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Effect of polyelectrolyte concentration on the rate of the catalytic reduction of methyl viologen with hydrogen in an aqueous solution in the presence of platinum nanoparticles

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The reduction of methyl viologen with hydrogen in water catalysed by platinum nanoparticles was studied; the reaction rate was found to decrease significantly as the concentration of sodium polyacrylate in solution was increased.

It is well known[1,2] that metal nanoparticles (primarily, platinum group metal nanoparticles) selectively catalyse many reactions. Determining the effect of concentration of a stabilising polymer additive on the catalytic activity of nanoparticles belongs to the most topical problems.

Previously,[3,4] it was reported that platinum nanoparticles prepared using different methods and different in the surface states are noticeably different in selectivity and catalytic activity. Here, we studied the kinetics of catalytic reduction of methyl viologen (MV^{2+}) with hydrogen in the presence of platinum nanoparticles and the effect of the concentration of polyacrylate ions on the rate of the reaction.

Platinum nanoparticles were prepared by the reduction of a 1×10^{-4} M K_2PtCl_4 solution containing 5×10^{-4} M NaOH with hydrogen. This solution was allowed to stand for a day until the complete reduction of Pt^{II} ions. The size of the resulting spherical particles varied within the range 5–8 nm, and the average particle size was equal to 7.0 nm. Note that particles with almost the same size (the average size of about 4.4 nm) were also prepared by the reduction of Pt^{II} ions with hydrogen in the presence of sodium polyacrylate (5×10^{-4} M). Sodium polyacrylate from Aldrich had a molecular mass of 5100. The OH^- ions and the polyelectrolyte had a stabilising effect on the resulting platinum sols. In the absence of these substances, the reduction of Pt^{II} ions with hydrogen was accompanied by the formation of a grey metal precipitate.

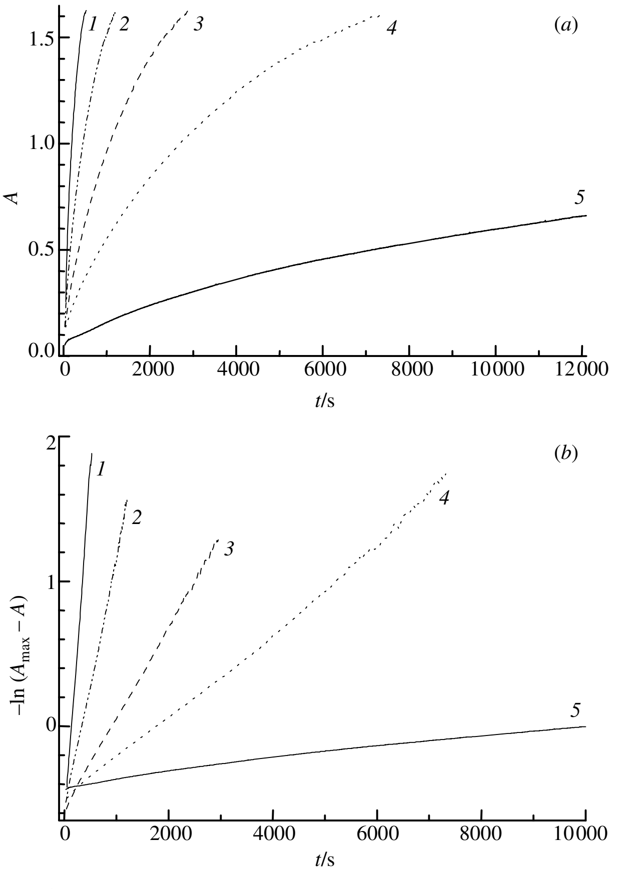

Figure 1 (*a*) Kinetic curves of formation of MV^+ radical cations (absorbance at 600 nm, $\varepsilon = 1.1\times10^4$ dm^3 mol^{-1} cm^{-1}) in the reaction of MV^{2+} reduction with hydrogen in the presence of 2×10^{-6} M Pt^0 (average sol size of 7 nm). Solution: 3×10^{-4} M MV^{2+}, 1×10^{-2} M NaOH, saturated with hydrogen (1 atm). Polyacrylate concentrations, mol dm^{-3}: (*1*) 0, (*2*) 1×10^{-4}, (*3*) 2×10^{-4}, (*4*) 3×10^{-4} and (*5*) 5×10^{-4}. Optical path length $l = 0.5$ cm. (*b*) The above kinetic curves on the $-\ln (A_{max} - A_t)$–t coordinates.

We studied the reaction kinetics of MV^{2+} reduction with hydrogen. Platinum nanoparticles prepared in the presence of an alkali were used as a catalyst. The addition of the polyacrylate was used to study its effect on the rate of the catalytic reaction. The experiments were performed in accordance with the previously published procedure. A 0.1 M NaOH solution (1 cm^3) was added to 10 cm^3 of an evacuated solution containing known catalyst and methyl viologen concentrations; next, hydrogen was passed. The concentration of reduced methyl viologen was determined by spectrophotometry. The absorption of the radical cation MV^+, which exhibits an intense absorption band with a maximum at 600 nm ($\varepsilon = 1.1\times10^4$ dm^3 mol^{-1} cm^{-1}),[5] was measured.

The electron microscopic studies were performed on a Phillips CM12 instrument equipped with an EDAX 9800 analyser. Test samples were prepared by applying a drop of the test solution to a copper–carbon plate followed by drying.

In alkaline media, the potential of the $2H^+/H_2$ pair is approximately equal to –0.8 V, which is noticeably higher than the potential of the MV^{2+}/MV^+ pair, which is –0.45 V.[6] Therefore, under these conditions, MV^{2+} ions are reduced by hydrogen in the overall reaction

$$2MV^{2+} + H_2 \longrightarrow 2MV^{+} + 2H^{+} \tag{1}$$

As a result, MV^+ radical cations are formed, which are detected by the appearance of a characteristic intense absorption band with a maximum at 600 nm and shoulders at 580, 660 and 730 nm.

Figure 1(*a*) demonstrates the kinetics of the appearance of the optical signal of the MV^+ radical cation, which is formed in reaction (1) in a 2×10^{-6} M aqueous solution of colloidal platinum Pt^0 saturated with hydrogen at different polyacrylate concentrations (the concentration was measured by the number of monomer units). It can be seen that the reaction rate of MV^{2+} reduction with hydrogen noticeably decreased with increasing polyacrylate content. The concentration $[MV^+]_t$ at the point t in time is equal to A_t/ε, where A_t is the absorbance of MV^+ and ε is the molar absorption coefficient at 600 nm. The methyl viologen concentration $[MV^{2+}]_t$ at time t is proportional to the value of $(A_\infty - A_t)$. Here, A_∞ is the absorbance of MV^+ upon the complete reduction of MV^{2+}. The value of A_∞ can also be calculated from the initial methyl viologen concentration $[MV^{2+}]_0$ in solution using the known value of ε for MV^+. It can be seen [Figure 1 (*b*)] that the kinetics of MV^{2+} reduction with hydrogen is adequately described on the coordinates of a first-order reaction equation. Figure 2(*a*) illustrates the value of k as a function of poly-

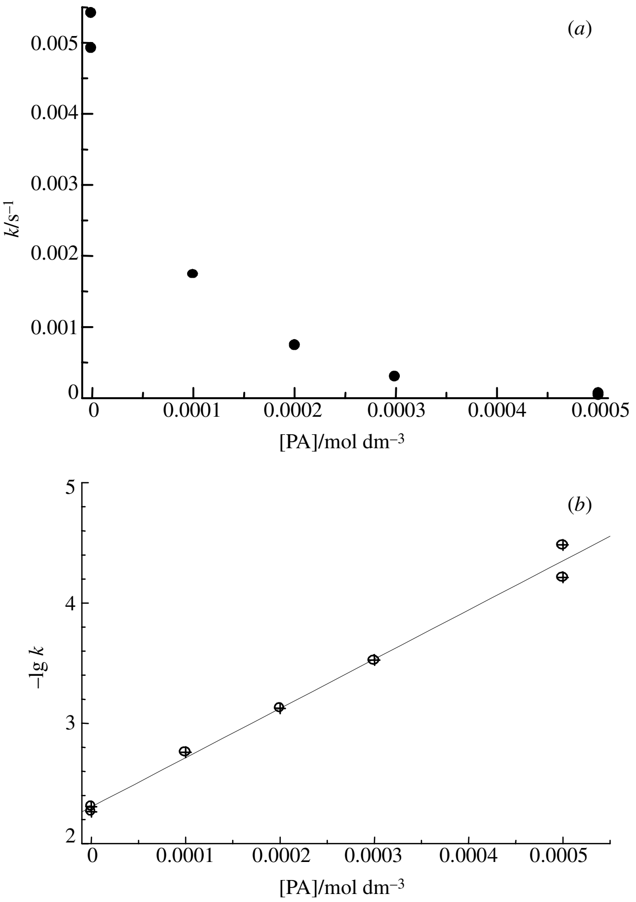

Figure 2 (*a*) Dependence of the effective reaction rate constant k of MV^{2+} reduction with hydrogen on polyacrylate concentration [PA]. (*b*) The above concentration dependence on the –lg(k)–[PA] coordinates.

electrolyte concentration (the determination error of k was no higher than ±10%). It can be seen that the addition of 1×10^{-4} M polyacrylate decreased the reaction rate constant by a factor of about three, whereas this constant decreased by almost two orders of magnitude in the presence of 5×10^{-4} M polyacrylate. The value of $-\lg k$ linearly increased with polyacrylate concentration [see Figure 2(*b*)]. The k–[PA] relationship is adequately approximated by the expression $k = k_0\exp(-\beta[\text{PA}])$, where k_0 is the rate constant of MV^{2+} reduction with hydrogen catalysed by platinum sols in the absence of polyacrylate, and β is a constant, which was calculated from Figure 2 to be equal to 9.4×10^3 dm^3 mol^{-1} (±10%).

Note that the character of the relationships found remains unchanged if the values of $\Delta A/\Delta t$, where ΔA is the change in the absorbance in the time interval Δt at the initial step of the catalytic reaction of methyl viologen reduction with hydrogen, are used in place of the constants k.

In our experiments, we used the same solution of platinum sols with an average size of 7 nm. It would be expected that the addition of polyacrylate, which is a highly efficient stabilizer, to the solution has no effect on the size of nanoparticles. This conclusion was supported by electron microscopic studies. Therefore, it is reasonable to relate the considerable decrease observed in the catalytic activity of platinum sols in the presence of polyacrylate to the sorption of the polyelectrolyte on the nanoparticle surface. The thickness of the sorption layer increases with polymer content; this makes the catalyst surface inaccessible to reactants and the removal of reaction products becomes difficult; thus, the reaction rate decreases.

References

1 L. N. Lewis, *Chem. Rev.*, 1993, **93**, 2692.
2 V. I. Bukhtiyarov and M. G. Slin'ko, *Usp. Khim.*, 2001, **70**, 167 (*Russ. Chem. Rev.*, 2001, **70**, 147).
3 A. Henglein, B. G. Ershov and M. Malow, *J. Phys. Chem.*, 1995, **99**, 14129.
4 B. G. Ershov, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 600 (*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 626).
5 P. A. Trudinger, *Anal. Biochem.*, 1970, **36**, 222.
6 P. Wardman, *J. Phys. Chem. Ref. Data*, 1989, **18**, 1637.
7 P. Galletto, P. F. Brevet and H. H. Girault, *J. Phys. Chem. B*, 1999, **103**, 8706.
8 S. De, A. Pal and N. R. Jana, *J. Photochem. Photobiol. A*, 2000, **131**, 111.

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