

Preparation of Polyoxometalate-Stabilized Colloidal Solutions of Palladium Metal and Catalysts Supported on Them

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Abstract—Sols containing Pd(0) clusters with polyoxo anions are prepared by the reduction of colloidal solutions of polyhydroxo complexes of Pd(II) in the presence of Mo(VI), W(VI), V(V), and Nb(V) polyoxo anions. The cluster sizes varied within the limits of 1–10 nm depending on the nature of the polyoxo anion. The stability of sols toward coagulation depends on the ratio between the palladium and polyoxo anion amounts in solution and on the composition of the solvent. Supported Pd catalysts are obtained by the adsorption of particles from sols; Pd can exist in these catalysts as individual particles or associates or form filamentary structures.

INTRODUCTION

Colloidal solutions of metals (sols) are of great interest in catalysis [1–4]. Many procedures for metal sol preparation, including palladium sols, are known. The chemical method, which has many modifications, is most commonly used. According to this method, a metal salt solution is treated with a reducing agent in the presence of a stabilizing additive, such as an excess reducing agent, a soluble polymer, or a surfactant (see [1–5] and references therein). Sols themselves can be used as catalysts; however, they are more frequently intermediates in the production of supported metal catalysts [2, 3]. However, the presence of a stabilizing additive in a solution often complicates the preparation of supported catalysts. Such a stabilizing additive prevents the adsorption of a colloid on a support or contaminates the surface of metal particles [4]. These factors have a negative effect on the catalyst performance. Therefore, the development of new preparation procedures for metal sols and the search for efficient stabilizing additives to sols are topical problems.

Polyoxometalates are a broad class of polyoxo anions, which can be represented by the general formula $M_mO_y^{x-}$ (isopoly anions) or $X_nM_mO_y^{x-}$ (heteropoly anions), where M is Mo, W, V, and Nb (more rarely), or a mixture of these elements in the highest oxidation states, and X is a heteroatom [6, 7]. The simplest polyoxometalates $V_{10}O_{28}^{6-}$ (decavanadate), $Mo_7O_{24}^{6-}$ (heptamolybdate) and $H_2W_{12}O_{42}^{10-}$ (paratungstate) are formed upon acidification of $NaVO_3$, Na_2MoO_4 , and Na_2WO_4 solutions to $pH \sim 5$ [6]. It was found [8] that palladium metal can be retained in a colloidal state in a solution in the presence of the polyoxometalate

$PMo_{12}O_{40}^{3-}$; however, the properties of the sol were not examined.

We found that Pd(II) is retained as a stable colloid of the polyhydroxo complexes in aqueous solutions in the presence of polyoxometalates and Cl^- at $pH > 2–3$. For M = Mo, the optimum molar ratio is M : Pd = 2–0.5 [9]. The treatment of such solutions with reducing agents results in the formation of Pd(0) sols. The aim of this work was to examine Pd sols obtained in the presence of polyoxometalates and the applicability of these sols to the preparation of supported catalysts.

EXPERIMENTAL

The most convenient Pd(II) compound for the synthesis of sols in the presence of polyoxometalates is K_2PdCl_4 , which was prepared according to the procedure in [10]. In some instances, $PdCl_2$ of reagent grade was used, which was dissolved in Na_2MoO_4 or Na_2WO_4 solutions [9]. To synthesize polyoxometalates, $Na_2WO_4 \cdot 2H_2O$, $Na_2MoO_4 \cdot 2H_2O$, and $NaVO_3 \cdot 2H_2O$ of analytical grade and Nb_2O_5 of reagent grade were used. The $SiW_{11}O_{39}^{8-}$, $Nb_6O_{19}^{8-}$, $Nb_2W_4O_{19}^{4-}$, $\alpha_2-P_2W_{17}O_{61}^{10-}$, and $PMo_{12-n}V_nO_{40}^{(3+n)-}$ species were prepared as described in [11–15], respectively. Isopoly compounds of W, Mo, and V were not specially prepared; they were formed upon mixing a solution of an M compound with dry $PdCl_2$ or with a freshly prepared K_2PdCl_4 solution, which exhibits an acidic character. Other chemicals and solvents of reagent or analytical grade were used without additional purification.

Palladium(0) sols were prepared by the treatment of colloidal solutions of Pd(II) polyhydroxo complexes, which were prepared according to [9] with reducing agents. In a typical procedure, a K_2PdCl_4 solution

(or dry PdCl_2) was mixed with a polyoxometalate (or a metal compound) solution. The mixture was heated to the boiling point (it became dark, indicating that a colloidal solution of Pd(II) polyhydroxo complexes was formed), then cooled, and treated with a reducing agent (for example, by bubbling H_2) to the complete blackening of the solution. As a rule, initial solutions contained Pd(II) in a concentration of 0.010–0.025 mol/l. Before reduction, they were diluted to a required concentration of palladium.

Supported Pd catalysts were prepared by the adsorption of palladium particles on a support upon stirring a suspension of the powdered support in a sol. The course of adsorption was monitored visually by observing the disappearance of color of the sol with the subsequent chemical analysis of the catalysts. Ground γ -Al₂O₃ ($S = 120 \text{ m}^2/\text{g}$), a Norit carbon ($S = 1380 \text{ m}^2/\text{g}$), a Sibunit carbon ($S = 420 \text{ m}^2/\text{g}$), TiO₂ ($S = 70 \text{ m}^2/\text{g}$), SiO₂ ($S = 340 \text{ m}^2/\text{g}$), etc., were used as supports.

The size of palladium particles was determined using a JEM-100CX electron microscope (with an accelerating voltage of 100 kV; and with a point resolution of 0.45 nm). Drops of colloidal solutions were supported on carbon films formed on copper gauze. Before supporting, the catalysts were dispersed in ethanol using ultrasound with a frequency of 35 kHz. To construct bar graphs of the particle-size distribution, ~500 particles were sorted manually. Chemical analysis was performed by atomic absorption spectrophotometry.

RESULTS

Black colloidal solutions of Pd(0) were prepared by the treatment of polyoxometalate-containing solutions of Pd(II) polyhydroxo complexes with reducing agents. The following reducing agents were used: N_2H_4 , $NaOOCH$, KH_2PO_2 , $NaBH_4$, C_2H_5OH , CO , C_3H_6 , and H_2 . Stable sols were obtained by bubbling gaseous reducing agents, of which H_2 was the best. The process of reduction is convenient to monitor visually: the solution gradually darkened to black and the disappearance of a brown color indicated that the reaction was complete. Very dilute solutions ($[Pd] < 10^{-4}$ mol/l) were dark brown. Table 1 summarizes some of the results. The time of Pd(0) sol formation depends on the composition of polyoxometalates, the molar ratio polyoxometalate (M): Pd, and the temperature. At room temperature, polyoxometalate species with the respective central metal atom can be arranged in the following series according to the time (in minutes) required for the complete blackening of solution (visually determined) at $[Pd] = [M] = 0.005$ mol/l:

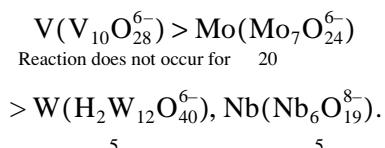


Table 1. Conditions and results of Pd(II) reduction in poly-oxometalate solutions. Pd : M = 1 mol/mol

Polyoxometalate	T, °C	[Pd], mol/l	Reducing agent	Result
$\text{H}_2\text{W}_{12}\text{O}_{42}^{10-}$	20	0.010	H_2	sol
$\text{V}_{10}\text{O}_{28}^{6-}$	60	0.010	H_2	sol
$\text{Nb}_6\text{O}_{19}^{8-}$	20	0.010	H_2	sol + precipitate
$\text{Nb}_6\text{O}_{19}^{8-}$	50	0.002	H_2	sol
$\text{SiW}_{11}\text{O}_{39}^{8-}$	20	0.010	H_2	sol
$\text{Nb}_2\text{W}_4\text{O}_{19}^{4-}$	50	0.010	H_2	sol
$\text{Mo}_7\text{O}_{24}^{6-}$	20	0.010	H_2	sol
$\text{Mo}_7\text{O}_{24}^{6-}$	50	0.010	C_3H_6	precipitate
$\text{Mo}_7\text{O}_{24}^{6-}$	20	0.010	CO	sol
$\text{Mo}_2\text{W}_4\text{O}_{19}^{2-}$ *	20	0.002	H_2	sol
$\text{Mo}_4\text{V}_2\text{O}_{19}^{4-}$ *	20	0.002	H_2	precipitate
$\text{V}_2\text{W}_4\text{O}_{19}^{4-}$ *	20	0.002	H_2	precipitate
$\text{PMo}_8\text{V}_4\text{O}_{40}^{7-}$	20	0.010	H_2	precipitate
$\text{PMo}_9\text{V}_3\text{O}_{40}^{6-}$	20	0.010	H_2	sol + precipitate
$\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}^{10-}$	20	0.010	H_2	sol + precipitate

* Empirical formula calculated from the amounts of starting compounds.

For $M = V$, the reduction of Pd(II) took place only in hot (above 60°C) solutions. The polyoxometalate type does not play a crucial role; the rate of sol formation primarily depends on the polyoxometalate ligand. If a mixed-ligand polyoxometalate is used, sol formation requires medium time. In some cases (for $M = Nb$, for mixed-ligand W–Nb polyoxometalates, and occasionally for $M = W$), the solution remained unchanged during the first minutes of bubbling hydrogen. Then, the solution abruptly blackened for ~10 s.

Table 2. Stability of water-organic Pd(0) sols to sediment formation. Reducing agent: H₂. [Pd] = 0.003 mol/l; Mo : Pd = 0.5 mol/mol

Solvent	Stability	Note
Water	1 year	Not tested for a longer time
98% methanol	—	Sol was not formed
90% methanol	30 min	—
50% methanol	8 days	—
90% acetone	—	Starting compounds are insoluble
40% acetone	3 days	—
90% dimethylacetamide	—	Sol was not formed
50% dimethylacetamide	6 h	—
90% hexamethylphosphoramide	6 months	Not tested for a longer time
90% sulfolane	—	H ₂ did not reduce
60% ethanol	6 h	—
90% acetic acid	—	Starting compounds are insoluble
60% acetic acid	6 h	—
90% 1,4-dioxane	—	Starting compounds are insoluble
60% 1,4-dioxane	—	H ₂ did not reduce
50% <i>n</i> -propanol	3 days	—
90% dimethylformamide	3 days	—
50% diethylamine	30 min	—
40% acetylacetone	—	Sol was not formed
50% pyridine	—	Sol was not formed
50% triethanolamine	3 days	—

The stability of Pd(0) sols depends on the solvent, the concentration of palladium, and the M : Pd ratio. In water at [Pd] = 0.01 mol/l, the solutions were stable (no sedimentation was observed for weeks) at $4 \geq \text{Mo : Pd} \geq 0.5$, $2 \geq \text{W : Pd} \geq 0.5$, or $\text{V : Pd} \geq 2$; at [Pd] = 0.001 mol/l, the solutions were stable at $\text{Mo : Pd} \geq 0.5$, $\text{W : Pd} \geq 0.5$, $\text{V : Pd} \geq 2$, or $\text{Nb : Pd} \geq 1$. An excess of a polyoxometalate and the presence of ballast substances (such as KCl) negatively affected the stability of sols toward coagulation. Therefore, the use of PdCl₂ is more appropriate for preparing sols in some cases. Of the polyoxometalates studied, Mo₇O₂₄⁶⁻ and Nb₂W₄O₁₉⁴⁻ provided the highest stability of sols, whereas the use of vanadium-containing polyoxometalates was unfavorable. For M = Mo, a maximum Pd concentration of 0.05 mol/l was attained in a hydrosol; this value is difficult to attain using other methods for the preparation of Pd(0) sols. At [Pd] = 0.005–0.001 mol/l, sols can be boiled, and some solu-

tions remained stable when heated to 180°C for several hours.

Various polar liquids can be used as solvents. Here, the main criterion is the solubility of the polyoxometalate and K₂PdCl₄ or PdCl₂. Water and hexamethylphosphoramide are the best solvents (Table 2).

According to electron microscopic and microdiffraction patterns, palladium metal particles were present in the sols. In sols with homoligand polyoxometalates, particles were round or weakly faceted. The average particle size (Figs. 1–3) increased in the following order for metal ligands:

$$\text{V (3.6 nm)} < \text{Mo (4.5 nm)} < \text{W (5.5 nm)}.$$

For M = W, both individual particles and their chains were observed in the sols. The concentration of palladium within the limits of 0.01 to 0.001 mol/l and the solvent exerted almost no effect on the particle size and morphology (water, water–methanol, and water–

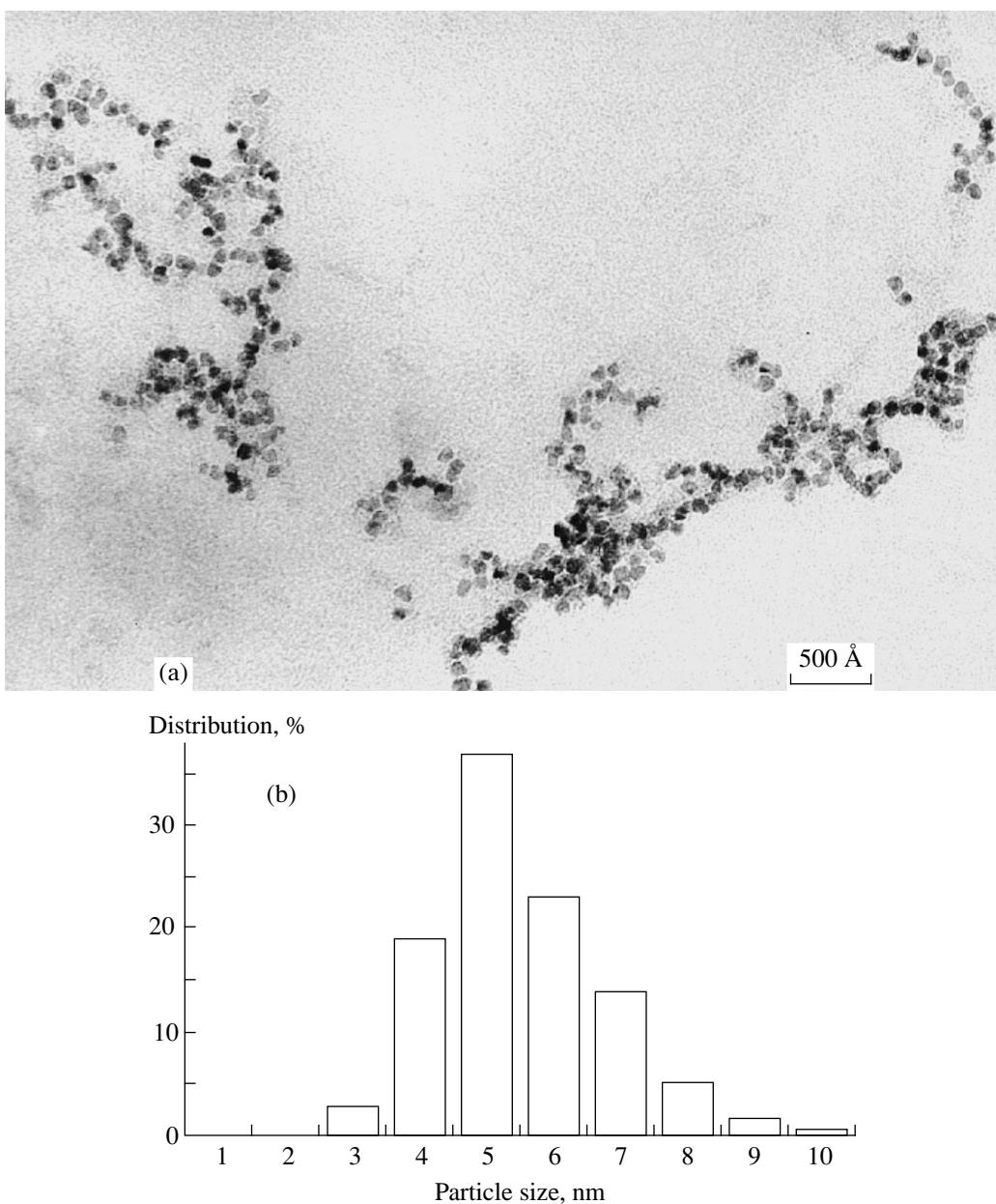


Fig. 1. (a) Electron microscopic pattern of particles in an aqueous sol at $[Pd] = 0.01$ mol/l and $Pd : W = 2$ and (b) a bar graph of the particle-size distribution.

hexamethylphosphoramide solvents were tested). A change in the $M : Pd$ ratio also affected the sol particle size only slightly. Thus, for $M = Mo$ in the range $Mo : Pd = 4-0.5$, the average particle size varied within the limits of 3.5 to 5.5 nm with a weak tendency for a decrease in the particle size as the above ratio increased. At $V : Pd = 2$, the average metal particle size was 3.6 nm, whereas the size of almost all particles did not exceed 3 nm at $V : Pd = 4$.

The capabilities of various supports to adsorb palladium particles from aqueous sols were examined at $Mo : Pd = 1$. According to the time it takes for

preparing 1% Pd supported catalysts at room temperature, the supports were arranged in the following series:

$MgO, MgSiO_3, BaCO_3, Cd(OH)_2$
15–60 s

> Norit > $\gamma\text{-Al}_2\text{O}_3$ > Sibunit
15–30 min 0.5–1 h 1–4 h

> TiO_2, SiO_2 , paper.
Do not absorb

Palladium particles were rapidly adsorbed by alkaline supports from a sol regardless of conditions. Conversely, acidic supports did not adsorb these particles

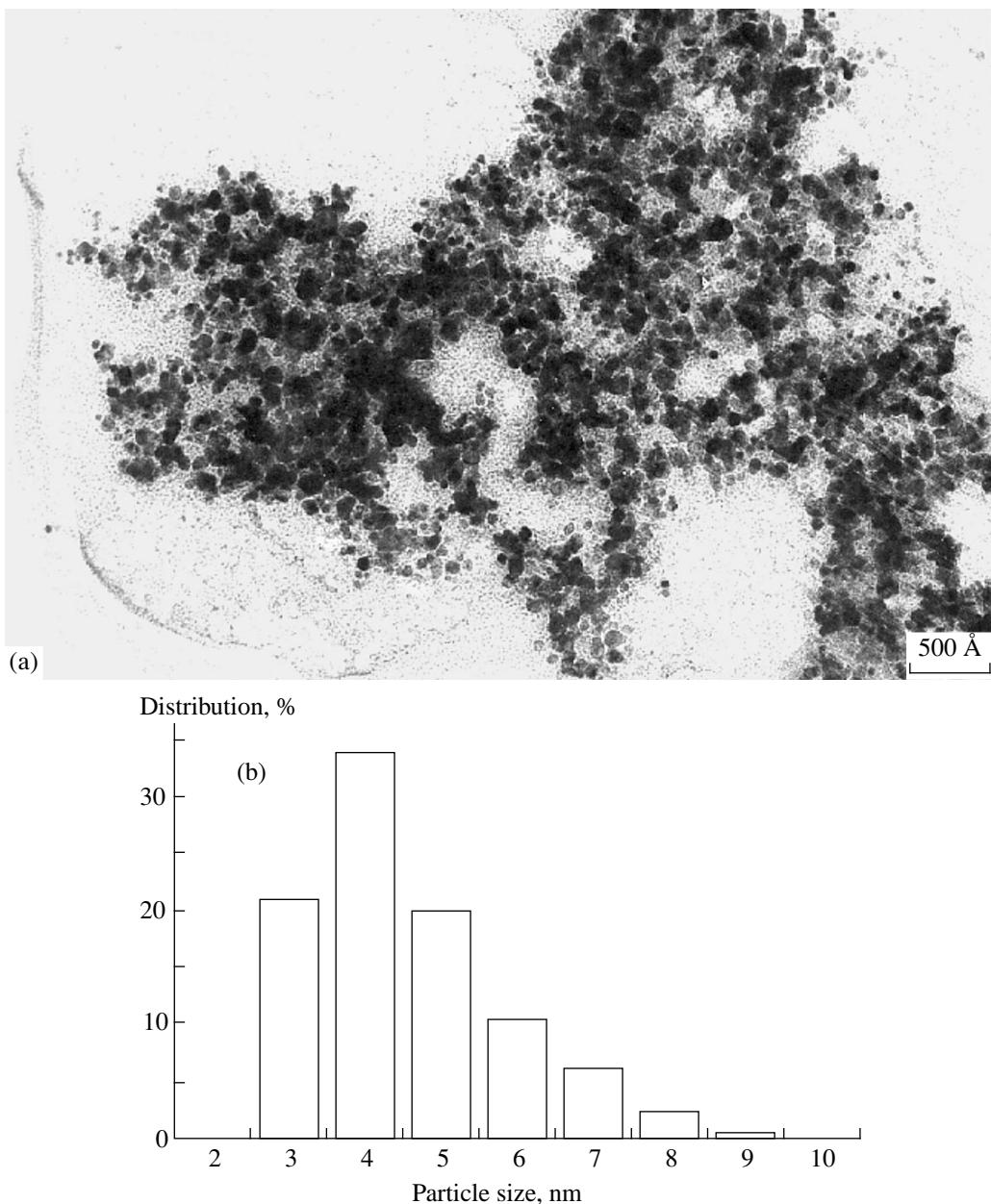


Fig. 2. (a) Electron microscopic pattern of particles in an aqueous sol at $[Pd] = 0.01$ mol/l and $Pd : Mo = 2$ and (b) a bar graph of the particle-size distribution.

regardless of conditions. The time and completeness of adsorption by neutral supports depended on the following conditions: temperature, $[Pd]$, particle size, the $M : Pd$ ratio, the support surface area, and the required palladium concentration in the catalyst. The following catalysts can be prepared: 5% $Pd/Norit$, 1–4% $Pd/Sibunit$, and 1–2% $Pd/\gamma-Al_2O_3$.

It follows from the electron microscopic patterns that the metal particle size remained unchanged upon supporting palladium from sols (Figs. 4, 5). Using the polyoxometalates $Nb_2W_4O_{19}^{4-}$ and $SiW_{11}O_{39}^{8-}$, 4% $Pd/Sibunit$ catalysts were prepared, in which palladium had a filament

structure with an average filament thickness of 3–6 nm (in the case of $SiW_{11}O_{39}^{8-}$, Fig. 6) or 5–15 nm (in the case of $Nb_2W_4O_{19}^{4-}$). Palladium was supported as particle associates on alkaline supports.

A polyoxometalate portion (2–50% of the initial amount) was also irreversibly adsorbed on a support. The degree of adsorption of polyoxometalates depends on the type of supports and on the nature of polyoxometalates. Polyoxometalate molecules can be adsorbed both directly on the support and on metal particles (being tightly bound to the particles already in the start-

ing sol). To evaluate the amount of polyoxometalates tightly bound to palladium particles, a sol with $[Pd] = 0.002 \text{ mol/l}$ obtained at $Mo : Pd = 4$ was treated with a mixture of KU-2-8 and AV-17-10 ion-exchange resins in H^+ and OH^- forms, respectively, for 1 h to remove cations and molecules of polyoxometalates unbound to colloid particles. According to the chemical analysis data, ~95% of Pd remained in solution, whereas K, Na, and Mo were not detected analytically. The sol was coagulated by boiling for a long time, and the Pd-containing black precipitate was filtered and washed. Using chemical analysis, 3.5 wt % of molybdenum was found in the precipitate; this value is ~1% of the Mo amount that was present in the starting solution.

DISCUSSION

In the presence of polyoxometalates, stable and reproducible Pd(0) sols were obtained only in the cases when the acidity of the solution before and after reduction corresponded to the stability region of the polyoxometalate, and a colloid of Pd(II) polyhydroxo complexes was formed beforehand. An ideal case is when the pH value of the solution before reduction is close to the upper pH limit of the stability of a chosen polyoxometalate (for example, pH ~5.5 for $Mo_7O_{24}^{6-}$ and $V_{10}O_{28}^{6-}$, pH ~8 for $SiW_{11}O_{39}^{8-}$, pH ~7 for $H_2W_{12}O_{42}^{10-}$, etc.), because the solution becomes acidified upon the reduction of Pd(II). If a colloid of Pd(II) polyhydroxo complexes was not formed or the reduction was performed in acidic ($pH < \sim 3$) solutions, Pd(0) black or a turbid unstable sol was produced. An analysis of well-known chemical methods for preparing noble metal sols demonstrated that, in the majority of cases, a solution of polyhydroxo complexes is a precursor of the sols. Thus, in principle, the method for the preparation of Pd(0) sols in the presence of polyoxometalates is no different from well-known chemical methods. Its novelty consists in the use of particular stabilizing agents, polyoxometalates, which can be considered as specific polyelectrolytes and soluble inorganic polymers.

The composition of polyoxometalates has an insignificant effect on the rate of formation and the stability of colloidal solutions of polyhydroxo complexes (polyoxometalate–Pd(II) chemical bonds were not found) [9]. However, it strongly effects the rate of formation and the stability of Pd(0) sols. It is likely that the composition of a polyoxometalate affects its adsorption ability to be adsorbed, in particular irreversibly, on a metal surface. The phenomenon of irreversible adsorption of polyoxometalates is known for Au [16], Ag [17], Ir [4], and a number of non-noble metals [18–20]; however, its nature is not understood. As a result of the interaction of polyoxometalates with colloid metal particles, clusters were formed, whose composition was determined for Ir at $M : Ir = 18$. For example:

$Ir_{\sim 300}^0 \cdot (P_4W_{30}Nb_6O_{123}^{16-})_{\sim 33}$, for which the average par-

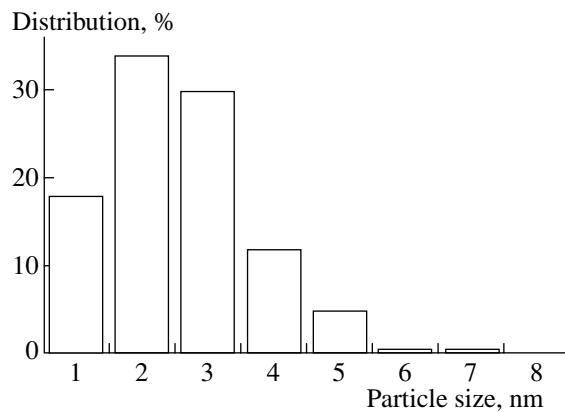


Fig. 3. Bar graph of the Pd(0) particle-size distribution in an aqueous sol at $[Pd] = 0.01 \text{ mol/l}$ and $V : Pd = 2$.

ticle size of Ir(0) was 2 nm [4]. For $Mo : Pd = 4$, we obtained clusters of the composition $Pd_{\sim 2300}^0 \cdot (Mo_7O_{24}^{6-})_{\sim 13}$ at an average particle size of 4 nm. Assuming that all polyoxometalate molecules are arranged on the surface of metal particles, this composition corresponds to the case when approximately one-seventh of the surface area of a Pd(0) particle is covered with polyoxometalate molecules, with a diameter of ~0.8 nm. The Cl^- ions can also exist on the surface of a cluster. A comparatively low particle surface coverage with polyoxometalate molecules can be due to the experimental conditions under which the coagulate was examined. However, the fact that tightly bound Mo was detected in the composition of clusters is indicative of the important role polyoxometalates play in preventing metal particles from coagulation. It should be noted in this connection that Mo(VI) additives prevent the agglomeration of particles in supported Pd catalysts [21, 22]. Note that the stability of the prepared Pd(0) sols cannot be explained by the presence of bulky alkylammonium cations, the use of a Pd(II)–polyoxometalate compound prepared beforehand, or the stabilization of metal particles in the matrix of a bulky polyoxometalate (the stability of sols even increased after the removal of unbound polyoxometalate molecules from a Pd(0) sol using ion-exchange resins), as was the case in Ir(0) sols in the presence of a tetrabutylammonium polyoxometalate [4]. It is likely that the stability of Pd(0) and Ir(0) sols in the presence of polyoxometalates is due to the same phenomenon associated with the strong adsorption of polyoxometalates on the surface of metal particles.

Pd(0) sols containing polyoxometalates are generally no different from Pd(0) sols prepared by chemical methods in particle size and morphology (for example, see [3] for sols prepared using sodium citrate). The particle size can be controlled within certain limits (1–10 nm) by varying the composition of polyoxometalates. It is likely that the effect of the polyoxometalate composition on

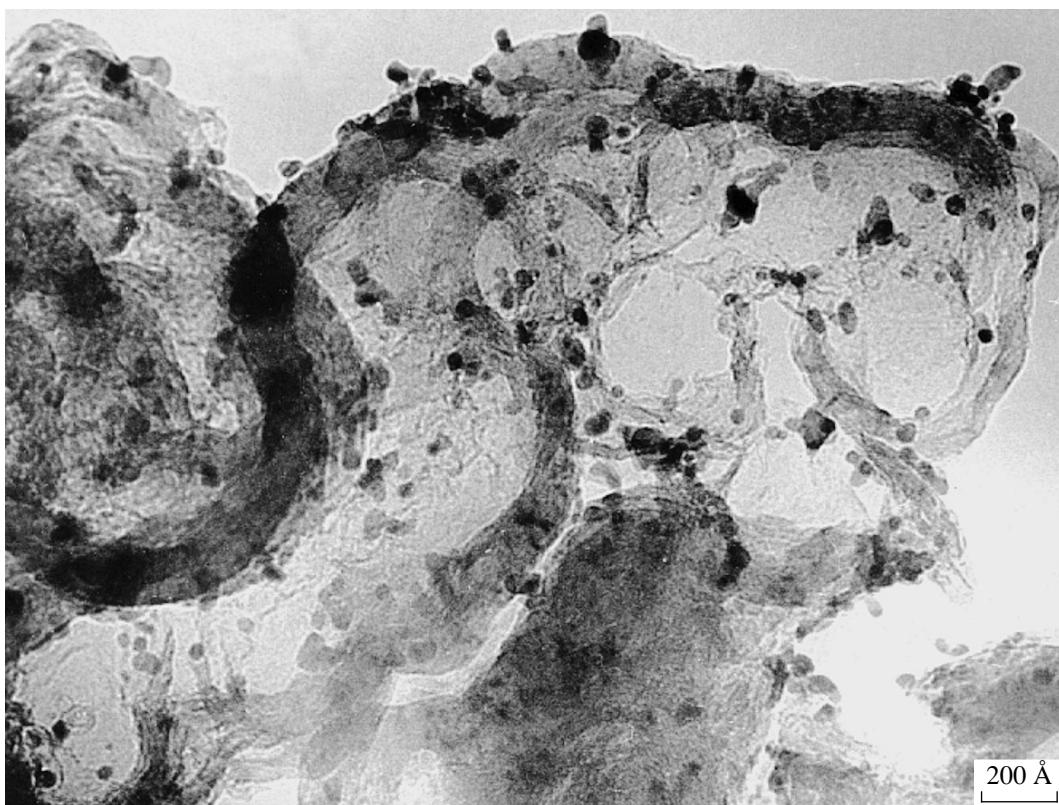


Fig. 4. Electron microscopic pattern of a 4% Pd/Sibunit catalyst prepared from an aqueous sol at $[Pd] = 0.01$ mol/l and $Pd : Mo = 2$.

the particle size is exhibited even at the stage of preparing the colloidal solution of a polyhydroxo complex. Variations in polyoxometalates and $[Pd]$ in starting solutions combined with $Pd(II)$ reduction under controlled conditions (temperature, composition of the reducing gas, etc.) can serve as additional tools for the preparation of sols with controlled particle sizes and narrower particle-size distributions.

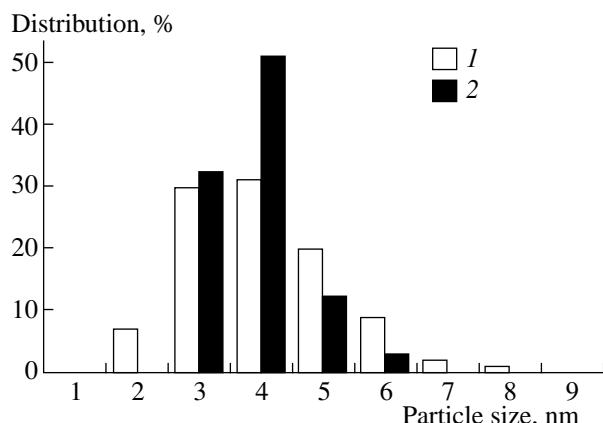


Fig. 5. Bar graph of the $Pd(0)$ particle-size distribution: (1) in an aqueous sol at $[Pd] = [Mo] = 0.001$ mol/l and (2) in a 1% Pd/Sibunit catalyst prepared from this sol.

The preferential adsorption of palladium particles from sols on alkaline rather than acidic supports indicates that metal particles are negatively charged as typical noble metal sols [2–4]. In this case, particles acquire a charge because of the presence of polyoxometalate molecules on their surface. Negative charges at palladium particles restrict the method for preparing supported catalysts with respect to acidic supports. At the same time, $Pd(0)$ particles (in particular, in the presence of polyoxometalates) are efficiently trapped by the corresponding precursor gels: silicic acid, titanic acid, and $Al(OH)_3$. In all cases, it should be taken into account that catalysts prepared by the adsorption of $Pd(0)$ particles from sols by supports contain some polyoxometalates or their decomposition products because polyoxometalates are known to be adsorbed, often irreversibly, on the supports [23, 24].

In some cases, a spatial network structure of filament palladium particles was formed on the surface of a support (Fig. 6), in which the particle size in the filaments can be controlled. We failed to find published data concerning the synthesis of catalysts of this kind. This structure provides additional opportunities to modify the properties of supported palladium catalysts. It should also be expected that the composition of $Pd(0)$ –polyoxometalate cluster particles will significantly affect the catalytic properties of palladium catalysts. Thus, the reversible adsorption of hydrogen found

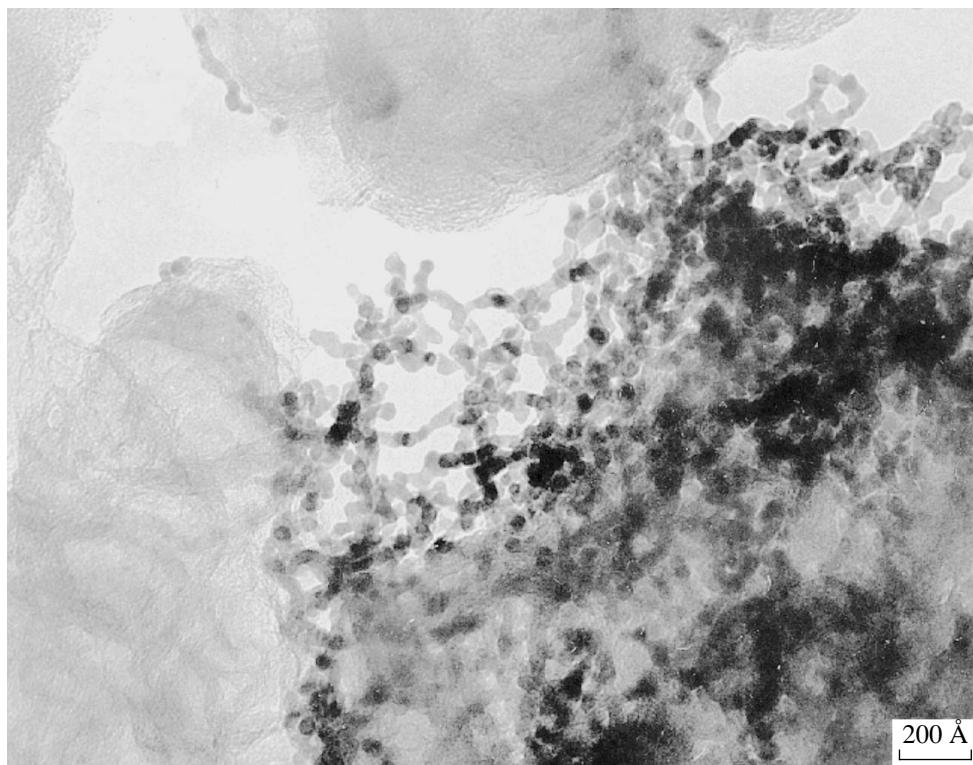


Fig. 6. Electron microscopic pattern of a 4% Pd/Sibunit catalyst prepared from an aqueous sol in the presence of the polyoxometalate $\text{SiW}_{11}\text{O}_{39}^{8-}$.

for Ir(0)–polyoxometalate clusters [4] and expected for Pd(II)–polyoxometalate clusters will depend on the composition and amount of polyoxometalates on the surface of particles, because different polyoxometalates exhibit different capabilities for redox reactions.

Thus, many polyoxometalates can be efficient inorganic stabilizing agents for sols in which metal–polyoxometalate clusters are sol-forming particles. These sols are suitable for the production of supported metal catalysts with controlled metal particle sizes.

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