SUPPORTING INFORMATION

Continuous Flow Transfer Hydrogenation of Nitroarenes, Azides and Alkenes using Maghemite-Pd Nanocomposites

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EXPERIMENTAL SECTION

Materials and reagents

All commercial reagents were used as received unless otherwise mentioned. For analytical and preparative thin-layer chromatography, Merck, 0.2 mm and 0.5 mm Kieselgel GF 254 pre-coated were used, respectively. The spots were visualized with iodine, and UV light.

The reactions were performed on Thales Nano H-Cube continuous flow hydrogen reactors, utilising water electrolysis to generate hydrogen. The conversion and selectivity of the individual hydrogenation reactions were analyzed by GC employing chromatograph Agilent 6820 (Agilent, United States) equipped with flame ionisation detector (FID) and chromatographic column DB5 (30x0.250x0.25). Following experimental parameters were applied: initial temperature 100 °C, increased to 250°C with a rate of 10 °C/min. Yield determined against internal standard.

Characterization techniques

X-ray powder diffraction (XRD) patterns from maghemite and maghemite-pd samples were recorded at room temperature using a X'Pert PRO MPD diffractometer (PANalytical) in Bragg–Brentano geometry with iron-filtered, Co-Kα radiation (40 kV, 30 mA, λ = 0.1789 nm) equipped with an X'Celerator detector and programmable divergence and diffracted beam antiscatter-slits. The angular range of measurement was set as 2θ = 10 – 105°, with a step size of 0.017°. The identification of the crystalline phases in the experimental XRD pattern was obtained using the X'Pert High Score Plus software that includes a PDF-4+ and ICSD databases. Scanning Electron Microscope (SEM) Hitachi SU6600 with accelerating voltage15 kV., Energy Dispersive Spectrometry (EDS) was acquired in SEM by Thermo Noran System 7 with Si(Li) Detector. Accelerating voltage was 15 kV and acquisition time was 300 s. Each sample in small eppendorf tube was added purified water and ultra-sonified for 5 minutes

Microscopic images were obtained by HRTEM TITAN 60-300 with X-FEG type emission gun, operating at 80 kV. This microscope is equipped with Cs image corrector and a STEM high-angle annular dark-field detector (HAADF). The point resolution is 0.06 nm in TEM mode. The elemental mappings were obtained by STEM-Energy Dispersive X-ray Spectroscopy (EDS) with acquisition time 20 min. For HRTEM analysis, the powder samples were dispersed in ethanol and 5 min ultrasonicated. One drop of this solution was placed on a copper grid with holey carbon film. The sample was dried at room temperature.

XPS surface investigation has been performed on the PHI 5000 VersaProbe II XPS system (Physical Electronics) with monochromatic Al-Kα source (15 kV, 50 W) and photon energy of 1486.7 eV was employed. Dual beam charge compensation was used for all measurements. All the spectra were measured in the vacuum of 1.3 x 10-7 Pa and at the room temperature of 21 °C. The analyzed area on each sample was spot of 200 μm in diameter. The survey spectra was measured with pass energy of 187.850 eV and electronvolt step of 0.8 eV while for the high resolution spectra was used pass energy of 23.500 eV and electronvolt step of 0.2 eV. The spectra were evaluated with the MultiPak (Ulvac - PHI, Inc.) software. All binding energy (BE) values were referenced to the carbon peak C1s at 284.80 eV.

The transmission ^{57}Fe Mössbauer spectra were recorded on in-house manufactured Mössbauer spectrometer operating at a constant acceleration mode and equipped with 50 mCi^{57}Co(Rh) source. For low-temperature (5 K) and in-field (5 T) measurements, the sample was placed inside the chamber of the Spectromagcryomagnetic system (Oxford Instruments); with the Mössbauer spectrometer attached to the system, the setup works in a parallel geometry when the external magnetic field is applied in a parallel direction with respect to the propagation of γ-rays. For fitting the Mössbauer spectra, the MossWinn software program was used. The isomer shift values are referred to α-Fe at room temperature.

Table S1. Values of the Mössbauer hyperfine parameters of the synthesized and recovered samples[a]

Sample	T (K)	B_{ext} (T)	Component	δ ± 0.01 (mm/s)	ΔE_Q ± 0.01 (mm/s)	B_{hf} ± 0.3 (T)	B_{eff} ± 0.3 (T)	RA ± 1 (%)	Assignment
Maghemite-Pd	300	0	Sextet	0.32	0.00	44.3*	-----	100	T-, O-sites
	5	5	Sextet	0.38	−0.02	-----	53.3	37	T-sites
			Sextet	0.52	−0.05	-----	47.0	63	O-sites
Maghemite-Pd (recovered)	300	0	Sextet	0.33	−0.01	44.9*	-----	100	T-, O-sites
	5	5	Sextet	0.28	0.14	-----	54.2	34	T-sites
			Sextet	0.56	−0.08	-----	47.7	66	O-sites

[a] T - temperature, B_{ext} - induction of the external magnetic field, δ - isomer shift, ΔE_Q - quadrupole splitting, B_{hf} - hyperfine magnetic field, B_{eff} - effective hyperfine magnetic field (i.e., vector sum of B_{hf} and B_{ext}), and RA is the relative spectral area of individual components identified during fitting.* The average hyperfine magnetic field, derived from the B_{hf} distribution.

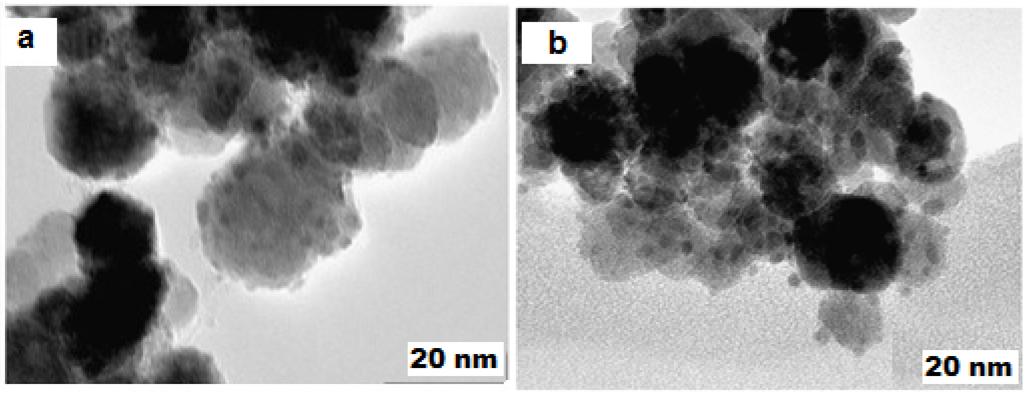
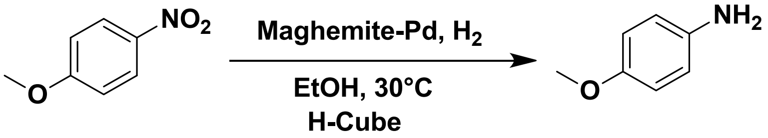


Figure S1. TEM-images a) fresh catalyst; and (b) reused catalyst after (12th run) reaction.

Table S2. Reusability study for the catalyst



Entry	Ist	2nd	3rd	4th	5th	6th	7th	8th	9th	10th	11th	12th
Conversion	>99	>99	>99	>99	>99	>99	>98	>99	>99	>97	>99	>99
[b]Yield %	94	94	93	93	94	95	93	94	92	93	94	93

Reaction condition: Nitro compound (1mmol), maghemite-Pd (6.2%), EtOH (5 mL), Temp 30°C, H_2 gas full mode. [a]Conversions calculated on the basis of GC analysis, [b] Isolated yield. t_r = 0.75 min., Reaction time - 10-15 min.

Table S3. Commonly used heterogeneous catalyst for flow reduction of nitro moieties

Entry	Catalyst	Conditions	Yield (%)	Ref.
1	ARP-Pt (0.073 mol Pt)	25-40°C, 1.5-2mL/min, H_2 (5 vol%)	40-99	1
2	10% Pd/Al_2O_3	25 °C, 2mL/min, H_2 (atm)	99	2
3	5% Pt/C(sulfided)	30 °C, 1ml/min, 30bar H_2	83	3
4	10% Pd/C or Raney Ni	25 °C, 1mL/min, 1 bar	95-99	4
5	$Fe(acac)_3$ (0.25mol%)	150 °C, 4mL/min, 20 mol% $N_2H_4.H_2O$ (H_2 source)	95-97	5
6	10% Pd/C	20-75 °C, 1mL/min, 1-100 bar H_2	41-96	7
7	Maghemite-Pd (6.2%)	30°C, 0.3-0.5mL/min, H_2 (gas flow rate 60 mL/min)	86-98	Present work

Table S4. Commonly used heterogeneous catalyst for flow reduction of alkene moieties

Entry	Catalyst	Conditions	Yield (%)	Ref.
1	ARP-Pt (0.073mol Pt)	25-40°C, 0.7-15mL/min, H_2 (5 vol%)	60-99	1
2	5% Pt/C(sulfided)	30 °C, 1ml/min, 30bar H_2,	100	3
3	10% Pd/C	25 °C, 1mL/min, 1 bar H_2	82-85	4
4	10%Pd/C	25 °C, 1mL/min, 15 bar H_2	quantitative	6
5	Raney/Ni (150 mg)	RT, 1-1.5 mL/min, H_2 full mode at atmospheric pressure	90-94	8
6	Maghemite-Pd (6.2%),	50 -70°C, 0.3mL/min, H_2 (gas flow rate 60 mL/min)	86-95	Present work

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