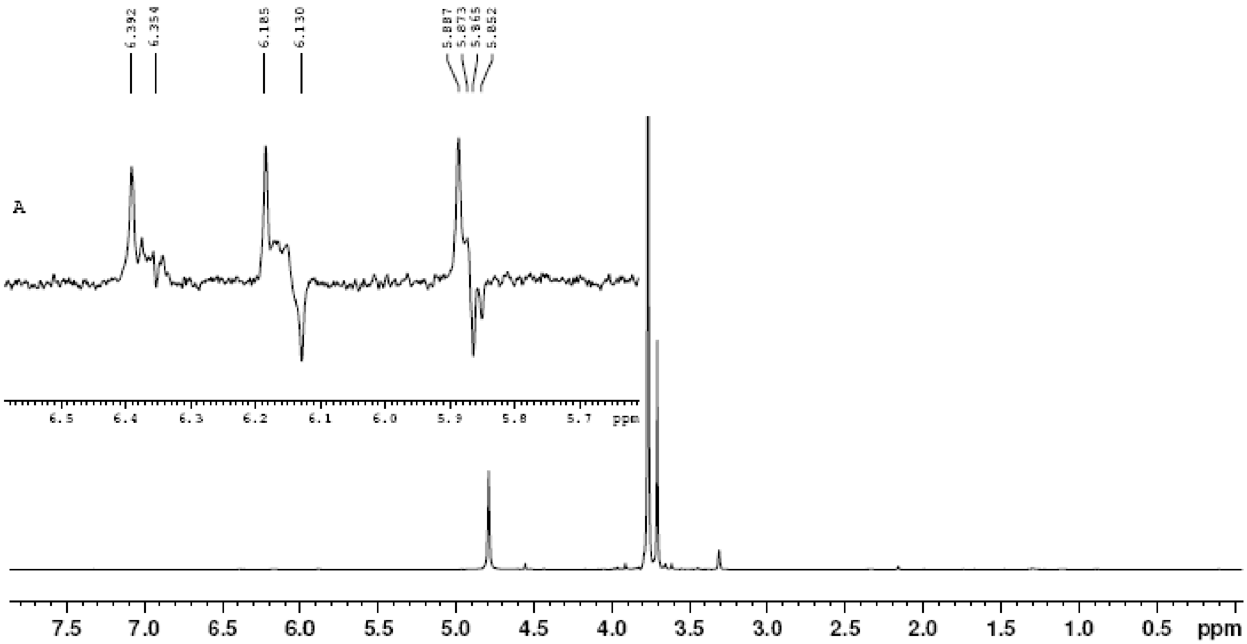
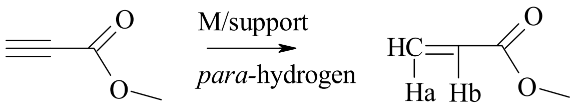


Figure S3. ^{1}H NMR spectra (1 scan) recorded in the heterogeneous hydrogenation of MePr in methanol-d4 using 0.5%Pt/MCM 48 catalyst. (A) PHIP enhancement clearly observed at 5.87 and 6.15 ppm, when hydrogenation is carried out in situ in the NMR probe.

Heterogeneous hydrogenation of MePr using 2%Pt/Al-SBA-15



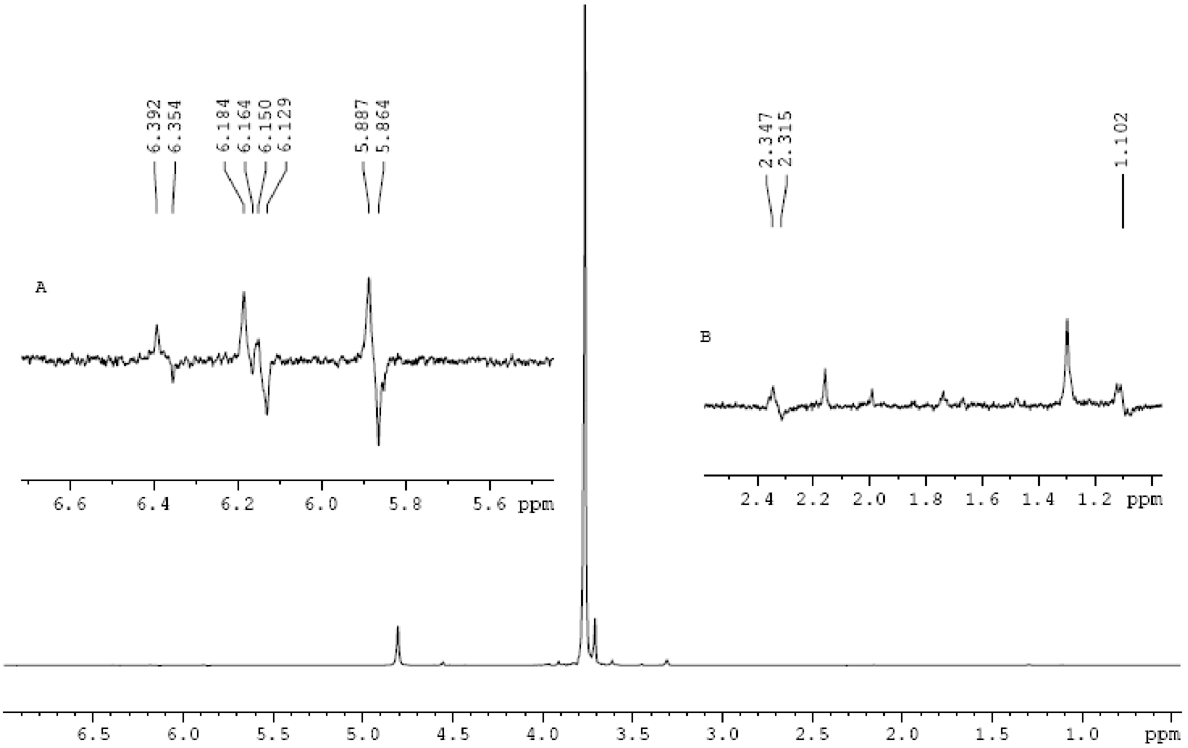


Figure S4. ^{1}H NMR spectra (1 scan) recorded in the heterogeneous hydrogenation of MePr in methanol-d4 using 2%Pt/Al-SBA-15 as catalyst. (A) PHIP enhancement clearly observed at 5.86, 6.15-6.16 and 6.35 ppm in the first step of hydrogenation from triple to double bond, when hydrogenation is carried out in situ in the NMR probe. (B) PHIP enhancement can also be observed in the final step of hydrogenation to single bond at 1.1 and 2.3 ppm.

References

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