Activation of gold due to the size effect for the isotopic reactions in molecular hydrogen

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Abstract. In this paper, it is shown that due to the size effect, we can create a catalytically active system based on gold nanoparticles. Gold, considered not so long ago, an inert metal, the transition in nanodispersed condition begins to show high catalytic activity in the reaction of ortho-para hydrogen conversion. It is shown that gold particle size from 1 nm to 40 nm possess high specific catalytic activity, which does not depend on the particle diameter in the size range. The assumption made that the hydrogen conversion proceed on magnetic mechanism, and, consequently, the gold particles become the new magnetic properties in comparison with diamagnetic massive metal.

1. Introduction

To test the catalytic properties of the various systems in this work uses two reactions involving molecular hydrogen:

\[
\begin{align*}
    \text{H}_2 + \text{D}_2 &\leftrightarrow 2\text{HD} \quad (1) \\
    \text{ortho-H}_2 &\leftrightarrow \text{para-H}_2 \quad (2)
\end{align*}
\]

Both reactions have practical applications in the industrial process of cryogenic distillation of hydrogen and the production of liquid para-hydrogen used as rocket fuel in the boosters and space launch complexes, super-heavy class. These reactions in the gas phase do not occur without catalysts, and therefore require catalytic reactors with highly efficient catalytic systems for the implementation of the above processes. Therefore, the development of highly efficient and affordable catalysts is relevant and timely task. One of perspective directions of creation of highly active catalysts is the synthesis of nanostructured systems based on nanoparticles of transition metals (Pt, Pd, Rh, Ru, etc.).

This paper presents part of the research of catalytic activity of gold nanoparticles activated by the dimensional effect, as it is well known that the massive metal is inert and has no catalytic activity in these reactions.

2. Results

2.1. Synthesis of gold nanoparticles

Gold nanoparticles were synthesized in solutions by six methods:

1. chemical reduction in reverse-micellar solutions (RMS);
2. radiation-chemical reduction in RMS;
3. chemical reduction by Tannin;
4. chemical reduction by citrate ions with heating by the method of Turkevich;
5. chemical reduction by citrate ions under UV light;
6. chemical reduction by citrate ions with the addition of an excess precursor and further reduction by hydrogen at room temperature.

1) \(\text{NPs}^{\text{RMS-Chem}}\) synthesis. Nanoparticles were synthesized by reduction of gold in RMS, which are an aqueous salt solution/surfactant/nonpolar solvent. As salt solutions 0.03 M, 1.1 M \(\text{AuCl}_3\) solutions, 0.3 M \(\text{HAuCl}_4\) solution were taken. As the surfactant used was bis(2-ethylhexyl) sulfo succinate (AOT, (Sigma-Aldrich). Isooctan was used as dispersion medium.
Chemical gold reduction was carried out under aerobic conditions with quercetin solution (Qr, 2-(3,4-dihydroxyphenyl)-3,5,7-trihydroxy-4H-1-benzopyran-4-one dihydrate, Merk). The reduction of gold ions occurs through a triple complex:

\[ \text{Qr} \cdots \text{O} \cdots \text{Au}^+ \]

2) **NPs\text{RMS-RadChem} synthesis.** Radiation-chemical reduction of gold was carried out in anaerobic conditions under the influence of \( \gamma \)-radiation of cobalt \( ^{60}\text{Co} \) source. A dose of 30 kGy. Solvent electrons and radicals on water-organic micellar solutions of gold salts act as a reduction agent. In the process of irradiation, the reaction of gold ions reduction initiates the process of metal nanoparticles formation:

\[ \text{Au}^+ + e_{\text{aq}} \rightarrow \text{Au}^0 \]

The size of gold nanoparticles depends on the diameter of the micelle pool, which characterized by coefficient of solubilisation \( \omega=[\text{H}_2\text{O}]/[\text{AOT}] \). In this paper, it is: 3.0, 4.0, 5.0, 8.0 – for the chemical reduction (NPs\text{RMS-Chem}), and: 1.5, 3.0, 5.0 – for the radiation-chemical reduction (NPs\text{RMS-RadChem}).

3) **NPs\text{Tannin} synthesis.** Gold nanoparticles were obtained by reduction of tannin (C\( _{76} \)H\( _{52} \)O\( _{46} \), «Purified» Germany). Gold hydrosol was prepared at room temperature by reduction of the 0.025 M 0.025 M precursor (AuCl\( _3 \), “Aldrich”) solution with tannin. Tannin in the reduction of gold goes into phlobaphene C\( _{76} \)H\( _{52} \)O\( _{49} \). The reaction takes place in an excess of tannin, so it can be assumed that the free metal ions in the colloidal solution are absent.

4) **NPs\text{Cit-T} synthesis.** The required amount of sodium citrate HOC\( _3 \)H\( _4 \)(COONa)\( _3 \) (CitNa\( _3 \)) added to the hot solution Na[AuCl\( _4 \)] (T = 368 ÷ 373 K). The resulting solutions were quickly brought to a boil in a water bath and boiled for 15 minutes with constant stirring (stirring speed – 800 rpm). Then the solutions were left in a water bath to cool to room temperature.

5) **NPs\text{Cit-h} synthesis.** The solution containing 2.0\( \cdot 10^{-4} \) M Na[AuCl\( _4 \)] (Aldrich) and sodium, citrate CitNa\( _3 \) with a concentration of 1.0\( \cdot 10^{-3} \) M, was deaerated using a vacuum rotary vane pump NVR-4,5D «Vacma», equipped with a nitrogen trap with a residual pressure of \( P = 1.5 \cdot 10^{-2} \) Torr = 2.0 Pa. After that, the solution in the quartz cell was irradiated with UV light of a low-pressure xenon pulse lamp with a total flow rate of \( I_{\text{UV}} = 6.0 \cdot 10^{20} \) Kvант/s = 1.0\( \cdot 10^{-3} \) Einstein/s. As result, there was a complete reduction of Au(III) ions.

6) **Reduction of gold NPs\text{Cit-H2}** was carried out in several stages: obtaining priming in the form of metal particles of gold by citrate ions; adding an excess of ions Au\( ^{3+} \) followed by hydrogen reduction at room temperature.

All solutions were prepared using deionized water (\( \kappa = 17.0 \text{\Omega} \cdot \text{m} \)).

Control of nanoparticle synthesis, and obtaining composite catalytic systems by sorption of gold nanoparticles on support, was carried out on the optical absorbance spectras obtained on spectrophotometers Hitachi U-3010, Varian Cary 100 Scan UV-Vis.

Fig. 1 shows the absorbance spectrum in the process of gold nanoparticles synthesis by various methods, Fig. 2 shows the absorbance spectrum in the process of gold nanoparticles adsorption on the support, which are \( \gamma \)-aluminum oxide (brand «Trilistnik», Redkino Catalyst Company).
2.2. Microscopy investigations

Sizes of the nanoparticles $\text{NPs}_{\text{Cit-hv}}$, $\text{NPs}_{\text{Cit-T}}$, $\text{NPs}_{\text{Cit-H2}}$ were determined on an Leo-912 AB Omega; C. Zeiss transmission electron microscope. Sizes of the nanoparticles $\text{NPs}^{\text{RMS-Chem}}$, $\text{NPs}^{\text{RMS-RadChem}}$, $\text{NPs}^{\text{Tannin}}$ were determined on an EnviroScope 5.30 atomic force microscope.

Fig. 3 shows AFM-images of gold nanoparticles and histogram of particle size. Fig. 4 shows TEM-images of gold nanoparticles in basic colloidal solution and nanoparticles supported on $\gamma$-$\text{Al}_2\text{O}_3$. 

Figure 1. Absorbance spectrum of synthesis of gold nanoparticles.

Figure 2. Absorbance spectrum of process of gold nanoparticles adsorption on support.

Figure 3. AFM-image of gold nanoparticles and histogram of particle size distribution.
The synthesized nanoparticles have spherical form and mainly narrow unimodal size distribution. Changes in the shape or size of nanoparticles during sample preparation and research of catalyst samples do not occur. This is confirmed by TEM-images (Fig. 4) and indicates that the particles are firmly fixed on the surface of the support. The results of microscopic studies of all samples are presented in Table 1.

### Table 1. Microscopy investigations results.

| Synthesis method | Dominating size, nm |
|------------------|---------------------|
| НЧ RMS-Chem       | 0.7±0.2             |
| НЧ RMS-Chem       | 1.4±0.3             |
| НЧ RMS-Chem       | 1.7±0.2             |
| НЧ RMS-Chem       | 4.2±0.7             |
| НЧ RMS-RadChem    | 0.9±0.2             |
| НЧ RMS-RadChem    | 1.1±0.3             |
| НЧ RMS-RadChem    | 1.0±0.2             |
| НЧ Cit-hv         | 4.6±0.8             |
| НЧ Cit-T          | 19.4±4.2            |
| НЧ Cit-T          | 28.3±3.1            |
| НЧ Cit-T          | 40.1±5.4            |
| НЧ Cit-H2         | 7.4±1.1             |
| НЧ Cit           | 14.4±2.2            |
| НЧ2 mm            | 20.5±4.5            |

2.3. **Hydrogen adsorption**

The active surface (the surface of the deposited metal) was determined by hydrogen adsorption. The measurements were carried out using volumetric method in a pressure range of from $1\cdot10^{-2}$ to $2\cdot10^{-1}$ Torr at $T = 77$ K.

The value of the active surface was calculated by the formula:

$$S_{H_2} = 2n_m \cdot N_A \cdot \sigma_{Me},$$

where $n_m$ is an amount of chemisorbed hydrogen corresponding to the plateau on the adsorption isotherm, $N_A$ is the Avogadro number, $\sigma_{Me}$ is the average area occupied by one surface metal atom on which one hydrogen atom is adsorbed. The value of $\sigma_{Me}$ for the gold is taken to be $6.51 \, \text{Å}^2$. 

![Figure 4. TEM-images of gold nanoparticles in basic colloidal solution (a) and nanoparticles deposited on γ-Al₂O₃ (b).]
Gold nanoparticles of all sizes from 0.7 nm to 40 nm are able to adsorb molecular hydrogen at 77 K. Based on the obtained experimental data, adsorption isotherms of a similar kind are constructed: a pronounced plateau is observed which is taken as a monolayer of chemisorbed hydrogen (Fig. 5).

Experiments to determine the fraction of weakly bound hydrogen on the surface of gold nanoparticles showed that all hydrogen is weakly bound and easily removed from the surface by pumping at the adsorption temperature. This is evidenced by the coincidence of primary and secondary adsorption isotherms (Fig. 5).

During the research it was revealed that hydrogen adsorption on gold nanoparticles is observed at higher temperatures, up to room temperature. However, when the temperature increases from 77 K to 110 K, there is a sharp decrease in the adsorption value.

On the example of a sample with a nanoparticle diameter of 19.4 nm, the ratio of the amount of adsorbed hydrogen and the amount of metal in the catalytic system was estimated.

The concentration of gold in the colloidal solution of nanoparticles was \( C_{Au} = 3 \times 10^{-4} \) M. According to the optical absorbance spectrums almost all gold nanoparticles were adsorbed onto the \( \gamma \)-Al\(_2\)O\(_3\) (Fig. 2). The nanoparticles deposition was carried out on the basis of the ratio of 5 ml of solution to 1 g of support. Then, the amount of metal on the surface of 1 g of the catalytic system is \( n_{Me} = 15 \times 10^{-7} \) mol. Taking into account the proportion of surface atoms \( \sigma \approx 8\%\), the number of surface gold atoms in 1 g of the catalytic system is \( n_{Me, surf} \approx 1.2 \times 10^{-7} \) mol.

From the experimental data on hydrogen adsorption it follows that the amount of adsorbed molecular hydrogen on the sample catalytic system (weight \( m = 0.7122 \) g) was \( n_m = 7.7 \times 10^{-7} \) mol H\(_2\) (Fig. 5). Thus, the catalytic system weighing 1 g is able to adsorb \( 10.8 \times 10^{-7} \) mol H\(_2\), which is 9 times the number of surface gold atoms. Assuming that all hydrogen (fully or partially) is adsorbed with dissociation of molecules, the amount of adsorbed hydrogen in the form of atoms and molecules exceeds the total amount of metal, which, it would seem, can not be. However, the obtained results can be explained both by the dissolution of partially dissociated hydrogen in the volume of nanoparticles and, more likely, by the manifestation of the effect of the hydrogen spillover to the support. Estimates for other samples showed that the amount of adsorbed hydrogen exceeds the number of surface gold atoms in particles from 4 to 17 times. Similar results are comparable with the results of the study of hydrogen spillover on catalytic systems Pt/Al\(_2\)O\(_3\) и Pd/Al\(_2\)O\(_3\) [1].
2.4. Catalytic activity

The reactions were studied under static conditions without gas circulation at an operation pressure of 0.5 Torr. The analysis of the gas mixture was carried out continuously by the method of thermal conductivity based on various rotational thermal conductivity of gas mixtures of hydrogen isotopes and protium ortho-para modifications heat transfer of the platinum filament heated by a current in a cylindrical vessel (cell). The working cell (1 on Fig. 6) is part of reaction volume, and the comparison cell (2 on Fig. 6) is filled with a mixture of the original composition. The volumes of both cells are equal, are in identical conditions, and are included in the Wheatstone bridge circuit (Fig. 6). Copper coils located next to each other, which prevents temperature drift during operation are used in the circuit to stabilize the microvoltmeter (3 on Fig. 6).

Specific catalytic activity ($K_{sp}$) is defined as the first-order rate constant ($k_0$) taking into account the number of molecules in the reaction volume at the reaction temperature ($N_T$) and divided by the catalyst active surface area ($S_{H2}$):

$$K_{sp} = k_0 \cdot \frac{N_T}{S_{H2}}$$

2.4.1. $H_2$-$D_2$ exchange

Protium-deuterium exchange reaction was studied in the wide range of temperature from 77 K to 530 K. All samples of catalytic systems based on gold nanoparticles ranging in size from 0.7 nm to 40 nm are shown high catalytic activity and have positive size-effect in $H_2$-$D_2$ exchange reaction [2]. Based on experimental data dependences of specific catalytic activity values on temperature are made in coordinates of the Arrhenius equation. (Fig. 7). Characteristic fractures conditionally divide the dependence graphs into two temperature regions, the reaction of which flows through various mechanisms with different values of activation energies. Because of experiments, it is shown that regardless of the method of obtaining nanoparticles, the reaction rate and the character of the kinetic curve coincide.
2.4.2. Ortho-para protium conversion

The ortho-para protium conversion reaction can proceed both by chemical and by magnetic mechanism, in which the change of the nuclear spin occurs under the influence of an inhomogeneous magnetic field.

The reaction was carried out at 77 K and 110 K. The results of experiments showed that all samples of catalytic systems showed extremely high catalytic activity, the value of which does not depend on the particle size and averages $K_{sp} = (3.9 \pm 1.2) \times 10^{14}$ molecules/cm$^2$/s, which exceeds the value of catalytic activity in the reaction of isotope exchange for small nanoparticles by 2-3 times, and for large nanoparticles with a diameter of 20÷40 nm to 400 times (Fig. 8).

Such a high value of catalytic activity of composite system based on gold nanoparticles is comparable with the most effective catalysts in the reaction of ortho-para protium conversion based on rare earth metals (Gd, Dy, Ho etc.), which by their nature have high magnetic moment values due to the presence of unpaired 4f-electrons. Thus, such a significant difference in the rates of reactions protium-deuterium exchange and ortho-para conversion of protium may indicate fundamentally different mechanisms of reaction. This proves that gold nanoparticles in contrast to massive metal have magnetic moment, which allows proceeding the reaction of o-p protium conversion on magnetic mechanism [3].

![Figure 7](image1)

Figure 7. The dependence of specific catalytic activity on temperature in coordinates of the Arrhenius equation.

![Figure 8](image2)

Figure 8. The dependence of average specific catalytic activity on size nanoparticles.
3. Conclusion

1) Due to the dimensional effect, during the transition from the catalytic inert massive gold to the nanostructured state, high-active composite catalytic systems in reactions involving molecular hydrogen were obtained, comparable in activity with catalysts based on transition metals;

2) It is shown that the specific catalytic activity of gold nanoparticles in the H₂-D₂ exchange reaction significantly depends on the particle size;

3) The specific catalytic activity of gold nanoparticles in the o-p protium conversion reaction does not depend on the particle size on the range of size from 1 nm to 40;

4) It is shown that the o-p protium conversion reaction flows through the magnetic mechanism, and, therefore, gold particles acquire magnetic properties in contrast to diamagnetic massive metal.

4. References

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