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Catalytic activity of SiO_2/Au heteronanoparticles in hydrogen peroxide decomposition reaction

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A comparative quantitative study of catalytic activity of Au nanoparticles and SiO_2/Au heteronanoparticles of various sizes in decomposition reaction of H_2O_2 aqueous alkaline solutions. It has been established that the catalytic activity increases with the dispersity of gold hydrosol particles and decreases as the diameter of silica dielectric core grows. The catalytic activity of SiO_2/Au heteronanoparticles depends on amount of gold on the silica surface and the heteronanoparticle size.

Проведено сравнительное количественное исследование каталитической активности наночастиц Au и гетеронаночастиц SiO_2/Au различного размера в реакции разложения водно-щелочных растворов H_2O_2. Установлено, что каталитическая активность растет при увеличении степени дисперсности частиц для гидрозолей золота и снижается при увеличении диаметра диэлектрического ядра кремнезема для гетеронаночастиц SiO_2/Au. Каталитическая активность гетеронаночастиц SiO_2/Au зависит от количества золота на поверхности кремнезема и размеров гетеронаночастиц.

Recently, the catalytic activity of metal nanoclusters is under intensive investigation. The unique structure of nanoclusters imparts to those a series of new properties as compared to usual metals and other chemical compounds. The specific features of nano- and microgeometry as well as a high specific surface of nanosystems offer new possibilities in development of active and highly selective catalysts [1]. Consideration of literature data shows that gold nanoparticles exhibit a high catalytic activity in gas phase oxidation reactions of carbon monoxide, while nanosized gold catalysts on silica and alumina surfaces prepared using impregnation show a high selectivity in 1,3-butadiene hydrogenation to buten. It is just the nanoparticle size that defines the catalyst activity [2–4]. In the methanol synthesis reaction, Ag and Au nanoparticles deposited onto zirconium oxide surface demonstrated a high catalytic activity [5]. Gold nanoparticles of less than 4 nm size exhibit a high catalytic activity in propylene epoxidation reactions [6]. Several works of past years are known devoted to catalytic activity of gold hydrosols in the standard reaction of hydrogen peroxide decomposition [7, 8]. The rate constant of hydrogen peroxide decomposition has been shown to depend on the dispersity of gold hydrosols.

Our previous studies have shown that the size of silica dielectric core as well as the SiO_2/Au heteronanoparticle structure influence considerably the properties of gold metal attached to its surface [9]. It seems to be of importance to ascertain to what extent the catalytic properties of gold nanoparticles will become apparent when the particles are fixed at silica nanoparticles of much larger size. To determine the effect of silica dielectric core size and structure on catalytic properties of gold nanoparticles, it is of interest to study the catalytic activity of SiO_2/Au heteronanoparticles in the liquid-phase reaction of hydrogen peroxide decomposition that is a well-studied model of catalytic redox reactions. Since in heterogeneous catalysis, the reaction rate change is associated with the intermediate chemical interaction between the reactants and catalyst, and at redox reactions, the intermediate interaction is defined by electron transitions between the catalyst and reactants, the processes running in the catalytic H_2O_2 decomposition are typical of that reaction kind. There are no literature data on the catalytic activity of such nanostructures. The purpose of this work is to study the catalytic activity of SiO_2/Au heteronanoparticles in the liquid-phase reaction of hydrogen peroxide decomposition and to compare it to the activity of gold hydrosols of various dispersity.

The monodisperse spherical silica particles were obtained using a procedure similar to that described in [10]. SiO_2/Au heteronanoparticles were obtained by colloidal synthesis according to procedures elaborated by authors [9]. Aqueous colloidal solutions of SiO_2/Au heteronanoparticles with various core diameters (40, 120, and 350 nm) at the same metal shell thickness (3 nm) were obtained as well as those of SiO_2/Au heteronanoparticles with SiO_2 diameter of 40 nm and separate gold clusters fixed at the surface thereof. The metal shell on the core surface is uncontinuous. Therefore, the shell thickness means an "effective" one determined from the ratio of total volume of gold nanoparticles to the core surface area [9]. Gold hydrosols with particle size of 2, 3, and 10 nm were prepared using the colloidal synthetic methods [11]. The SiO_2 and Au particle sizes were determined by transmission electron microscopy using an EM-125 microscope at 100 kV accelerating voltage and a JEOL-820 scanning electron microscope. The samples were prepared according to the standard procedure including application of the nanoparticle solutions onto copper films coated with a carbon film and removal of the excess solution using filter paper.

The catalytic activity of SiO_2/Au heteronanoparticles, gold hydrosols, and SiO_2 nanoparticles in the standard reaction of hydrogen peroxide decomposition was studied in a water thermostat at 25±0.5 °C. Gold concentration in all the solutions under study was the same and amounted $3\cdot10^{-6}$ g-atom per liter. The concentration of colloidal SiO_2 solutions was selected to be equal to SiO_2 concentration in the solutions of SiO_2/Au heteronanoparticles and amounted 10^{13} particles per liter. The catalytic activity was studied in alkaline aqueous solutions according to [7]. In a dry flask, the necessary volume of the colloidal solution to be studied was mixed with water up to 30 ml volume, 2.7 ml of 0.4 M NaOH solution and 2 ml of 3% H_2O_2 solution were added. To analyze, the reaction mixture samples of 2 ml volume were taken every 15 min, mixed with 0.4 ml of 1 M H_2SO_4 solution and titrated with 0.002 M $KMnO_4$ solution. The blank experiment (without the catalyst) was carried out in parallel.

Table. Averaged values of rate constant for H_2O_2 decomposition by SiO_2/Au heteronanoparticles and Au sols. The mean geometric parameters of particles are presented.

System studied	$k\cdot10^4$, s^{-1}
Au sol (10 nm)	1.7
Au sol (3 nm)	7.0
Au sol (1–2 nm)	11.3
SiO_2/Au (350/3 nm)	0.2
SiO_2/Au (120/3 nm)	0.62
SiO_2/Au (40/3 nm)	2.4
SiO_2/Au (40 nm/separate Au clusters)	0.12

Since the H_2O_2 decomposition is a first-order reaction, the reaction rate constant was calculated using the formula [7, 8]

$$k = \frac{2.303}{\Delta t}\, lg \frac{a}{a - x}$$

where a (ml) is the volume of $KMnO_4$ solution used in the preceding titration; $(a-x)$, the volume of the solution at the time interval Δt. The titrations were carried out in triplicate. The determination error for k was 6% on average and did not exceed 10%. The reproducibility in parallel experiments was approximately the same. The study results both of SiO_2 nanoparticles and SiO_2/Au heteronanoparticles by electron microscopy evidence that the surface structure and appearance of the particles remain unchanged during the kinetic experiments in alkaline aqueous solutions (pH = 11.4) where the H_2O_2 decomposition reaction runs. In the heteronanoparticles, the gold nanoclusters remain fixed at the SiO_2 surface, neither aggregation no dissolution of the SiO_2 nanoparticles take place. The initial SiO_2 nanoparticles do not show any catalytic activity.

As expected, the catalytic activity of gold metal hydrosols is in correlation with the particle dispersity. A similar dependence is seen clearly for SiO_2/Au heteronanoparticles, too (see Table). Comparison of the H_2O_2 decomposition rate constants for SiO_2/Au heteronanoparticles with 40 nm core diameter and various extent of the silica surface coating with gold nanoclusters (separate clusters, the shell thickness 3 nm) shows that the reaction rate is defined by Au amount fixed at the SiO_2 surface (0.12 and $2.4 \cdot 10^4$ s^{-1} respectively).

To explain the distinctions in the rate constant values for the system studied, let a simplified model be considered where SiO_2 spheres are coated with a thin continuous gold layer. Simple calculations based on the numerical concentration values (equal to the number of gold particles per unit volume) and geometric parameters of the nanoparticles show that the total area of the Au/H_2O interface in gold hydrosols amounts $9.2 \cdot 10^{16}$, $6.2 \cdot 10^{16}$, and $1.8 \cdot 10^{16}$ nm^2 (for 2, 3, and 10 nm size, respectively), while for heteronanoparticles, it is $2.5 \cdot 10^{16}$, $2.2 \cdot 10^{16}$, and $2.1 \cdot 10^{16}$ nm^2 (for 46, 126 and 350 nm particle size, respectively). These results explain well the reaction rate constant drop for gold hydrosols as the particle size increases, but the sharp drop of k (from $2.38 \cdot 10^{-4}$ to $0.2 \cdot 10^{-4}$) in the case of heteronanoparticles remains unexplained.

Another model seems to be more plausible. In its frame, the Au nanoparticles fixed at the support (SiO_2) retain their individual structure, including the high specific surface, in spite of the fact that it is decreased somewhat due to fixation at the silica surface area. Thus, the picture is reduced to the statement that Au nanoparticles become concentrated at larger SiO_2 spheres. Such concentrating should no doubt influence the hitting probability of H_2O_2 molecules onto the catalyst surface. Perhaps this may be the reason for the appreciable decrease of the reaction rate constant from $6.95 \cdot 10^{-4}$ s^{-1} (pure gold sol) and $2.38 \cdot 10^{-4}$ s^{-1} (SiO_2 diameter 40 nm) to $0.20 \cdot 10^{-4}$ s^{-1} (SiO_2 diameter 350 nm). It is to note that the k value is defined not only by the specific surface of Au nanoparticles on the SiO_2 surface but also by other factors. In particular, both SiO_2 and Au nanoparticles are known to have a complex fractal structure [12–14] that seems to favor the reactant diffusion to the catalyst surface and the start of elementary act of the catalytic reaction.

Thus, the experimental studies carried out in this work evidence that SiO_2/Au heteronanoparticles show a catalytic activity in the liquid-phase reaction of hydrogen peroxide decomposition. That activity is due to catalytic activity of gold nanoclusters. In the specific experimental conditions, the catalytic activity of heteronanoparticles is somewhat lower than that of gold hydrosols, although the k values are rather close to one another (1.7 and 2.4) for Au nanoparticles of 10 nm diameter and SiO_2 (40 nm)/ Au (3 nm) heteronanoparticles, respectively. On the other hand, in the heteronanoparticle structure, the catalyst is already fixed on the solid support, therefore, its use in specific practical tasks can be found to be more effective than in the case of metal nanoparticles.

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Каталітична активність гетеронаночастинок SiO_2/Au у реакції розкладання пероксиду водню

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Проведено порівняльне кількісне дослідження каталітичної активності гетеронаночастинок SiO_2/Au різних розмірів та складу і наночастинок гідрозолів Au у реакції розкладання водно-лужних розчинів H_2O_2. Установлено, що каталітична активність зростає при збільшенні ступеню дисперсності частинок для гідрозолів золота і зменшується при зростанні діаметру діелектричного ядра кремнезему для гетеронаночастинок SiO_2/Au. Каталітична активність гетеронаночастинок SiO_2/Au залежить від кількості Au на поверхні кремнезему та розмірів гетеронаночастинок SiO_2/Au.