Supporting Information

Magnetic gold (nanocat-Fe-Au) nanocatalyst: catalytic applications for the oxidative esterification and hydrogen transfer reactions

Manoj B. Gawande,*†a Anuj K. Rathi,†a Jiri Tucek,[a] Klara Safarova,[a] Nenad Bundaleski,[b] Orlando M. N. D. Teodoro,[b] Libor Kvitek,[a] Rajender S. Varma,*c and Radek Zboril*a

[a]Regional Centre of Advanced Technologies and Materials, Faculty of Science, Department of Physical Chemistry, Palacky University, Šlechtitelů 11, 783 71, Olomouc, Czech Republic.

[b]Centre for Physics and Technological Research (CeFITec), Department of Physics, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829–516 Caparica, Portugal.

[c]Sustainable Technology Division, National Risk Management Research Laboratory, US Environmental Protection Agency, MS 443, 26 West Martin Luther King Drive, Cincinnati, Ohio, 45268, USA.

†Both authors contributed equally

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, ninhydrine, and UV light.

Characterization techniques

X-ray diffraction (XRD) was performed on a D-800 Siemens diffractometer, with Ni-filtered Cu-Kα radiation. 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 analyses, 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 measurement has been performed on a VSW XPS system with the Class 100 energy analyzer being a part of an experimental setup assembled for surface investigation using the non-monochromatic Mg-Kα line (photon energy of 1256.3 eV). Nanocatalyst fine powders were prepared for XPS by pressing on an indium plate as a matrix in order to provide both mechanical support and electrical contact and analyzed 'as received'. For the energy axis calibration Ag (110) and polycrystalline Au samples (previously cleaned by ion sputtering) were used. The detailed XPS lines were taken in FAT 22 mode with 0.1 eV energy step, while the survey spectra was taken in FAT 44 mode with 0.5 eV energy step. The shift of the energy axis due to charging has been determined from the discrepancy of the main contribution of the C 1s peak, assuming it corresponds to adventitious carbon which should be at 284.8 eV. The binding energy axis was shifted accordingly for 0.7 eV.

The transmission ^{57}Fe Mössbauer spectra were recorded employing a 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 cryomagnetic 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.

Mössbauer analysis of nanocat-Fe-Au

Table 1. Values of the Mössbauer hyperfine parameters, derived from the least-square fitting of the Mössbauer spectra of the nanocat-Fe-Au, where T is the temperature of the measurement, B_{ext} is the induction of the external magnetic field, δ is the isomer shift, ΔE_Q is the quadrupole splitting, B_{hf} is the hyperfine magnetic field, B_{eff} is effective hyperfine magnetic field (i.e., a vector sum of B_{hf} and B_{ext}), and RA is the relative spectral area of individual spectral components identified during fitting.* The average hyperfine magnetic field, derived from the B_{hf} distribution

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
300	0	Sextet	0.31	− 0.01	45.3*	-------	100	T-, O-sites
5	5	Sextet	0.36	0.00	-------	53.9	37	T-sites
		Sextet	0.50	0.00	-------	46.9	63	O-sites

XPS survey spectrum of the nanocat-Fe-Au

In the XPS survey spectrum of the nanocat-Fe-Au, the main lines of oxygen, iron and carbon are clearly visible. Since the sensitivity factor of Au 4f is high, this indicates very low concentration of gold; though it is not quantitative technique to determine the gold content. Indeed, after performing analysis with very prolonged acquisition time, Au 4f line was observed. The XPS spectrum of Au 4f line is shown in Figure 1, after correcting the energy axis to compensate the charging problems. The position of Au $4f_{7/2}$ line is at 83.9 eV, perfectly matching to that of the metallic gold at 83.96 eV.[1]

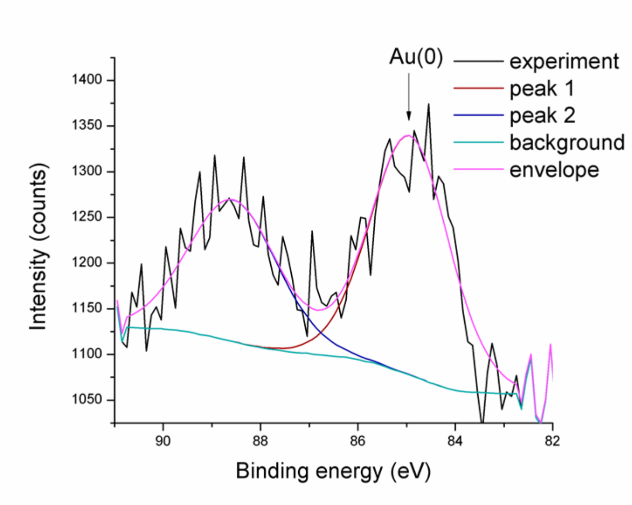

Figure 1. XPS spectrum of Au 4f line taken from nanocat-Fe-Au. The position of the Au $4f_{7/2}$ line for the metallic gold is denoted by arrow.

The XPS spectrum of Fe $2p_{3/2}$ line taken from nanocat-Fe-Au sample, after correcting the energy axis due to the charging, is shown in Figure 2. This line is characterized by large width and specific shape due to the multiplet splitting effects. The fitting has been performed by using the peak model proposed in the study of Biesinger et al. [2] for Fe_2O_3, consisting of 5 GL(30) pseudo-Voigt contributions with constraints for their relative intensities, positions and widths. The background was of the Shirley type, also according to the same reference.

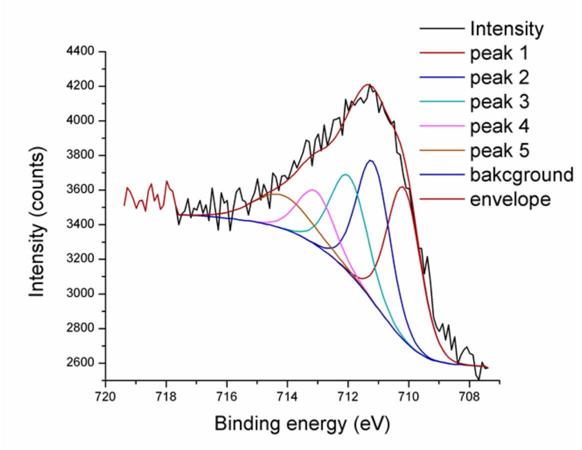

Figure 2. XPS spectrum of Fe $2p_{3/2}$ line taken from nanocat-Fe-Au and the corresponding fit for Fe_2O_3 phase. The peak model is taken from

Reusability

The reusability of the nanocat-Fe-Au was investigated for oxidative oxidative esterification of 4-chlorobenzaldehyde and reduction nitrobenzene. For both reactions excellent reusability was observed (Table 2 and 3).

Table 2. Reusability for oxidative esterification of benzaldehyde

Cycle	1	2	3	4	5
% Yield	92	91	91	90	88

Reaction condition: 4-chlorobenzalde (1 mmol), K_2CO_3 (10 mol%), nanocat-Fe-Au (50 mg), MeOH (3 mL), O_2.

Table 3. Reusability for reduction of nitrobenzene

Cycle	1	2	3	4	5
% Yield	94	93	92	91	89

Reaction condition: Nitro benzene (1 mmol), $HCOONH_4$ (8 mmol), nanocat-Fe-Au (80 mg), EtOH (3 mL), Temp 70°C.

References

1. NIST XPS database http://srdata.nist.gov/xps/Default.aspx.
2. M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A. R. Gerson, R. S. Smart, Appl. Sur. Sci., 2011, 257, 2717-2730.