Bimetallic Cu-Pd Nanoparticles Supported on Bio-silica as an Efficient Catalyst for Selective Aerobic Oxidation of Benzylic Alcohols

Eduardo Buxaderas\textsuperscript{a}, Marilyn Graziano-Mayer \textsuperscript{a}, María Alicia Volpe\textsuperscript{b}, and Gabriel Radivoy\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a} Instituto de Química del Sur, INQUISUR (CONICET-UNS), Departamento de Química, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina.
\textsuperscript{b} Planta Piloto de Ingeniería Química, PLAPIQUI (CONICET-UNS), Camino La Carrindanga Km 7, CC 717, 8000 Bahía Blanca Argentina.

Supporting Information

1. Preparation and characterization of the catalyst

Anhydrous copper(II) chloride (202 mg, 1.5 mmol) and palladium(II) chloride (177 mg, 0.3 mmol) were added to a suspension of lithium (28 mg, 4 mmol) and 4,4'-di-tert-butylbiphenyl (DTBB, 27 mg, 0.1 mmol) in THF (3 mL) at room temperature under a nitrogen atmosphere. The reaction mixture, which was initially dark blue, rapidly changed to black, indicating that the suspension of copper nanoparticles was formed. This suspension was diluted with THF (17 mL) followed by the addition of the bio-silica (HyFlo Super Cel\textsuperscript{®}, 1 g). The resulting mixture was stirred for 1 h at room temperature, filtered, and the solid successively washed with THF (20 mL) and diethyl ether (20 mL), and then dried under vacuum.

The catalyst was characterized by Transmission Electron Microscopy (TEM) in a JEOL JEM-2100F-UHR instrument, operated at an acceleration voltage of 200 kV. For their observation, the samples were mounted on holey-carbon coated 300 mesh gold- or copper grids. Near one hundred metal particles were measured to perform the particle size distribution. TEM analysis showed the presence of well dispersed spherical nanoparticles on the support, with an average particle size of 10.0 ± 2 nm (Figures 1 and 2).
**Figure 1.** Representative TEM micrographs of the Cu-PdNPs/bio-silica catalyst.

**Figure 2.** Size distribution graphic of Cu-PdNPs. The sizes were determined for 100 nanoparticles selected at random.
The XPS spectra were measured with a VG-Microtech Multilab 3000 electron spectrometer using a non-monochromatised Mg-Kα (1253.6 eV) radiation source of 300 W and a hemispheric electron analyser equipped with 9 channeltron electron multipliers. The pressure inside the analysis chamber during the scans was about 5·10⁻⁷ N·m⁻². After the survey spectra were obtained, higher resolution survey scans were performed at pass energy of 50 eV. The intensities of the different contributions were obtained by means of the calculation of the integral of each peak, after having eliminated the baseline with S form and adjusting the experimental curves to a combination of Lorentz (30%) and Gaussian (70%) lines. All the bond energies were referred to the line of the C 1s to 284.4 eV, obtaining values with a precision of ± 0.2 eV.

XPS analysis of the Cu-PdNPs/biosilica catalyst (Figures 3 and 4) showed Cu (2p3/2) peaks at 932.3, 934.6, 936.2, 941.5 and 944.7 eV, with the last two peaks being a satellite shake-up feature characteristic of Cu²⁺ species. On the other hand, XPS analysis revealed the presence of Pd (3d5/2) and Pd (3d3/2) peaks that, after deconvolution, showed two contributions at 336.2/337.6 eV for Pd (3d5/2) peak, and 341.3/342.9 eV for Pd (3d3/2) peak.

![Figure 3. XPS spectrum of PdNPs in the Cu-PdNPs/bio-silica catalyst.](image-url)
Copper and palladium contents of the supported catalyst were determined by Atomic Absorption Spectroscopy that was carried out in a Perkin Elmer AA700 spectrometer. The AAS analysis gave 2.25 mg of copper and 0.75 mg of palladium per 100 mg of catalyst.

2. Study about the heterogeneity of the catalytic process and metal leaching.

In order to study the metal leaching and to confirm the heterogeneity of the catalytic process, a “hot filtration” test was performed as follows. The oxidation of benzyl alcohol (1a) was carried out under the optimized conditions (in the absence of TEMPO), and the reaction was stopped at 30% conversion (2 h). The Cu-PdNPs/bio-silica catalyst was separated by hot filtration and the solid-free filtrate was allowed to stir under the same conditions for 12 h. After this time, the conversion did not show major changes (from 30 to 34%), thus proving the heterogeneity of the catalytic process and indicating that no significant metal leaching had occurred. Furthermore, the degree of copper or palladium leaching was below the atomic absorption spectrometry sensitivity threshold, since no presence of copper or palladium was detected by means of this technique.

Figure 4. XPS spectrum of CuNPs in the Cu-PdNPs/bio-silica catalyst.