Potentialities of silane-modified silicas to regulate palladium nanoparticles sizes

**N. Ivashchenko · V. Tertykh · V. Yanishpolskii ·
J. Skubiszewska-Zięba · R. Leboda ·
S. Khainakov**

Abstract A promising approach to control palladium nanoparticle sizes by application of silane modified silicas was suggested. The combination of reductive properties of silicon hydride groups and hydrophobic properties of alkylsilyl groups which act as agglomeration limiters for metal nanoparticles gives an opportunity to synthesize uniformly distributed particles with a specified size. Silicas modified with triethoxysilane (TES) and diisopropylchlorosilane (DIPCS), as well as, the combination of hexamethyldisilazane (HMDS) and triethoxysilane were applied for formation of such bifunctional matrices. Properties of the silane-modified silica samples and changes occurred during the formation of palladium nanoparticles were studied by IR spectroscopy. Thermal stability of surface chemical compounds was investigated by thermogravimetric analysis (TGA); low-temperature nitrogen adsorption was used to study structural properties of the applied materials. With the use of transmission electron microscopy (TEM) the dependence of palladium nanoparticle size on the nature of support surface layer was found.

Keywords Palladium · Nanoparticles · Bifunctional silicas · Silicon hydride groups · Particle size regulation

N. Ivashchenko (✉) · V. Tertykh · V. Yanishpolskii
Chuiko Institute of Surface Chemistry, National Academy
of Sciences of Ukraine, 17 General Naumov Str,
Kyiv 03164, Ukraine
e-mail: nadiia.iva@gmail.com

J. Skubiszewska-Zięba · R. Leboda
Maria Curie-Sklodowska University, pl. Maria
Curie-Skłodowskiej 3, 20-031 Lublin, Poland

S. Khainakov
Department of Chemistry, University of Oviedo,
8 Julian Claveria, 33006 Oviedo, Spain

Introduction

Preparation of metal nanoparticles is a field of current interest in material chemistry because of possible emerging of new physical and chemical properties when the particle sizes approach the nanometer range [1–3]. However, metal nanoparticles have a tendency to agglomerate and are quite difficult to recover because of their small size. To avoid the above-mentioned drawbacks, they are usually deposited on inorganic porous supports, such as silica, which prevents agglomeration and simplifies their processing and recovery [1]. Such metal-containing nanocomposites, especially those that carry supported noble metal nanoparticles, are widely used as catalysts in numerous catalytic reactions.

Nowadays a lot of research studies are devoted to the synthesis of such materials while seeking for possible ways to prevent undesirable aggregation processes and obtain the materials with uniform metal nanoparticles [4–6]. One of the possible ways to limit the growth of nanoparticles is their confinement in the pores of ordered mesoporous materials. However, even in this case, application of the commonly used reducing reagents, such as sodium borohydride, hydrazine, and hydrogen [4–10] often leads to considerable aggregation of particles under conditions of their synthesis. On the other hand, when the reducing agent is grafted to the support surface the immediate formation of nanoparticles occurs on the attachment sites of the reducing species due to instant reduction of metal ions [11]. In our previous researches the advantages of usage of silicas modified with the groups possessing reductive properties such as silicon hydride ($\equiv$SiH) groups were described. Thus, the preparation of silver, gold, and palladium nanoparticles on the surface of such hydride silicas was studied [7, 12–15]. Direct reduction of ions on the hydride silica surface allowed us to control the sizes of formed metal

particles within certain limits by varying the concentration of metal salt taken for reduction and the time of reduction.

Grafting of hydrophobic groups, such as trimethylsilyl, to the support surface was shown to diminish significantly the aggregation of metal nanoparticles formed on the surface and resulted in formation of uniformly distributed particles with a narrow size distribution [16]. In the present research the combination of these two approaches, namely the use of the grafted silicon hydride groups as reducing agents on the silica surface and the trimethylsilyl groups for suppressing metal particle aggregation, has been studied for the first time as a possible way to synthesize palladium nanoparticles with a desired size.

Experimental

Silicon hydride groups immobilized on the silica surface were used for in situ reduction of palladium ions. As a support we used Silochrom, a porous substance obtained from concentrated water suspensions of high-purity pyrogenic silica (Aerosil). Modification of silica with triethoxysilane (TES) was carried out under dry conditions according to the procedure described previously in [17]. Diisopropylchlorosilane (DIPCS) modified silica was synthesized by the similar procedure. TES (0.185 mL, 1 mmol) or DIPCS (0.179 mL, 0.1 mmol) was added dropwise to glacial acetic acid (5 mL). After stirring, the mixture was poured into the flask containing silica (5 g). After impregnation, the obtained mixture was transferred to the thermostat and heated there for 2 h at 90 °C. The modified silica samples were dried in air at 90 °C for 1 h and then heated in the oven at 150 °C for 2 h.

Another procedure consists of step by step modification of silica in order to fabricate the first layer of hydrophobic groups and then to graft silicon hydride groups on the silica surface. For this purpose silica (5 g) was first modified with hexamethyldisilazne (HMDS) in the toluene medium at 80 °C (0.08 mL, 0.38 mmol HMDS in 10 mL of toluene) for 10 h, then washed with ethanol and dried at 80 °C for 2 h. Then triethoxysilane (TES) in the acetic acid medium (0.185 mL, 1 mmol of TES in 5 ml of acetic acid) was added and the mixture was heated at 90 °C for 2 h and after-dried at 150 °C for 2 h.

These synthesized silane-modified silicas were denoted as TES-silica, DIPCS-silica, Meth–silica, and Meth–TES–silica, respectively. In all the samples the concentration of $\equiv$SiH groups was 0.2 mmol/g.

Introduction of palladium was performed by impregnating 2 g of modified silica with the palladium nitrate (0.026 mmol) solution at pH 1.6. Then the samples were washed with distilled water and dried at 100 °C for 3 h. Metal nanoparticles were formed at the immediate attachment sites of surface $\equiv$SiH groups as a result of reduction of palladium ions.

The content of palladium in the as-prepared composites was equal to 0.3 wt%, however, the samples were prepared on the basis of different modified silicas, so they were denoted as Pd/TES, Pd/DIPCS, and Pd/meth-TES. The metal content in the equilibrium solutions was checked by spectrophotometry with the use of thiourea [18]. Measurements were carried out by a SF 46 spectrophotometer (LOMO, Russia) at the 460 nm wavelength using cells with a layer thickness of 1 cm.

IR-spectra of the samples (the mixtures with KBr in the mass ratio 1:20) were recorded by a FTIR spectrometer (Thermo Nicolet Nexus FTIR, Germany).

Data of low-temperature adsorption/desorption of nitrogen were obtained with the use of an analyser of porosity and specific surface area (Micromeritics ASAP 2020, USA) at −196 °C. The total surface area was calculated by the BET method; the volume of pores and the pore-size distribution were obtained with the use of the BJH method.

TEM observations were performed on MET JEOL-2000 EX-II (Japan) transmission electron microscope. For the TEM analysis the materials were dispersed in ethanol and a drop of this suspension was deposited onto a carbon-coated copper grid.

Thermogravimetric analyses were carried out with the use of Derivatograph-C apparatus (MOM Budapest, Hungary) in the temperature range from 20 to 800 °C at 10 °C/min heating rate.

Results and discussions

For formation of a bifunctional layer which consists of silicon hydride groups for reducing the metal ions and hydrophobic groups for suppressing the growth of the formed metal nanoparticles on the silica surface two different approaches were applied.

The first approach is a two-step synthesis involving the modification of the silica surface with hexamethyldisilazane (HMDS) under conditions described in the experimental part to form grafted trimethylsilyl groups and the subsequent impregnation of such methylated silica with triethoxysilane to attach silicon hydride groups (Fig. 1a). Another approach is the modification of silica with diisopropyltrichlorosilane (DIPCS), molecules of which consist of both silicon hydride and diisopropyl groups allowing to solve two problems at once—to reduce the metal ions and to suppress aggregation of the formed nanoparticles (Fig. 1b). Also triethoxysilane (TES) modified silica was used as a reference material to control changes in palladium nanoparticles sizes brought about by application of bifunctional silicas (Fig. 1c).

Fig. 1 Schematic illustration of silica modification with silanes and subsequent palladium nanoparticles synthesis
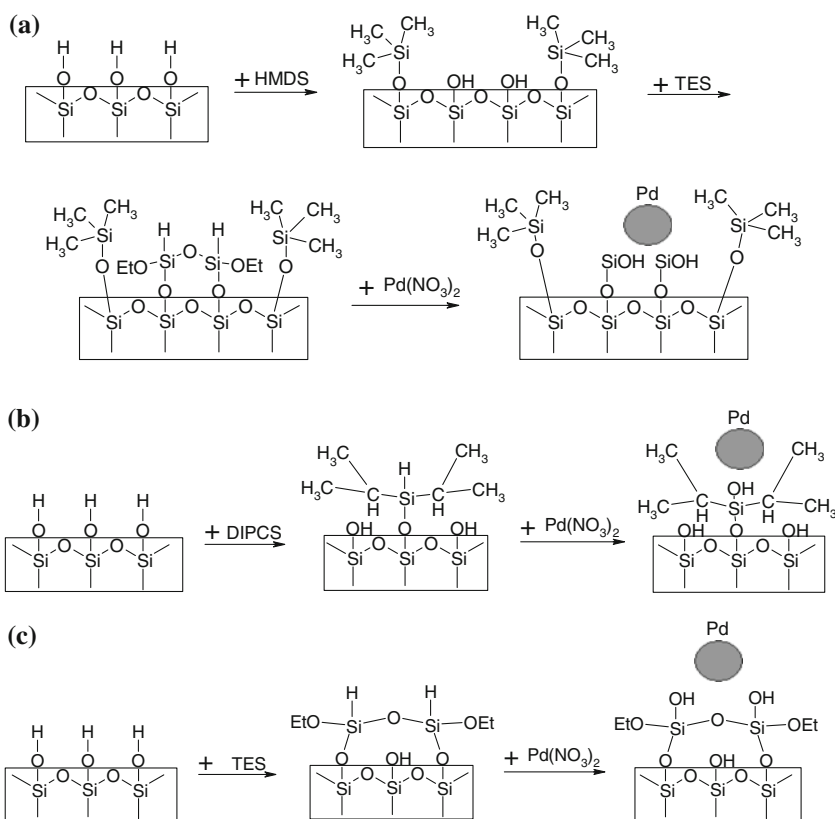
Changes occurring in the surface layer during the silica modification and following interaction of obtained hydride silica with the palladium nitrate solution are illustrated in Figs. 2 and 3.

Absorption bands of Si–H stretching vibrations provide evidence of the fact that attachment of silicon hydride groups occurred. For TES-modified silica this band is at 2260 cm^{-1}, for DIPCS the band of $\equiv$SiH groups is shifted to the high wavelength region and has maximum at 2130 cm^{-1}. The apparent peak position shift is caused by changes in substituents near the silicon atom; in comparison with the molecule of triethoxysilane, the branched isopropyl group in the molecule of diisopropylchlorosilane is a more active electron donor, leading to less
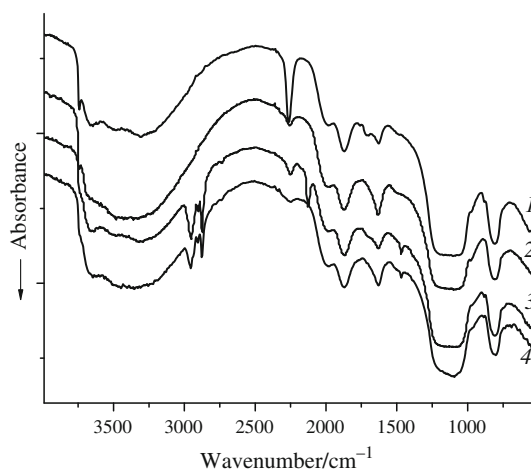

Fig. 2 FTIR-spectra of silicas modified with triethoxysilane (*1*), diisopropylchlorosilane (*2*), and palladium-containing composites on their basis (*3* and *4*, respectively)
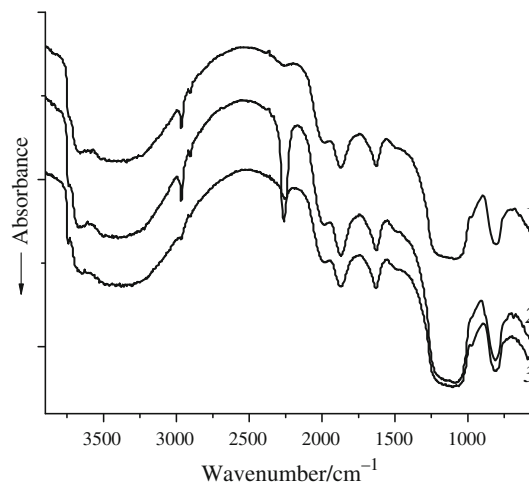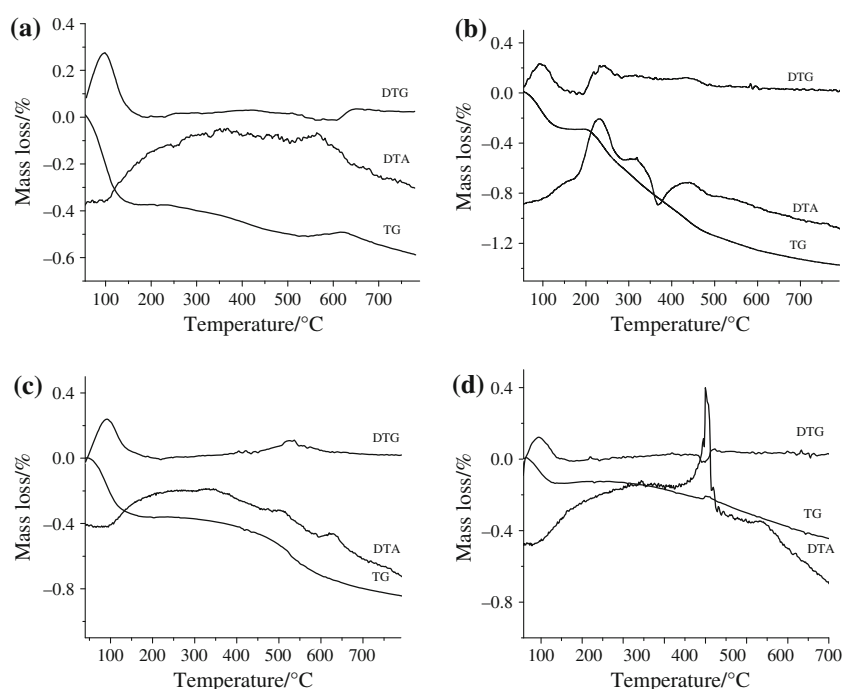

Fig. 3 FTIR-spectra of methylated silica (*1*), methylated silica after modification with triethoxysilane (*2*), and palladium-containing composite on its basis (*3*)

Fig. 4 DTA, DTG, and TG curves of TES-modified silica (**a**), DIPCS-modified silica (**b**), methylated silica (**c**), methylated silica modified with triethoxysilane (**d**)

polarization of Si–H bond and to the short wavenumber shift of the band [19]. Moreover, in the IR spectrum of DIPCS-modified silica the bands with absorption maxima at 2966 and 2877 cm^{-1} corresponding to the stretching vibrations of C–H in –CH_3 and $\equiv$CH groups are observed (Fig. 2). The absorption band at 2966 cm^{-1} is also presented in the spectrum of methylated silica (Fig. 2, 1). After modification of the methylated sample with

triethoxysilane the band at 2260 cm^{-1} appeared suggesting that the silicon hydride groups are grafted to the silica surface (Fig. 2, 2).

Substantial decrease in the intensity of the band assigned to silicon hydride groups for all samples after impregnation with the palladium nitrate solution (Figs. 2, 2, 4; 3, 3) is detected. It occurs simultaneously with appearance of the absorption band of silanol groups at 3750 cm^{-1}, suggesting

Fig. 5 DTA, DTG, and TG curves of Pd/Silica nanocomposites synthesized on the basis of TES-modified silica (**a**), DIPCS–modified silica (**b**), and methylated silica modified with triethoxysilane (**c**)
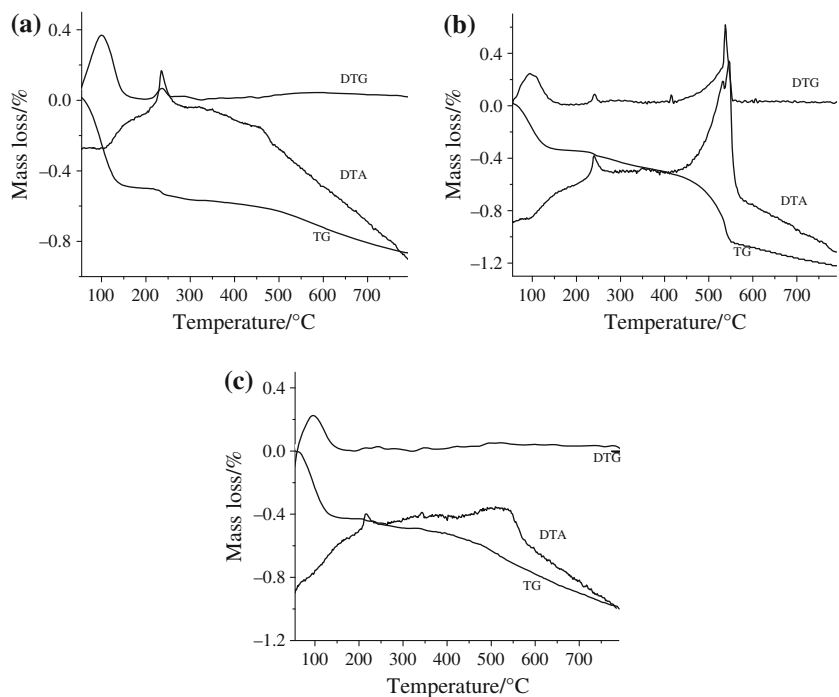
Fig. 6 a Isotherms of low-temperature ad(de)sorption of nitrogen at −196 °C for initial silica and samples after modification (TES-Silica, DIPCS-Silica, meth-Silica, meth-TES-Silica), **b** enlarged part of the graph

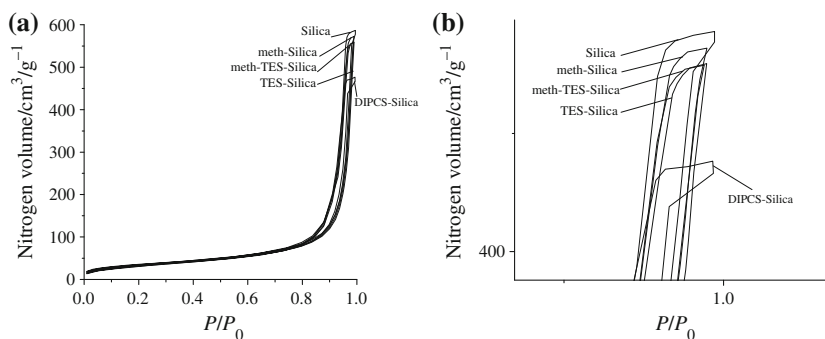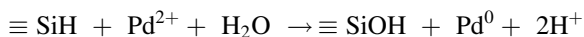**Table 1** Adsorption-structural characteristics of initial and silane-modified silicas

Parameter	Silica	TES-silica	DIPCS-silica	Meth-silica	Meth-TES-silica
d_{pores}/nm	25.3	25.1	20.3	22.5	24.3
S/m^{2}g^{-1}	127	123	116	121	118
V_{pores}/cm^{3}g^{-1}	0.89	0.85	0.73	0.85	0.88

hydrolysis of the silicon hydride groups during the formation of palladium nanoparticles:

$$\equiv SiH \ + \ Pd^{2+} + \ H_2O \ \rightarrow \equiv SiOH \ + \ Pd^0 + \ 2H^+$$

The presence of bands corresponding to C–H stretching vibrations remains, suggesting that no other changes occur in the surface layer of modified silica, except of silicon hydride groups hydrolysis. However, after hydride silica samples impregnation with the palladium nitrate water solution, width of broad band between 3000 and 3600 cm^{-1} assigned to water adsorbed on the silica surface increases, so above-mentioned bands related to $\equiv CH$ and –CH$_3$ groups are partially hidden.

Samples silane modified silica samples, as well as palladium-containing nanocomposites synthesized on their basis, were studied by thermogravimetric analysis. The TG, DTG, and DTA curves for all the samples are presented in Figs. 4 and 5.

Samples decomposition has a stepwise character. Total mass loss for TES-modified silica is 0.58%, for the silica modified with diisopropylchlorosilane is 1.37%, for the methylated silica after and before subjection of triethoxysilane values of mass loss amount to 0.84 and 0.46%, respectively (Fig. 4). Different hydrophobicity of the samples resulted in different mass loss in the region up to 150 °C. Thus, in the case of silica modified with TES, mass

Fig. 7 TEM micrographs of Pd nanoparticles supported on silica modified with TES (**a**), silica modified with DIPCS (**b**), and silica containing both trimethylsilyl and silicon hydride groups (**c**)
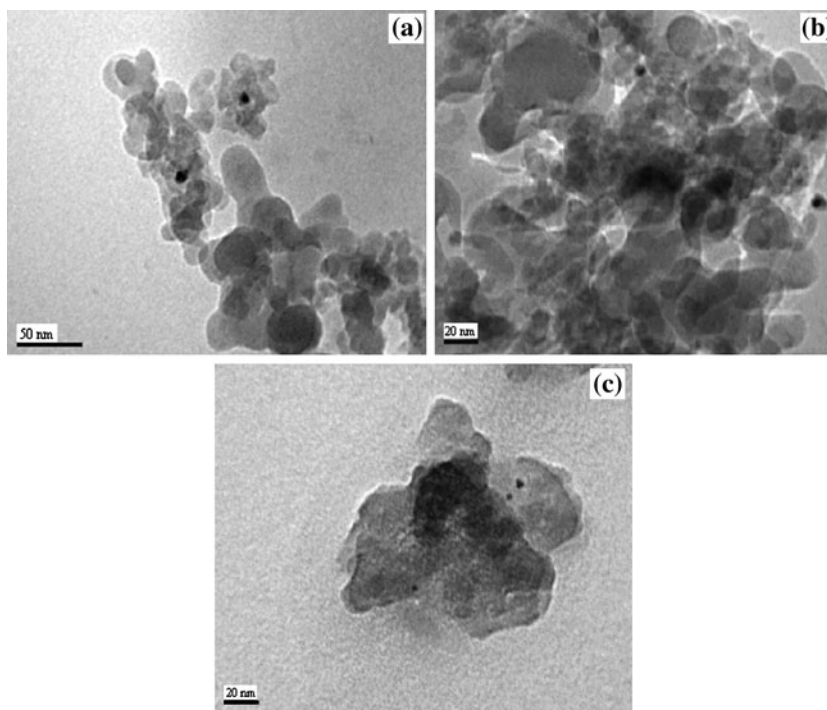
loss in this region is 0.37% (Fig. 3a), for the DIPCS-silica it equals to 0.28% (Fig. 3b). In the methylated silica after its additional modification with triethoxysilane, the mass loss caused by removal of physically adsorbed water decreased from 0.33 to 0.14%, respectively (Fig. 3c, d). It is attributed to increased sample hydrophobicity owing to substitution of surface silanols by hydrophobic triethoxysilane, diisopropyl, and trimethyl groups.

Hydride groups oxidation of to silanol ones by atmospheric oxygen, which according to the literature data begins at about 260–300 °C [20–22], goes simultaneously with decomposition of organic groups and it is very difficult to separate these processes.

At the temperature ranging between 500 and 600 °C, probably, dehydroxylation reaction between structural surface groups with simultaneous formation of siloxane bridges takes place. It results in a decrease of the sample weight, which can be seen in TG curve of all the samples (Fig. 4). These observations are in a good agreement with the literature data [20–23].

Mass loss in palladium-containing nanocomposites (Fig. 5) in the region up to 150 °C is slightly bigger than in the corresponding silane-modified silicas. This is 0.40% for the Pd-TES composite, and 0.38 and 0.40%, respectively, for the Pd-DIPCS and Pd-meth-TES samples. TG curves of the palladium-containing nanocomposites are not very different from those for silicas modified with organosilanes. Characteristic feature of DTA curves for all the samples containing palladium nanoparticles is an exothermal peak around 235 °C.

The mesoporous structure of silica material used as a support was confirmed by low-temperature nitrogen adsorption method. From isotherms displayed in Fig. 6 can be easily seen that modification does not affect porous structure of the silica support, however, volume of adsorbed nitrogen for silane-modified silicas is lower than in the case of the initial silica matrices.

The textural properties of initial silicas and palladium-containing composites are summarized in Table 1. Specific surface area (S_{BET}) and pore volume (V_{pores}) of modified silicas decrease slightly compared to initial silica matrices.

The confirmation of palladium nanoparticles formation on the surface of silica matrix can be obtained from transmission electron microscopy (TEM) data. Moreover our previous investigations [17] suggested that the reduction of palladium ions by silicon hydride groups leads to the formation of metallic palladium. X-ray diffractions studies of palladium-containing nanocomposites in the wide-angle region (10–70°) confirm the above statement. Diffractograms reveal three well-defined (111), (200), and (220) reflex ions typical for the palladium face-centered cubic lattice [24].

It can be assumed from the TEM images that the nature of surface layer strongly affects the size of formed metal particles. Interaction of palladium nitrate solution with TES-modified silica resulted in formation of metal nanoparticles having a quite large sizes distribution, particles from 7 up to 15 nm were detected on the support surface (Fig. 7a). However, in the cases, where DIPCS- or meth-TES-Silica are used the sizes of nanoparticles do not exceed 3–4 nm (Fig. 7b, c).

Conclusions

The usage of silicas containing in the surface layer silicon hydride groups as reducing agents along with hydrophobic groups was shown to suppress nanoparticles aggregation and allows one to obtain palladium particles with a narrow size distribution. Thus, in the case of silica modified with diisopropylchlorosilane (DIPCS-Silica) or silica containing both trimethylsilyl and silicon hydride groups (meth-TES-Silica) the size of formed palladium nanoparticles is 3–4 nm.

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