

Structural characterization of bimetallic Pd-Cu vapor derived catalysts

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Abstract. Pd-Cu bimetallic Solvated Metal Atoms (SMA) were synthesized by metal vapor synthesis technique and supported on PVPy resin. Since the catalytic activity, of the Pd-Cu system turned out to be quite high also compared to the corresponding monometallic system, a structural characterization, using electron microscopy techniques and X-ray Absorption Fine Structure spectroscopy, was performed. HRTEM analysis showed the presence of Pd particles distributed in a narrow range with a mean diameter of about 2.5 nm while the XAFS analysis, confirmed the presence of the Pd nanoparticles but revealed also some alloying with Cu atoms.

1. Introduction

Bimetallic catalysts are of great interest from both a scientific and an industrial point of view thanks to their catalytic, electronic and optical properties often different from their corresponding mono-metal systems. Among the numerous structural features which can influence their catalytic efficiency, such as particles size and shape like in the monometallic systems, the chemical states and the distribution of the two metals within the individual nanoparticles (e.g., alloying, core-shell or segregation) play a crucial role [1-3]. Bimetallic catalysts which include a combination of a group VIII, such as Pd, and a group IB, such as Cu, have been extensively studied in many processes such as hydrogenation or oxidation reactions but only a smaller number of studies concern their use in Sonogashira coupling reaction that is a very powerful method for the formation of $C_{sp^2} - C_{sp}$ bonds [4-6]. The Pd/Cu co-catalyzed $C_{sp^2} - C_{sp}$ coupling reaction of an aryl or vinyl halide and an alkyne (Sonogashira reaction), is a powerful tool to prepare important precursors of natural products, agrochemicals and pharmaceuticals, as well as molecular materials (optical or electronic) [7]. The development of supported catalysts is a promising way to ensure an easy separation and reusability of the catalytic systems avoiding the environmental pollution from heavy metallic ions [7]. Recently, Pd-Cu bimetallic nanoparticles also embedded in an ion-exchange resin have been reported to be active in Sonogashira coupling reactions performed in acetonitrile as solvent [6]. In the last years many efforts have been made to develop new Pd-Cu bimetallic systems. In this study the structural characterization of a Pd-Cu bimetallic catalyst derived from Pd and Cu vapors, according to metal vapor synthesis (MVS) technique and supported on a commercially available polyvinylpyridine crosslinked with



divinylbenzene (PVPy) resin, that showed high catalytic activity in Sonogashira carbon-carbon coupling reactions, is reported.

2. Sample preparation

The synthesis of the Pd-Cu bimetallic system was achieved by the simultaneous co-condensation of Pd and Cu vapors with a mixture of 1-hexene and mesitylene vapors, according to the Metal Vapor Synthesis (MVS) procedure [8]. The MVS approach allowed to easily deposit the metal nanoparticles onto the PVPy polymeric support avoiding further additional treatments (e.g. high temperature calcinations or reducing steps). A quantitative analysis (ICP-OES) performed on the Pd-Cu/PVPy sample revealed a 1.0 wt.% of Pd and 0.3 wt.% of Cu.

3. Results and discussion

The structural features, the metal particle size distribution and the metal dispersion on the PVPy support, of all samples were investigated by high resolution transmission electron microscopy (HRTEM) (Fig. 1) and X-ray absorption fine structure (XAFS) spectroscopy.

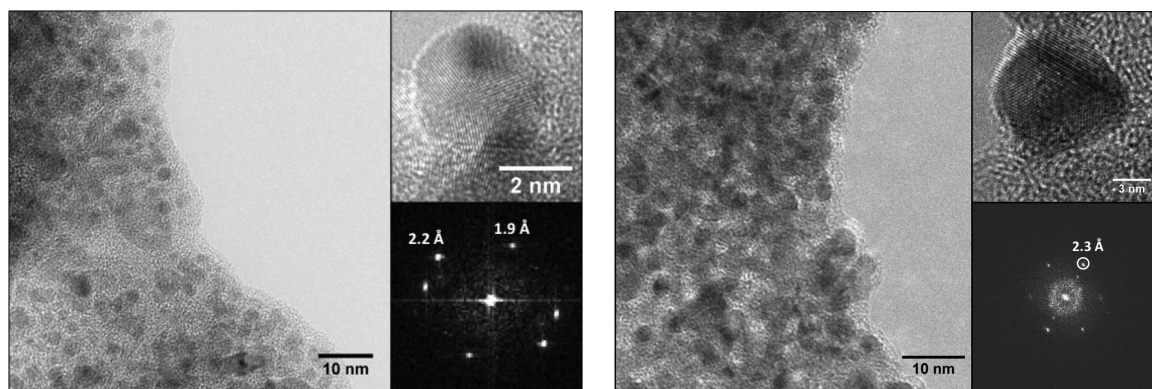


Figure 1. HRTEM and lattice fringe analysis of the PVPy-supported bimetallic Pd-Cu (left) and monometallic Pd (right) samples.

The HRTEM analysis was performed using a 200 KV Zeiss LIBRA 200FE analytical transmission electron microscope, equipped with a STEM facility and an EDS probe for chemical analysis. The local atomic structure around the Pd and Cu atoms was investigated by XAFS spectroscopy. Here we report the results achieved at the Pd K absorption edges of the Pd monometallic and Pd-Cu bimetallic samples at the Italian GILDA beamline [9] of the European Synchrotron Radiation Facility (ESRF, Grenoble - France). XAFS data analysis was performed using the IFEFFIT program [10] to best fit experimental data to simulated spectra with theoretical amplitudes and phases provided by the FEFF code [11]. In the analysis, the palladium foil data, where used to calibrated in energy the different spectra and determine and fix to 0.82 the S_0^2 parameter.

3.1. Catalytic activity

The high catalytic performances of the bimetallic Pd-Cu/PVPy system, compared to the ones of the Pd/PVPy monometallic system in Sonogashira-type carbon-carbon coupling of iodobenzene with phenylacetylene, are reported in Table 1. The reaction conditions were: 2 mmols of aryl iodide, 2.4 mmols of phenyl acetylene, 4 mmols of pyrrolidine, 21.2 mg of catalyst (molar ratio iodide/Pd = 1000, molar ratio iodide/Cu = 2000), 5 mL of H₂O, 1 mmol of TBAB, 95°C, under air. The catalytic system was effectively used for three catalytic runs showing only a slight decrease of the catalytic activity (second run: TOF = 496 h⁻¹, third run: TOF = 481 h⁻¹).

Table 1. Catalytic performances of the bimetallic and monometallic samples; a) Evaluated by gas-chromatographic analyses; b) Calculated as moles of aryl iodide converted/moles of Pd per hour; c) wt.% of metal leached respect to the available starting amount.

Catalyst	Time (h)	Conversion ^{a)} (%)	Turnover Frequency (TOF) (h ⁻¹) ^{b)}	Metal leaching ^{c)} (wt. %)
Pd-Cu/PVPy (1.0 Pd wt.%, 0.3 Cu wt.%)	0.5	26.5	520	-
	2.5	100	-	<0.1 (Pd) <1.8 (Cu)
Pd/PVPy (1.0 wt.%)	0.5	14.5	289	-
	4	100	-	0.5 (Pd)

3.2. Structural characterization using HRTEM and XAFS

HRTEM analysis (Fig. 1) has shown that in the bimetallic Pd-Cu sample, the PVPy resin, appears densely populated by nanostructured metal particles mainly distributed in a narrow range (1.0 nm - 4.5 nm) with a mean diameter of about 2.5 nm. STEM-EDS analysis performed on different grains of the bimetallic Pd-Cu system revealed a constant Pd/Cu molar ratio which was in agreement with above reported quantitative analysis. Fourier transforms analysis (FFT) of the high-resolution images of individual particles of the bimetallic system showed spots at 2.2 Å and 1.9 Å (see Fig. 1). This values are compatible (within the experimental errors) with the presence of small Pd nanoparticles [12], having a face cubic centered (fcc) structure, showing a contraction of the spacings of the {111} and {200} lattice planes with respect to the monometallic Pd system that gives a value of 2.3 Å, typical of pure metallic Pd. Comparing the bimetallic system with the monometallic Pd/PVPy one, synthesized using the same procedure, the latter contains metal particles with larger mean diameters of about 2.9 nm and a broader size distribution (1.0 nm - 7.5 nm) showing that the presence of Cu has an effect on the size and on the distribution of the metal particles in the bimetallic catalyst. HRTEM lattice fringe analysis and EXAFS analysis (Fig. 2) indicated, for the monometallic and bimetallic samples, the presence of fcc Pd nanoparticles. The monometallic sample, showed the presence of metallic Pd nanoparticles ($N_{Pd-Pd} = 8$, $R_{Pd-Pd} = 2.74$ Å and $\sigma^2_{Pd-Pd} = 0.0049$ Å²) and of a little Pd-O ($N_{Pd-O} = 0.7$, $R_{Pd-O} = 2.02$ Å and $\sigma^2_{Pd-O} = 0.0024$ Å²) contribution coming from the superficial oxidation of the Pd nanoparticles [13]. Moving to the bimetallic, Pd-Cu sample the EXAFS data analysis showed the presence of three different Pd-O, Pd-Cu and Pd-Pd contributions. Compared to the monometallic sample, the coordination number of the Pd-O contribution in the bimetallic catalyst is higher but has the same interatomic distance ($N_{Pd-O} = 1.3$, $R_{Pd-O} = 2.02$ Å and $\sigma^2_{Pd-O} = 0.002$ Å²). The higher coordination number probably comes from the smaller nanoparticle dimensions and consequently to the higher surface to volume ratio of the bimetallic catalyst. A small amount of hetero-atomic Pd-Cu bonds ($N_{Pd-Cu} = 0.7$, $R_{Pd-Cu} = 2.68$ Å and $\sigma^2_{Pd-Cu} = 0.008$ Å²) and a shortening of the Pd-Pd distance ($N_{Pd-Pd} = 5$, $R_{Pd-Pd} = 2.72$ Å and $\sigma^2_{Pd-Pd} = 0.0068$ Å²) were also observed. The shorter Pd-Pd interatomic distance of the bimetallic sample, compared to monometallic one, can be due to the smaller nanoparticles dimension [14] (fcc structure is still observable). Considering that the monometallic and bimetallic samples were prepared using the same Metal Vapor Synthesis (MVS) procedure [8], the main structural effects of the presence of Cu, seems to be some alloying probably present only in the immediate subsurface layers and the reduction of the mean dimension and of the size distribution of the produced nanoparticles as seen by HRTEM. Taking into account the catalytic results these findings suggest that, the presence of

Cu (Pd-Cu heteroatomic bonds) and of smaller Pd nanoparticle dimensions, could be responsible of the enhanced catalytic efficiency.

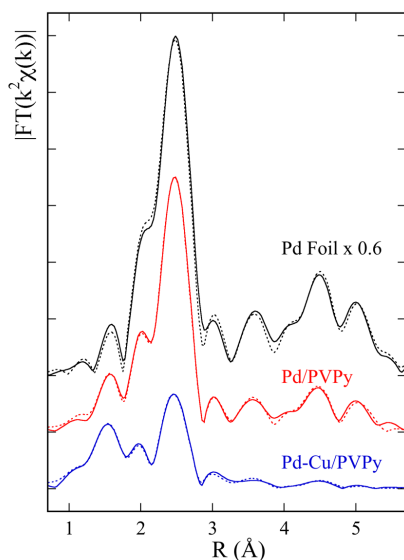


Figure 2. FT of the EXAFS signals and their best fit (dotted lines).

4. Conclusions

A Pd-Cu/PVPy catalyst, used in Sonogashira type carbon-carbon coupling reactions, resulted largely more active than the corresponding monometallic Pd catalyst. In the bimetallic Pd-Cu/PVPy sample, HRTEM analysis showed the presence of metal particles distributed in a narrow range with a mean diameter of about 2.5 nm. XAFS analysis indicated the presence of small Pd nanoparticles with contracted interatomic distances and of heteroatomic Pd-Cu bonds. The structural effects due to presence of Cu were related to the higher catalytic activity of the Pd-Cu sample.

5. References

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