Supporting information

Magnetically recyclable magnetite-palladium (Nanocat-Fe-Pd) nanocatalyst for the Buchwald-Hartwig reaction

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1. General Methods

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 percoated were used, respectively. The spots were visualized using UV light.

Transmission electron microscopy (TEM) experiments were performed on a Hitachi H8100 microscope, with a ThermoNoran light elements EDS detector and a CCD camera for image acquisition. The Nanocat-Fe-Pd fine powder was placed on carbon stub and the images were recorded at 5-15 kV using LFD detector under low vacuum.

Elemental analysis was done by using ICP-AES (Inductively coupled plasma-atomic emission spectrometer) using a Horiba Jobin-Yvon, France, Ultima, model equipped with a 40.68 MHz RF generator, Czerny-Turner monochromator with 1.00 m (sequential), autosampler AS500 and CMA (concomitant metals analyzer).

Scanning electron microscopy images were acquired using a JEOL JSM7001F FEG-SEM.

Elemental analysis was performed using a light elements EDS detector from Oxford. The Nanocat-Fe-Pd powder was spread on a double-sided carbon tape and analyzed using 25kV acceleration voltage.

For SIMS, (secondary ion mass spectrometry) positive secondary ion spectra were collected in the mass range of 0 -100 m/z (T=10 min) with an upgraded VG Ionex IX23LS TOF-SIMS set-up based on the Poschenrieder design. A focused liquid Ga^+ gun in pulsed mode (6 kHz) was used as a source of the analytical ions. A beam current in dc mode at 14 keV was ca. 15 nA with a raster size of 300 X 300 μm2. Sample potential was 5 kV. Vacuum during the experiments was maintained in the range of (2-3) $X10^{-9}$ mbar in the analytical chamber.

XPS measurements were performed on VSW XPS system with the Class 100 energy analyzer being a part of an experimental setup assembled for surface investigation. The spectra were taken in fixed analyzer transmission mode with the pass energy of 22 eV i.e. FAT 22. Nanocat-Fe-Pd fine powder was prepared for XPS by pressing on an Indium plate as a matrix in order to reduce the charging problems and providing a mechanical support. For the energy axis calibration Ag(110) and polycrystalline Au samples (previously cleaned by ion sputtering) were used. NMR spectra were recorded on a Bruker 400, 5 mm probe at 400 MHz.

Characeterization of Nanocat-Fe-Pd

1. XRD profile of Nanocat-Fe-Pd

The X-ray powder diffraction patterns were obtained using a Rigaku DMAX-III C conventional powder diffractometer operating in the Bragg–Brentano (θ/2θ) geometry. Graphite monochromatized Cu-Kα radiation was used, with excitation conditions of 40 kV and 30 mA, in the 2θ range from 20º to 80º, an acquisition time of 1 s and 2θ increments of 0.04º. For crystallite size determination sake, the 311 line was selected and refined scans were performed with a 2θ increment of 0.01º and an acquisition time of 5 s.

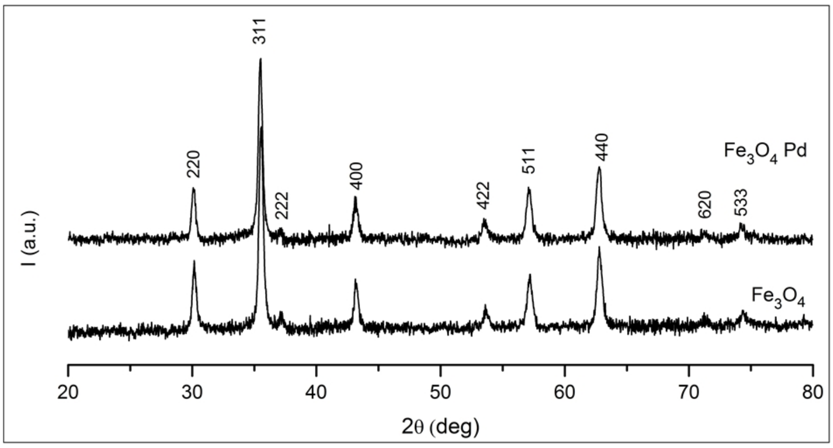

Figure 1. XRD pattern obtained from Fe_3O_4 and Nanocat-Fe-Pd. All indexed lines correspond to cubic Fe_3O_4 (JCPDS 75-1610).

2. XPS profile of reused Nanocat-Fe-Pd

In figures 2, show XPS spectrum of Pd 3d line taken from of recovered catalyst and the relative ratio between Pd(0) and PdO phases is 38:62 (reused catalyst), being identical, in the frame of the experimental error, to the result obtained for the fresh catalyst is 41:59.

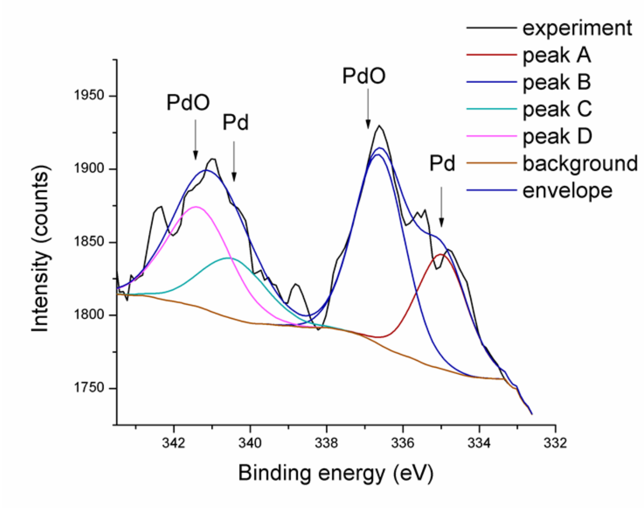

Figure 2. XPS spectrum of Pd 3d line taken from reused Pd-Fe nanocatalyst, sample 2. The expected line positions in the case of metallic Pd as well as of PdO are marked by arrows.