Supporting Information

Highly Selective Wacker Oxidation of Terminal Olefins Using Magnetically Recyclable Pd–Fe_3O_4 Heterodimer Nanocrystals

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General

All commercially available chemicals were purchased from Aldrich Chemical Co. or Tokyo Chemical Industry Co. and used without further purification unless otherwise noted. All reaction products were identified through comparison with the authentic compounds and quantified through GC analysis using a Hewlett Packard 5890 Gas Chromatograph with mesitylene as an internal standard. All Transmission Electron Microscopy (TEM) images were obtained on a JEOL EM-2010 microscope at an accelerating voltage of 200 kV. The powder X-ray diffraction (XRD) was performed using a Bruker AXS D8 FOCUS (2theta : 5-100, scanspeed : 2degree/min, Cu Kαradiation: λ=1.54056nm, Generator : 40kV, 40m). Magnetic Property Mesurement System (MPMS) was performed using a Quantum Design

Experimental

Preparation of the catalyst

$Pd(acac)_2$ (200 mg, 0.660 mmol) and $Fe(acac)_3$ (14.0 g, 40.0 mmol) were added to a mixture of 120 mL of oleylamine (350 mmol) and 80 mL of oleic acid (250 mmol). The mixture was heated to 120 ^oC under reduced pressure while being stirred vigorously for 2 h. The resulting mixture was heated to 220 ^oC under Ar atmosphere at a heating rate of 2 ^oC /min and kept at this temperature for 30 min. Then it was further heated to 300 ^oC at the same heating rate and aged for 30 min. Subsequently the mixture was cooled to room temperature and washed with 250 mL of ethanol and a black supernatant was decanted. The residue was dispersed in EtOH (250 mL) through sonication and products were collected by centrifugation (1700 rpm, 15 min). The Pd–Fe_3O_4 product was again dispersed in 150 mL of hexane and collected through the use of an external magnet. This washing process was repeated until the decanted hexane did not show any color. After repeated washing cycles, the catalyst was collected and dried under vacuum to furnish 2.45 g of dark solid.

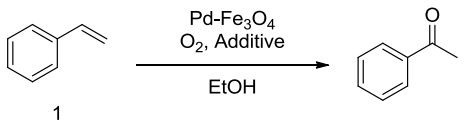
General procedure for Wacker oxidation

Pd–Fe_3O_4 nanocrystal catalyst (1.0 mmol) in ethanol (3.0 mL) was placed in a sealed vial and the mixture was heated to 75 ^oC. After 60 min, styrene (1 mmol), CuCl (0.1 mmol) and H_2O (0.75 mL) were added to the mixture and an O_2 balloon was attached to the vial. The sealed vial was sonicated for 1 minute for dispersion of the Pd-Fe_3O_4 and the reaction mixture was stirred for 36 h at 75 ^oC. After the reaction mixture was cooled to room temperature, the catalyst was separated from the mixture through the use of an external magnet.

General procedure for recycling

After the reaction was complete, ethanol (5 mL) was added and the mixture was sonicated for 1 min. Then the Pd–Fe_3O_4 catalyst was separated with the use of an external magnet. The recovered catalyst was washed five times with EtOH (20 mL), twice with water H_2O (10 ml), and finally twice with ethanol (10 mL) and dried before use for the next reaction.

Table S1. Study on the effect of temperature and amount of CuCl [a]



1

Entry	Additive	Temp (°C)	Conversion (%)[b]	Yield (%)[b]
1	None	70	0	-
2	CuCl (0.1 eq)	70	>99	75
3	CuCl (0.3 eq)	70	>99	75
4	CuCl (1 eq)	70	>99	60
5	CuCl (0.1 eq)	50	14	13
6	CuCl (0.1 eq)	60	40	38

[a] Reaction conditions: Compound 1 (1.0 mmol), Pd-Fe_3O_4 (1.0 mol%), solvent (3.0 mL), mesitylene (1.0 mmol, an internal standard), O_2 balloon. [b] All product composition and yields were determined though GC analysis.

Figure S1. Magnetic separation of Pd-Fe_3O_4 after the reaction.

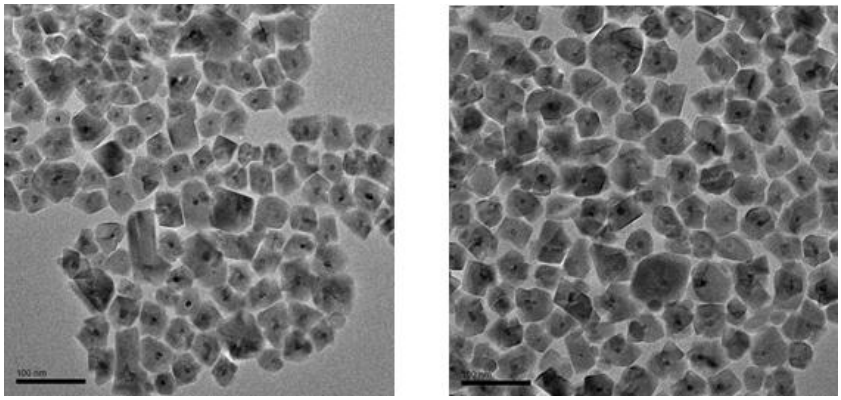


Figure S2. TEM images of pristine Pd-Fe_3O_4

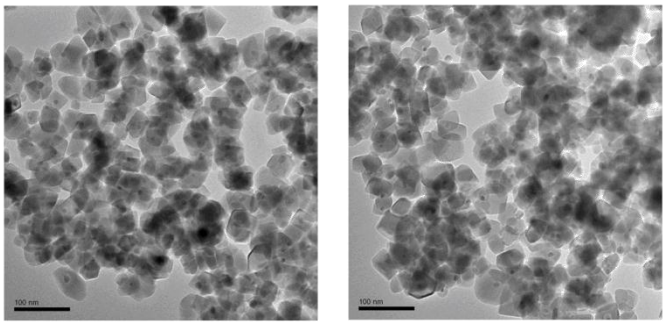
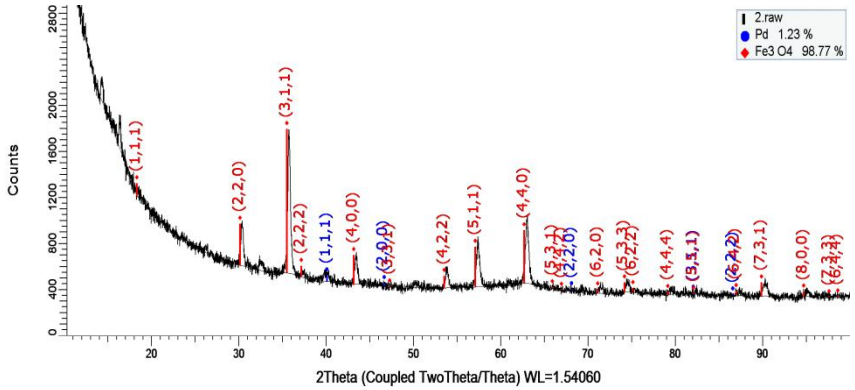
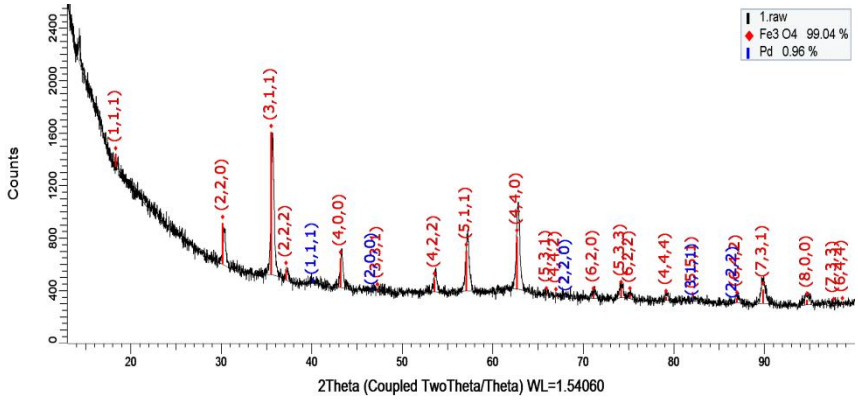


Figure S3. TEM images of Pd-Fe_3O_4 after fifth recycling experiment



Pattern #	Compound Name	Formula	S-Q	System	Space Group	a	b	c
PDF 03-065-2867	Palladium, syn	Pd	1.23%	Cubic	Fm-3m (225)	3.8908		
PDF 01-071-6336	Magnetite, syn	Fe_3O_4	98.77%	Cubic	Fd-3m (227)	8.3778		

Figure S4. XRD pattern of pristine Pd-Fe_3O_4 heterodimer nanocrystals



Pattern #	Compound Name	Formula	S-Q	System	Space Group	a	b	c
PDF 03-065-2867	Palladium, syn	Pd	0.96%	Cubic	Fm-3m (225)	3.8908		
PDF 01-071-6336	Magnetite, syn	Fe_3O_4	99.04%	Cubic	Fd-3m (227)	8.3778		

Figure S5. XRD pattern of Pd-Fe_3O_4 heterodimer nanocrystals after the fifth recycling experiment Pd-Fe_3O_4