The nature of colloidal platinum in aqueous solution: features of catalytic reactions

B. G. Ershov

Institute of Physical Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117915 Moscow, Russian Federation.
Fax: +7 (095) 335 1778. E-mail: ershov@ipc.rssi.ru

The specific features of the catalytic reduction of methylviologen by dihydrogen in water in the presence of platinum colloids synthesized by various methods are studied. The colloids prepared by the radiation-chemical reduction of $PtCl_4{}^{2-}$ in the presence of polyacrylate or polyphosphate as stabilizers and colloids prepared by the reduction with dihydrogen efficiently catalyze the reaction. The "citrate" colloids synthesized by the reduction of $PtCl_6{}^{2-}$ with citric acid are characterized by a prolonged induction period after which these colloids also gain the catalytic activity. We assume that the "citrate" platinum colloids are giant clusters with the close-packed metal core containing the "magic" number of platinum atoms (Pt_{561}), which are coordinated by the ligand molecules blocking the surface of the metal particle. In the presence of H_2, the ligand molecules are decomposed or removed from the surface, which is accompanied by the appearance of the catalytic activity.

Key words: colloids, nanoparticles, clusters, platinum, reduction, catalysis, optical absorbance.

Metal colloids and clusters, and first of all, those of platinum group metals, exhibit a high and selective ability to catalyze various reactions.[1,2] Elucidation of the mechanism of the catalytic effect and its interrelation to the structure and nature of clusters and colloids is among the most urgent problems.

We have previously[3] found that platinum colloidal particles prepared by various methods differ noticeably in catalytic activity. For example, the "radiolysis" colloids,* synthesized by the radiation-chemical reduction of Pt^{II} ions in the presence of polyacrylate, polyethyleneimine, polyphosphate, and other polyelectrolytes as stabilizing additives (solvate mechanism of protection), are oxidized to Pt^{II} by ~30% with dioxygen. This does not occur either for "hydrogen" colloids, which were prepared by the reduction with H_2 in the presence of the same stabilizers, or for "citrate" colloids prepared by the reduction of Pt^{IV} in the presence of citric acid. It was found that the "radiolysis" colloids reduce $Au(CN)_2{}^-$ under argon to colloidal gold but do not catalyze the reduction of $Au(CN)_2{}^-$ by H_2. By contrast, the "hydrogen" platinum colloids do not reduce $Au(CN)_2{}^-$ ions but catalyze their reduction by dihydrogen. These differences in chemical activity of the "radiolysis" and "hydrogen" colloids were explained by a noticeable difference in their size and shape. The first colloids are nonregular particles 1—3 nm in diameter, and the second colloids are spherical particles with a diameter of 5—8 nm. However, the "citrate" colloids also have a spherical shape, the almost monodispersed particle distribution, and an average diameter of 2.5 nm. Nevertheless, they differ substantially in properties from the "radiolysis" and "hydrogen" colloids. For example, they neither reduce $Au(CN)_2{}^-$, nor catalyze the reduction of $Au(CN)_2{}^-$ by dihydrogen. However, their preliminary exposure for ~20 min to an H_2 atmosphere initiates the oxidation by the $Au(CN)_2{}^-$ ions in argon. The "radiolysis" and "hydrogen" colloids catalyze isopropyl alcohol autooxidation to acetone, but the "citrate" colloids do not manifest this ability. The specific features of the reactivity of the latter were related to the oxidation of their surface by dioxygen during synthesis.

In this work, we continued a study of the catalytic activity of platinum colloids using the reduction of methylviologen by molecular hydrogen as an example. Previous and new results suggest that in the "citrate" colloids, unlike the platinum colloids with solvate protection ("radiolysis" and "hydrogen" colloids), the stabilizing ligands block active sites on the surface of platinum nanoparticles preventing some catalytic reactions.

Experimental

Various platinum colloids were prepared by previously described methods.[3]

In the case of the "radiolysis" colloids, the radiation-chemical reduction of Pt^{II} was performed by γ-irradiation from a ^{60}Co source of $(1—5) \cdot 10^{-4}$ mM solution of K_2PtCl_4 containing 0.01 mM isopropyl alcohol and $5 \cdot 10^{-4}$ mM sodium polyphosphate or polyacrylate as a stabilizer. The formed platinum sols have an irregular structure and rather broad size distribution

---

* Hereinafter we used the names of colloidal platinum particles accepted previously[3] according to the method of preparation.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 4, pp. 600—605, April, 2001.

with a predominant diameter of 1—3 nm. The average particle size is ~1.8 nm.

The same stock solution was used to prepare the "hydrogen" platinum colloids. With this purpose, the solution was saturated with H_2 at 1 atm and ~20 °C and stored for 1 day for complete Pt^{II} reduction. The size of the spherical particles that formed ranges from 5 to 8 nm, and the average size is 7.0 nm.

The "citrate" colloids were synthesized by a known procedure.[4] A 1% solution of Na citrate (25 mL) was added to a boiling $3 \cdot 10^{-4}$ *M* solution of K_2PtCl_6 (500 mL). After boiling for 1 h, the solution gained a brown color. After cooling to room temperature, the solution was passed through a column packed with the Amberlite MB 1 ion-exchange resin. Deionization of the solution decreases its electroconductivity from 500 ro 20 μSm cm^{-1}. The particle size of the "citrate" colloids with almost monodispersed distribution was 2.5 nm.

The reaction of H_2 with methylviologen (MV^{2+}) (dimethyl-4,4′-bipyridine) catalyzed by colloidal platinum was studied using the following procedure. A 0.1 *M* solution of NaOH (1 mL) and a $5 \cdot 10^{-2}$ *M* solution of methylviologen (1 mL) were added to an evacuated solution (10 mL) containing the catalyst, and then H_2 (1 atm) was let in. The concentration of reduced methylviologen was determined spectrophotometrically by the absorbance of the $MV^{+\bullet}$ radical cation, which has an intense absorption band with λ_{max} = 600 nm ($\varepsilon_{max} = 1.1 \cdot 10^4$ L mol^{-1} cm^{-1}).[5]

Electron microscopic studies were performed on a Phillips CM12 instrument equipped with an EDAX 9800 analyzer. Specimens were prepared by the deposition of a solution droplet on a copper-carbon support followed by drying. The specimens were prepared and studied without contact with air.

Results and Discussion

Catalytic reduction of methylviologen. The reduction of the methylviologen ion (MV^{2+}) with molecular hydrogen in an alkaline aqueous solution catalyzed by the "radiolysis" and "hydrogen" colloids occurs according to the overall reaction

$$2\,MV^{2+} + H_2 = 2\,MV^{+\bullet} + 2\,H^+. \qquad (1)$$

The standard potential of the MV^{2+}/MV^+ redox pair is −0.4 V,[6] *i.e.*, it is much more negative than that of the $2H^+/H_2$ pair equal to zero. In neutral and acidic media, the $MV^{+\bullet}$ radical cations are oxidized over platinum colloids to evolve hydrogen, *i.e.*, the reaction inversed to (1) occurs. Colloidal platinum and methylviologen are used in combination with other components in photoactive systems to obtain dihydrogen from water.[7] However, in an alkaline medium, due to a decrease in the concentration of H^+ ions, the potential of the hydrogen system becomes much more negative reaching ~−0.8 V. Under these conditions, the direction indicated for reaction (1) becomes possible.

Our experiments showed that, in the case of the "radiolysis" and "hydrogen" colloids, the $MV^{+\bullet}$ radical cation formed immediately after H_2 was let in an alkaline aqueous solution of MV^{2+}. Its appearance is detected by the characteristic intense absorbance with λ_{max} = 600 nm and shoulders at 580, 660, and 730 nm (Fig. 1). The reaction is accelerated when the concentrations of colloidal platinum and methylviologen increase. In the presence of $1.0 \cdot 10^{-4}$ *M* colloidal platinum and $5.0 \cdot 10^{-3}$ *M* MV^{2+}, when H_2 is let in and the solution is rigorously stirred, already 2—4 min after (the time necessary for measuring the optical absorption spectrum), more than 50% MV^{2+} ions are reduced. If the solution is not stirred, MV^+ is also formed immediately after hydrogen was let in. However, the reaction further develops much more slowly, which indicates that the dissolution of H_2 in water is the limiting stage of reduction. When O_2 is introduced, the $MV^{+\bullet}$ radical cations are oxidized, and the system returns to its initial state. The reduction-oxidation procedure can multiply be repeated. However, this results in a gradual accumulation of the products of methylviologen partial decomposition, the solution gains a green color, and an additional absorption band with a maximum at 390 nm appears in its optical spectrum (in air).

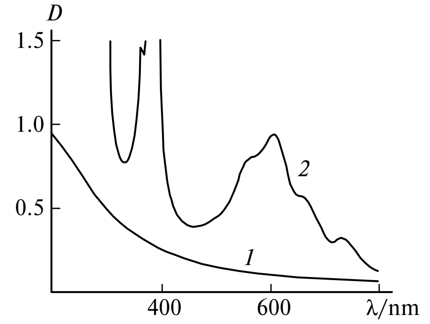

Fig. 1. Absorption spectra of a solution containing $1 \cdot 10^{-4}$ mol L^{-1} Pt^0 ("radiolysis" platinum colloids), $1 \cdot 10^{-2}$ mol L^{-1} NaOH, and $1 \cdot 10^{-4}$ mol L^{-1} methylviologen: evacuated (*1*) and after letting in H_2 (*2*).

The reaction with the "citrate" colloids is substantially different. In this case, at the indicated above composition of the solution, an induction period of ~25 min is observed (Fig. 2). Then the $MV^{+\bullet}$ radical

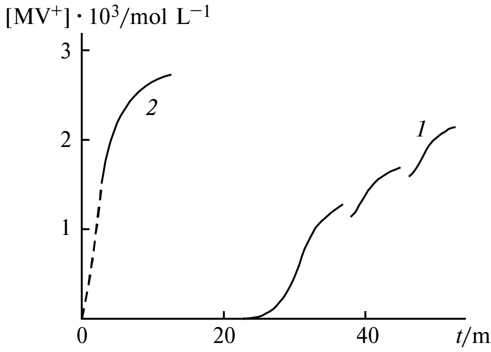

Fig. 2. Kinetic curves of formation of the $MV^{+\bullet}$ radical cation in the reaction of methylviologen MV^{2+} with hydrogen in the presence of the "citrate" platinum colloids (solid lines *1*). The break points correspond to mixing of the solution. Dotted line (*2*), a solution of the "citrate" platinum colloids pre-stored for 3 h in an H_2 atmosphere. Solution: $1 \cdot 10^{-4}$ mol L^{-1} Pt^0, $1 \cdot 10^{-2}$ mol L^{-1} NaOH, and $5 \cdot 10^{-3}$ mol L^{-1} methylviologen, saturated with H_2.

cations are formed, and the reaction rate at the initial stage increases. In the absence of stirring, after several min, the reaction is retarded, and a "pseudo-steady-state" state is achieved. After mixing the solution, a new jump in the formation of the reaction product is observed, and almost complete reduction of methylviologen present in the solution is gradually achieved by "steps". When the reaction is performed with intense stirring, the induction period is shortened only insignificantly during the time of smooth achievement of the limiting concentration of the reaction product. The reduction of the MV^{2+} ions with H_2 on platinum "microelectrodes" has, most likely, an electrochemical nature. In the absence of stirring, at a sufficiently high current density, the reduction rate increases to the value at which diffusion does not already provide the transfer of the reactant to the electrode. The reduction rate decreases because of the "transport" hindrances. Diffusion is a slower process than electrochemical reduction and, as a result, the kinetics is limited, as a whole, by the diffusion rate. In our opinion, this is a reason for the "steps" observed during methylviologen reduction by H_2 in the absence of stirring. When electrochemical reduction goes to the diffusion region, the further potential shift cannot already increase the rate of process because diffusion does not provide reactant supply to the electrode. During stirring the solution gets renewed in the near-electrode space, which results in a new jump of the reduction rate.

For the "citrate" colloids pre-stored in an H_2 atmosphere for 3 h, we did not observe an induction period in methylviologen reduction (Fig. 2), and they differ slightly in their catalytic activity from the "radiolysis" and "hydrogen" colloids.

Note that after storing in air the platinum colloids (including the "citrate" colloids pre-treated with H_2) do not loose their capability of catalyzing methylviologen reduction immediately after the removal of air and introduction of H_2.

We found that the "citrate" colloids, unlike "radiolysis" and "hydrogen," do not reduce $Au(CN)_2^-$ and do not catalyze reduction by H_2.[3] However, pre-storing for ~20 min in H_2 initiates the subsequent oxidation of colloidal platinum by the $Au(CN)_2^-$ ions in an Ar atmosphere.[3] It is noteworthy that the specific properties of the "citrate" platinum colloids appear in reduction reactions and also in oxidation processes. For example, unlike "radiolysis" and "hydrogen" colloids, they do not catalyze the autooxidation of isopropyl alcohol to acetone. However, they gain this capability after pre-storing in an H_2 atmosphere. This procedure was found to be universal for the transformation of the "citrate" colloids into colloids with the same catalytic properties as the "hydrogen" colloids in redox processes. The found peculiarities of the reactivity of the "citrate" colloids have previously[3] been ascribed to the oxidation of their surface by air oxygen during their synthesis. However, the data obtained indicates that the "citrate" colloids originally possess several chemical properties, which are not gained at a simple contact of the "radiolysis" and "hydrogen" colloids with air, *i.e.*, when their surface is oxidized, and are not returned to the "citrate" colloids being pre-treated with H_2 when they are oxidized by air oxygen.

Absorption spectra of colloids. The optical absorption of platinum nanoaggregates is due to the oscillation of surface plasmons (electron gas) and intraband electron transitions.[8,9] The optical properties depend substantially on the size and shape of the particles and are also very sensitive to the state of the surface. It has previously[3] been shown that the absorption spectra of the "radiolysis" and "hydrogen" platinum colloids are the same and almost independent of the form of the used stabilizer (sodium polyacrylate or polyphosphate). They represent single bands with a maximum at 215 nm, whose intensity decreases smoothly on going to the long-wave region, and the molar absorption coefficient at λ_{max} is equal to $6 \cdot 10^3$ L mol^{-1} cm^{-1} (±10%). In the recent work,[10] the platinum nanoparticles with a diameter of 1—3 nm were obtained by the reduction of $PtCl_6^{2-}$ with ethanol in the presence of poly-*N*-isopropylacrylamide in water-ethanol mixtures (according to the terminology used in this work, we define them as "ethanol" platinum colloids). They have the same optical parameters as those observed for the "radiolysis" and "hydrogen" colloids.

The optical spectra (normalized at 500 nm) of the platinum colloids studied in this work and "citrate" colloids are shown in Fig. 3. It is seen that the absorption spectra of the "radiolysis" and "hydrogen" colloids are virtually the same in the whole region of wavelengths from 200 to 800 nm and exhibit a maximum at 215 nm. The absorption typical of platinum nanoparticles predominates in the whole optical spectrum of a solution of the "citrate" colloids and increases smoothly and monotonically toward the UV region. However, the absorption band does not exhibit a maximum and is somewhat more

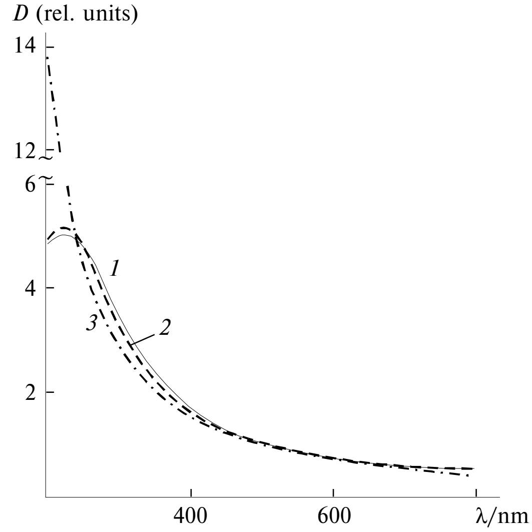

Fig. 3. Normalized absorption spectra of the "radiolysis" (*1*), "hydrogen" (*2*), and "citrate" (*3*) platinum colloids in an aqueous solution. The absorbance at 500 nm was accepted as unity.

narrow than that in the case of the "radiolysis" and "hydrogen" platinum colloids. The found distinction could be related to both the state (different from the "radiolysis" and "hydrogen" colloids) of the surface of these nanoparticles and the presence of chemical compounds, which were formed during the reduction of the platinum ions and were not completely removed by purification, in the solution along with sols of "citrate" platinum. However, the deionization of the solution with the Amberlite MB 1 ion-exchange resin decreases its electroconductivity (see Experimental). The initial compounds and products appeared during the synthesis of the platinum colloids are almost completely removed. The residual electroconductivity corresponds to the maximum concentration of the unreacted citrate ions of $\leq 10^{-6}$ mol L^{-1}, which does not explain the sufficiently intense absorption at ~200 nm. We found that the repetition of the purification procedure has no noticeable effect on the absorption spectrum of a solution of the "citrate" colloids. It is noteworthy that the optical spectrum of the "citrate" colloids is smooth and has no inflections and special points, which could be expected if it was a sum of the spectral components. Therefore, it is reasonable to assume that the observed absorption spectrum is due, in fact, to the particles defined by us as "citrate" colloids. They behave as specific particles or giant molecules for which the absorption by the metallic core and the absorption by the ligands on its surface cannot be separated as individual absorption bands.

The previous study[9] of the optical absorbance of spherical platinum nanoaggregates showed that when their diameter increases up to 10 nm the shape of the optical absorption band, position of its maximum, and absorbance remain virtually unchanged. The calculated optical parameters (the position of a maximum and absorbance) agree well with the experimental values for the "radiolysis," "hydrogen," and "ethanol" colloids with spherical particles 1—3, 5—8, and 1—3 nm in diameter, respectively. The absorption bands of sols with the particle diameter >20 nm are broadened and shifted to the long-wave region, and their intensities decrease with an increase in the particle size. In the case of needle-like particles, an additional band appears, which is shifted to the visible region when the particles elongate. Thus, theoretical calculations do not predict differences in the absorption spectra of the "citrate," "radiolysis," "hydrogen," and "ethanol" colloids.

The absorption spectrum of the "citrate" platinum colloids changes depending on the exposure time in an aqueous solution saturated with hydrogen. The absorption intensity (Fig. 4) at $\lambda \leq 250$ nm decreases and at longer waves, by contrast, increases. The solution darkens. Several hours after, the spectrum stops changing. This resulting spectrum is a smoothly descending absorption from the UV to visible region with an inflection at ~230 nm. This spectrum can be deconvoluted to a broad band with a maximum at 220—230 nm, which is imposed by the smoothly increasing to the UV region absorption without a maximum. The electron microscopic study shows (Fig. 5) that, when the "citrate" colloids (with the size distribution of particles close to the monodispersed distribution and an average diameter of 2.5 nm) are treated with H_2, they flocculate to form fractals (prolate chains and branched structures). The latter explains the more intense absorbance of the platinum particles in the visible region as compared to that of the "radiolysis" and

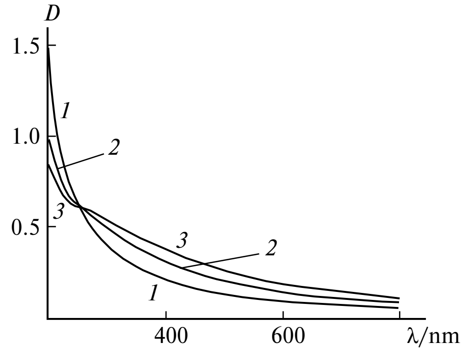

Fig. 4. Changes in the spectrum of optical absorbance of a solution of the platinum "citrate" colloids ($1 \cdot 10^{-4}$ mol L^{-1} Pt^0) saturated with H_2 at storage times of 0 (*1*), 60 (*2*), and 180 min (*3*).

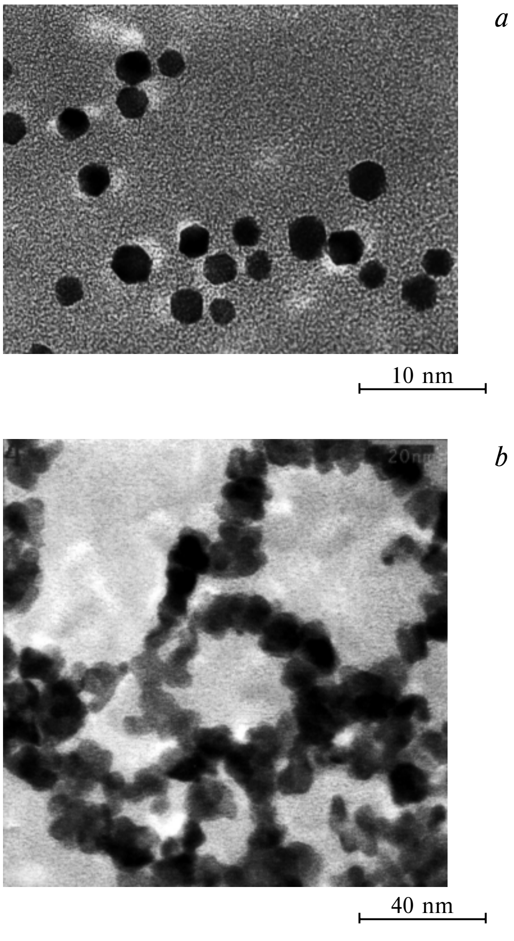

Fig. 5. Electron microphotographs of the starting platinum "citrate" colloids (*a*) and after their storage with H_2 for 3 h (*b*).

"hydrogen" colloids with approximately the same size (due to a great contribution of light scattering). In addition, the size of individual particles increases to 5—8 nm. The observed additional low-intensity absorption at $\lambda < 220$ nm (Fig. 4) corresponds, most likely, to compounds that composed the ligand shell of the "citrate" colloids and underwent chemical transformations or were simply displaced into the solution bulk due to the interaction of the platinum colloids with molecular hydrogen.

Nature of platinum colloids. In our opinion, the distinction in properties of the "radiolysis" and "hydrogen" platinum colloids, on the one hand, and "citrate" colloids, on the other hand, is due to the different states of their surface. This is likely related to different methods for their preparation and mechanisms of colloid stabilization. The first colloids exhibit a solvate mechanism of protection by polymers (polyelectrolytes, polyphosphates or polyacrylates), which are linked to the surface of metallic particles mainly by van der Waals forces. The second, *i.e.*, "citrate," colloids are metallic nanoparticles protected by anions of citric acid or products of its decomposition formed during the reduction of $PtCl_6^{2-}$ to the metal. In a "terminological" sense, they can be attributed to giant clusters containing a positively charged close-packed core including a preferential number of metal atoms. The main principle in organization of such idealized clusters is that the metal atoms in it form layers around the central atom, which are packed similarly to the packing in the bulky metal, and the cluster structure has a polyhedron shape typical of crystallites of this metal. Clusters of this type[11—14] form families of particles with the discrete, "magic" number of atoms equal to 13, 55, 147, 309, 561, *etc.* The metallic core of these clusters is stabilized by coordinated ligands and outer-sphere anions. The latter can be the determining distinction of a giant cluster from a metal sol, which has not, most likely, a specific structure of chemical bonds on the surface. Presently, representatives of all indicated and even more complex families of clusters have been synthesized and their structures have been solved by modern physical methods. Thus, the "citrate" platinum colloids can be attributed to particles with a specific size and a rigidly determined structure of chemical bonds between the ligand and surface. In fact, as was already mentioned, their size distribution is virtually monodispersed with an average particle size of 2.5 nm. The monodispersed character of distribution with the same size of platinum particles (2.0—2.5 nm) has previously been found in Ref. 15, where the "citrate" method of their preparation was also used. For the platinum cluster with this size and close-packed HCC structure, we can expect five layers of the metal atoms around one central atom and the total number of atoms of ~561. Of course, we imply the idealized cluster to which the real "citrate" platinum particles are very close in size. Anions of citric acid and products of its decomposition form, most likely, the ligand shell of the cluster thus providing its stability and the appearance of specific, as compared to standard colloids, properties. In particular, this relates to the catalytic properties and specific optical parameters, which differ from those for metal sols with solvate protection.

Unlike "the radiolysis" and "hydrogen" colloids, the "citrate" platinum colloids are incapable of catalyzing the reduction of methylviologen reduction by H_2 or oxidation of isopropyl alcohol to acetone.[3] This probably due to the fact that the catalytic sites on the particle surface are blocked by the ligand molecules. It is substantial that the ligand blocks the surface of the platinum particles with respect to its catalytic effect in both the reduction and oxidation processes. This indicates a strong chemical binding of the surface platinum atoms by the ligand molecules. In the presence of molecular hydrogen, the ligand protection decomposes due to either ligand displacement or their decomposition in the reaction with H_2. This is manifested as a change in the optical spectrum of the platinum nanoaggregates: the absorption of the "ligand" giant "citrate" platinum cluster is changed by the absorbance typical of sols of this metal. As a consequence, the formed sols gain the catalytic properties inherent in the "radiolysis" and "hydrogen" platinum colloids.

The author thanks Prof. A. Henglein (Germany) for fruitful discussion.

This work was financially supported in part by the Russian Foundation for Basic Research (Project No. 00-03-32107) and the Ministry of Science and Technology of the Russian Federation (Project No. 9.2.08 "Chemical Transformations with Nano- and Ultramolecular Systems").

References

1. L. N. Lewis, *Chem. Rev.*, 1993, **93**, 2692.
2. B. C. Gates, *Chem. Rev.*, 1995, **95**, 511.
3. A. Henglein, B. G. Ershov, and M. Malow, *J. Phys. Chem.*, 1995, **99**, 14129.
4. K. Aika, L. L. Ban, I. Okura, S. Namba, and J. Turkevich, *J. Res. Inst. Catal., Hokkaido Univ.*, 1976, **24**, 54.
5. P. A. Trudinger, *Anal. Biochem.*, 1970, **36**, 222.
6. G. W. Buxton, C. L. Greenstock, W. P. Helman, and A. B. Ross, *J. Phys. Chem. Reference Data*, 1988, **17**, 513.
7. E. Amouyl and P. Koffi, *J. Photochemistry*, 1985, **29**, 227.
8. J. A. Creighton and D. G. Eadon, *J. Chem. Soc., Faraday Trans. 1*, 1991, **87**, 3881.
9. N. L. Sukhov and N. B. Ershov, *Zh. Fiz. Khim.*, 2001, **75**, No. 8 [*Russ. J. Phys. Chem.*, 2001, **75**, No. 8 (Engl. Transl.)].
10. C. W. Chen and M. Akashi, *Langmuir*, 1997, **13**, 6465.
11. P. Chini, *J. Organometal. Chem.*, 1980, **200**, 37.
12. M. N. Vargaftik, V. P. Zagorodnikov, and I. P. Stolarov, *J. Chem. Soc., Chem. Commun.*, 1985, 937.
13. G. Schmid, *Chem. Rev.*, 1992, **92**, 1709.
14. M. N. Vargaftik, N. Yu. Kozitsyna, N. V. Cherkashina, R. I. Rudnyi, D. I. Kochubei, B. N. Novgorodov, and I. I. Moiseev, *Kinet. Katal.*, 1998, **39**, 1 [*Kinet. Catal.*, 1998, **39** (Engl. Transl.)].
15. D. N. Furlong, A. Launikonis, and W. H. Sasse, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 571.

Received July 13, 2000