Catalytic Decomposition of Hydrazine in Weakly Alkaline Solutions on Platinum Nanoparticles

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Abstract—The kinetics and stoichiometry of catalytic decomposition of hydrazine in 0.01 M NaOH solutions in the presence of unstabilized ("gray" colloid) and stabilized with sodium polyacrylate ("brown" colloid) platinum nanoparticles were studied. The main decomposition products are ammonia and N₂ with H₂ impurity (up to 1.5%), i.e., hydrazine decomposition predominantly follows the stoichiometric equation $3N_2H_4 = 4NH_3 + N_2$. The catalytic activity was studied as influenced by nanoparticle size distribution. Despite higher nanoparticle dispersion, the catalytic activity of the stabilized "brown" colloid is lower than that of the "gray" colloid. The reaction mechanism is discussed.

Owing to high reduction activity, hydrazine is widely used in wet processes of the nuclear fuel cycle as stabilizer of actinide ions in lower oxidation states [1] or as nitrite scavenger [2]. The presence of hydrazine in aqueous waste is undesirable, because it often complicates treatment of liquid radioactive waste, in particular, in the course of chemical denitration [3]. It was found [4–6] that hydrazine is effectively decomposed in the presence of finely dispersed platinum catalyst supported on silica. However, this Pt/SiO_2 catalyst can be used only in acidic solutions because of low chemical stability of the support (silica) in alkaline and carbonate solutions. Hence, search for new catalytic materials stable in the above media is of particular importance.

Colloids of platinum group metals are highly selective catalysts for many chemical reactions [7, 8]. Platinum nanoparticles exhibit catalytic properties both in oxidation (e.g., of 2-propanol [9]) and reduction (reaction of molecular hydrogen with methylviologen [10]) processes. It was found [10] that the catalytic activity of platinum nanoparticles prepared by various procedures is considerably different.

In this work we continued a study of the catalytic properties of platinum nanoparticles, with hydrazine decomposition in weakly alkaline solutions as example.

EXPERIMENTAL

Preparation of Platinum Nanoparticles and Their Properties

Catalytic decomposition of hydrazine was studied using two types of colloids prepared by different procedures. In the first procedure, colloidal platinum was prepared directly in the reaction system by injection of an aliquot of H_2PtCl_6 solution into a temperaturecontrolled working solution of sodium hydroxide (10⁻² NaOH) containing excess hydrazine. In this case, platinum was rapidly reduced to the finely dispersed metal and the solution became gray due to platinum colloid; the "gray" colloid was stable within the entire experimental time. This colloid catalyzed decomposition of excess hydrazine.

In the second case, platinum nanoparticles were prepared according to the standard procedure [10] by reduction of H_2PtCl_6 or K_2PtCl_6 in 10^{-2} M NaOH solution with molecular hydrogen in the presence of sodium polyacrylate stabilizer. As a result, stable brown colloidal solution was prepared ("brown" colloid).

The size distributions of platinum nanoparticles in "gray" and "brown" colloids, determined by the atomic-force microscopy, are shown in Fig. 1. The particle size distribution in the "gray" colloid is non-uniform (Fig. 1a): it contains significant amount of 4-8-nm nanoparticles along with fairly coarse aggregates of 20-40 nm size. The gray color of the solution is determined by light scattering on these large aggregates. The "brown" colloid is virtually monodisperse (Fig. 1b), and the average particle size is about 4 nm.

The absorption spectra of both colloids are shown in Fig. 2. The "brown" colloid exhibits specific absorption in the near-UV region, which monotonically decreases with increasing wavelength. Such a spectrum, typical of fine colloids with the particle size less



Fig. 1. Atomic-force microscopic patterns and size distribution of platinum nanoparticles. (a) "Gray" colloid and (b) "brown" colloid.

than 10 nm, is determined by intraband electronic transitions [11]. There is no absorption maximum in the case of stabilizer-free "gray" colloid, and the smooth shape of the spectrum indicates that the total absorption of the colloid solution is predominantly due to the light scattering on the coarse particles.

Experimental Procedure

The kinetic experiments were performed in a temperature-controlled glass reactor equipped with a reflux condenser to prevent evaporation of the working solutions. The reaction system was stirred with a magnetic stirrer with a controllable stirring rate. The catalytic decomposition of hydrazine was initiated either by addition of an aliquot of H_2PtCl_6 solution into the working solution ("gray" colloid) or by injection of the required amount of N_2H_4 into the "brown" colloid solution. Aliquots (0.1 ml) of the working solutions were sampled at certain intervals in the course of the experiment. The current concentration of hydrazine in solution was determined spectropho-

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tometrically with *p*-dimethylaminobenzaldehyde (DMAB) [12].

The stoichiometry of catalytic decomposition of hydrazine in the presence of platinum colloids was studied by analysis of the gaseous reaction products, performed on a Chrom 5 chromatograph equipped with a 2-m column packed with zeolite 5A (0.4-0.5 mm particle size) and a katharometer (argon carrier gas, 30 ml min⁻¹ flow rate, room temperature).



Fig. 2. Absorption spectra of colloid solutions $(1 \times 10^{-4} \text{ M} \text{ Pt})$: (1) "gray" colloid and (2) "brown" colloid.



Fig. 3. (a) Kinetic curves of catalytic decomposition of hydrazine in the presence of platinum nanoparticles ("gray" colloid of various concentrations) and (b) rate of catalytic decomposition of hydrazine as influenced by the concentration of the "gray" colloid at $[N_2H_4]_0 = 2 \times 10^{-3}$ M, [NaOH] = 0.01 M, $T = 74^{\circ}$ C. (a) Colloid concentration, M: (1) 5×10^{-6} , (2) 1×10^{-5} , (3) 5×10^{-5} , and (4) 1×10^{-4} .



Fig. 4. Kinetic curves of catalytic decomposition of hydrazine in the presence of "gray" colloid (5×10^{-5}) at $[N_2H_4]_0 = 2 \times 10^{-3}$ M, [NaOH] = 0.01 M, and temperature, °C: (1) 30, (2) 40, (3) 56, and (4) 74.

RESULTS AND DICUSSION

Catalytic Decomposition of Hydrazine in the Presence of "Gray" Colloid

Our preliminary experiments showed that hydrazine completely decomposes within 2.5 h upon addition of H₂PtCl₆ (5×10^{-6} M) to the solution of N₂H₅OH (2×10^{-3} M) at 80°C. This is probably due to its catalytic decomposition on the Pt nanoparticles arising from stoichiometric reduction of PtCl₆²⁻ ions with excess hydrazine.

The kinetic curves of the catalytic decomposition of hydrazine $(2 \times 10^{-3} \text{ M})$ in 0.01 M NaOH solution in the presence of platinum $(5 \times 10^{-6} - 1 \times 10^{-4} \text{ M})$ at 74°C are shown in Fig. 3a. The kinetic dependences are linear, which suggests the zero reaction order with respect to hydrazine concentration. With increasing platinum concentration over the above range, an additional component of the first order is observed in the kinetic curves. These changes in the reaction order with respect to the hydrazine concentration are probably due to the adsorption mechanism of the heterogeneous-catalytic decomposition of this compound. The zero reaction order is realized when the concentration of the reacting species in solution is much higher than the volume concentration of the active catalytic centers. Under these conditions, the reaction rate is independent of the current concentration of hydrazine and is determined only by the concentration of platinum nanoparticles in solution.

To exclude uncertainty due to the variable reaction order, we performed a series of experiments at low platinum concentrations ($\leq 10^{-4}$ M), when the reaction order with respect to the hydrazine concentration was mainly zero. The reaction rate constants were calculated using the zero-order equation d[N₂H₄]/d $\tau = k_0$.

With increasing catalyst concentration in the 5×10^{-6} – 1×10^{-4} M range at 74°C, the rate of hydrazine decomposition increases:

[Pt], M	$k_0, \text{ mol } l^{-1} \text{ min}^{-1}$
$5 imes 10^{-6}$	1.03×10^{-5}
1×10^{-6}	1.92×10^{-5}
5×10^{-5}	9.04×10^{-5}
1×10^{-4}	$1.63 imes 10^{-4}$

In the $\ln [Pt] - \ln k_0$ coordinates, this dependence can be plotted as a straight line with a slope of 0.93 (Fig. 3b), which can be formally interpreted as an apparent reaction order with respect to the concentration of the active catalytic centers in the reaction system.

The effect of temperature on the kinetics of catalytic decomposition of hydrazine upon addition of H₂PtCl₆ is unusual. With decreasing temperature of the reaction mixture, the reaction order deviates from zero. Moreover, temperature changes in the 30-74°C range do not affect the rate of hydrazine decomposition (Fig. 4). Even for diffusion-controlled reactions, the temperature dependence of the reaction rate should correspond to the activation energy $E^* = 19 \text{ kJ mol}^{-1}$ [13]. In the case of catalytic decomposition of hydrazine in the presence of H₂PtCl₆, we failed to reveal a statistically significant effect of temperature on the reaction rate. This phenomenon is probably due to a decrease in the rate of platinum reduction to metal with decreasing temperature. The catalytic activity of hydrated platinum dioxide and oxide forming successively as the intermediates after addition of H₂PtCl₆ into the alkaline solution of hydrazine may be higher than the catalytic activity of metallic particles of the "gray" colloid, which is the final reduction product. These processes strongly affect the reaction kinetics, and thus the reliable interpretation of the experimental data obtained under given experimental conditions is impossible. At least, this unusual phenomenon requires additional study.

The catalytic activity of the "gray" colloid decreases at its reuse. This is probably caused by coarsening of platinum nanoparticles due to coagulation and by decrease in the active surface area of the catalyst in the absence of stabilizer. Certain fraction of the "gray" colloid precipitates as platinum black within several hours.

Catalytic Decomposition of Hydrazine in the Presence of "Brown" Colloid

The kinetics of the catalytic decomposition of hydrazine in the presence of "brown" platinum colloid ($[Pt] = 1 \times 10^{-4}-3 \times 10^{-4}$ M) stabilized with sodium polyacrylate (NaPA) was studied at 74°C, at $[N_2H_4 \cdot H_2O]_0 = 1.77 \times 10^{-2}$ M and [NaOH] = 0.01 M. The Pt/NaPA molar ratio was constant (1 : 2) in all the experiments. Under these experimental conditions, hydrazine decomposition is a zero-order reaction with respect to the hydrazine concentration (Fig. 5a). With increasing catalyst concentration in the $1 \times 10^{-4}-3 \times 10^{-4}$ M range, the rate of hydrazine decomposition increases:

[Pt], M	$k_0, \text{ mol } l^{-1} \text{ min}^{-1}$
1×10^{-4}	5.22×10^{-5}
2×10^{-4}	1.06×10^{-4}
3×10^{-4}	$1.66 imes 10^{-4}$

In the ln–ln coordinates, this dependence is linear (Fig. 5b). Similarly to the case of "gray" colloid, the slope corresponding to the apparent reaction order with respect to the concentration of the active centers is close to 1 (1.05), which is common for heterogeneous catalytic reactions in aqueous media.

Now, let us compare the rates of hydrazine decomposition in the presence of "gray" and "brown" colloids (Figs. 3 and 5). Despite smaller particle size and thus more developed surface area of the "brown" colloid, its catalytic activity is lower than that of the "gray" colloid by a factor of approximately 3. This decrease in the catalytic activity is probably due to blocking of the catalyst active surface with the stabilizer molecules (NaPA), which decreases the accessibility of the catalyst surface for the reacting compounds. Similar phenomenon was observed in catalyt-



Fig. 5. (a) Kinetic curves of catalytic decomposition of hydrazine in the presence of platinum nanoparticles ("brown" colloid of various concentrations) and (b) rate of catalytic decomposition of hydrazine as influenced by the concentration of the "brown" colloid at $[N_2H_4]_0 = 1.77 \times 10^{-2}$ M, [NaOH] = 0.01 M, $T = 74^{\circ}$ C. (a) Colloid concentration, M: (1) 1×10^{-4} , (2) 2×10^{-4} , and (3) 3×10^{-4} .



Fig. 6. Catalytic activity of the "brown" colloid at reuse, as influenced by the catalyst aging. (1) Freshly prepared colloid, (2) second run in 24 h, (3) third run in 72 h, and (4) colloid prepared in advance.

ic reduction of methylviologen with molecular hydrogen on platinum nanoparticles [14]. It was found that the reaction rate decreases linearly with increasing ln [NaPA].

The "brown" colloid solution can be prepared in situ by addition of H_2PtCl_6 aliquot to the working solution containing NaPA stabilizer and excess hydrazine. The catalytic activity of this freshly prepared "brown" colloid is significantly higher than that of the catalyst prepared by the procedure [10] involving reduction of platinum with molecular hydrogen. As seen from Fig. 6, the reused catalyst prepared *in situ* exhibits lower catalytic activity, which gradually decreases to the activity of the stabilized colloid prepared accoding to [10]. This decrease in the catalytic activity is probably caused by a decrease in the specific surface area due to the particle coarsening at colloid aging. This fact is confirmed by changes in the absorption spectra recorded at reuse of the colloids in the catalytic reaction; the intensity of absorption in the UV region decreases, whereas in the visible spectral range it increases. These spectral changes suggest that the colloid particle size and, thus, the contribution of the light dispersion increase (Fig. 2).

Chromatographic analysis of the gaseous reaction products was performed with the "brown" colloid prepared *in situ*. The main reaction product is nitrogen with 1–1.5% of hydrogen. It should be noted that hydrogen is liberated only in the first reaction stage (up to 30% conversion). Sodium hydroxide solution (0.01 M) containing 0.01 M N₂H₄ in the presence of platinum (1×10⁻⁴ M) and NaPA stabilizer (2×10⁻⁴– 2×10⁻³ M) liberates 0.30±0.06 mol of N₂ and (4.8±3)×10⁻³ mol of hydrogen per mole of decomposed hydrazine. These data suggest that the catalytic decomposition of hydrazine in weakly alkaline solutions in the presence of platinum nanoparticles follows the stoichiometric equation

$$3N_2H_4 = 4NH_3 + N_2$$

Certain amount of hydrogen in the gaseous products of hydrazine decomposition indicates that, initially, the following reaction also takes place:

$$2N_2H_4 = 2NH_3 + N_2 + H_2.$$

However, the contribution of this reaction to the overall process of hydrazine decomposition does not exceed 1.5%.

With certain approximation, we assumed that, similarly to catalytic decomposition of hydrazine in acidic solutions, the limiting stage of the process is the dissociation of hydrazine molecules adsorbed on the catalyst surface, followed by subsequent rapid reaction of sorbed NH_2^* radicals with hydrazine molecules in solution [5].

$$N_2H_{4_{ads}} \rightarrow 2NH_{2_{ads}}^*,$$

 $NH_{2_{ads}}^* + N_2H_{4_{sol}} \rightarrow NH_{3_{ads}} + N_2H_{3_{sol}}^*$

In turn, $N_2H_3^*$ radicals decompose to form ammonia and nitrogen:

$$2N_2H_{3_{sol}}^* \rightarrow N_2 + 2NH_3.$$

The rate of this reaction is very high $(k > 3 \times 10^{12} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1})$ [15].

Appearance of hydrogen in the reaction products is probably due to dissociation of sorbed NH^{*}₂ radicals followed by recombination of H atoms:

$$\begin{split} \mathrm{NH}_{2 \ \mathrm{ads}}^{*} &\to \mathrm{NH}_{\mathrm{ads}}^{*} + \mathrm{H}_{\mathrm{ads}}^{*}, \\ & 2\mathrm{H}_{\mathrm{ads}}^{*} \to \mathrm{H}_{2}. \end{split}$$

The rate of this process is significantly lower than the rate of reaction of NH^{*}₂ radicals with hydrazine molecules; this explains low yield of molecular hydrogen in the course of catalytic decomposition of hydrazine.

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