

# 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<sub>2</sub> pressure and  $T = 50^\circ\text{C}$ ). 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.

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## 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<sub>2</sub> [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  $>0.14 \text{ s}^{-1}$  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  $70^\circ\text{C}$  and 7 bar of  $\text{H}_2$ . 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  $\text{CO}_2$  conditions) for hydrogenation of different substrates. They obtained TOF values as high as  $11,111 \text{ s}^{-1}$  (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  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (depending on the final colloid composition) were added to the mixture, and the system was submitted to stirring for 3 h at  $80^\circ\text{C}$ . 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  $0^\circ\text{C}$  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  $100^\circ\text{C}$  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  $\text{HNO}_3$ .

### 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  $\text{H}_2$  for another

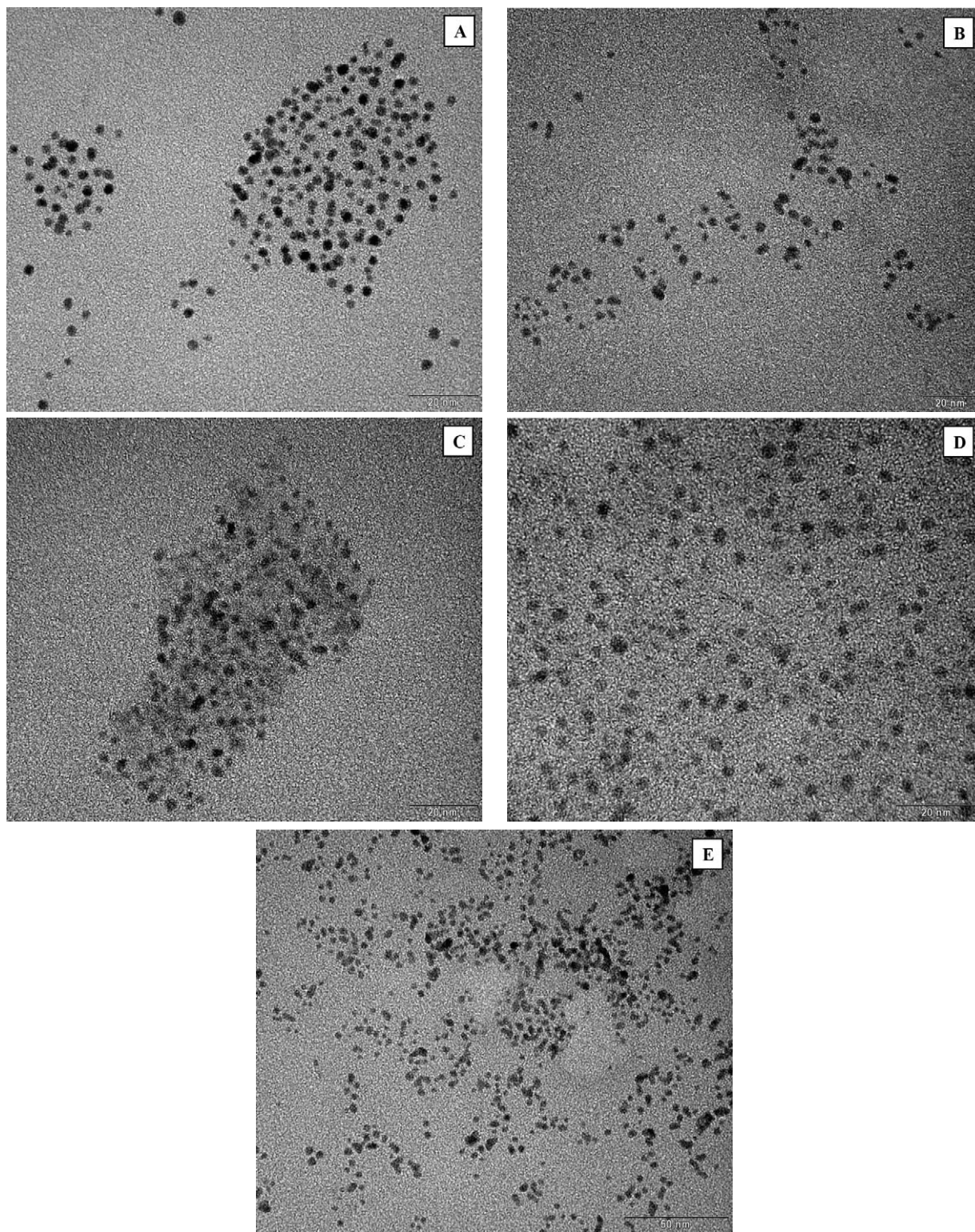


Fig. 1. TEM images of a purified (A) Pt colloid, (B) Pd colloid, (C) Fe/Pd 50:50 bimetallic colloid, (D) Ni/Pd 70:30 bimetallic colloid, and (E) Mg/Pd 50:50 colloid.

30 min. After purging, 10 ml (9300 mg) of phenylacetylene were added to the reaction mixture, and the  $H_2$  flow was regulated by a needle valve. This time was considered the start of the catalytic reaction. The final volume of the solution in the flask was always 100 ml. All reactions were performed up to a 100% conversion, and this was taken as the end of the reac-

tion. Agitation was done with a magnetic stirring bar covered with a glass capsule to prevent colloid agglomeration. The reactions were performed at a temperature of 50 °C. The progress of the reaction was monitored using a gas chromatograph (HP 6890) equipped with a capillary column (HP-1 cross-linked methyl siloxane). Aliquots were taken from the reaction mix-

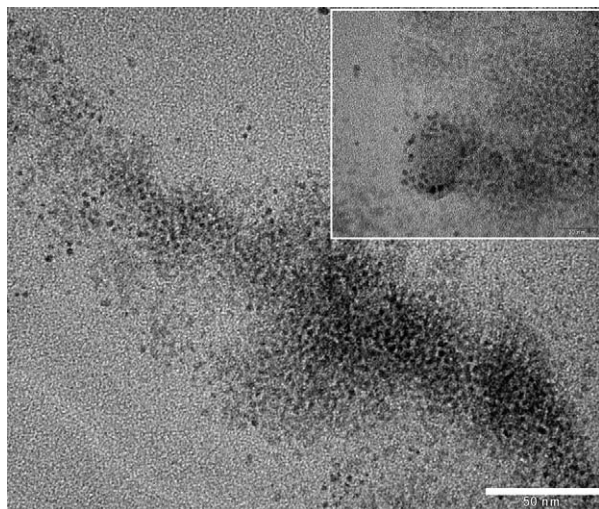


Fig. 2. TEM image of a Mg/Pd 50:50 colloid with PVP. Inset: Detailed view showing the bimetallic nanoparticles (dark spots) and the PVP flakes.

ture at the desired times, diluted to a 1:100 ratio, and injected by means of a microsyringe in the chromatograph. In addition, some experiments were performed using the nonpurified colloid for comparison purposes.

### 3. Results

#### 3.1. Colloid characterization

The synthetic procedure followed for colloid preparation allowed the preparation of stable and very small nanoparticles with a narrow particle size distribution as observed by TEM. Fig. 1 shows TEM images of some of the prepared colloids after purification, which are representative of the materials prepared. Fig. 1 confirms the adequateness of the purification method used, because there is no sign of the protecting polymer (PVP) around the nanoparticles as seen in the nonpurified nanoparticles of Fig. 2, where PVP molecules appear as translucent flakes in the TEM pictures.

The particle size distributions of the colloids were measured from the TEM observations. Fig. 3 shows the histograms corresponding to the particle size distributions of the prepared colloids based on a 100-particle count. Table 1 gives the average particle sizes of the prepared colloids, as measured by TEM. The results indicate that for all the bimetallic catalysts and compositions, the preparation method allowed us to obtain small particles with narrow particle size distributions similar to the pure Pd nanoparticles.

The bulk composition of the metallic nanoparticles was assessed by ICP-OES, dissolving the colloid in  $\text{HNO}_3$ ; the results provide a good agreement with the desired composition, except for the Mg/Pd material (Table 2). To obtain information on the homogeneity of the chemical composition of the nanoparticles prepared, the composition of the resulting materials was measured by energy-dispersive spectroscopy (EDS), coupled to the TEM equipment. Considering the spatial resolution of the analytical TEM used (about 15 nm) and the error of the technique (experimental error was never  $>5\%$ ), the compositions of about

Table 1  
Colloid particle size distributions

Colloid	Mean particle size (nm) <sup>a</sup>	Standard deviation <sup>a</sup>
Ni/Pd 70:30	2.3	$\pm 0.3$
Ni/Pd 50:50	2.2	$\pm 0.5$
Ni/Pd 30:70	2.4	$\pm 0.4$
Pd	2.4	$\pm 0.5$
Pt	2.6	$\pm 0.5$
Fe/Pd 50:50	2.1	$\pm 0.3$
Mg/Pd 50:50	2.5	$\pm 0.4$

<sup>a</sup> Based on a 100-particle count.

Table 2  
Composition of the prepared bimetallic nanoparticles obtained from inductively coupled plasma and energy dispersive spectroscopy

Colloid	ICP-AES		EDS	
	%Pd	%M <sup>a</sup>	%Pd	%M <sup>a</sup>
Ni/Pd 70:30	29.40	70.59	$32.38 \pm 4.08$	$67.61 \pm 4.08$
Ni/Pd 50:50	53.33	46.67	$54.05 \pm 3.60$	$46.05 \pm 3.60$
Ni/Pd 30:70	28.33	71.67	$29.59 \pm 1.44$	$70.41 \pm 1.44$
Fe/Pd 50:50	51.56	48.43	$55.67 \pm 2.08$	$44.33 \pm 2.08$
Mg/Pd 50:50	75.56	24.43	$90.42 \pm 0.69$ $36.01 \pm 0.50$	$9.58 \pm 0.69$ $63.99 \pm 0.50$

Note. All relative standard deviations for EDS are calculated taking a confidence interval of 95%.

<sup>a</sup> Alloying metal.

five particles were evaluated in each analysis. At least four regions of each sample were analyzed. Table 2 gives the metallic ratios as determined by ICP-OES for the bulk materials and by TEM-EDS for several isolated particles. The results show that for Fe and Ni, the homogeneity in composition of the synthesized nanoparticles was high, and the synthetic procedure used for the different compositions was successful. However, for Mg/Pd nanoparticles, the local composition was rather heterogeneous, and wide ranges of compositions were detected for the particles analyzed. The collected TEM images indicate that the material consisted of two separate phases, the first formed by Mg/Pd nanoparticles (with a lower Mg content than expected) and the second formed by pod-like structures several microns in size. These structures were analyzed by EDS, showing that it was a Mg compound (magnesium sulfate). Moreover, the bulk composition of the sample shows that the final material has a quite different composition with respect to that expected (25:75 vs 50:50). Note that although we keep the nomenclature of the sample as Mg/Pd 50:50, our calculations and discussion take into account the correct composition of the material.

In summary, from the results presented above, we can conclude that the reduction-by-solvent method appears to be a very suitable method for preparing metallic nanoparticles with sizes ranging from approximately 2 nm and narrow size distributions and different chemical compositions that are homogeneous in the case of Pd nanoparticles containing Fe and Ni.

#### 3.2. Catalytic tests

The hydrogenation of phenylacetylene was performed in the presence of several different bimetallic colloids under different

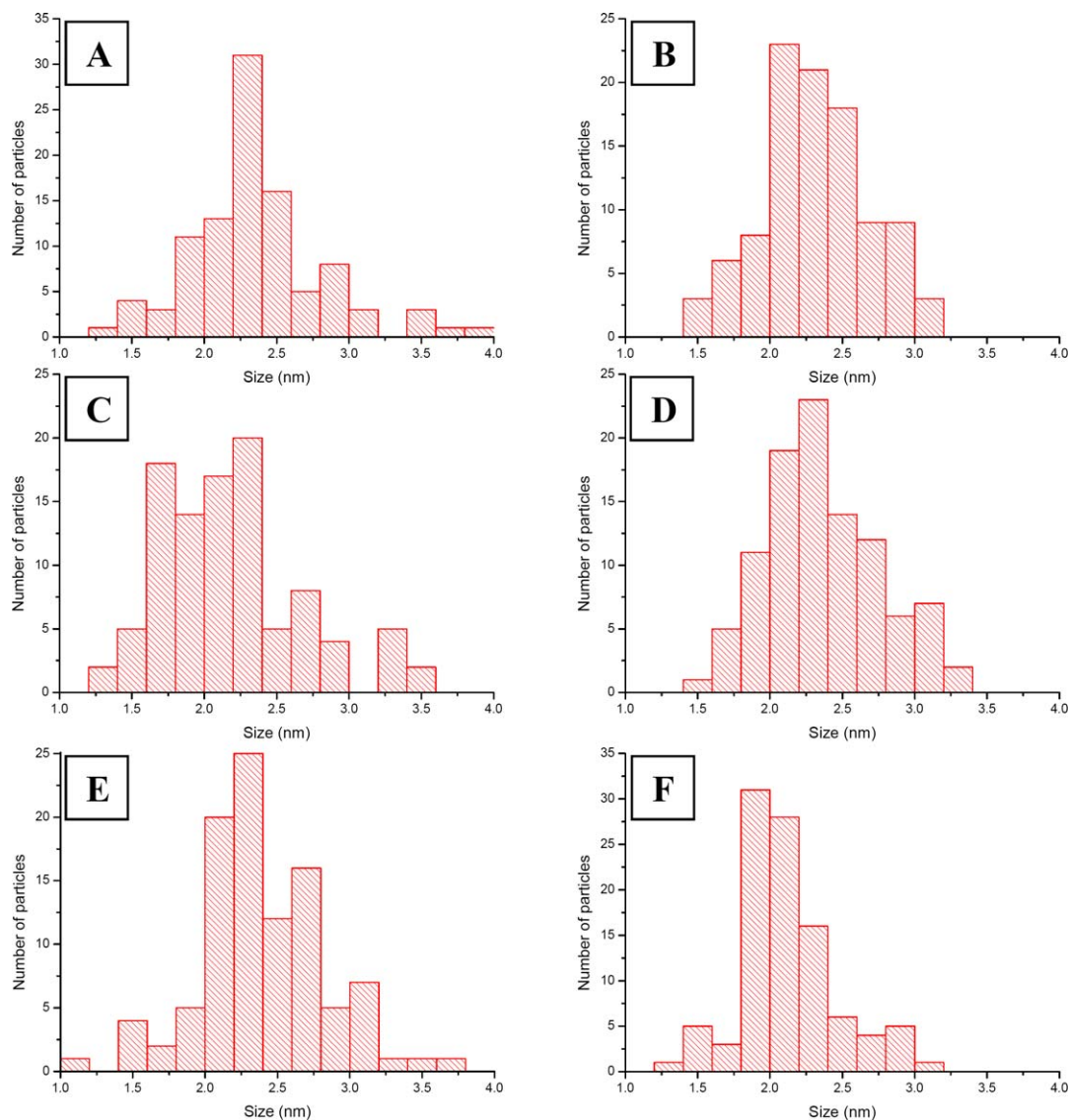


Fig. 3. Particle size distribution histograms corresponding to a (A) Pd, (B) Ni/Pd 70:30, (C) Ni/Pd 50:50, (D) Ni/Pd 30:70, (E) Mg/Pd 50:50, (F) Fe/Pd 50:50 colloid.

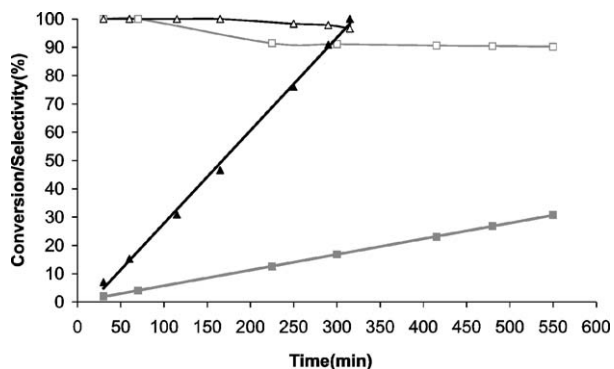


Fig. 4. Conversion (full symbols) and selectivity (hollow symbols) graphs for the semihydrogenation of phenylacetylene in MeOH at 50 °C using a (▲) Ni/Pd 50:50 colloid or a (■) Pt colloid. H<sub>2</sub> pressure = 1 bar (flow = 30 ml/min), amount of metallic colloid: 1.3 mg. Substrate-to-colloid ratio: 7450 (g/g).

conditions. Fig. 4 shows, for some of the prepared nanoparticle suspensions, the evolution of the conversion of phenylacetylene versus time together with the corresponding selectivity toward

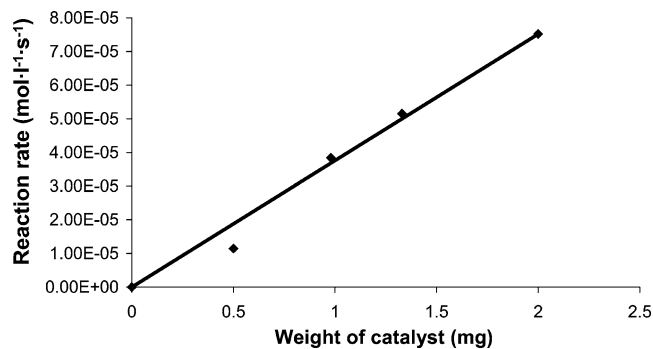


Fig. 5. Reaction rate vs weight of catalyst plot for a Ni/Pd 50:50 catalyst.

styrene. Initial experiments were performed to verify the absence of mass transfer limitations; thus, agitation rate and hydrogen bubbling were increased until the reaction rate remained constant. At the selected agitation rate and hydrogen bubbling, the Koros-Nowak criterion was applied to confirm that the reaction rates were free of mass transfer effects [37]. For this

Table 3  
Results of the hydrogenation of phenylacetylene performed with the studied colloids

Colloid <sup>a</sup>	H <sub>2</sub> flow (ml/min)	Temperature (°C)	Time (min) <sup>b</sup>	Selectivity <sup>c</sup> (%)	TOF <sup>d</sup> (s <sup>-1</sup> )	TOF <sup>e</sup> (s <sup>-1</sup> )
Pd	30	50	327	95.6	1.01	1.01
Ni/Pd (70:30)	30	50	360	95.1	0.59	1.97
Ni/Pd (50:50)	30	50	315	96.6	0.73	1.46
Ni/Pd (30:70)	30	50	285	97.3	0.99	1.41
Fe/Pd (50:50)	30	50	355	96.5	0.61	1.22
Mg/Pd (50:50)	30	50	255	94.0	0.81	1.08
Pt	30	50	550 <sup>f</sup>	90.2	0.38	–

<sup>a</sup> Amount of metallic colloid: 1.3 mg. Substrate-to-colloid ratio: 7450 (g/g).

<sup>b</sup> Until conversion reached 100%.

<sup>c</sup> Toward styrene for a 100% conversion.

<sup>d</sup> (Mol substrate) (mol surface catalyst)<sup>-1</sup> s<sup>-1</sup>.

<sup>e</sup> Per mol of surface Pd, calculated assuming homogeneous composition.

<sup>f</sup> Conversion 30.8%.

purpose, the reaction rates for different weights of the catalyst (0.5–2.0 mg) were measured. The results, shown in Fig. 5, demonstrate that the reaction rate is proportional to the amount of catalyst, thus confirming that the measurements under the experimental conditions studied, are within the kinetic regime.

From experiments like those shown in Fig. 4, the performance of the prepared catalysts was evaluated. Note that according to Fig. 4, the reaction seems to be of zero order to phenylacetylene under the reaction conditions studied ( $T = 50\text{ }^{\circ}\text{C}$ ,  $P_{\text{H}_2} = 1$  bar, and a phenylacetylene-to-metal weight ratio near 7500). This observation agrees with what is usually observed at similar reactions conditions with Pd catalysts [38–41].

Table 3 summarizes the results of the catalytic tests performed with the different prepared colloids (using 1.3 mg of colloid and a substrate-to-colloid ratio of 7450 g/g). The table includes the experimental conditions used (H<sub>2</sub> flow and temperature), the time at which the 100% conversion is reached, and the selectivity toward styrene for a 100% conversion and the TOF (included in the sixth column in Table 3). The TOFs were calculated from the TEM average particle sizes determined for each colloid, assuming that the particles are spherical (dispersion  $\approx 0.9/d$  (nm) [42]). Fig. 6 plots the TOF data collected in Table 3 for a better indication of the trends among the samples.

As can be seen from Figs. 4 and 6 and Table 3, the Pd-based catalysts show very good activity and selectivity throughout the course of the reaction. It is particularly remarkable that the selectivity values remain very close to 100% until conversion values exceed 80%, showing a similar trend to that reported by Costa et al. [22], although the drop in selectivity at higher conversions presented in this work is much lower, with final selectivity values  $>95$  for 100% conversion in most cases.

Fig. 6 shows that the Pd nanoparticles are those with the highest activity and that Pt is the sample with the worst performance in terms of activity and selectivity. This last observation is expected because Pt is known to have lower activity and selectivity than Pd for hydrogenation of highly unsaturated hydrocarbons [43]. Regarding the bimetallic nanoparticles, the results show that the TOFs are smaller in all cases compared with pure Pd nanoparticles, although some interesting tendencies merit mention. Thus, TOF decreases significantly with increasing Ni

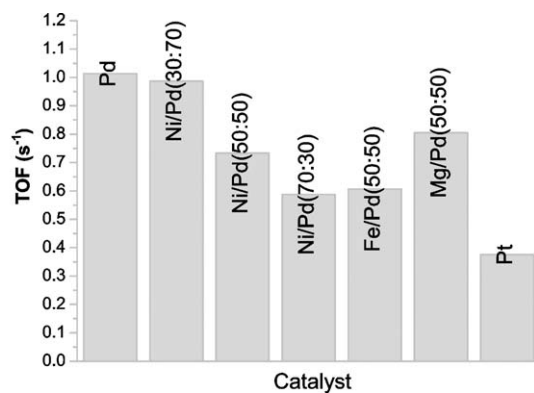


Fig. 6. TOF values for the catalysts shown in Table 3 at 50 °C.

content, and the performance of the Fe-containing colloid is worse than that of the Ni/Pd sample. In addition, the value for the Mg-containing nanoparticles (Mg/Pd 50:50, with a real composition of 25:75) is very similar to that of the corresponding Ni/Pd 50:50 colloid and lower than that of the Ni/Pd 30:70 sample. Regarding the selectivity of the catalysts, it is very high in all the materials and slightly higher for some bimetallic colloids compared with pure Pd nanoparticles (see the selectivity of Ni/Pd 50:50, Ni/Pd 30:70, and Fe/Pd 50:50 vs Pd in Table 3).

Table 3 also includes the TOF data calculated per mol of surface palladium (see the last column). These results were calculated assuming that the prepared nanoparticles have a homogeneous composition. This consideration is valid for Ni/Pd and Fe/Pd and is supported by the work of Lu et al. [36], in which, after thorough characterization of reduced by solvent Ni/Pd nanoparticles by HRTEM, XANES, and EXAFS, the authors concluded that their structure corresponds to a random Ni/Pd alloy. Since both Ni and Fe can form alloys with Pd with complete solubility [43] and considering that the synthesis procedure followed in this study is almost the same as that used previously [36], it may be safely assumed that the structure of both colloids corresponds to a random alloy of both metals. On the other hand, the TOF value calculated per mol of surface Pd for the Mg/Pd sample is not correct and should be used only for comparison purposes. In fact, Mg and Pd form intermetallic phases [44], and thus the Mg/Pd material prepared is very heterogeneous.

When the TOF is calculated per mol of surface Pd in the catalyst (see the last column of Table 3), all catalysts show higher TOFs than the pure Pd colloid. The TOF values obtained in the various experiments are comparable to the results found in the literature for heterogeneous Pd-hydrotalcite and Pd-pumice catalysts [26,39] and for homogeneous Pd-based catalysts [20,21], although with higher selectivity.

#### 4. Discussion

The kinetic model and reaction mechanism for hydrogenation of alkynes was discussed previously [39,41,45]. It is proposed that the hydrogenation of the alkynes to the corresponding alkenes and alkanes proceeds through a two-path mechanism in which either the direct hydrogenation of the triple bond to

single bond, or a two-step hydrogenation, may occur and that the process involves formation of single or multiple adsorbed species. In addition, carbonaceous deposits are formed, especially for hydrogenations occurring in the gas phase. According to this reaction scheme, a zero-order kinetics is observed at experimental conditions similar to those used in this study [38–41], which agrees with our catalytic tests.

The results obtained when using Pt colloids clearly show that the rate was much slower than when using its Pd counterpart. Moreover, when the conversion reached values around 30%, the selectivity value had already begun to drop to values around 90%. These observations are expected because it is known that Pt is less active and selective than Pd for hydrogenation of highly unsaturated hydrocarbons [45]. The strength of the alkene–Pt bond is greater than that of the alkene–Pd bond, explaining the higher selectivity of Pd toward the alkene [45]. The higher activity and selectivity of Pd is the reason why most of the recent studies on heterogeneous catalysts for this reaction focus on this active phase. This conclusion could also be extended to homogeneous catalysts, because the performance of Pd-based complexes is one of the most widely studied.

In terms of the bimetallic Pd colloids, there are interesting differences with respect to pure Pd nanoparticles that depend on the composition and nature of the second metal. We discuss these differences in more detail later, but note here that the first aspect to remark, due to its relevance from an applied standpoint, is that adding a 30% of Ni atoms in the Pd colloid produces a material with activity and selectivity very close to those of the monometallic counterpart (Table 3, Fig. 6). In this sense, we must, from a practical standpoint, acknowledge the reduced cost of the catalyst, because nickel sulfate is much cheaper than palladium acetate.

The effect of a second metal on Pd activity and selectivity has been studied in sufficient detail for heterogeneous Pd catalysts. This issue has been reviewed previously [42]. Both the selectivity and activity can be influenced by the addition of a second metal due to either electronic or geometric effects. In the first case, the presence of the second metal may modify the electron density of Pd atoms, thus modifying the strength of the adsorption of the hydrocarbon molecules and hydrogen. An increase in electron density results in decreased adsorption strength of the unsaturated hydrocarbons and, consequently, an increase in selectivity toward the alkene. Regarding the geometric effect, the existence of large ensembles of Pd atoms with an appropriate geometry allows the formation of multiple adsorbed species that seem to be responsible for complete hydrogenation of the alkyne.

The above comments on the influence of a second metal on Pd activity are useful to understand the results found with the bimetallic colloids used in this work (Table 3, Fig. 6). Assuming nanoparticles with homogeneous composition, the decrease in TOF with increasing Ni content can be explained considering that an increased number of Ni atoms in the nanoparticles will dilute the Pd active sites. This argument is also valid for Fe-containing nanoparticles. In addition, the presence of Ni or Fe will decrease the amount of large Pd ensembles, thus increasing the selectivity toward the alkene. However, electronic effects

cannot be discarded if we look at the TOF calculated per mol of surface Pd (see the last column in Table 3).

Once the results found for the nanoparticles with different compositions have been explained, we should recall our attention to the fact that we are using bimetallic nanoparticles in homogeneous phase for the hydrogenation of phenylacetylene. The use of these catalysts presents one clear advantage compared with other results in the literature, in which different metallic complexes are used in very similar (or sometimes the same) reactions [21–23,46,47]: Preparation of the catalytically active species involves the formation of a metal complex, which sometimes requires the use of expensive moisture-sensitive and/or air-sensitive compounds, and also may take a significant amount of time. The catalysts presented herewith are prepared with comparatively cheap raw materials (with the exception of palladium acetate) and can be prepared in 4 h. Because of these results, the reduction-by-solvent method has proven to be suitable for preparing metallic colloids due to its simplicity and reproducibility. Moreover, because no specific reduction agent is used (such as sodium tetrahydroborate or hydrazine), the reagent cost and byproduct generation are minimized. Furthermore, and from the results presented in this study, the activity of the prepared bimetallic nanoparticles is comparable to that reported in the literature for homogeneous catalysts, if not higher in some cases (except for the results of Niessen et al. [35a]). In the case of selectivity, the values presented in this work are higher than those reported in the literature for homogeneous reactions [20–22,31–34], with values around 97% (Ni/Pd 30:70 at 50 °C), among the best results presented to date in terms of selectivity. Moreover, the values are very similar to the results presented by Martín-Astorga et al. [40], in which a heterogeneous reaction is involved.

A step of paramount importance when working with metallic nanoparticles is separation of the metallic species from its respective protecting agent (in our case, the polymer PVP). This step is called the purification of the colloid (see, e.g., Ref. [4b]). In our case, we repeated one of the experiments with the non-purified colloid to establish the effect of the protecting polymer surrounding the metallic nanoparticle. From our results, using PVP-Ni/Pd 50:50 at 50 °C and with a H<sub>2</sub> flow of 30 ml/min, the activity was the same as with the purified sample of the colloid, and the selectivity reached 91%, similar to that of the purified nanoparticle dispersion. This observation may be due either to the diffusion of the reagent through the protecting polymer layer around the nanoparticle or to the dispersion of the polymer in the reaction medium (MeOH), making the nanoparticles available for reaction. In any case, these results may greatly simplify the procedure for performing the catalytic reaction, enabling the storage of the as-prepared colloids for their direct use as the catalytically active species.

## 5. Conclusion

This paper describes the preparation of bimetallic nanoparticles with different metallic compositions and metallic ratios by the reduction-by-solvent method together with their catalytic testing in the hydrogenation of phenylacetylene in homoge-

neous phase. Ni/Pd and Fe/Pd nanoparticles are homogeneous in composition and can be prepared with different metallic ratios, but Mg/Pd nanoparticles are heterogeneous in composition and chemical state. The prepared bimetallic catalysts have proven very active and selective under very mild conditions (ambient temperature and low H<sub>2</sub> pressures), showing similar or better results compared with those obtained using pure Pd nanoparticles. An interesting advantage of using bimetallic nanoparticles is to bring down the cost of production by using fewer amounts of noble metal precursors. The results obtained with the prepared metallic nanoparticles are very interesting compared with other homogeneous catalysts especially in terms of selectivity, reaching values very close to 97%, accounting for the interest in these nanoparticles for different reactions of industrial importance.

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