

Synthesis of Poly (vinylpyrrolidone) protected Pd-Ag Bimetallic Nanoparticles by Polyol Method

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Bimetallic Pd-Ag nanoparticles (NPs) were obtained by polyol method in the presence of poly (vinylpyrrolidone), PVP, as capping agent. The reduction of silver and palladium precursors was performed in argon inert atmosphere by successive reduction, or coreduction approach. In the successive reduction, AgNO₃ solution was injected in the ethylene glycol solution of PVP at 140°C, followed by the injection of [Pd(NH₃)₄]Cl₂ solution. The obtained bimetallic Pd-Ag NPs exhibited cluster structure, with the surface reach in silver. The NPs size was in the range of 30 – 58.5 nm with the average dimension of 41.5 nm. The coreduction approach consists in the hot injection of both metal precursors as complex ammine dissolved in ethylene glycol. By this method, smaller Pd-Ag NPs with the average sizes in the range 16 – 30 nm were obtained, depending on the synthesis parameters. The influence of metal cations : PVP molar ratio, metal cations concentration, Ag : Pd atomic ratio and the reduction temperature on the composition and morphology of the bimetallic NPs was studied. For both reduction approaches, based on the experimental data, two different reduction pathways were proposed.

Keywords: bimetallic nanoparticles, Ag, Pd, PVP, polyol method, coreduction, successive reduction

In many applications such as catalysis, data storage, biomedicine, metallic nanostructures are of great interest. To control the morphology of metallic NPs during the synthesis is a key factor that plays a significant role in determining their physical and chemical features [1-4]. Electrical, optical and magnetic properties of metallic nanocrystals (NCs) vary widely with their size and shape. Nonspherical noble metal NCs, which provide different crystallographic facets and increased number of edges, corners and defects showed enhanced catalytic properties [5,6]. Noble metal nanoclusters consisting of several to tens metal atoms have molecular-like properties, including luminescence and unique charging properties due to the spatial confinement of free electrons [7,8].

Various chemical synthetic routes based on the solution-phase colloidal chemistry were developed to synthesize uniform-sized metallic NPs with various dimensions and shapes. Colloidal methods, usually performed in the presence of a stabilizer, involve either the reduction reaction of a noble metal salt using different reducing agents, such as hydrogen, sodium borohydride, tetrabutylammonium borohydride, polyalcohols, or the thermal decomposition of an organometallic precursor, or a metal-surfactant complex [1,2,5,9-11]. The synthesis of metallic NPs by polyol method involves the reduction of metal cations with a polyalcohol, which acts also as solvent. The main advantage of polyalcohols (ethylene glycol, 1,2-propylene glycol, 1,5-pentadiol etc.) is their high boiling points, associated with their high viscosity that is of great importance in the control of the diffusion and growth processes, which assist the metallic NCs formation [9,10].

The steric stabilizer employed in the metallic NPs synthesis, which can be a soluble polymer or a surfactant, plays an important role in the control of the NPs morphology by acting as ligand for metal ions and preventing their agglomeration. One of the most efficient capping agents

in the solution phase synthesis of several colloidal particles is poly (vinylpyrrolidone) that is soluble in several reaction media, including water and could be completely removed in the washing step. Xiang et al. [12] reported that the hydroxyl-terminated PVP (present due to the water and hydrogen peroxide used in the PVP obtaining) could serve as mild reducing agent in the kinetics controlled synthesis of Ag and Au nanoplates or Pd and Pt NPs with different shapes. They also reported that a higher concentration of hydroxyl groups in poly (vinylalcohol) (PVA) than in PVP polymer led to the formation of NPs with thermodynamic stable shapes as result of a faster reduction reaction of metal ions. Tsuji et al. [13] established that in the case of Pt NPs synthesis by polyol method in the presence of NaNO₃ and PVP, the selective interaction between PVP and various crystalline planes of Pt NPs caused the growth of metallic seeds along {100} crystallographic direction resulting the formation of Pt NPs with shapes of triangle, tetrahedron and octahedron.

Bimetallic nanoparticles, composed of two different metals assembled in one entity, are of greater interest than monometallic NCs from both scientific and technological perspectives [2,4]. The bimetalization, that creates new properties, determines enhanced catalytic properties, especially selectivity for several chemical reactions [14,15]. Thus, bimetallic NPs can be used as catalyst for nitrate ions reduction from waste water (Pd-Cu, Pd-Sn, Pd-Ag, Pt-In etc.) [15-18], electrocatalyst for methanol oxidation at anode in PEM fuel cells (PtCo bimetallic NPs) [19], aerobic oxidation of glucose (Ag@Au) [20] etc.

Previously, we reported the synthesis parameters for the obtaining of monodisperse, spherical Pd NPs, with a very narrow size distribution between 5-10 nm and an average size of 7.5 nm, by polyol method using ethylene glycol as reducing agent and PVP as protecting agent [21]. The aim of the present work was to obtain bimetallic Pd-Ag NPs in

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order to be applied as catalyst for nitrates removal from waste waters by hydrogen reduction process. It was proved that Pd-Ag bimetallic NPs were effective catalysts for this reaction [22]. For this purpose, we apply the polyol method, using ethylene glycol as reducing agent and PVP as protecting agent, in order to obtain Pd-Ag bimetallic nanostructures with controlled morphology as stable colloidal suspensions.

Experimental part

Pd-Ag bimetallic NPs were synthesized by polyol method using different approaches: co-reduction and successive reduction. In a typical polyol procedure, the corresponding amount of polyvinylpyrrolidone (PVP, Sigma-Aldrich, M=10000), dissolved in ethylene glycol was placed in a three-neck flask equipped with a condenser. The ethylene glycol solution of the metal precursors was added to PVP solution by hot injection, when the reaction mixture reached the desired temperature. The reaction mixture was continuously purged with argon to ensure inert atmosphere during the reduction reaction of metal ions. The initial transparent solutions were turned to dark-colored because of the bimetallic NPs formation.

In the successive reduction method, firstly, silver NPs were obtained by the reduction of 5 mmol AgNO₃ (Merck, ≥ 99.9%) at 140°C, 1h and followed by the reduction of 5 mmol palladium chloride (Sigma-Aldrich, 99%), previously dissolved in concentrated aqueous solution of ammonia and ethylene glycol, and added to the reaction mixture at the same temperature. The total concentration of metal ions in ethylene glycol was 5 mM and the Ag : Pd : PVP molar ratio was 1 : 1 : 20.

Pd-Ag bimetallic NPs were also synthesized by coreduction approach in similar conditions. A solution of both inorganic salts dissolved in concentrated aqueous ammonia solution and ethylene glycol, was injected to the PVP solution in ethylene glycol, kept at the reduction temperature, 140°C for 90 min., in inert atmosphere. The synthesis conditions of different Pd-Ag samples are listed in table 1.

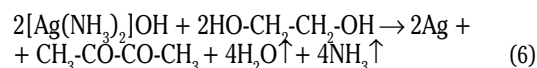
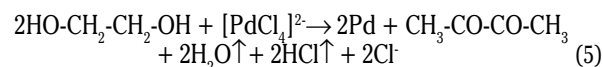
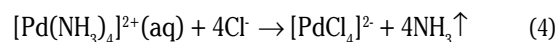
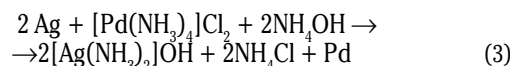
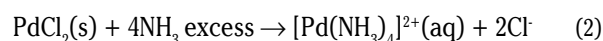
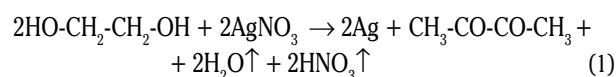
The Pd-Ag NPs were isolated by centrifugation and washed intensively with ethanol to remove the organic compounds. The samples were structural analyzed by powder X-ray diffraction (XRD) performed on a Rigaku Miniflex II diffractometer with Ni filtered CuKα radiation, in the range of 2θ, 20-70°, scan rate of 2°/min. and step size of 0.02°. The morphology of bimetallic NPs was investigated by transmission electron microscopy, using a high resolution transmission electron microscope (HRTEM) TECNAI F30 G² with a linear resolution of 1Å. X-Ray Photoelectron Spectroscopy (XPS) analyses were performed on VG Esca 3 Mk II spectrometer using Al Kα radiation source with energy of 1486.7 eV.

Results and discussions

Synthesis of bimetallic Pd-Ag NPs by successive reduction approach

In the first step of the successive reduction approach, silver ions, the less noble metal, was reduced for 1h at 140

°C to form PVP stabilized Ag NCs (1). The solution of tetrammine Pd(II) ions (2) was injected in the reaction mixture containing colloidal silver nanocrystals at 140 °C. The presence of silver NCs favored the reduction of palladium ions on the surface of Ag NCs probably by a metathesis reaction (3). A similar reaction was observed in the case of Pt ions reduction on the surface of spherical silver NPs and exploited for the obtaining of platinum empty nanospheres [23]. Even if Pd is more electropositive element than Pt, it is still noble enough to be reduced by metallic Ag. Moreover, for this step, we found that an excess of ammonia was necessary to avoid the precipitation of AgCl, which can occur because of the presence in the reaction mixture of both Cl⁻ and Ag⁺ ions resulted from reoxidation of silver NCs. On the other hand, it was previously proved by Uv-Vis spectra that the reduction of [Pd(NH₃)₄]Cl₂ in ethylene glycol produces [PdCl₄]²⁻ ions [21,24] as intermediary species (4 and 5). These two processes led to the nucleation and deposition of Pd nanocrystals on the Ag NPs surface. Finally, silver ions were reduced (6) with the formation of bimetallic Pd-Ag nanostructures. Figure 1 illustrates the formation steps of Pd-Ag NPs by successive reduction.



The HRTEM image revealed the obtaining of these nanostructures consisting in silver core covered by a metallic palladium shell decorated on the surface with clusters of silver nanocrystals. In the HRTEM image of Pd-Ag NPs obtained by successive reduction, it can be observed the fringes separated by 2.24 Å characteristic for {111} lattice spacing of face centered cubic metallic palladium and the fringes separated by 2.35 Å specific for Ag nanocrystals that belong to Fm3m symmetry group (fig. 2). The particle size distribution calculated by means of ImageTool software, by measuring around 100 particles from TEM images (fig. 3), displayed particles in the range of 30 – 58.5 nm with an average size of 41.5 nm (fig. 4). The selected area electron diffraction analysis showed the characteristic patterns of both metals and demonstrated the bimetallic NPs formation (fig. 2, insert). XRD patterns, also proved the bimetallic NPs formation with cubic symmetry (fig. 5). The chemical composition of the NPs,

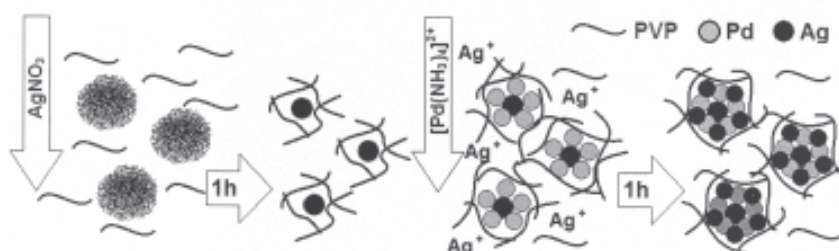


Fig. 1. The scheme of Pd-Ag NPs formation by successive reduction approach

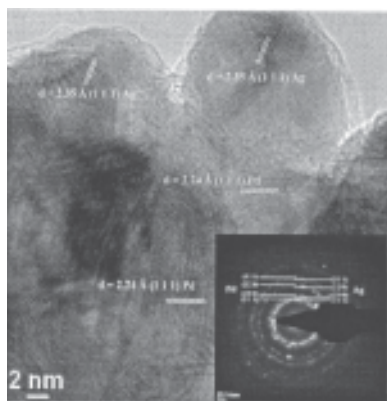


Fig. 2. HRTEM image of Pd-Ag NPs obtained by successive reduction. Inset, the SAED patterns

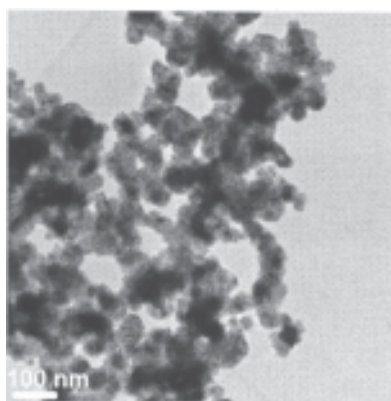


Fig.3. TEM image of Pd-Ag NPs obtained by successive reduction

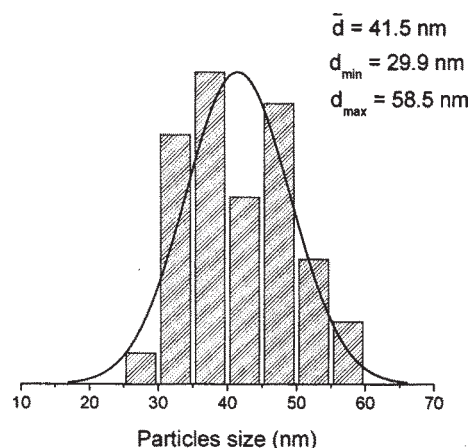


Fig. 4. The size distribution of Pd-Ag NPs obtained by successive reduction calculated from TEM image

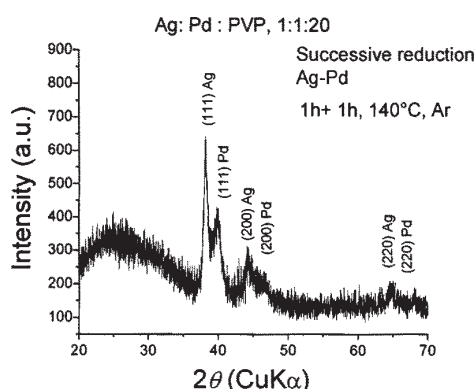


Fig. 5. XRD patterns of Pd-Ag NPs obtained by successive reduction

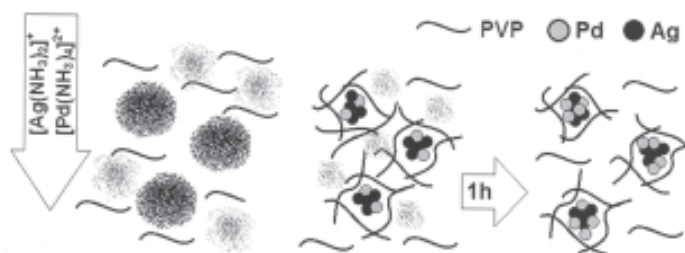


Fig. 6. The scheme of Pd-Ag NPs formation by coreduction

determined by EDX microanalysis was Pd 45.2% (at.) and Ag 54.8% (at.), with a slightly lower concentration in Pd than the theoretical one, explained by the high stability of $[PdCl_4]^{2-}$ ions. Although, very spectacular in morphology, the obtained nanostructures were too large for the purpose of our study.

Synthesis of bimetallic Pd-Ag NPs by coreduction approach

Different to the successive reduction, the presence of silver and palladium ammine complex ions in the reaction mixture allowed a simultaneous nucleation of both metals and a kinetic control of the bimetallic NCs growth process. The first step of the bimetallic NPs synthesis by coreduction was the nucleation of Ag (6) and Pd (4, 5). The high temperature of the reaction mixture at the moment of injection allowed an almost instantaneous nucleation of metallic silver, whereas the nucleation of palladium took longer. Once the silver seeds produced, the reduction of palladium ions around these seeds accelerated and led to the formation of Pd-Ag bimetallic nanostructures. The

second step is the growth of these nanostructures and the formation of bimetallic NPs. It is worth to mention that the obtained bimetallic NPs were formed by association of distinct Pd and Ag crystals and not their alloy. Figure 6 presents a scheme of the bimetallic Pd-Ag NPs formation by coreduction method. Surprisingly, considering the simultaneous presence of Ag and Pd precursors in the reaction mixture, this method has a good separation between the nucleation and the growth steps and allows a control of the morphology of bimetallic Pd-Ag NPs [25]. Because smaller bimetallic NPs were obtained by coreduction, the influence of different synthesis parameters (molar ratio of metallic cations / PVP, metallic cations concentration, molar ratio Pd/Ag and temperature) on the bimetallic NP morphology were studied (table 1).

As it was noticed in successive reduction method, a lower content of palladium in the NPs was awaited in the coreduction method too, because of the stability of the palladium complex ions. Different to the previous method, when silver dominated the surface of the NPs, a higher content in Pd was expected on the surface of NPs obtained

Sample	Initial molar ratio $Pd^{2+}:Ag^+:PVP$	Concentration of metal cations [mM]	Reaction parameters $T [^{\circ}C], t [h]$	Average particle size $d [nm]$	Atomic ratio Pd : Ag [at% : at%]
S1	0.5 : 0.5 : 10	5	140°C, 1.5 h	24	46.5 : 53.5
S2	0.5 : 0.5 : 20	5	140°C, 1 h	26	43 : 57
S3	0.5 : 0.5 : 20	2.5	140°C, 1 h	16	40 : 60
S4	0.9 : 0.1 : 20	5	140°C, 1 h	28	82 : 18
S5	0.8 : 0.2 : 20	5	140°C, 1 h	28	72 : 28
S6	0.5 : 0.5 : 20	5	110°C, 2 h	12-45	32 : 68

*Pd/Ag atomic ratio determined from EDX

Table 1
THE AVERAGE PARTICLE SIZE AND Pd/Ag ATOMIC RATIO OF BIMETALLIC NPs OBTAINED BY COREDUCTION APPROACH

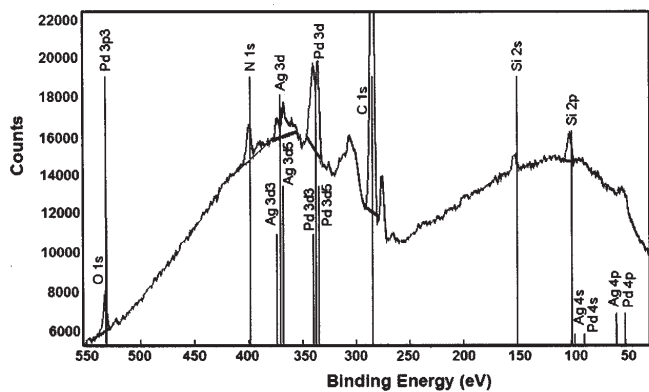
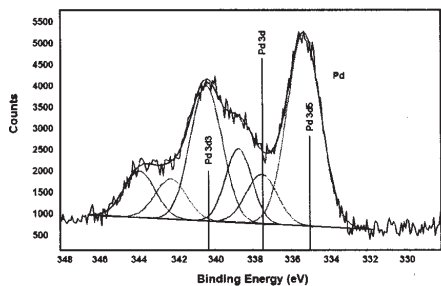
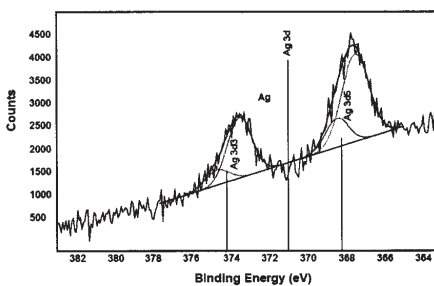


Fig. 7 XPS survey of the sample S1 (a). The Pd3d (b) and Ag3d (c) core level spectra

a)



b)



c)

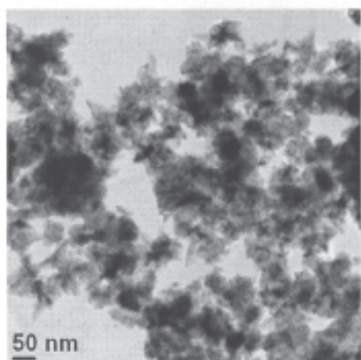


Fig. 8 TEM image of sample S1

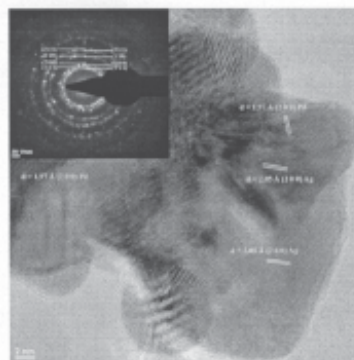


Fig. 9 HRTEM of sample S1 (insert SAED)

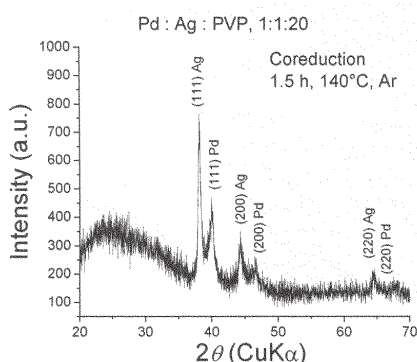


Fig. 10. XRD patterns of sample S1

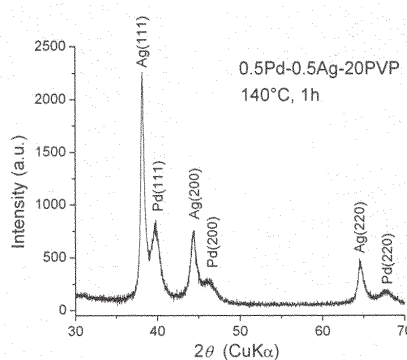


Fig. 11 XRD patterns of sample S2

by coreduction approach. This was confirmed by the XPS data for the sample S1. From XPS survey, the surface composition of Pd-Ag NPs synthesized by coreduction is 40%(at) Ag and 60%(at) Pd. The NPs surface was richer in Pd than the overall composition established by EDX analysis (Ag : Pd atomic ratio, 53.5 : 46.5). The XPS spectrum deconvolution showed the presence of Pd(0) besides PdO and PdO₂ species. The presence of the oxidized species on the surface of the NPs was predictable as long as the XPS analysis was performed without a surface cleaning.

A chemical composition closer to the theoretical one was obtained when low concentration of PVP was used. S1 sample, with a final composition Pd 46.5% (at), Ag 53.5% (at) was synthesized at metal cations : PVP molar ratio, 1 : 10. The morphology of this sample was different than all other samples, presenting dendritic NPs as TEM investigation proved (fig. 8 and 9). The low concentration of the capping agent, let different free facets of the NCs, favoring the growth of the NPs in multiple directions. Selected area electron diffraction (SAED) analysis (fig. 9

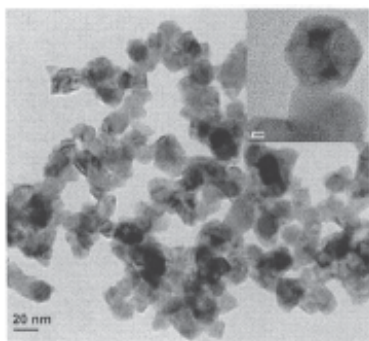


Fig. 12 TEM image of sample S3, inset HRTEM

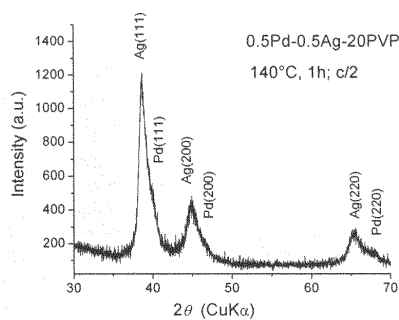


Fig. 13 XRD patterns of sample S3

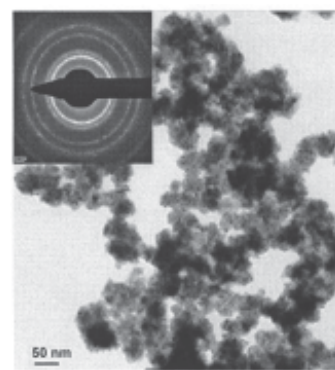


Fig. 14 TEM image of sample S4, inset SAED

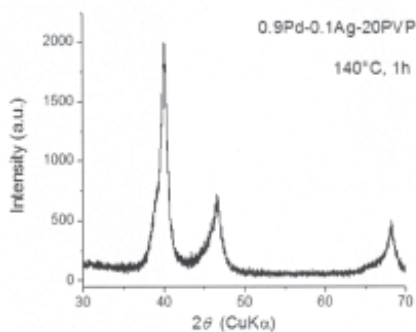


Fig. 15. XRD patterns of sample S4

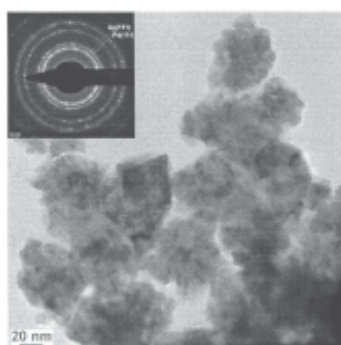


Fig. 16 TEM image of sample S5, inset SAED

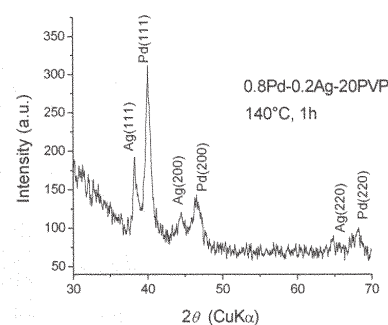


Fig. 17. XRD patterns of sample S5

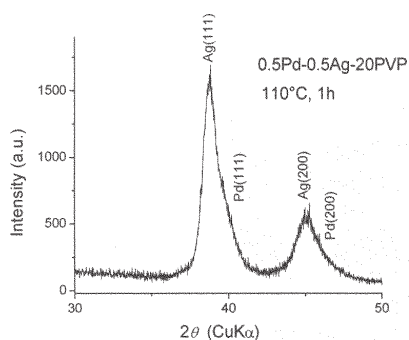


Fig. 18. XRD patterns of sample S6

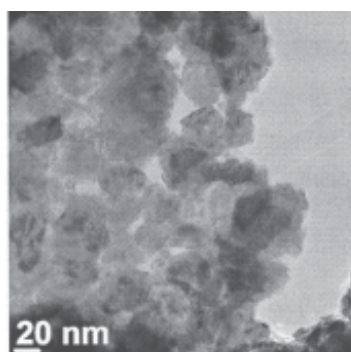


Fig. 19. TEM image of sample S5

inset), as well as XRD data (fig. 10) confirmed the obtaining of Pb-Ag bimetallic NPs.

By increasing the PVP content in the reaction mixture, no significant differences were noticed in the structure (fig. 11) of the S2 sample, only a decrease of Pd : Ag molar ratio.

A lower concentration of metal cations (S3 sample) led to polyhedral bimetallic particles with size ranging between 13 and 23 nm, with a narrow size distribution as TEM investigation has demonstrated (fig. 12). In this case, it can be noticed that crystallites, measured by X-ray diffraction, are smaller too (fig.13).

The variation of Pd : Ag molar ratio (0.9 Pd : 0.1, S4 and 0.8 Pd : 0.2, S5) did not modify significantly the structure and the morphology of Pd-Ag NPs (fig. 14 – 17). The average size of these bimetallic NPs was 28 nm.

When the reduction reactions were performed at lower temperature, 110°C, XRD results proved the formation of bimetallic NPs (fig. 18), but with a chemical composition even richer in silver than in the case of the samples obtained at 140°C, which can be assigned to the incomplete reduction of palladium ions. TEM investigation showed the formation of Pd-Ag NPs with polyhedral shape and larger size distribution in comparison with the samples prepared at 140°C because of a thinner shell of palladium (fig. 19)

Conclusions

Bimetallic Pd-Ag NPs were obtained by polyol method using ethylene glycol as solvent and PVP as protecting agent. The reduction of silver and palladium precursors was performed by successive reduction, as well as coreduction approach. For both methods, the chemical composition of obtained bimetallic NPs is slightly lower in palladium than the molar ratio of the precursors. This was assigned to the higher stability of palladium chloro-complexes formed in the reaction medium. In the successive reduction, the prepared bimetallic Pd-Ag NPs exhibited cluster structure, with the average size of 41.5 nm and the surface reach in silver. In the coreduction approach, when a mixture of Pd and Ag ammine complex was injected, smaller Pd-Ag NPs than in the case of successive reduction method, with the average sizes in the range of 16 – 30 nm were obtained. The bimetallic NPs obtained at a higher metal cations / PVP molar ratio presented a dendritic morphology, unlike the polyhedral one for the other samples. Smaller NPs were obtained at low concentration of metal cations. The Pd : Ag molar ratio had no influence on the size of the obtained bimetallic NPs. A lower reduction temperature caused a decrease of NPs crystallinity and a higher silver content than the

theoretical. Unlike the successive reductions, the NPs obtained by coreduction method had a higher palladium concentration on their surface. Based on all these observations, we have proposed for each method a mechanism for the formation of bimetallic Pd-Ag NPs.

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