Silica-supported palladium nanoparticles show remarkable hydrogenation catalytic activity

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Abstract

Palladium nanoparticles (1.9 nm) stabilized on silica were obtained from the reduction of an organometallic precursor (palladium(II) bis-dibencylidene acetone) with dihydrogen. This material was investigated in the hydrogenation catalysis of different substrates (1-hexene, cyclohexene, benzene, 2-hexanone, cyclohexanone and benzonitrile). The solid was used as a heterogeneous catalyst. The highest hydrogenation rate was found with 1-hexene with a TOF of 38,250 mole of product/(mole of metal/h) at 25 °C and 30 psi pressure. The [Pd/SiO$_2$] nanocatalyst has shown remarkably high activity for the catalytic hydrogenation of cyclohexene (TOF 33,000) and benzene (TOF 10,000). This is the first reported palladium nanocatalyst with high catalytic activity towards the hydrogenation of 2-hexanone TOF 16,000, cyclohexanone TOF 15,000 and benzonitrile TOF 5000 reported to the date.
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Keywords: Palladium nanoparticles; Nanocatalyst; Hydrogenation catalysis

1. Introduction

Over the last decade, due to the unique properties of metal nanoparticles, the interest in synthetic routes that could generate new nanostructured materials has shown significant growth. For noble metal colloids, the interest mainly focuses on catalytic applications [1,2]. The advantages of colloidally dispersed noble metal are precisely the advantages derived of colloidal particles, in general:

- a large surfaces area;

- unique activities and spectroscopic features due to the size quantization of most electronic properties.

Catalytic hydrogenation represents only a small part of the industrial organic syntheses. Nevertheless, it represents an essential part of hydrotreatment of crude in the oil industry, which eliminates aromatics and unsaturated hydrocarbons during diesel and aero fuel production. The increase in oil consumption between the years 2000 and 2010 is forecast to be around 17% and by the year 2010 the relation petrol–diesel is expected to change in favor of diesel. These facts reveal the importance of the development of new catalytic materials with substantially incremented activities and selectivities that could imply costs reductions, especially in hydrogenation process [3].

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Table 1
Catalytic activity of [Pd/SiO$_2$] in the catalytic hydrogenation of various organic substrates

Substrate	[Catalyst]/[substrate] ratio	Reaction conditions	Reaction time	Conversion (%)	TOF (mole of product/ (mole of metal/h))
1-Hexene	1/160,000	25 °C; 30 psi	10 min	21	38,247
Cyclohexene	1/340,000	25 °C; 40 psi	100 min	16.5	33,000
Benzene	1/235,000	140 °C; 120 psi	2 h	14	10,000
2-Hexanone	1/170,000	125 °C; 30 psi	6 h	32	16,000
Cyclohexanone	1/200,000	133 °C; 30 psi	6 h	25	15,000
Benzonitrile	1/205,000	145 °C; 120 psi	24 h	46	5000

Different groups have reported the catalytic activities of various palladium and other transition metal nanostructured materials [4–8] supported mainly on polymeric matrixes, which have superior or at least comparable catalytic activities to that of bulk metal catalysts. These, provide enough evidence of the potential of nanostructured catalyst compared to bulk catalysts.

Within this context, this study presents a new nanostructured palladium material supported on silica, which exhibits very high catalytic hydrogenation activities towards various organic substrates Table 1.

2. Experimental

The synthesis of the palladium nanoparticles was carried out under argon atmosphere using standard Schlenck techniques. The silica gel (Gomasil G-200) used as inorganic support has a reported BET surface area of 223 m^2/g, with a mean grain size of 0.5 μm and 98.8% SiO$_2$ and 0.69% NaSO$_4$ content. The material was donated by Rhodia Silices de Venezuela C.A. The silica gel was activated at 300 °C under vacuum, during 72 h then kept under argon atmosphere previous to its use.

Routine IR-FT was performed on a Perkin-Elmer 1760-X spectrometer using CsI disks. The elemental analyses were carried out by atomic emission with coupled inductive plasma on a Thermo Jarrel ASH, model IRIS H12. The transmission electron microscopy (TEM) was performed on JEOL JEM 1220 electron microscope operating at an accelerating voltage of 120 kV. Samples were prepared using carbon-coated copper grids. One drop of a tetrahydrofurane (THF) suspension of [Pd/SiO$_2$] was placed on the carbon-coated grid using a microsyringe. GC analyses were performed on a Perkin-Elmer Autosystem XL with FID detector, equipped with a PE–alumina capillary column (30 m). GC–MS was performed on a HP6890 equipped with a mass selective detector 5973.

2.1. Catalyst preparation

Palladium nanoparticles were prepared by dissolving 2.9 mmole (1 g) of palladium(II) bis-dibenzylidene acetone in 50 ml of previously dried and degassed THF. This solution was mixed with a suspension of 10 g of silica in 400 ml of THF and stirred for 24 h in a Fischer Portter bottle. After this time, 25 psi of dihydrogen were introduced into the system and stirred at room temperature during another 24 h period. At the end of this time, the suspension had changed from purple to dark gray.

The solvent was evaporated under reduced pressure and the solid was washed several times with dichloromethane. Then the solid was dried once again under reduced pressure and stored under argon atmosphere. The elemental analysis for this material gave 0.1 wt.% palladium content.

2.2. Hydrogenation experiments

The catalytic reactions were carried out in a 125 ml stainless steel autoclave under constant pressure (30 and 120 psi). The reaction temperatures were maintained using a Parr thermo-programmed oven. The reaction was maintained under constant stirring. The catalyst/substrate ratio was calculated according to the palladium atom concentration contained in the [Pd/SiO$_2$] catalyst.

In a typical experiment, the nanostructured material (10 mg [Pd/SiO$_2$], 0.1% Pd content) is introduced into the autoclave; 2 ml (22 mmole) benzene is added and
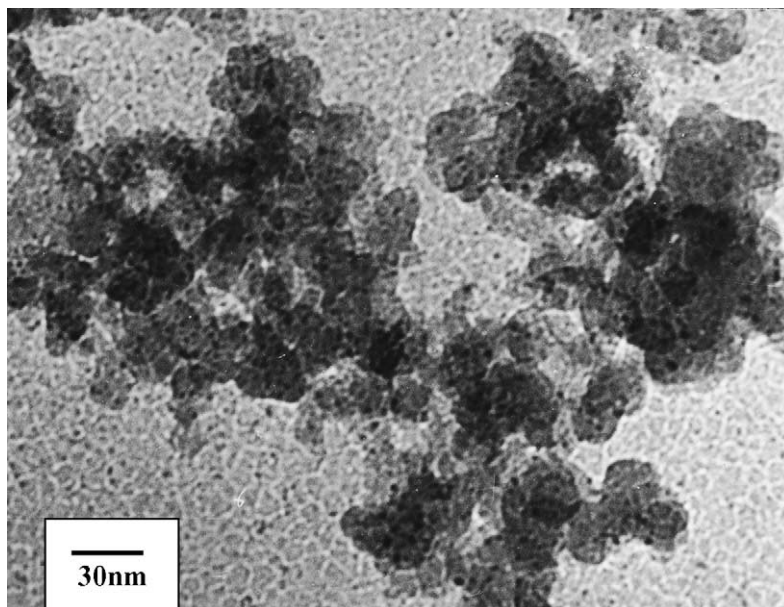
Fig. 1. Pd/SiO$_2$ before reaction.

dihydrogen is introduced (120 psi), the oven is then programmed to 140 °C. Once the oven has reached the programmed temperature, the reaction is carried out over 2 h and then cooled to room temperature. The autoclave pressure is liberated and the reaction mixture analyzed by GC and GC–MS.

3. Results and discussion

3.1. Synthesis and characterization of silica-supported palladium nanoparticles

The silica-supported palladium nanoparticles [Pd/SiO$_2$] were obtained by the reduction of palladium(II) bis-dibenzylidene acetone in a silica–THF suspension under 25 psi of dihydrogen, following the same procedure used by Chaudret et al. [9] for the synthesis of palladium colloids on nitrocellulose. Although the same authors have used this procedure, to generate colloidal nanoparticles stabilized on polyvinylpyrrolidone, it has never been reported for the synthesis of palladium nanoparticles supported on inorganic matrixes.

The [Pd/SiO$_2$] nanostructured material was characterized by transmission electron microscopy as shown in Fig. 1. The micrograph shows very small metal particles, which are well dispersed within the inorganic support. Fig. 2 reveals that this material has a mean size of 1.9 nm, with a stretch size distribution that ranges between 1.0 and 5 nm. This material is stable
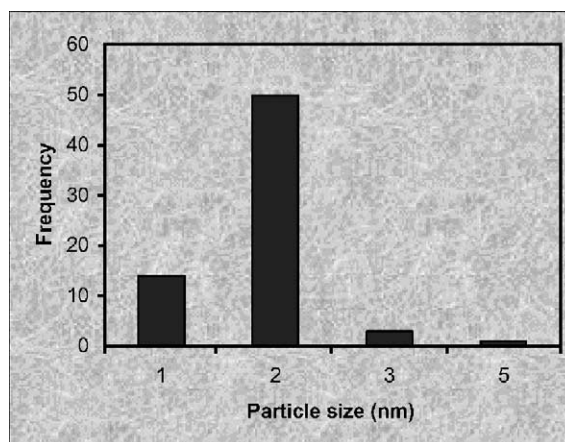

Fig. 2. Particle size distribution for Pd/SiO$_2$.

Table 2
Comparison of different nanostructured palladium systems with the [Pd/SiO$_2$] reported in this work

Functional group	Organic substrate	Reported TOF mole of product/(mole of metal/h)	Reference
Alkenes	1-Hexene	38,250	Pd/SiO$_2$[a]
		33,000	Pd/SiO$_2$[a]
	Cyclohexene	164	[7]
		200	Aldrich 1 wt.% Pd on activated carbon [7]
Aromatic	Benzene	10,000	Pd/SiO$_2$[a]
Carbonyl	Hexanone	16,000	Pd/SiO$_2$[a]
	Cyclohexanone	15,000	Pd/SiO$_2$[a]
	Acetophenone	45.5	[8]
	Ethyl pyruvate	468	[14]
Nitrile	Benzonitrile	5,000	Pd/SiO$_2$[a]

[a] This work.

for months when kept under an argon atmosphere and it also shows great stability in air.

3.2. Hydrogenation reactions

The catalytic hydrogenation of alkynes, alkenes and aromatics is a very common reaction in heterogeneous metal catalysis, and in this sense palladium-based catalysts are well established as one of the most efficient catalysts for this process (Table 2). Taking this into account, a preliminary series of catalytic hydrogenation of 1-hexene, cyclohexene, benzene, 2-hexanone, cyclohexanone and benzonitrile were performed in order to investigate the catalytic activity of the [Pd/SiO$_2$] nanostructured material. Table 1 summarizes the reaction conditions, conversion and TOF values obtained for each of the hydrogenation catalysis studied in this work. The hydrogenation of 1-hexene was carried out using temperatures between 80 and 25 °C under 30 psi H$_2$ at 2 h reaction time, in a heterogeneous system with catalyst/1-hexene ratio of 1/160,000. The hexane formation was quantified via GC. This study revealed that even at 25 °C the nanostructured material hydrogenated all the substrate in this time.

It was possible to determine a turn over frequency (TOF) of 38,250 mole of product per mole of palladium per hour, when the reaction time was reduced to 10 min at 25 °C. After completion of the reaction, the catalyst was dried under an argon flow at 100 °C for 24 h. The same sample of catalyst was used in four different batch reactions and no significant decrease in activity was observed. However, after the fourth batch reaction the TEM analysis of the material showed a 30% increase in size, from 1.9 to 2.9 nm (see Figs. 3 and 4).

The hydrogenation study of cyclohexene was carried out at 100 °C under 30 psi H$_2$ at 2 h reaction time. After completion of the reaction the GC analysis showed total conversion of the substrate. Due to this result milder reaction conditions were used to determine the TOF the [Pd/SiO$_2$] nanocatalyst. The study was carried out at 25 °C under 40 psi H$_2$ during 100 min. At the end of this time the GC analyses revealed 16.5% conversion of the cyclohexene to cyclohexane, with a TOF of 33,000.

Given that the most important application in industrial catalytic hydrogenation is probably the conversion of benzene to cyclohexane [10], the study of the catalytic activity of [Pd/SiO$_2$] in this reaction was undertaken. This study was carried out at 140 °C under 120 psi H$_2$ over 2 h reaction time, in a heterogeneous system with catalyst/benzene ratio of 1/235,000. For this reaction the TOF was 10,000. The TEM analysis of the material after the reaction reveals an increase in size from 1.9 to 2.8 nm, at this temperature, (see Figs. 5 and 6). This result indicates that even at 140 °C the size increase is the same than the one observed for the studied done after four-batch reactions. It is noteworthy that silica-stabilized nanoparticles have the advantage of enduring much higher reaction temperatures than their organic polymeric counterpart.
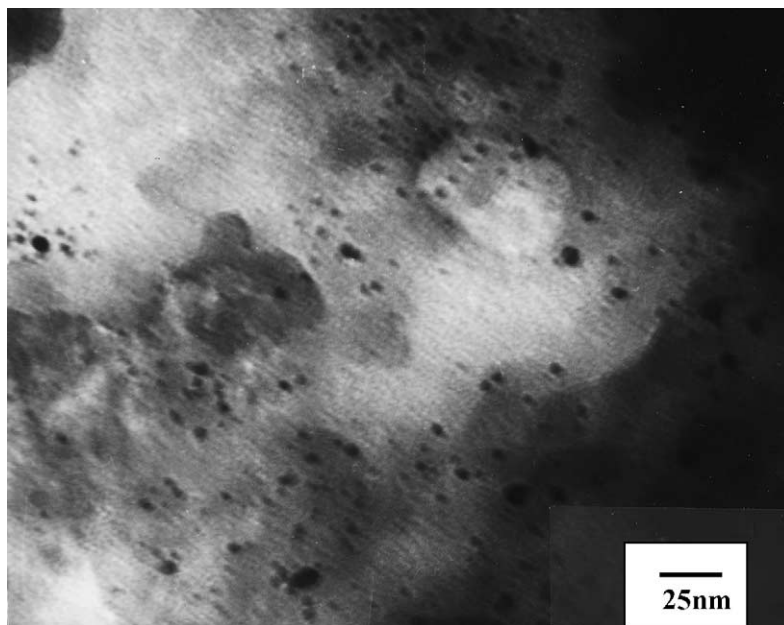
Fig. 3. Pd/SiO$_2$ after four-batch hydrogenation reactions of 1-hexene.

Although there are many reports of catalytic hydrogenation of unsaturated molecules in the presence of colloidal noble metal particles supported on organic polymers, most of these refer to cyclohexene hydrogenation [7,11–13]. Table 2 gives a comparative data between the results obtained in this work and those relevant reported in the literature. To the best of our knowledge, one of the most active nanocatalytic

Fig. 4. Pd/SiO$_2$ after four-batch hydrogenation reactions of 1-hexene.

systems for the cyclohexene hydrogenation is reported by Anttonetti et al. [7] using a palladium block copolymer-stabilized colloids which has a TOF 164 at 30 °C and 1.10 bar H$_2$. These authors also report the TOF of commercial Pd on activated carbon (Aldrich, 1 wt.% Pd) as 200 at the same experimental conditions. Although these results cannot be directly compared with the results obtained in this work, since the pressure used is slightly higher they show that [Pd/SiO$_2$] nanomaterial is much more active than previously reported palladium nanomaterial, and even more than the commercial carbon-supported material in the hydrogenation of cyclohexene.

The catalytic activity of the [Pd/SiO$_2$] nanomaterial was further investigated in the hydrogenation of carbonyl and nitrile groups. Carbonyl group hydrogenation of 2-hexanone and cyclohexanone was performed at temperatures of 125 and 133 °C, respectively, under 30 psi H$_2$ during 6 h. After the completion of the reaction, the conversion and TOF were determined by GC analysis. Under these conditions, in the case of 2-hexanone a 32% conversion to 2-hexanol was obtained with a TOF of 16,000. For cyclohexanone a 25% conversion to cyclohexanol was obtained with a TOF of 15,000. There are very
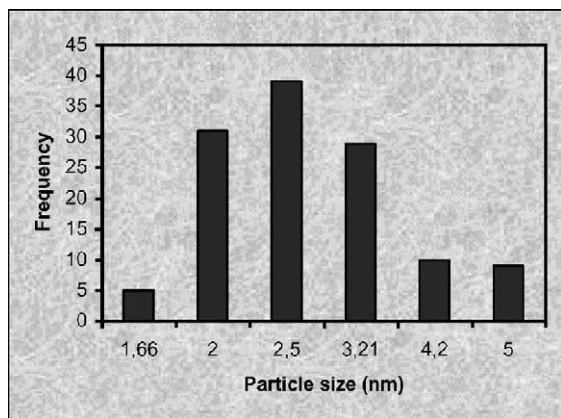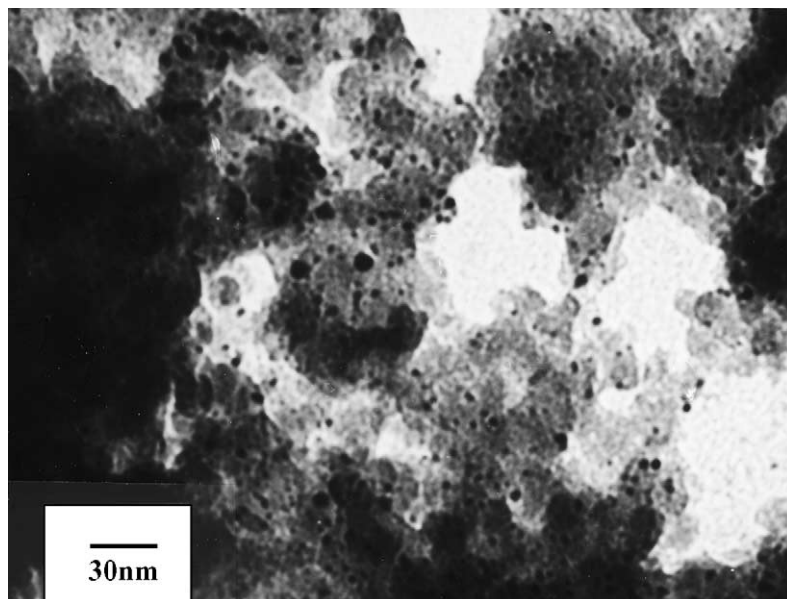
Fig. 5. Pd/SiO$_2$ after hydrogenation of benzene at 140 °C.

few reports of carbonyl group hydrogenation in the presence of palladium nanoparticles. Schmid et al. [8] report large ligand-stabilized palladium clusters (3–4 nm) stabilized on TiO$_2$ which are capable of hydrogenating acetophenone to phenyl ethanol at 60 °C 100 bar H$_2$ with a TOF of 45.5. Much more recently, Whyman and coworkers [14] reported the enantioselective hydrogenation of ethyl pyruvate in the presence of solvent-stabilized palladium nanomaterials at room temperature under 70 bar H$_2$ pressure
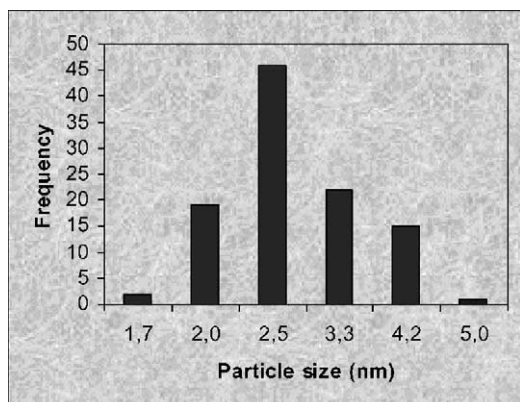

Fig. 6. Particle size distribution after reaction.

with TOF of 468. Evidently, the activities of these reported materials is well below the activity shown by the [Pd/SiO$_2$] nanocatalyst reported within.

For nitrile group hydrogenation benzonitrile was chosen. In this case, the consumption of the benzonitrile was determined after the reaction, which was carried out at 145 °C under 120 psi H$_2$ pressure during 24 h. The catalytic results reveal a 46% consumption of benzonitrile with a TOF of 5000. Even though, there are a only a few reports of catalytic hydrogenation of nitrogen containing aromatic compounds in the presence of palladium nanoparticles, these only refer to nitro and azo groups [15,16]. Thus, [Pd/SiO$_2$] is also a highly effective nanocatalyst for nitrile hydrogenation. Further results on the catalytic hydrogenation activity of [Pd/SiO$_2$] towards nitro groups will be reported shortly.

At the moment studies of methanation and oxygen transfer reactions are also underway with this material.

4. Conclusions

As mentioned before, there are many reports of polymer-stabilized palladium colloids in catalytic hydrogenation of olefinic substrates. Nevertheless, the

nanocatalyst reported within, has the highest hydrogention catalytic activity for the different substrates that have been studied here, especially in the case of carbonyls and nitrile groups, for any nanostructured material reported to date.

It is important to underline, that most recently Pellegatta et al. [17] have reported the hydrogenation of benzene in the presence of polyvinylpyrrolidone-stabilized rhodium colloids. The TOF for this material is 250 using a [catalyst]/[substrate] ratio of 1/2000, at 30 °C and 7 bar H_2. Taking into account that the established order in bulk metals for catalytic aromatic hydrogenation is accepted as Pt > Rh > Ru > Ni > Pd [18], this in conjunction with the result within, seems to imply that the order of catalytic activity with nanomaterials is rather different to that of metal bulk materials.

We can conclude that the catalytic potential of the $[Pd/SiO_2]$ synthesized by an organometallic route renders an extremely active nanomaterial which shows very little aggregation after catalytic reactions even at 145 °C. This nanomaterial is not only far more active than what to our knowledge is reported in the literature to date for benzene, 2-hexanone and cyclohexanone hydrogenation but it is also the first palladium nanomaterial reported to have efficient catalytic activity towards benzonitrile hydrogenation.

Acknowledgements

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