

## A general one-pot methodology for the preparation of mono and bimetallic nanoparticles supported on carbon nanotubes.

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### Abstract

The decomposition of organometallic metal complexes in the presence of stoichiometric amounts of ligands have demonstrated to be an effective method for the preparation of well-defined metal nanoparticles under mild conditions.<sup>1</sup> Recently, a new procedure for synthesizing small and well-defined NHC-stabilized NiNPs has been developed.<sup>2</sup> This methodology permitted the preparation of not only colloidal nanoparticles but also the direct immobilization on carbon nanotubes by a simple “one-pot” procedure. The supported Ni NPs/CNTs revealed to be efficient catalysts in the selective hydrogenation of internal alkynes into the corresponding (Z)-alkenes. In the present contribution, the “one-pot” methodology was extended for the preparation of monometallic (Cu and Pd) and bimetallic nanocatalysts (NiCu and PdCu) stabilized by a N-heterocyclic carbene ligand. Both colloidal and supported nanoparticles (NPs) on carbon nanotubes (CNTs) exhibited welldefined control on their size, morphology and composition and were evaluated in the selective hydrogenation of alkynes and alkynols. PdCu/CNTs revealed to be an efficient catalytic system providing highly selectivity in the hydrogenations of terminal and internal alkynes. Moreover, this catalyst was tested in the semihydrogenation of acetylene in industrially relevant acetylene/ethylene-rich model gas feeds displaying excellent stability even after 40 h of reaction.

A facile and straightforward methodology for the preparation of monometallic (copper and palladium) and bimetallic nanocatalysts (NiCu and PdCu) stabilized by a N-heterocyclic carbene ligand is reported. Both colloidal and supported nanoparticles (NPs) on carbon nanotubes (CNTs) were prepared in a one-pot synthesis with outstanding control on their size, morphology and composition. These catalysts were evaluated in the selective hydrogenation of alkynes and alkynols. PdCu/CNTs revealed an efficient catalytic system providing high selectivity in the hydrogenation of terminal and internal alkynes. Moreover, this catalyst was tested in the semi-hydrogenation of acetylene in industrially relevant acetylene/ethylene-rich model gas feeds and showed excellent stability even after 40 h of reaction.

Bimetallic nanoparticles represent attractive catalytic systems thanks to the synergy between both partners at the atomic lev-

el, mainly induced by electronic effects which in turn are associated with the corresponding structures (alloy, core-shell, hetero-dimer). This type of engineered material can trigger changes in the kinetics of catalyzed processes by variations on the electrophilicity/nucleophilicity of the metal centers involved and also promote cooperative effects to foster organic transformations, including multi-component and multi-step processes. Solvents become a crucial factor in the conception of catalytic processes, not only due to their environmental impact, but also because they can preserve the bimetallic structure during the catalytic reaction and therefore increase the catalyst life-time. In this frame, the present review focuses on the recent works described in the literature concerning the synthesis of bimetallic nanoparticles in non-conventional solvents, i.e., other than common volatile compounds, for catalytic applications.

Furthermore, one can envisage the concomitant synthesis of both BMNPs and the solid support, such as silica, by in situ methodologies from metal salts and organosilicates. As a highly valuable and sophisticated impregnation method, Zhang et al. reported the synthesis of CuNi@SiO<sub>2</sub> from the reverse-microemulsion of Cu(NO<sub>3</sub>)<sub>2</sub>•3H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O in a mixture of Brij®58 (polyethylene glycol hexadecyl ether) and cyclohexane, followed by aqueous ammonia treatment and tetraethyl orthosilicate (TEOS) hydrolysis at the oil/water interface to trigger the formation of a 3-D network structure Cu(II)/Ni(II)@SiO<sub>2</sub>. After drying, Cu(OH)<sub>2</sub>/Ni(OH)<sub>2</sub>@SiO<sub>2</sub> was generated, followed by CuO/NiO@SiO<sub>2</sub> after calcination at 500 °C. Finally, CuO and NiO were reduced to CuNi@SiO<sub>2</sub> under H<sub>2</sub> atmosphere at a high temperature (350 °C). The size and composition of these as-prepared BMNPs were characterized by FT-IR (Fast Transform-Infrared spectroscopy), TEM, XPS, XRD, and ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry). As a catalyst for the reduction of p-nitrophenol in water by NaBH<sub>4</sub>, the calculated activation energy of Cu<sub>54</sub>Ni<sub>46</sub>@SiO<sub>2</sub> (CuNi BMNPs showed a mean size of 5.7 nm) was much lower (16.6 kJ/mol) than that of monometallic Cu@SiO<sub>2</sub> (29.0 kJ/mol) and Ni@SiO<sub>2</sub> (39.5 kJ/mol). This CuNi@SiO<sub>2</sub> nanocatalyst was recycled up to 10 times whilst preserving its reactivity (>90% conversion for 10th run).

Fe-Ni BMNPs supported on montmorillonite (MMT, soft phyllosilicate mineral) have recently been developed by Chikate

and coworkers. Thus, an aqueous solution of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  was mixed with a suspension of  $\text{Na}^+$ -MMT in de-ionized water, before being reduced by the dropwise addition of  $\text{NaBH}_4$  under  $\text{N}_2$  atmosphere. The as-prepared composites were characterized by XRD, TEM, and  $\text{NH}_3$ -TPD (Temperature Programmed Desorption) and were then applied as catalysts for the reductive cyclization of levulinic acid (LA) to  $\gamma$ -valerolactone (GLV). The reduction of LA took place on the bimetallic sites, while the subsequent cyclization to GLV was favored on the strong acidic sites of MMT. Despite the high reactivity (conversion of 90% after 1 h), substantial leaching of iron was observed when using water as the solvent.

Another example of a co-reduction methodology by Yamauchid et al. yielded AuPd alloys supported on graphene oxide (GO) nanosheets by the treatment of a GO water suspension with an aqueous solution of  $\text{H}[\text{AuCl}_4]$  and  $\text{PdCl}_2$ , using ascorbic acid as the reducing agent. The resulting material was employed as an efficient photocatalyst for the degradation of phenolic compounds in water and it could be recycled up to five times. Long et al. reported the preparation of FePd BMNPs supported on chelating resin from  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{PdCl}_2$  using  $\text{NaBH}_4$  as the reducing agent in water; these catalysts were used for the selective reduction of nitrate into nitrogen .