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Triazine-Based Polymers as Nanostructured Supports for the Liquid-Phase Oxidation of Alcohols

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Abstract: A covalent triazine framework (CTF) was used as support for palladium nanoparticles (NPs) and Pd/CTF was applied as the catalyst in the selective oxidation of benzyl alcohol. N groups in the CTF appeared more efficient than those created on carbon nanotubes (CNTs) by NH_3/high-temperature treatment in stabilizing Pd NPs against growth during the immobilization step. This assured a high metal dispersion, which led to a highly active and stable catalyst in the alcohol oxidation reaction. Indeed, Pd on the CTF was more stable in recycling than Pd on activated carbon (AC) and on nitrogen-doped CNTs, particularly avoiding leaching of Pd NPs. Moreover, Pd on the CTF was less sensitive than Pd on AC to the decrease of reactant concentration. This in turn led to a higher selectivity to benzaldehyde (98 %) with a considerable activity (turnover frequency 1453 h^{-1}).

Keywords: alcohols · oxidation · palladium · polymer frameworks · supported catalysts

Introduction

The finding of new supports able to stabilize metal nanoparticles (NPs) is of importance as restructuring and leaching of metal NPs often arise in liquid-phase reaction.[1–3] However, the main limitation in their scaling up is represented by the often occurring rapid deactivation. Different catalysts (homogeneous and heterogeneous) have been investigated in alcohol oxidation with molecular oxygen or hydrogen peroxide.[4–7] The oxidation mechanism as well as the nature of the palladium active sites, Pd^0, have already been largely investigated.[5] Together with the formation of an alkoxide, anion Pd−H is formed, which is then oxidized by O_2 resulting in the formation of Pd^0 species and H_2O. Heterogeneous catalysts based on platinum and palladium supported on activated carbon (AC) are among the most studied systems for the liquid-phase oxidation of alcohols.[8–11] Indeed, AC as support is commercially available, cheap, exhibits high specific surface area (of about 800–1200 $m^2 g^{-1}$), and is stable in both acidic and basic media.[12] More expensive, nanostructured carbon materials such as carbon nanotubes (CNTs) have been tested as the support of metal NPs.[13–16] A direct comparison between AC and CNTs as support for Pd NPs was carried out in the Heck reaction of styrene and iodobenzene and for the Suzuki coupling of phenylboronic acid and iodobenzene.[17,18]

In these cases Pd/CNTs were more active than Pd/AC. When the surface of the CNTs is further functionalized, for example with nitrogen groups, the activity and stability of the corresponding catalysts can be enhanced. Indeed, as reported by Jiang et al.,[19] the introduction of nitrogen functionalities on the surface of CNTs increases the dispersion and stability of gold NPs during catalytic reactions. We have recently also demonstrated that nitrogen functionalities incorporated on carbon nanostructures led to the improvement of the catalytic performance in the selective oxidation of alcohols.[20] Considering the catalytic activity, as Freund suggested, “it may be desirable to control not only particle size and morphology but also interparticle distances”.[21] In this view, by controlling the distribution of N groups on the support, a better control of the interparticle distance of metal NPs should be possible.

Metal–organic frameworks (MOFs) have raised a lot of attention because of their high surface area and tunable pore size.[22] This class of porous materials consists of metal ions and organic ligands with highly regular and controllable nanometer-sized cavities or channels,[23–25] and has recently been increasingly used for catalytic applications. MOFs

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functionalized with amino groups are active in the Knoevenagel condensation of benzaldehyde with ethyl cyanoacetate and ethyl acetoacetate,[26] aza-Michael condensation, and ethyl decanoate transesterification.[27] The synthesis of metal-containing MOFs was successful and their efficiency in liquid-phase reaction has been largely demonstrated.[24,28–34] However, as described by Proch et al.,[35] one of the drawbacks of some supports (MOF-177) for the oxidation of alcohol is the sensitivity towards water, which is produced in a stoichiometric way during the oxidation process. Kuhn et al. reported on a new class of material,[36–39] the covalent triazine framework (CTF), which is highly stable in water. CTFs can be prepared as periodic frameworks with defined porosities[40] upon heating dicyano compounds in salt melts at 400 °C. Further heating yields amorphous yet highly porous frameworks showing high surface areas up to 3000 $m^2 g^{-1}$ and hierarchical porosity.[36] CTFs (Figure 1) incorporate high amounts of nitrogen (~10 wt %), thus facilitating the coordination of metals[41] and metal NPs.[42]

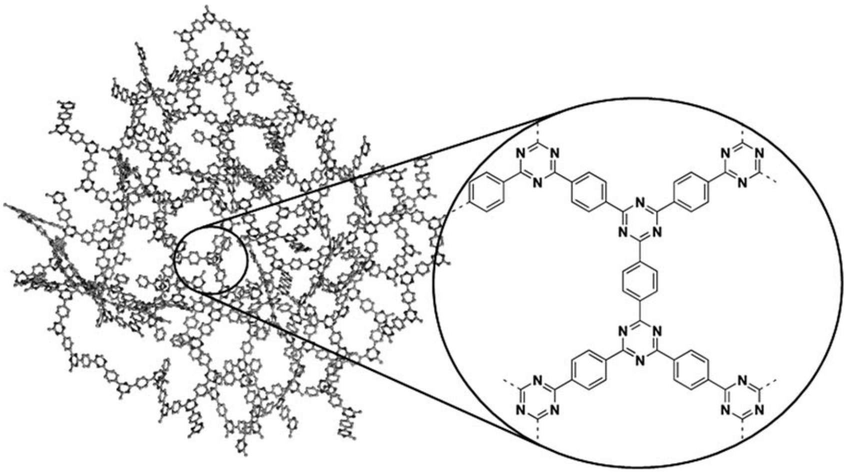

Figure 1. Structure of a CTF prepared from 1,4-dicyanobenzene at 400 and 600 °C in molten $ZnCl_2$.[42]

We have recently reported[42] that CTFs can immobilize palladium NPs more efficiently than AC, which results in a more stable (and active) catalyst in the glycerol-selective oxidation. The longer lifetime of the Pd/CTF was explained by the higher stabilization of Pd NPs through interaction with the nitrogen groups contained in the framework (Figure 1). However, glycerol represents a particular class of alcohols (polyols) that are highly soluble in water. Because the polymer framework is hydrophobic, in the present work we investigated the performance of the catalyst in a nonpolar (cyclohexane) solvent for extending the use of Pd/CTF to alcohols that are scarcely soluble in water. Thus, we studied as a model reaction the benzyl alcohol oxidation in cyclohexane using Pd/CTF as catalyst and O_2 as oxidant. We also compared the performance of Pd/CTF with those of Pd/AC, Pd/CNTs, and Pd/nitrogen-doped carbon nanotubes (N-CNTs) similarly prepared by the colloid immobilization method.[43] The comparison between Pd/CTF and Pd/N-CNTs will help to better clarify the influence of N-containing groups in terms of amount and type of functionalization on the catalytic activity and stability of Pd systems.

Results and Discussion

Palladium supported on CTFs was previously used as catalyst in glycerol oxidation in an aqueous medium.[42] However, the CTF is hydrophobic, and thus we expected to increase the wettability and in turn make access to the active sites easier by using an organic solvent such as cyclohexane. In this work we extended the use of Pd/CTF in cyclohexane by using benzyl alcohol as a representative substrate that is highly soluble in organic solvent. Pd/CTF was then compared to Pd supported on AC, a typical support used for this kind of reaction.[44]

Moreover, we also made a comparison with the activity of Pd supported on CNTs and N-CNTs (prepared by a gas-phase procedure as described elsewhere[45]), to better clarify the influence of N-containing groups. CTFs exhibit very high surface areas and high amounts of nitrogen functionalities (9 wt %[42]).

Due to the fully covalent structure, CTFs possess high thermal and chemical stability. The pore volume of 1.79 $cm^3 g^{-1}$ is similar to that of microporous AC (pore volume of 1.50 $cm^3 g^{-1}$). Both materials are amorphous and have a high surface area (934 vs. 2814 $m^2 g^{-1}$ for AC and CTF, respectively[42]). CNTs and N-functionalized CNTs are characterized by a lower surface area (43 $m^2 g^{-1}$[46]).

Pd-based catalysts were synthesized by the sol immobilization technique ($NaBH_4$/poly(vinyl alcohol) (PVA)),[43] in which identical preformed Pd NPs were deposited on the different supports. TEM characterization results are in agreement with those reported in refs. [20,42]. The particle size of the four catalysts is shown in Table 1 and an overview of the particle dispersion can be seen in Figure 2, in

Table 1. Statistical median and standard deviation of particle size analysis for Pd catalysts.

Catalyst	Statistical median [nm]	Standard deviation σ
unsupported Pd NPs	2.7	0.62
Pd/CTF	3.1	0.60
Pd/AC	4.0	1.23
Pd/CNTs	4.4	1.49
Pd/N-CNTs	3.2	0.97

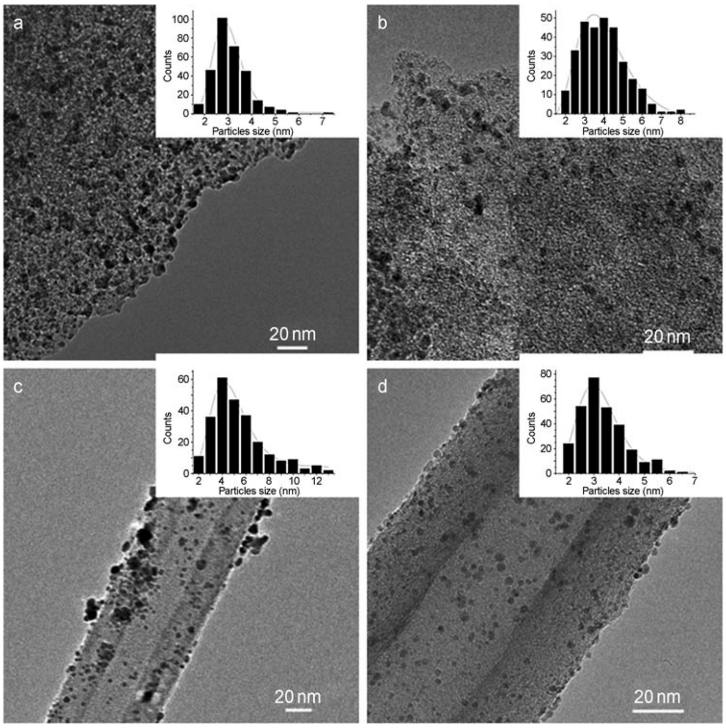

Figure 2. TEM images of Pd-based catalysts. a) Pd on CTF; b) Pd on AC; c) Pd on CNTs, and d) Pd on N-CNTs. Insets: particle size distributions of NPs.

which the insets report the particle size distribution calculated on at least 300 NPs. During the immobilization of Pd (PVA) NPs, an increase of the particle size occurred (from 2.7 nm for unsupported NPs to 3.1 for Pd/CTF, 4.0 for Pd/AC, 4.4 for Pd/CNTs, and 3.2 nm for N-CNTs) even though preformed particles are deposited on the materials. However, it is noted that the presence of N functionalities limited the growth of the NPs and it should also be noted that the standard deviation (σ) is minimized in these cases (CTF and N-CNTs in Table 1). Moreover, the presence of nitrogen groups has a positive effect in terms of particle dispersion avoiding particle aggregation, as highlighted in particular upon moving from Pd/CNTs to Pd/N-CNTs (Figure 2c and d).

Table 2 reports the catalytic activity expressed in terms of turnover frequency (TOF; calculated at 15 min of reaction) and Figure 3 shows the corresponding reaction profiles. Selectivity was compared at iso-conversion (90%). Pd/CTF is the most active catalyst (Table 2). Indeed, Pd/CTF showed a TOF of 4917 h^{-1} whereas the TOFs obtained with Pd/AC, Pd/CNTs, and Pd/N-CNTs were 2678, 1518, and 4438 h^{-1}, respectively. The activity reflects the trend of particle size.[47] Pd/CTF and Pd/N-CNTs showed a similar initial activity (TOF) and presented a similar particle size (3.1–3.2 nm), whereas Pd/AC and Pd/CNTs showed a lower activity corresponding to a larger particle size (4.0–4.4 nm). We can thus conclude that the presence of nitrogen functionalities in the support (CTF and N-CNTs) facilitates the immobilization of Pd NPs, which limits their growth and in turn enhances the catalytic activity. The lower activity of Pd/N-CNTs in comparison to that of Pd/CTF can be better highlighted by comparing the reaction profiles (Figure 3). On the basis of particle size (Table 1) we expected an opposite trend; a possible reason for this finding could lie in the different number of nitrogen groups in N-CNTs relative to CTF (2% in N-CNTs and 9% in the CTF).[42] All the catalysts showed a similar selectivity to benzaldehyde.

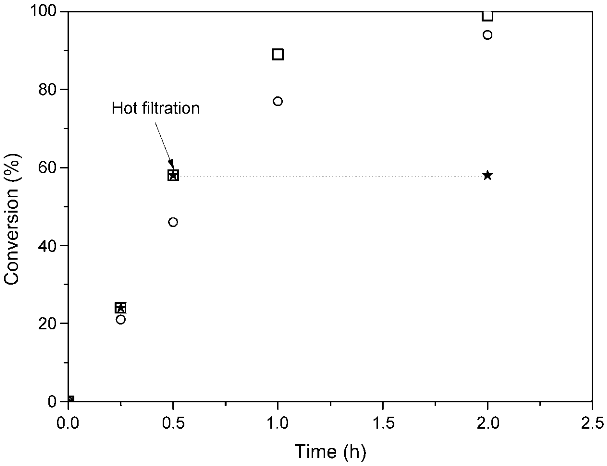

Figure 3. Reaction profiles of Pd/CTF, Pd/N-CNTs, and a hot filtration test with Pd/CTF. Reaction conditions: alcohol/metal: 5000 (□ = Pd/CTF, ○ = Pd/N-CNTs, ★ = Pd/CTF hot filtration), $T = 80\,°C$, $pO_2 = 2$ atm, benzyl alcohol/cyclohexane ratio 50:50.

To generalize the method, the effect of substrate/solvent ratio was also studied by increasing the amount of solvent (benzyl alcohol/cyclohexane ratio from 50:50 to 10:90 vol%, Table 3). Upon increasing the amount of solvent, the activity decreased as expected. In terms of selectivity to benzaldehyde, no obvious changes were observed from 50:50 to 25:75 (selectivity ~70%), whereas for a 10:90 ratio a strong enhancement in aldehyde selectivity and a consistent decrease in the formation of toluene were observed (selectivity to benzaldehyde >95%). However, unknown products were formed (2% for CTF as support and 5% for AC, not shown here). By comparing the

Table 2. Oxidation of benzyl alcohol using supported Pd NPs.[a]

Catalyst	TOF[b] [h^{-1}]	Selectivity[c]				
		Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate	Unknown
Pd/CTF	4917	31	66	1	1	1
Pd/AC	2678	29	70	1	–	–
Pd/CNTs	1518	33	67	–	–	–
Pd/N-CNTs	4438	30	69	1	–	–

[a] Reaction conditions: alcohol/metal: 5000, $T = 80\,°C$, $pO_2 = 2$ atm, benzyl alcohol/cyclohexane ratio 50:50. [b] TOF calculated after 15 min of reaction based on the total metal loading. [c] Selectivity calculated at 90% conversion.

Table 3. Oxidation of benzyl alcohol: effect of benzyl alcohol/cyclohexane ratio.[a]

Catalyst	Benzyl alcohol/ Cyclohexane ratio	TOF[b] [h^{-1}]	Selectivity[c]			
			Toluene	Benzaldehyde	Benzoic acid	Benzyl benzoate
Pd/AC	50:50	2678	29	70	1	–
Pd/CTF	50:50	4917	31	66	1	1
Pd/N-CNTs	50:50	4438	30	69	1	–
Pd/AC	25:75	1592	40	56	1	2
Pd/CTF	25:75	4162	30	68	1	–
Pd/N-CNTs	25:75	3392	32	65	–	–
Pd/AC	10:90	1059	–	95	–	–
Pd/CTF	10:90	1453	–	98	–	–
Pd/N-CNTs	10:90	1094	–	>99	–	–

[a] Reaction conditions: alcohol/metal: 5000, $T=80\,^{\circ}C$, $pO_2=2$ atm. [b] TOF calculated after 15 min of reaction based on the total metal loading. [c] Selectivity calculated at 90% conversion.

TOF of Pd/CTF with those of Pd/N-CNTs and Pd/AC (Table 3), we observed that the three catalysts behaved differently even though all of them decreased in activity upon increasing the amount of solvent. Pd on CTF always showed the highest activity and Pd/AC the lowest. On the contrary, Pd/N-CNTs behaved similarly to CTF when the organic solvent was 50 vol%, but similarly to AC when the solvent reached 90 vol%. When a large amount of cyclohexane was present (90%), the difference among the three activities decreased (1453, 1094, and 1059 h^{-1} for Pd/CTF, Pd/N-CNTs, and Pd/AC, respectively). AC with respect to CTF is a less hydrophobic support due to the presence of carboxylic and hydroxylic groups on the surface. Thus, in these two cases, it is not surprising that by decreasing the polarity of the medium (i.e., increasing the amount of cyclohexane) CTF could interact with a polar reactant better than AC. On the contrary, the behavior of N-CNTs highlights the double nature of this support, in which N functionalities such as pyridine, pyrrole, and pyridone[45] coexist with typical hydrophilic functionalities of AC (carboxylic acid, phenols, etc.). The capability of N functionalities to enhance the stability of Pd NPs during catalytic reaction is of particular importance from an industrial point of view. We have already shown that Pd/CTF is a much more durable catalyst than Pd/AC for glycerol oxidation in water.[42] In addition, we also showed that Pd/AC deactivates rapidly in the oxidation of benzyl alcohol in cyclohexane, probably because of a consistent leaching of metal.[48] Herein, the durability of Pd/CTF was investigated and compared with that of Pd/N-CNTs by performing several reactions successively (recycling). Each run was carried out under the same conditions (alcohol/metal: 5000, 80 °C, 2 atm O_2, 1250 rpm, cyclohexane 50 vol%) for two hours.

The catalyst was reused after separation from the solution without any other treatment. Pd/CTF showed a similar conversion (about 100%) along the nine runs and the selectivity to benzaldehyde (66% taken at 90% conversion) did not change (Figure 4). On the contrary, Pd/N-CNT deactivated faster than Pd/CTF as observed for Pd/AC.[48] Similarly to the case of Pd/AC, the deactivation of Pd/N-CNTs is explained by consistent leaching of Pd (5% on the used catalyst). In the case of Pd/CTF, no leaching of Pd was observed by inductively coupled plasma (ICP) measurements on both the collected solution from recycling and the used catalyst (see Experimental Section). To confirm the absence of leached Pd, the "hot filtration" test was performed.[49] After 30 min of reaction, the catalyst was isolated by filtration without cooling the reaction mixture and ICP measurements on the filtrate excluded the presence of Pd.

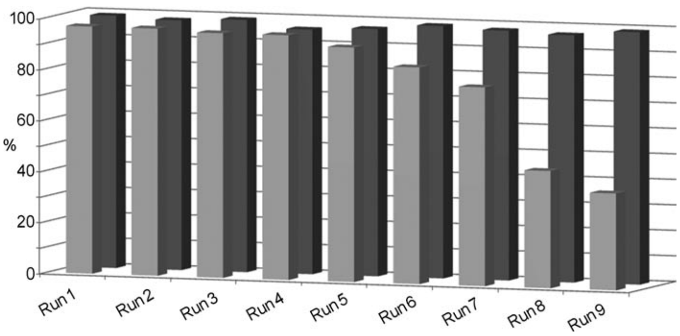

Figure 4. Recycling test with Pd/CTF (dark gray) and Pd/N-CNT (light gray): benzyl alcohol/cyclohexane 50:50, alcohol/metal: 5000, $T=80\,^{\circ}C$, $pO_2=2$ atm.

Moreover, the filtrate was maintained under the reaction conditions ($T=80\,^{\circ}C$, $pO_2=2$ atm, stirring) and samples were analyzed after an additional hour to check any changes in the product distribution. No changes occurred. To definitely exclude a possible contribution of soluble Pd^{II} species to catalysis, an additional test was performed with $Pd(OAc)_2$ (Ac = acetyl) as the catalyst under the same reaction conditions as those used with Pd/CTF. No conversion of benzyl alcohol was detected after one hour.

Conclusion

By the use of a CTF, a triazine-rich material, as the support for Pd NPs, it was established that a large number of N groups (9 wt%) with a controlled morphology greatly increased the catalyst performance in alcohol oxidation in cyclohexane relative to AC and CNTs. Pd/CTF showed an initial activity similar to that of Pd on N-doped CNTs and this confirmed the beneficial effect on catalytic activity of the presence of N functionalities. Pd NPs similarly prepared (from PVA sol) revealed a better stability during the immobilization on CTF and N-CNTs than AC and CNTs. This property allows a better catalytic performance in alcohol oxidation due to a higher dispersion of Pd NPs. However, Pd on the CTF resulted in a really resistant catalyst (tested in recycling experiments) whereas Pd on N-doped CNTs deactivated. This finding supports the conclusion that the number of N groups (9 vs. 2 wt % for CTF and N-CNTs, respectively) and probably also their nature have a positive effect on the activity of the catalyst in the benzyl alcohol oxidation reaction. Moreover, the hydrophobicity of CTF was useful in allowing better catalytic performances when organic solvents were used as reaction media in large amounts.

Experimental Section

Materials: 1,4-Dicyanobenzene was purchased from Alfa Aesar and was used as received. Zinc chloride (Alfa Aesar, anhydrous, 98 %) was stored in a glove box and used as received. $Na_2PdCl_4 \cdot 2H_2O$ was from Aldrich (99.99 % purity) and AC from Camel (X40S; surface area = 900–1100 $m^2 g^{-1}$; pore volume = 1.5 $mL g^{-1}$). Commercial CNTs were supplied by Applied Science. $NaBH_4$ of purity > 96 % from Fluka and PVA (M_w = 13 000–23 000; 87–89 % hydrolyzed) from Aldrich were used. Gaseous oxygen from SIAD was 99.99 % pure.

Synthesis of the support: The support was prepared according to refs. [36–39] by modifying the preparation as described by Chan-Thaw et al.[42] 1,4-Dicyanobenzene, the monomer, and $ZnCl_2$ in a 1:5 molar ratio were transferred into a quartz ampoule (3 × 12 cm) under an inert atmosphere. The ampoule was then evacuated, sealed, and heated within 30 min to 400 °C. After 20 h at 400 °C the ampoule was further heated within 1 h to 600 °C and held at this temperature for an additional 20 h. The ampoule was then cooled to room temperature and opened. The resulting reaction mixture was washed several times with diluted HCl (0.1 M) under stirring to remove most of the $ZnCl_2$. The resulting black powder was washed with water until a neutral pH was obtained. After filtration, the material was dried at 150 °C and finely ground to give the CTF. A yield of 98 % was obtained. The residual Zn content was checked by ICP measurements and resulted in a maximum amount of 0.3 wt %.

Sol immobilization: Pd sol ($Na_2PdCl_4 \cdot 2H_2O$, 0.043 mmol) and freshly prepared PVA solution (2 wt %, 880 μL) were added to H_2O (130 mL). After 3 min, $NaBH_4$ solution (0.1 M, 860 μL) was added to the yellow-brown solution under vigorous magnetic stirring. The brown Pd^0 sol was immediately formed. A UV–visible spectrum of the Pd sol was recorded to ensure the complete reduction of Pd^{II}. Within a few minutes of its generation, the suspension was acidified at pH 2 by sulfuric acid and the support was added under vigorous stirring. The catalyst was isolated by filtration and washed several times with distilled water. The samples were dried at 80 °C for 2 h. The amount of support was calculated to obtain a final metal loading of 1 wt %. The obtained catalysts were labeled Pd/CTF, Pd/AC, Pd/CNTs, and Pd/N-CNTs when CTF, AC, CNTs, and N-CNTs were used as supports, respectively. ICP (Jobin Yvon JY24) analyses of the filtrate confirmed the actual loading on the support to be 1 wt %.

Catalytic tests: The reactions were carried out in a thermostatted glass reactor (30 mL) provided with an electronically controlled magnetic stirrer connected to a large reservoir (5000 mL) containing oxygen at 2 atm. The oxygen uptake was followed by a mass flow controller connected to a PC through an analog/digital board. Oxidation experiments were carried out in the presence of a solvent (0.0125 mol substrate, substrate/metal = 5000 (mol/mol), benzyl alcohol/cyclohexane 50:50 vol %, 80 °C, $pO_2 = 2$ atm). Samples were periodically withdrawn from the reactor. Recoveries were always 98 ± 3 % with this procedure. The effect of substrate/solvent ratio on the catalytic activity was studied by varying the benzyl alcohol/cyclohexane ratio from 50:50 to 10:90 vol %. For the identification and analysis of the products, GC-MS and GC (Dani 86.10 HT gas chromatograph equipped with a capillary column, BP21 30 m × 0.53 mm, 0.5 μm film, made by SGE) were carried out for comparison of the authentic samples. For quantification of the reactant products the external calibration method was used.

Sol characterization: UV–visible spectra of sols in H_2O in a quartz cuvette were obtained between 190 and 1200 nm on HP8452 and HP8453 Hewlett–Packard spectrophotometers.

Catalyst characterization: The metal content was checked by ICP analysis of the filtrate or alternatively directly on the catalyst after burning off the carbon, with a Jobin Yvon JY24 instrument. The Pd content of the support material was estimated by ICP mass spectrometry measurements conducted with a Perkin–Elmer ELAN 6000 instrument. Samples were digested with concentrated HNO_3 under microwave power then diluted, and the results were compared with calibration data obtained for Pd species. The morphology and microstructures of the catalysts were characterized by TEM and SEM. Powder samples of the catalysts were ultrasonically dispersed in ethanol and mounted on copper grids covered with holey carbon film. A Philips CM200 LaB6 electron microscope, operating at 200 kV and equipped with a Gatan CCD camera, was used for TEM observation.

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