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Magnetite-supported palladium single-atoms do not catalyse the hydrogenation of alkenes but small clusters do

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Materials and Methods

Synthesis. The synthesis of nanoparticles Fe_3O_4dopPPh_2@Pd was as follows: Fe_3O_4dopPPh_2 NPs (100 mg) were sonicated in 12 ml of water for 10 min. Then, potassium tetrachloropalladate(II) was added to the suspension and the mixture was magnetically stirred (1000 rpm) for two hours at room temperature. The resulting nanoparticles were isolated and washed three times with water and finally with acetone and dried under vacuum. After this, the nanoparticles were sonicated in 11 ml of water for 10 min followed by addition of a solution of 2.6 mg of $NaBH_4$ in 1 ml of water. The mixture was magnetically stirred (1000 rpm) for 2 h and washed three times with water, acetone and dried. The potassium tetrachloropalladate(II) required for each sample was the following: sample 1 (0.18 w% Pd), 0.7 mg (2.1 µmol); sample 2 (0.38 w% Pd), 1.4 mg (4.5 µmol); sample 3 (0.63 w% Pd), 2.3 mg (7.5 µmol); sample 4 (0.90 w% Pd), 3.3 mg (10.7 µmol); sample 5 (3.48 w% Pd), 3.9 mg (12 µmol) and the loading was repeated two additional times on the resulting NPs.

IR (KBr): spectrum ν=3431cm^{-1} (O-H+N-H), 2962 cm^{-1} (arC-H), 2923 and 2852 cm^{-1} (Csp^3-H), 1632 cm^{-1} (N-C=O), 1489 cm^{-1} (arC-C), 579 cm^{-1} (Fe-O).

Sample characterization. The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) data was acquired with a double spherical aberration-corrected JEOL JEM-ARM200F microscope operated at 200 kV. A probe semiconvergence angle of 25.3 mrad was set yielding a probe size of about 80 pm. The annular semidetection range of the annular dark-filed detector was calibrated at 90-370 mrad. Samples for STEM were prepared by dispersing the catalyst nanoparticles in ethanol and dropping the dispersion onto a lacey carbon coated grid and allowing the solvent to evaporate in air. In addition, the samples were gently plasma cleaned with an Ar (75%)/O_2 (25%) plasma for a few seconds to remove hydrocarbon contamination from the surfaces of the nanoparticles.

X-ray photoelectron spectroscopy (XPS) was performed on a SPECS system equipped with an Al anode XR50 source operating at 150 mW and a Phoibos MCD-9 detector. The pass energy of the hemispherical analyzer was set at 25 eV and the energy step was set at 0.1 eV. The pressure in the analysis chamber was kept below 10^{-7} Pa. Data processing was performed with the CasaXPS program (Casa Software Ltd., UK). Atomic fractions were calculated using peak areas normalized on the basis of acquisition parameters after background subtraction, experimental sensitivity factors and transmission factors provided by the manufacturer.

ICPoes (inductively coupled plasma optical emission spectrometry) measurements were carried out in a Perkin–Elmer Optima 3200RL spectrometer.

Catalysis experiments. The catalysis experiments were carried out using a Fisher-Porter tube with magnetic stirring (500 rpm). Reaction samples were analyzed by gas chromatography (Agilent 6890N) using a 30m HP-5 capillary column and the products identified by gas chromatography-mass spectroscopy, using a Agilent 7820A gas chromatograph equipped with a 30m HP5 capillary column with a mass spectrometry detector (Agilent 5975). Typical reaction conditions, 30 mg of the appropriate Fe_3O_4dopPPh_2@Pd catalyst, 1.177 g (11.3 mmol) of styrene and 25 ml of isopropanol were charged into the reactor, which was purged with hydrogen three times and then pressurized with 3 bar of H_2 and the mixture was stirred for 1 h at room temperature. On stopping the reaction, the reactor was degased slowly and the catalyst separated by using an external magnet. The reaction product was analyzed by gas chromatography. No catalytic activity was detected in the absence of the catalyst.

The catalytic hydrogenation of 1-octene and cyclohexene were performed following identical procedure to that described above. The glass reactor was loaded with 1.268 g (11.3 mmol) of 1-octene or 0.928 g (11.3 mmol) of cyclohexene. Sample 1 was shown to be inactive with both substrates and with sample 2 the conversion to octane and to cyclohexane was achieved with TOFs (h^{-1}) of 2667 and 286, respectively at 3 bar of H_2 and 20ºC.

In order to test the recyclability of the catalyst the following procedure was done. After completion of the reaction, the catalyst was separated by an external magnet and extensively rinsed with isopropanol (3x25 ml) in the Fisher-Porter tube. After that, more styrene and isopropanol was added and the reaction was carried out as described above.

TOFs based on Pd surface atoms[1]

Pd load	NPs: Diameter	Radius	Volume	Total atoms	Total atoms surface	TOF
0.38%	1.2 ± 0.2 nm	0.6	0.9048 nm^3	61	46	7854
0.63%	2.4 ± 0.3 nm	1.2	7.2382 nm^3	491	228	10567
0.90%	2.5 ± 0.4 nm	1.28	8.7845 nm^3	792	263	8379
3.48%	4.3 ± 0.4 nm	2.15	41.6298 nm^3	2827	805	9303

Pd:Face-centered cubic structure (FCC); $a = b = c$ = 389.08 pm (0.38908 nm)
Atomic Pd radius = 0.1374 nm (rcov 139 pm)
Volume unit cell = $a^3 = 0.0589$ nm^3
Pd atoms for unit cell (FCC) = 4
Total Pd atoms = $1/3(10n^3 - 15n^2 + 11n - 3)$
Total Pd surface atoms = $10n^2 – 20n + 12$

1. M. F. Ashby, P. J. Ferreira, and D. L. Schodek , *Nanomaterials, nanotechnologies and design. An introduction for enginers and architects.* Elsevier, Amsterdam, 2009.