Electronic Supplementary Information (ESI)

Parahydrogen-Induced Polarization (PHIP) in heterogeneous hydrogenations over bulk metals and metal oxides

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Hydrogenation and NMR experiments

^{1}H NMR spectra were recorded on a 300 MHz Bruker AV 300 NMR spectrometer with 8 signal averages (unless stated otherwise). H_2 was enriched with parahydrogen up to 50% by passing it through FeO(OH) powder maintained at liquid N_2 temperature. For hydrogenation of gaseous substrates (propylene, 1,3-butadiene, 1-butyne), the 1:4 mixtures of corresponding gases with hydrogen were used. For 1,3-butadiene heterogeneous hydrogenation the highest catalytic activity (conversion >90%) was observed for Pd, PdO and $Pd(OH)_2$, 40-80% conversion of 1,3-butadiene was observed for Pt and PtO2 and low level of conversion (5-10%) was detected for CaO, Cr_2O_3 and $Pt(OH)_2$. The reaction was carried out at atmospheric pressure in the high magnetic field of the NMR spectrometer (the PASADENA experiment) or in the earth magnetic field with subsequent transfer of reaction products to NMR spectrometer for analysis (the ALTADENA experiment). In the case of PASADENA experiment the catalyst (0.03 g) was placed in a 10 mm NMR tube positioned inside the magnet bore of the NMR spectrometer and maintained at 130 °C. The mixture of gases was supplied to the heterogeneous catalyst through a Teflon capillary extended to the bottom of the NMR tube where the catalyst was placed. For acrolein hydrogenation, the hydrogen gas was bubbled into the flask with liquid acrolein. Then the mixture of hydrogen and acrolein vapor (with acrolein fraction 36 % according to its vapor pressure) was supplied to the NMR tube. The NMR spectra were always acquired while the gas was still flowing through the NMR tube, using a single 45º rf pulse to maximize the observed PASADENA polarization. In the ALTADENA experiments, hydrogenations were performed in the straight part of a copper tube reactor at different temperatures with the catalyst (30 mg) packed between two pieces of fiberglass tissue. Gaseous mixture of reagents was supplied to the reactor and from there via a Teflon capillary to an empty NMR tube for analysis. A single 90º rf pulse was used for signal detection. The gas flow rate was 6.8 ml/s unless stated otherwise. Therefore, gas transfer time from reactor to NMR tube in ALTADENA experiments was approximately 0.7s.

Catalysts preparation, activation and characterization by XPS

Commercially available calcium oxide was purified using the following procedure. Calcium oxide was dissolved in distilled water. The residue obtained after decantation of the liquid from the top of the beaker was moved to a Petri dish and dried at 120 °C. The residue was placed inside a quartz vessel and calcined for 2 hours at 800 °C. Then it was transferred to the NMR tube under argon atmosphere.

Chromium oxide was prepared in two different ways: (i) volcano reaction (thermal decomposition of ammonium dichromate) and (ii) urea leaching. In (i), approximately 0.5 g of $(NH_4)_2Cr_2O_7$ was placed on a salver. Decomposition was initiated by the touch of a glass rod preliminarily heated in the flame of an alcohol lamp. Chromium oxide (30 mg) formed in the reaction was transferred to the NMR tube or copper reactor depending on the type of experiment. In (ii), 100 ml of chromium nitrate solution (0.04 M) was mixed with 40 ml of 1 M urea solution. The obtained mixture was maintained at 95 °C under continuous stirring until solution color changed from dark blue to dark green and flaky precipitate was formed. During the procedure, the solution pH changed continuously until reaching 8. Then the liquid was decanted. Precipitate was washed and left in the oven at 120 °C overnight.

CeO_2 and ZrO_2 were manufactured by TSP (Ekaterinburg, Russia). Granulated fractions (0.25-0.50 μm) were prepared from as received material by the following procedure: granules were grinded and successively sifted through 0.5 μm and 0.25 μm sieves. The first and the last fractions were excluded and thus the granulated ceria and zirconia of 0.25-0.50 μm fractions were obtained. They were dried at 120 °C overnight and calcined at 500 °C for 4 hours.

Palladium black was prepared using the reduction of H_2PdCl_4 solution by sodium formate at 80 °C. 1.8 g of $PdCl_2$ was dissolved in 10 ml of hot 2M HCl solution. The pH value was increased to 10 by the addition of NaOH. After that, 1.5 g of HCOONa was added. The formed black precipitate was filtered and washed with 200 ml of hot water to remove chloride ions. Then the metallic palladium was additionally reduced in hydrogen flow at 300 °C for 3 hours.

Platinum black was made by decomposition of 2.8 g of $H_2PtCl_6 \times 6H_2O$ at 200 °C for 3 hours in a furnace. The obtained metallic platinum was washed with 200 ml of hot water and reduced in hydrogen flow at 300 °C for 3 hours.

Palladium hydroxide was prepared from H_2PdCl_4 via precipitation with NaOH. 2.52 g of $PdCl_2$, 2.20 ml of HCl (12 M) and 4.30 ml of H_2O were mixed resulting in H_2PdCl_4 formation. The obtained solution was heated to 85 °C. Then 11.10 ml of 20 wt% NaOH solution was added, resulting in the formation of yellow-brown precipitate. Palladium hydroxide precipitate was dried in air atmosphere at 35°C for 48 hours.

Platinum(II) hydroxide was prepared from H_2PtCl_6. 0.22 g of hydrazine chloride $N_2H_4 \cdot 2HCl$ was added to the solution of H_2PtCl_6 (2.20 g) in 14 ml H_2O. Then the solution of Na_2CO_3 (4 g) in 50 ml of H_2O was added dropwise to the obtained mixture with simultaneous CO_2 removal. The formation of black precipitate started after the addition of ~20 ml of Na_2CO_3 aqueous solution. Finally, the black precipitate of $Pt(OH)_2$ formed was filtered, washed with 200 ml of hot water and dried at 35°C for 48 hours on air.

Photoelectron spectra were recorded using SPECS spectrometer with PHOIBOS-150-MCD-9 hemispherical energy analyzer and X-ray monochromator FOCUS-500 (Al Kα, irradiation, hν = 1486.74 eV, 200 W). The samples were supported onto double-sided conducting copper scotch tape. Binding energy (BE) scale was preliminarily calibrated by the position of the peaks of Au4f7/2 (BE = 84.0 eV) and Cu2p3/2 (BE = 932.67 eV) core levels. The binding energy of peaks was calibrated by the position of the C1s peak (BE = 284.8 eV) corresponding to the surface hydrocarbon-like deposits (C-C and C-H bonds). The ratio of surface atomic concentrations of the elements was calculated from the integral intensities of photoelectron peaks corrected by corresponding atomic sensitivity factors.

Additional figures

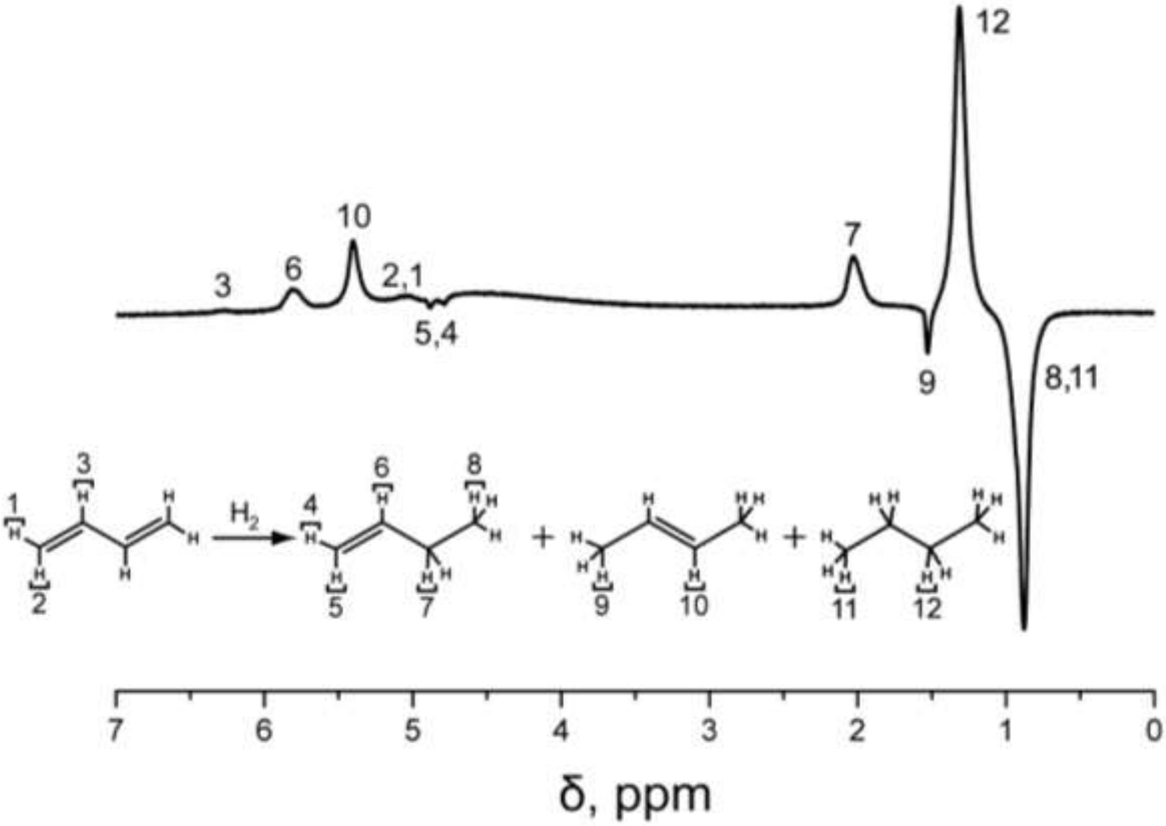


Figure S1. ^{1}H NMR spectrum detected upon hydrogenation of 1,3-butadiene over CaO at 500 °C in an ALTADENA experiment. The flow rate of gaseous mixture was 10.2 ml/s. Polarization is observed for all reaction products, including the protons of the CH and CH_2 groups of the vinyl fragment of 1-butene.

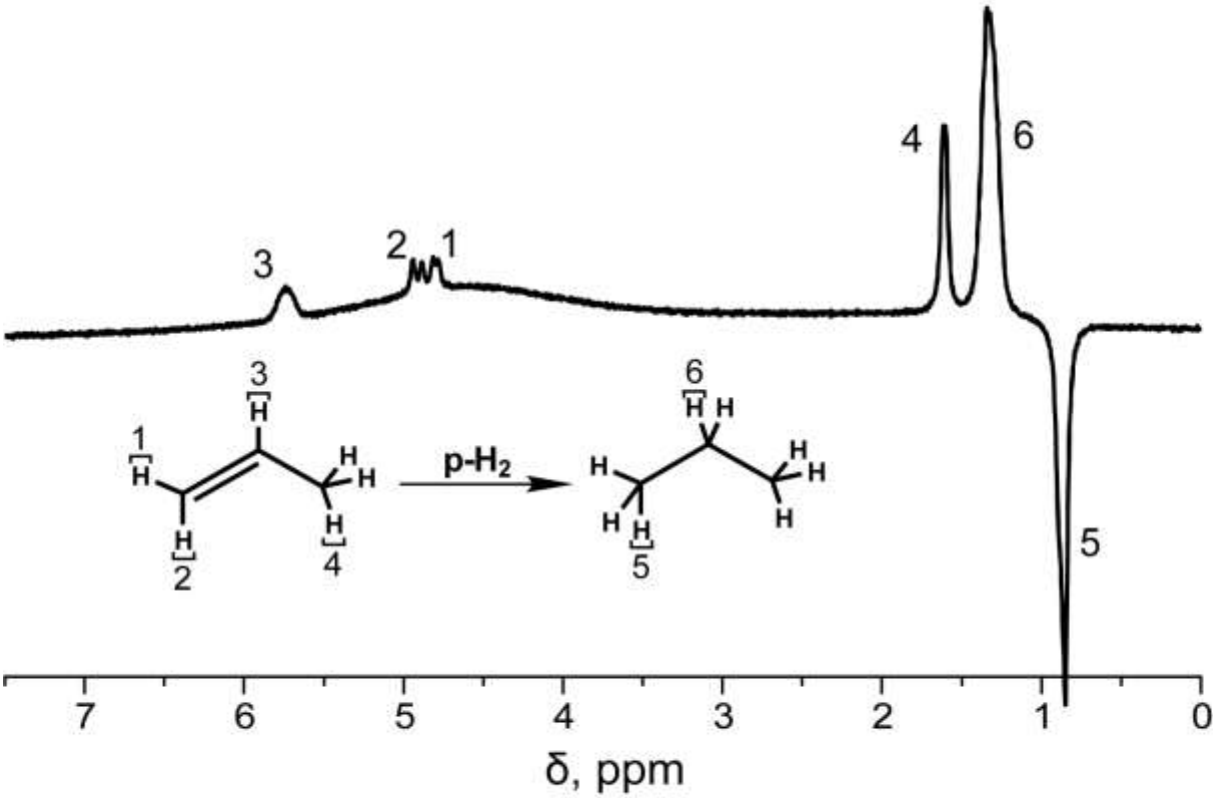


Figure S2. ^{1}H NMR spectrum detected upon hydrogenation of propylene over CaO at 400 °C in an ALTADENA experiment. the flow rate of gaseous mixture was 10.2 ml/s. Polarization is observed for the CH_2 and CH_3 protons of propane.

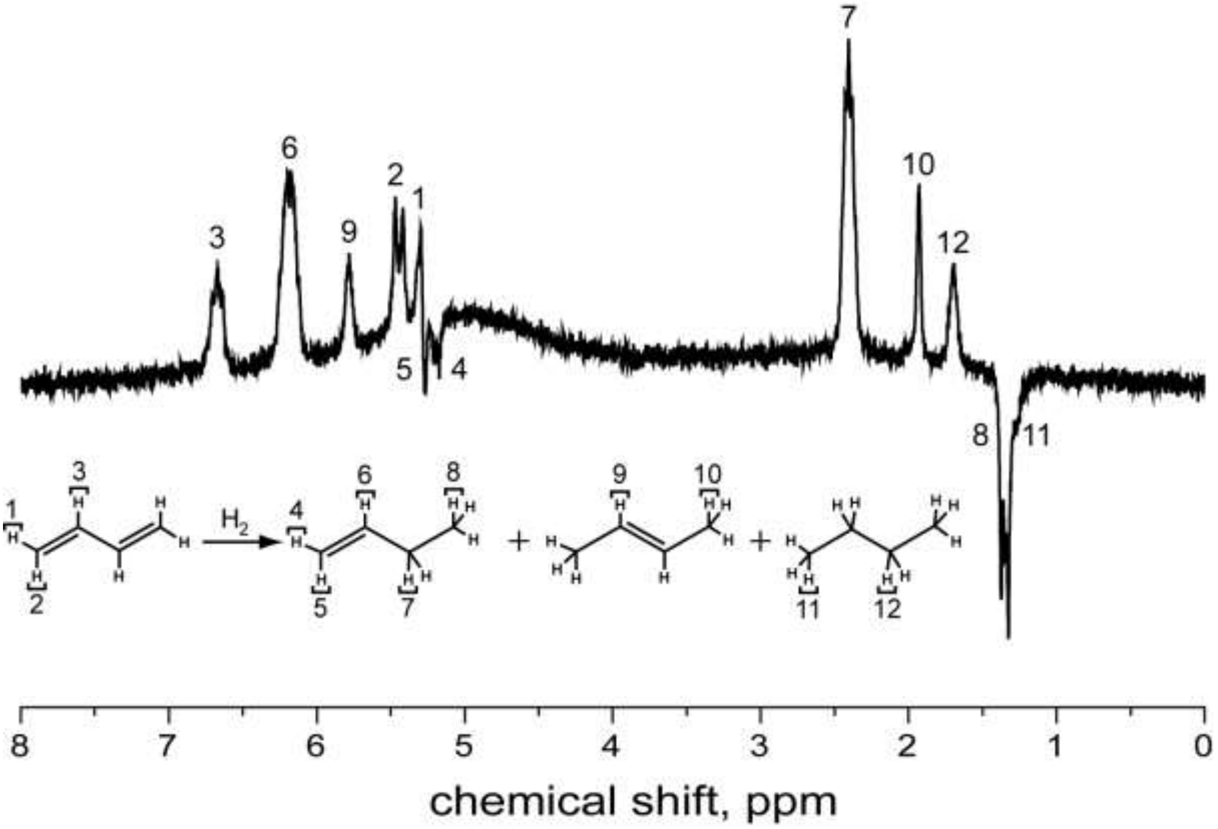
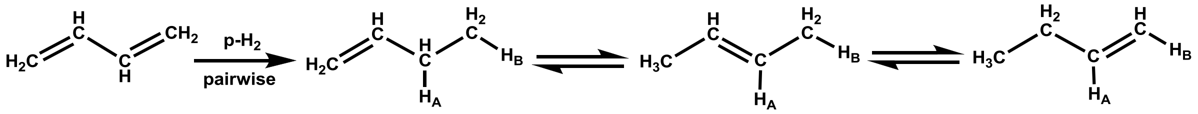


Figure S3. ^{1}H NMR spectrum detected upon hydrogenation of 1,3-butadiene over Cr_2O_3 at 400 °C in an ALTADENA experiment. The flow rate of gaseous mixture was 10.2 ml/s. Polarization is observed for all reaction products, including the protons of the CH and CH_2 groups of 1-butene (the spectrum was recorded with one scan, i.e., without signal accumulation). The Cr_2O_3 sample used in this experiment was prepared using ammonium dichromate decomposition (procedure (i)). Similar results were obtained with Cr_2O_3 produced by urea leaching, but conversions and polarization levels were lower.



Scheme S1. The suggested mechanism for the formation of 1-butene with polarized NMR signals of CH_2 and CH protons of the vinyl fragment in the heterogeneous hydrogenation of 1,3-butadiene with parahydrogen over bulk CaO and PtO_2 catalysts.

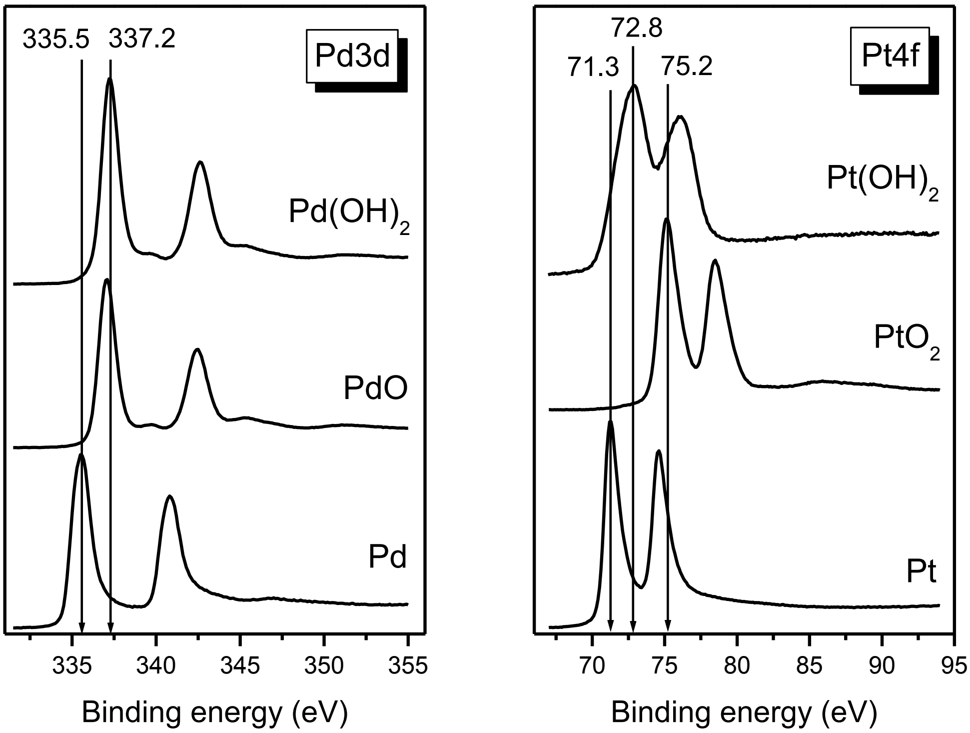


Figure. S4. X-ray photoelectron spectra of Pd3d(left) and Pt4f (right) regions, respectively. Binding energies of different metal charge states are shown with arrows.

Fig. S4 (left) presents Pd3d core-level spectra obtained over Pd-black, PdO and Pd(OH)2 samples. The Pd3d5/2 peak at 335.5 eV, can be attributed to metallic Pd, i.e., Pd(0) [1-3,6]. The peak with binding energy at 337.0±0.2 eV is typical for palladium (II) [1-6].

Fig. S4 (right) presents Pt4f core-level spectra obtained over Pt-black, Pt(OH)2 and PtO2 catalysts. The Pt4f7/2 peak at 71.3 eV can be attributed to metallic Pt, i.e., Pt(0) [1,7,9,10]. The peak with binding energy at 72.8 eV is characteristic of the Pt(II) species [1,9,10]. The peak with binding energy at 75.2 eV can be attributed to Pt(IV)[1,7-10].

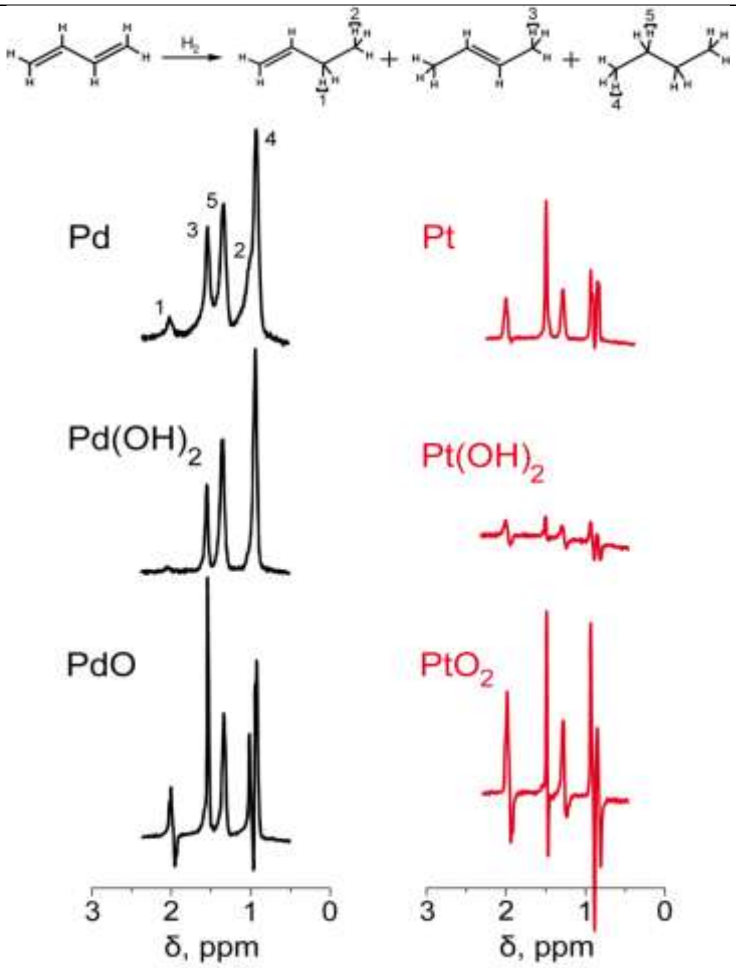


Figure S5. ^{1}H NMR spectra detected upon heterogeneous hydrogenation of 1,3-butadiene with parahydrogen over different Pt- and Pd-containing catalysts at 130 °C in a PASADENA experiments. All spectra were recorded at identical conditions. The spectra are scaled individually to fill the picture evenly.

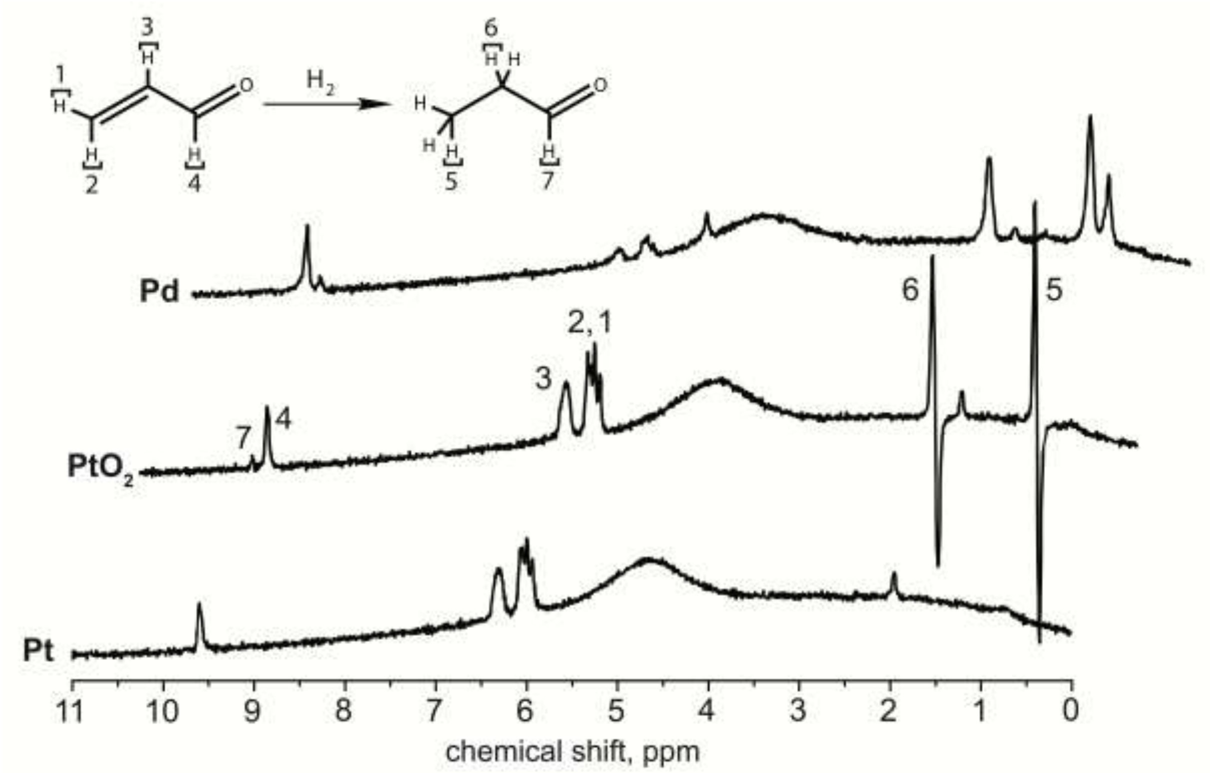


Figure S6. ^{1}H NMR spectra detected upon hydrogenation of acrolein by parahydrogen over Pd black, PtO_2 and Pt black in a PASADENA experiment.

References

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