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Semihydrogenation of phenylacetylene catalyzed by metallic nanoparticles containing noble metals

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Abstract

Stable mono and bimetallic nanoparticles have been prepared from colloids developed by a simple and reproducible method, based on a reduction-by-solvent process. This method allows for the preparation of metallic nanoparticles with different compositions (i.e., Ni-Pd, Fe-Pd, Mg-Pd, Pd, and Pt) and metallic ratios, and an average size of about 2 nm. Purified and nonpurified metallic species were used in the selective hydrogenation of phenylacetylene to styrene in liquid phase under very mild conditions (1 bar H_2 pressure and $T = 50\,^{\circ}\mathrm{C}$). The catalysts prepared show high selectivity and activity toward styrene at very high loadings of phenylacetylene (substrate-to-catalyst weight ratio near 7500). Therefore, these materials are highly interesting as selective hydrogenation catalysts for reactions of great industrial importance.

Keywords: Homogeneous; Nanoparticles; Semihydrogenation; Phenylacetylene; Styrene; Metallic colloids; Selectivity

1. Introduction

The preparation of bimetallic colloids has attracted increasing attention during the last years [1–8], due mostly to the fact that the addition of a second metal generally improves some properties of the final catalyst, including activity, selectivity, and stability in certain reactions [9]. One of the main aspects in heterogeneous catalysis is the preparation of the catalyst, which, despite the large diversity of methodologies [10], makes tuning of the size and composition of the catalyst particles a difficult task. In this sense, the preparation of bimetallic nanoparticles is envisaged as a suitable alternative to conventional methods, because both composition and particle size can be controlled [11,12]. Thus, it is possible to prepare bimetallic alloy nanoparticles with a perfectly defined composition and structure [11], even though the synthesis conditions must be carefully controlled, because many variables (even the miscibility of the precursors) may have a great influence in the resulting material.

Phenylacetylene removal by semihydrogenation is a process of great industrial importance [13,14] because phenylacetylene is a poisoning impurity in styrene feedstocks, causing deactivation of the styrene polymerization catalyst. This makes the decrease in phenylacetylene concentration to values close to 10 ppm mandatory. The reaction of hydrogenation of phenylacetylene proceeds at relatively mild conditions, and the desired product is the intermediate (styrene), making it very convenient for the evaluation of process design [14,15] and testing of hydrogenation catalysts [16–19]. In this sense, we can find a substantial amount of literature (both homogeneous [20–22] and heterogeneous [23–29] catalysis) exploring highly selective processes toward the semihydrogenation of alkynes.

In relation to the present paper, dealing with homogeneous catalysis, the literature concerning the hydrogenation of phenylacetylene in homogeneous phase must be taken into account. Adams et al. reported the synthesis of a bimetallic cluster complex for the hydrogenation of phenylacetylene at 80 °C and 30 psi (2.07 bar) of H_2 [30]; however, these catalysts did not show significant activity. Belykh et al. reported in a series of papers [20,31,32] the preparation and catalytic testing of several hydrogenation catalysts based on Pd complexes with phos-

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phines, resulting in very active phenylacetylene hydrogenation catalysts, but did not focus on the processes' selectivity toward styrene. Evrard et al. prepared homogeneous Pd catalysts based on phosphine complexes that reached values $>0.14\ \mathrm{s}^{-1}$ in TOF for the hydrogenation of phenylacetylene under very mild conditions [33], thus obtaining results similar to those reported by Rogolino and co-workers under very similar conditions [22,34]. In the former case, however, the issue of selectivity toward styrene was not addressed. In the latter case, on the other hand, the most abundant product was ethylbenzene after 24 h of reaction. A similar behavior was observed by Pellegatta et al. [28] using rhodium nanoparticles embedded in PVP at 70 °C and 7 bar of H_2. Some authors have even investigated the possibility of using supercritical conditions for the hydrogenation of phenylacetylene [35]. In fact, one of the best results observed hitherto is that reported by Niessen et al. [35a] using Pd nanoparticles (in supercritical CO_2 conditions) for hydrogenation of different substrates. They obtained TOF values as high as $11{,}111\ \mathrm{s}^{-1}$ (achieving 100% conversion after 8 min), with selectivity values slightly above 50% at conversions near 100%. Most of the above-cited examples make use of different metallic clusters prepared from different metallic complexes, which may involve a somewhat complicated preparation method and/or the use of expensive reagents. In this sense, it may be interesting to analyse the advantages of using metallic nanoparticles, which can be readily prepared using relatively cheap chemicals by fairly simple methodologies [12].

The main objective of the present study is to prepare stable colloidal bimetallic nanoparticles with different metallic compositions and metallic ratios and to test their catalytic performance in the semihydrogenation of phenylacetylene in homogeneous phase. Both purified and nonpurified materials were tested and their performance compared with that obtained for monometallic nanoparticles (Pd and Pt) and those reported in the literature.

2. Experimental

2.1. Bimetallic and monometallic colloid preparations

Metallic nanoparticles with different compositions and metallic ratios were prepared following a methodology similar to that described by Lu et al. [36], which is based on a reduction by solvent process. All experiments were performed in an inert atmosphere by means of a Schlenk system unless stated otherwise.

For solution 1, in a two-necked, round-bottom flask, 0.800 g of poly-*n*-vinyl pyrrolidone were added to 120 ml of anhydrous ethylene glycol. Different amounts of $NiSO_4 \cdot 6H_2O$ (depending on the final colloid composition) were added to the mixture, and the system was submitted to stirring for 3 h at 80 °C. The solution was light green in color. For iron-containing colloids, the corresponding metal precursor was iron(II) acetate; for magnesium-containing colloids, the corresponding metal precursor was magnesium sulfate heptahydrate.

For solution 2, in a two-necked, round-bottom flask, different amounts of palladium(II) acetate (depending on the final colloid composition) were dissolved in 50 ml of 1,4-dioxane under vigorous stirring for 2 h. The solution was dark orange in color. In the case of platinum-containing colloids, hexachloroplatinic acid was used as the metallic precursor. Note that in this case, MeOH was used as solvent instead of dioxane.

Solution 1 was cooled to 0 °C with an ice bath, and solution 2 was poured into solution 1 under stirring to ensure homogenization. The pH of the resulting mixture was adjusted to 9–10 by adding a 1 M NaOH solution. The resulting bright yellow solution was capped and heated at 100 °C under vigorous stirring. After a few min, the solution began to acquire a dark-brown color until it was no longer transparent, indicating that the colloid had formed. The heating was maintained for 2 h, after which the bath was removed and the colloidal suspension cooled to room temperature. The flask was sealed and kept for further use.

The stability of the prepared bimetallic colloids is acknowledged by the fact that the colloidal glycol dispersions remained stable for more than 8 months after preparation, with no noticeable amount of aggregated colloid.

2.2. Colloid purification

The prepared nanoparticles colloids were purified as follows. An aliquot containing the desired amount of nanoparticles was treated with a large excess of acetone. This treatment produced the extraction of the protecting polymer to the acetone phase, provoking flocculation of the metallic nanoparticles. This made purification possible by either decantation or centrifugation, depending on the metallic composition of the nanoparticles. After removal of the acetone phase, the purified colloids were redispersed in MeOH by very gentle stirring.

2.3. Catalyst characterization

The as-prepared bimetallic catalysts were characterized by transmission electron microscopy (TEM) using a JEOL JEM-2010 high-tilt instrument operating at 200 kV with a structural spatial resolution of 0.5 nm. The composition of the nanoparticles was measured by EDS coupled to the TEM equipment (OXFORD instruments model INCA Energy TEM100). The spatial resolution of the analytical TEM used (15 nm) allowed measurement of the composition of groups of about 5 particles, with a sufficient signal-to-noise ratio. The bulk composition of the nanoparticles was measured by ICP-OES (Perkin–Elmer Optima 4300) after an aliquot of the colloids was dissolved in HNO_3.

2.4. Catalytic tests

The homogeneous catalytic reaction was performed as follows. An aliquot of the purified colloid suspension containing the desired amount of purified bimetallic nanoparticles (0.5–2.0 mg) in MeOH was added to a 250-ml three-necked flask containing the appropriate amount of MeOH. A glass stopper was set in one of the necks, and the system was purged with Ar for 30 min. The flask was then purged with H_2 for another