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Sol-derived Pd/SiO$_2$ catalyst: characterization and activity in benzene hydrogenation

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Abstract

Pd/SiO$_2$ catalysts were prepared by adsorption of Pd sols on support Aerosil 200 and characterized by transmission electron microscopy (TEM), CO chemisorption and temperature programmed oxidation (TPO). The Pd hydrosols were generated from PdCl$_2$ solution and ethanol as reducing agent in the presence of poly(diallyldimethylammonium chloride), PDDA. The pH of the solution was increased to ensure adsorption of the Pd sol with high concentration of PDDA. The catalytic activity was tested in benzene hydrogenation. The presence of organic impurities and the role of morphology affecting the activity have been discussed in terms of the preparation procedure applied. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Pd sol; Pd particle size; PDDA polycation

1. Introduction

Reduction of noble metal cations to form colloids [1] can be performed using alcohols [2–4], polyols [5] or other reducing agents [6]. Changing the nature of the reducing agent [2,6,7], its concentration [3,8,9], the temperature [10] or the location of the nucleation process [11] one can control the size of the metal nanoparticles. Furthermore, the nature and the concentration of the stabilizing agent play an important role in the limitation of particle growth. Besides, the stabilizing agent provides protection against agglomerization. Nakao and Kaeriyama [12] have experienced that surfactant molecules influence the particle size to different extent depending on the type of both the surfactant and the metal. In contrast to this, the particle size in Pd sols was not affected by changing the amount of citrate stabilizer [13]. In the case of strongly adsorbing polymers (usually containing N atom) the most important factor which influences the particle size is the monomer/metal ratio [8]. Generally, upon increasing the concentration of polymer the size of metal particles decreases [14], since the adsorbed hydrocarbon chains on the particles retard continuously the transport of metal ions and the reducing agent. The adsorption strength of polymer and its solvatation in the liquid phase must be balanced to achieve sufficient stabilization, which still allows the reduction of metal ions [2]. Sol preparation method offers narrow particle size distribution, but the metal particles can be sensitive to air [2,3,15] and their size may change under subsequent hydrogen treatment [7,16]. In homogeneous catalysis metal sols have been applied without any special regards to the presence of stabilizing agent, which surely influences the activity [4,5,17]. However, in heterogeneous catalysis other problems should be considered, such as, depositing sols on the support is difficult [14], the supported metal can be

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leached out during the reaction and the size of metal particles may be changed upon immobilization [18].

In the present paper, our main goal is to produce stabilized Pd nanoparticles prepared by ethanol reduction and supported on silica, and to investigate their behavior in gas phase catalytic reaction with attention to the contamination of metal surface, which is almost inevitable. The structural feature and the catalytic behavior of the samples are compared with Pd/SiO_2 prepared by controlled colloidal synthesis (CCS) [19] and impregnation.

2. Experimental

2.1. Preparation of Pd sols

Pd sols (denoted by Sol1 and Sol2) were prepared from $PdCl_2$ (Aldrich) as metal source, which was dissolved by aqueous HCl for complexing Pd ions. We chose ethanol to reduce Pd ions, because this reducing agent was applied in our previous CCS method [19]. After dilution of 2 mM $PdCl_2$ solution to the required concentration aqueous solution of poly(diallyldimethylammonium chloride), PDDA polymer (Aldrich, 20 wt.% in water) was added into the same beaker. The solution, containing polymer and Pd^{2+} ions, was vigorously stirred for 20 min and then ethanol was introduced to perform reduction of the metal ions. During the reduction process, the color of the solution changed from greenish yellow to brown. The sol formation was allowed to proceed at 65 °C. The detailed parameters of the synthesis of two Pd sols with significantly different particle sizes are presented in Table 1.

2.2. Deposition of Pd nanoparticles on Aerosil

We have applied nonporous Aerosil 200 type silica as a support with an average particle diameter of 12 nm. The deposition of sol onto the support was carried out at room temperature during stirring. The sample Sol1 was adsorbed on silica within 1 day (producing Pd/SiO_2 denoted by S1). However, adsorption of Sol2 did not take place (the color of the liquid phase after 1 day still remained brown showing that a part of Pd particles was not bound to the support). Thus, we changed the pH value of Sol2 to 8.5 by adding sodium carbonate solution and ensured 5 h for adsorption (sample S2). The suspensions were then centrifuged and the solid phase was dried at 60 °C for 2 days.

Samples prepared by impregnation and by CCS served as references. The impregnation was carried out with $PdCl_2$ solution using Aerosil support. Sample IMP1 was oxidized in air at 500 °C for 3 h and reduced in H_2 at 500 °C for 3 h (for detailed characterization see Ref. [19]). Sample IMP2 was calcined in air at 300 °C for 1 h and reduced at different temperatures (see Table 3). For the preparation of sample CCS the same metal precursor and support was used, but the reduction of Pd^{2+} ions by ethanol took place in the solid/liquid interfacial layer of the support surface [19,20].

2.3. Sample characterization

The metal content of the samples was determined by X-ray fluorescence (XRF) method. The particle size of the sols and the supported samples was determined by a Philips CM20 transmission electron microscope (TEM) operating at 200 kV. After evaporating water from the carbon-coated grid, the electron micrographs of the particles were taken. The particle size distribution was obtained by counting more than 200 individual particles.

CO chemisorption was applied to measure the accessible Pd surface (dispersion, D_{CO} (%)) using $Pd_s/CO_a = 1.5$ adsorption stoichiometry [21]. From the chemisorption data the particle size was calculated

Table 1
Preparation parameters in sol formation

Sample	[EtOH] (mM)	[Pd^{2+}] (mM)	Monomer/ metal ratio	pH[a]	Temperature (°C)	Reduction time (h)	Particle diameter (nm)
Sol1	343	0.20	0.23	2.5	65	13	6.4 ± 2.1
Sol2	927	0.18	1.25	2.9	65	1.5	3.1 ± 0.9

[a] pH of the aqueous solution containing the Pd precursor and PDDA.

assuming spherical particles, d_{CO} (nm) = 113/ D_{CO} (%). The chemisorption was carried out in a pulse flow system (Sorbstar) equipped with QMS and thermal conductivity detector. CO pulses in He were introduced at room temperature. Previously, temperature programmed reduction (TPR) of the samples was conducted in the same apparatus in 1% H_2/Ar with 20 °C/min heating rate to reveal the presence of unreduced Pd species.

The removal of the carbonaceous materials was followed by temperature-programmed oxidation (TPO) in 1% O_2/He flow with 20 °C/min heating rate. The formation of CO_2 product was detected in the temperature range from 20 to 600 °C by means of a QMS linked to the system. The CO_2 signal intensity was calibrated by adding 0.1 ml CO_2 pulses into 1% O_2/He and the O_2 signal was used as an internal standard.

The catalytic activity of the samples was tested in benzene hydrogenation in an atmospheric plug flow reactor working under differential regime, and the product was analyzed by gas chromatograph. The only product observed was cyclohexane. The benzene content of the reaction mixture was set by passing H_2 stream above the surface of benzene in a saturator at 0 °C providing stable $H_2/C_6H_6 = 37$ ratio. The catalytic performance was measured at 120 °C in the "as-prepared" state as well as after oxidation and reduction at different temperatures. The reaction rate was expressed as number of transformations per second per site (turn over frequency, TOF, 1/s) based on site number estimated by CO chemisorption ($Pd_s = 1.5CO_a$).

3. Results and discussion

The PDDA polymer turned out to be a proper stabilizer even in low concentration. Due to its polycationic nature (containing quaterner nitrogen atom), PDDA (its structure is displayed in Fig. 1) stabilizes the Pd nuclei formed during the reduction. This assumption is based on the general observation that metal colloids prepared in chloride-containing solutions are negatively charged through Cl^- adsorption [14], thus, Coulomb interaction is generated between the metal particles and the cationic stabilizer. The positive charge of PDDA was used to attach the polymer to the silica surface. Deposition of sols on solid surfaces is a complicated process. The success of immobilization depends on the physicochemical properties of the support and the polymer and on the monomer/metal ratio as well [18]. We experienced difficulty in the adsorption of Sol2 because of its five times higher polymer concentration. It was shown that the polymer occupies the adsorption sites on the solid [14], so as a consequence, the surface charge of silica must have been adjusted by increasing the pH to produce higher concentration of anionic sites (the iso-electric point of silica is around 2). Thus, stronger interaction between the support and the polymer containing metal particles was generated. After immobilization of the Pd particles, they were dispersed on the support uniformly, as is shown in Fig. 2.

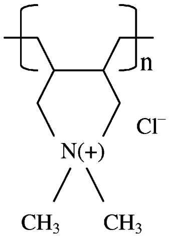

Fig. 1. Structure of PDDA polymer.

Our TPR experiments proved the absence of unreduced Pd species for both samples. Bulk oxidation of Pd particles on S1 produces a small peak (centered at 400 °C) in the O_2 signal as shown in Fig. 4a. PdO formation on S2 overlaps with the oxidation of organic impurities (Fig. 4b).

The different concentrations of the polymer and reducing agent (Table 1) resulted in the formation of nanoparticles of different particle size. The increase of these concentrations caused a decrease in the Pd particle diameter of Sol2. Table 2 shows the average particle size of silica-supported sols determined by TEM and CO chemisorption. The size distributions are presented in Fig. 3. The size of Pd particles did not change after immobilization on the support (compare d_{TEM} in Tables 1 and 2). For the sake of comparison, the samples previously prepared by impregnation and CCS [19,20] are also included in Table 2.

One of the main advantages of sol preparation is the possibility of producing close to uniform nanoparticles, which can then be deposited on a support in different concentrations. The CCS method can produce

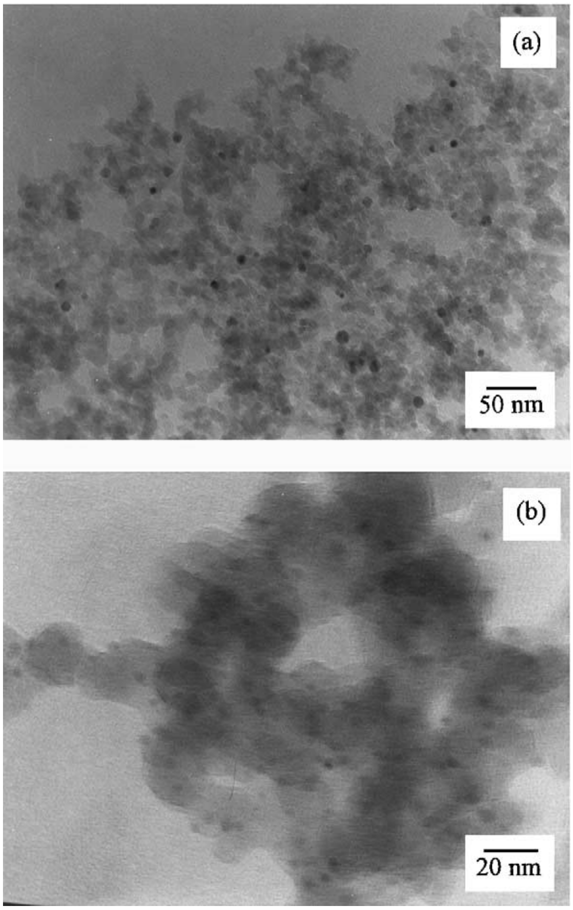

Fig. 2. TEM micrograph of sample S1 (a) and sample S2 (b).

relatively narrow size distribution of metal particles in controlled size, but in order to decrease the particle size a decrease in metal loading is needed [19]. The incipient wetness method is not convenient to obtain palladium particles of uniform size on Aerosil 200 (especially at higher metal content), because the silica applied here is nonporous, so by impregnation the uniform distribution of metal particles cannot be achieved. Each of the preparation steps, drying, calcination and reduction of the impregnated catalysts results in a dramatic change in the size distribution. In contrast to this, once metal particles are formed in liquid phase (sol method) they retain their size after depositing them onto a support.

Table 3
Dispersion of Pd/SiO_2 prepared by sol method and impregnation technique after oxidation at 300 °C/1 h and reduction at different temperatures

Sample	D_{CO} (%) after reduction at		
	80 °C	300 °C	500 °C
IMP2	51.0	32.5	23.0
S2	21.6	23.7	22.2

Table 3 compares the dispersion of sample S2 with that of the impregnated sample (IMP2) after treatments in hydrogen. The metal surface of S2 measured by CO chemisorption does not alter significantly, whereas the dispersion of the impregnated sample decreases during hydrogenation at higher temperatures. Apparently, the impregnated sample possesses higher dispersion initially, but the higher metal surface exposed cannot be maintained after H_2 treatment at higher temperatures. The impregnated sample after drying presumably contains $PdCl_2$ particles and Si–O–Pd^{n+} surface species [22], and the latter is transformed to a well-dispersed Pd metal by reduction, which may sinter during heating in hydrogen.

Presence of organic ligands is of great importance in connection with the restriction of particle growth.

Table 2
Particle size of Pd/SiO_2 samples and TOF in benzene hydrogenation in as-prepared state and after oxidation/reduction treatment

Sample	In as-prepared state					After oxidation at 300 °C and reduction at 80 °C		
	Pd content (wt.%)	d_{TEM} (nm)	d_{CO} (nm)	C (g_{cat}[a])	TOF_{CO} (s^{-1})	d_{TEM} (nm)	d_{CO} (nm)	TOF_{CO} (s^{-1})
S1	1.13	6.5 ± 2.4	8.5	2.0×10^{-4}	0.008	6.6 ± 2.6	8.7	0.024
S2	1.08	3.2 ± 0.97	8.1	4.4×10^{-4}	0.007	3.3 ± 0.7	5.2	0.023
CCS	0.98	8.8 ± 2.3	11.6	6.4×10^{-5}	0.011	9.3 ± 2.9	10.9	0.030
IMP1	1.85	13.0 ± 7.5	17.3	5.2×10^{-6}	0.020	–	17.2	0.026

[a] C (g_{cat}) in mol CO_2 (g_{cat}) (the TPO curve was integrated between 25 and 450 °C).

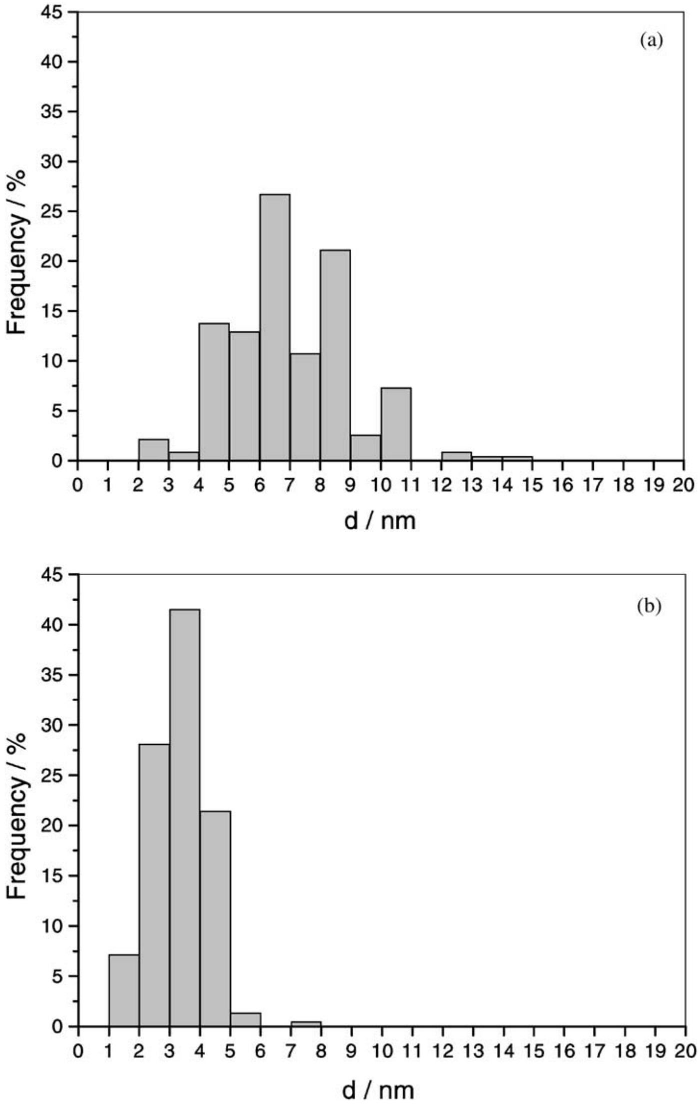

Fig. 3. Palladium particle size distribution on S1 (a) and S2 (b) samples.

However, both the sol stabilizer and the organic reducing agent (or the solvent itself) may poison the metal particles formed. Keeping these in mind, it is obvious that catalytic reactions may involve some difficulties when the activity is to be calculated. Usually, liquid phase hydrogenations catalyzed by metal sols are characterized by measuring the hydrogen consumption [4,23]. The catalytic performance originates from the presence of the metal but it is also affected by the surrounding weakly bound ligands, which may or may not allow the reactants to reach the metal surface. This working "ensemble" means a great chance to influence the catalytic behavior or selectivity by changing the ligand [24]. The only disadvantage is that the activity of the sols with different stabilizers is hardly comparable, since the reaction rates are not corrected for the accessible metal surface. There are some examples when the catalytic activity is based on the dispersion calculated from TEM pictures, but this is still an approximation [5,25]. Once the sol is supported on

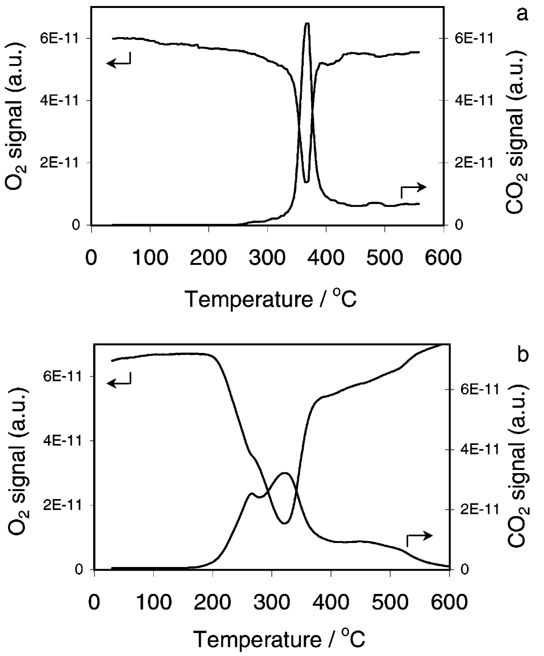

Fig. 4. CO_2 formation in temperature-programmed oxidation: sample S1 (a), sample S2 (b).

solid the effect of stabilizer on the catalytic reaction still remains a question. Comparisons were made with conventional catalysts on the basis of conversion [11] or hydrogen uptake [16], but the surface of the active metal sites was still unknown.

Reductions carried out by organic molecules result in the formation of carbonaceous residues bound to the support and/or the metal surface. The use of polymer stabilizer increases the carbon content. The presence of such carbonaceous residues is clearly indicated by Fig. 4 showing the TPO curves of S1 and S2. Sample S1 gave a rather narrow oxidation peak centered at 370 °C, S2 produced—probably due to the high concentration of stabilizer—a rather broad peak of CO_2 formation. The CO_2 peak shape is affected by several factors such as Pd dispersion, distribution of hydrocarbons on the support and metal particles, therefore unambiguous conclusions cannot be drawn about the coverage of residues on the metal sites.

Surprisingly, CO chemisorption indicated relatively "clean" metal particles in the case of S1: the particle size determined by TEM (d_{TEM}) only slightly differs from the particle size based on CO chemisorption data (d_{CO}), as can be seen in Table 2. An increase in the concentration of polymer and ethanol poisoned the palladium particles of S2, so the CO molecules have limited access to the metal surface (significant difference between d_{TEM} and d_{CO} for S2). Hindrance of CO chemisorption caused by the presence of adsorbed stabilizer was also observed in the paper of Bönnemann et al. [26]. When bulkier alkyl groups were applied as stabilizer a parallel decrease in CO chemisorption and in hydrogenation activity was experienced.

Oxidation of our samples at 300 °C removes the majority of deposits from the catalyst. Thus, the average diameter of S2 calculated from CO chemisorption approaches the TEM value (see Table 2).

Testing the catalytic performance in benzene hydrogenation, the samples exhibited reasonable activity even in the "as prepared" state, which means that metal atoms exposed to the surface are able to coordinate benzene and activate hydrogen. Table 2 shows that after oxidation at 300 °C followed by reduction at 80 °C the TOF values based on CO chemisorption (TOF_{CO}) increase. The increase of activity per surface Pd atoms cannot be solely explained by the removal of carbonaceous materials as it was proven in our previous work [20]. Benzene hydrogenation is considered to be a structure insensitive reaction, although there are several contradictions in the literature regarding this problem [21,27–30]. Small variations in TOF values depending on the synthesis method [29] and the pretreatment conditions [33] reflect that this problem needs further investigation. Moss et al. [21] in benzene hydrogenation have experienced a change in TOF with changing reduction temperature. The lower was the reduction temperature of Pd catalyst, the higher catalytic activity was obtained. They tried to explain this observation by the degree of dehydroxylation of the support and silicon incorporation into the palladium, but the presence of Pd_xSi_y was not supported by XRD measurements.

Our catalytic activity test on benzene hydrogenation reflects the complex effect of oxidation and reduction treatments. Inspecting Fig. 5, in which reaction rates versus pretreatment conditions are displayed for both samples, the following observations can be made. In the "as-received" state of S2 the difference between d_{TEM} and d_{CO} suggests the poisoning of metal sites. The oxidation at 150 °C results in an activity increase for S2, but causes no change in the case of S1, which

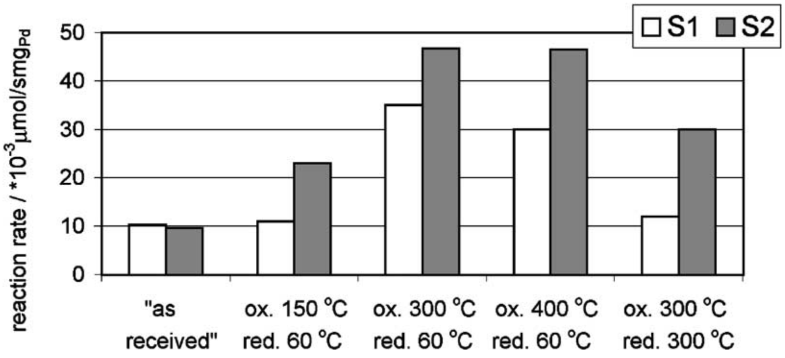

Fig. 5. Reaction rates in benzene hydrogenation after different treatments (Conditions: 120 °C, $P_{tot} = 101$ kPa, H_2/benzene = 37).

was assumed to be "free" of contamination on the metal surface. The oxidation of Pd samples at 300 and 400 °C, respectively, leads to PdO formation [20] and the subsequent reduction at 80 °C results in increased benzene conversion. However, if the reduction was carried out at 300 °C, the reaction rate decreased (see the last bar in Fig. 5), although the dispersion of Pd was not altered. The explanation for this latter observation may involve the restructuring of the metal surface upon oxidation and reduction. Pd metal during oxidation changes its morphology through the formation of pits and cavities as Chen and Ruckenstein [31] have observed. The reduction at low temperature produces a restructured metal surface, which is more active due to its disordered structure. Since the reaction mechanism is still not perfectly clarified, we may assume an increase in the number of sites activating hydrogen or being active in transformation of adsorbed benzene to cyclohexane, or, if the number of active sites is constant, we may suggest an enhanced intrinsic activity per site. Our findings are in accordance with the work of Sai Prasad et al. [27] who assigned the increased TOF to a distinctly different metal surface produced by the reduction of PdO formed under microwave heating.

The samples prepared by the three different methods show different TOF values in the as-prepared state (Table 2), presumably reflecting dissimilarity in Pd surface morphology. The same oxidation/reduction treatment generates similar Pd surfaces, which manifests itself in nearly identical TOF values. From literature data, the following TOF (1/s) values can be calculated for Pd/SiO_2 catalysts in benzene hydrogenation (conditions: $T = 120$ °C, 2.66 kPa benzene and 98.42 kPa H_2): 0.008–0.06 [32], 0.03–0.06 [33], 0.023 [34], 0.01 [21]. Our values, 0.023–0.03 (1/s), show satisfactory agreement with these data, particularly as the TOF depends on the support, impurities and pretreatment conditions.

4. Conclusion

Pd sols were prepared using ethanol as reducing agent and PDDA as stabilizer. Fixation of the Pd particles from the sol onto the surface of SiO_2 (Aerosil 200) was ensured by choosing the right pH of the solution.

It was established that the larger is the ethanol and PDDA concentration, the smaller is the particle size and the larger is the required negative charge on SiO_2 to keep the particles adsorbed on SiO_2.

The presence of impurities as tested by CO adsorption and benzene hydrogenation measurements affects to some extent the accessibility of Pd sites. Nevertheless, the prepared catalysts even without oxidative removal of hydrocarbon species can be used for hydrogenation. The increase in activity by a factor of 4 after oxidation and reduction treatments can be attributed not only to the removal of impurities, but also to morphological changes on Pd particles.

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