Low-Temperature Conversion of Hydrogen Modifications on Nanoparticles of 1B-Group Metals

O A Boeva*, E S Kudinova, N S Panyukova, N I Nesterova and K N Zhavoronkova
D. I. Mendeleev University of Chemical Technology of Russia 125480, st. Geroev Panfilovtsev, 20, Moscow, Russia
*E-mail: olga_boeva@mail.ru

Abstract. The catalytic properties of metal nanoparticles of the 1B group (Cu, Ag, Au) in the reaction of low-temperature ortho-vapor conversion of hydrogen are investigated. It is shown that, upon transition to nanoscale particles, inert bulk metals adsorb hydrogen at low temperatures and become active in the reaction of the conversion of hydrogen modifications. Among the metals studied, gold nanoparticles have the highest specific catalytic activity. Conversion occurs on all ortho-vapor nanoparticles by the physical magnetic mechanism, which indicates the presence of magnetic properties of copper, silver, and gold nanoparticles.

1. Introduction

Ordinary hydrogen under normal conditions consists of a mixture of two modifications: 75% ortho-hydrogen (o-H₂) and 25% para-hydrogen (p-H₂), which differ in nuclear spins. A change in temperature from 300 K to 20 K entails a change in the equilibrium concentrations of hydrogen modifications. At 20.4 K, the stable form of liquid hydrogen corresponds to almost pure para-hydrogen with a concentration of 99.8%. In liquid hydrogen, a spontaneous ortho-vapor conversion reaction takes place with a large thermal effect exceeding the heat of vaporization of hydrogen. In the gaseous state, the conversion reaction does not occur spontaneously; a catalyst is required to carry it out. Therefore, the stage of catalytic inversion of the nuclei spins in a hydrogen molecule is industrially important. It is necessary in the cryogenic production of liquid hydrogen and low-temperature distillation of hydrogen to obtain deuterium and heavy water (D₂O). Also, the reaction of the ortho-para conversion of protium is used as a model reaction in some catalytic studies. In the present work, the conversion reaction is used to test the catalytic properties of metal nanoparticles.

The scientific novelty of the work lies in the use of new approaches to the creation of catalytically efficient systems. Nanoparticles of metals of the IB group (copper, silver, gold) were taken as the active component for the fundamental direction of work. We emphasize that bulk metals are chemically inert with respect to the reaction under study. Upon transition to a nanostructured state, metals become catalytically active. The reaction rate may depend [1,4] or not depend [2,3] on the size of nanostructured particles. In addition to the size effect affecting the reaction rate, the transition to nanodispersed particles is often accompanied by the appearance of new physicochemical properties, for example, magnetic properties of metal nanoparticles [5]. It is possible to obtain magnetic nanoparticles from diamagnetic bulk gold, which, in turn, can uniquely affect the mechanism of ortho-vapor conversion of protium and lead to new approaches to the creation of highly efficient catalysts.

2. Results

2.1. Synthesis of nanoparticles

The objects of study are nanoparticles of various metals of the IB group (copper, silver, and gold) deposited on a γ-Al₂O₃ support (“trefoil” brand).

The synthesis procedure involves the preparation of nanoparticles immediately on a carrier by the method of thermal decomposition of a metal salt. Obtaining a catalytic system includes the following steps:

- Preparation of a metal salt solution of the desired concentration;
- Impregnation of the carrier with the salt solution;
Sample drying;
- Thermal decomposition of the metal salt of silver (AgNO₃) and gold (AuCl₃) by calcination. For samples containing copper (CuCl₂), simultaneous calcination and reduction of the metal in a stream of hydrogen.

2.2. Microscopy investigations

The size and shape of the nanoparticles were determined by transmission electron microscopy (TEM) on a JEOLJEM-1011 device. TEM images were processed using Nano Measurer 1.2 program.

a). Figs. 1 and 2 show TEM photographs of Au nanoparticles on the surface of a carrier and particle size distribution before and after studies. During studies of the adsorption and catalytic properties, the sample with nanoparticles was in a hydrogen atmosphere at temperatures from 77 K to 300 K and was also heated in a vacuum.

![Figure 1. TEM-images of Au nanoparticles deposited on Al₂O₃ before research (a) and after research (b).](image)

![Figure 2. Size distribution of gold nanoparticles before research (a) and after research (b).](image)

TEM images show a spherical shape of a gold nanoparticle. In the photo, agglomerates of nanoparticles consisting of 3-5 particles ranging in size from 2 to 5 nm are clearly distinguishable. The particle size distribution is rather wide 5 ÷ 10 nm, which is due to the synthesis technique. On a sample with gold nanoparticles, an increase in the number of particles with a large size (10-11 nm) is observed after studies in a hydrogen atmosphere in comparison with the initial particle size distribution (5-7 nm). This is not explained by the restoration of NPs in hydrogen, since the area of the active surface of the sample during the studies (more than 2 months) did not change.
Figure 3. TEM-images of NPs Cu deposited on \(\gamma\)-Al\(_2\)O\(_3\) before studies (a) and after studies (b).

b). Sizing of Cu nanoparticles before and after catalytic studies was also carried out by TEM (Fig. 3). The particle size distribution is shown in Fig. 4. In TEM images, copper particles are in the form of rods. Sizes range from 5 to 12 nm. Note that in the process of research, copper particles do not change their morphology and do not become larger, therefore, they are quite firmly fixed on the surface of the carrier.

Figure 4. Size distribution of NPs Cu deposited on \(\gamma\)-Al\(_2\)O\(_3\) before studies (a) and after studies (b).
c). Ag nanoparticles on the surface of γ-Al₂O₃ were studied by TEM after catalytic studies, the results are presented in Fig. 5. The particles have a spherical shape. The size of the nanoparticles is 4-6 nm.

![Image of TEM images of nanoparticles Ag/γ-Al₂O₃ and size distribution.](image)

**Figure 5.** TEM-images of nanoparticles Ag/γ-Al₂O₃ and size distribution.

### 2.3. Hydrogen adsorption

The active surface (the surface of the deposited metal) was determined by hydrogen adsorption. The measurements were carried out using the volumetric method in a pressure range of from $1 \cdot 10^{-2}$ to $2 \cdot 10^{-1}$ Torr at $T = 77$ K.

Adsorption studies have shown that upon transition to the nanoscale state, hydrogen adsorption on copper, silver, and gold becomes possible at temperatures from 77 to 297 K (Fig. 6a). A plateau is observed on isotherms of hydrogen adsorption, which is taken as a monolayer of chemisorbed hydrogen ($n_{H_2}$).

This value is used to calculate the active surface of the catalytic system ($S_{Me}$), which in turn is necessary to calculate the specific catalytic activity ($K_{sp}$).

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

$$S_{Me} = 2 \cdot n_{H_2} \cdot N_A \cdot \sigma_{Me}$$  \hspace{1cm} (1)

where $n_{H_2}$ 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.

Hydrogen adsorption on samples with metal nanoparticles was measured in a wide temperature range from 77 K to 300 K. An isobar of hydrogen adsorption was constructed from these data (Fig.6b). It is shown that with increasing temperature the amount of adsorbed hydrogen decreases sharply. For a sample with Au NPs at 300 K, the amount of adsorbed hydrogen is 5-6 times less than at a temperature of 77 K. Hydrogen adsorption is an exothermic process.
Figure 6. Typical hydrogen adsorption isotherm on Cu nanoparticles (a) and isobar of hydrogen adsorption on Au NPs (b).

Hydrogen adsorption was measured repeatedly during catalytic studies. The active surface area of the Au/γ-Al₂O₃ sample did not change throughout the study (66 days) and remained equal to 200 cm². Unlike samples with silver and gold nanoparticles, the surface of the copper sample was less stable. As a result of the first experiments on hydrogen adsorption, the active surface was 70 cm². After 11 days, the active surface decreased to 30 cm², and therefore, heating was carried out in a hydrogen atmosphere for 1 hour at a temperature of 540 K. Hydrogen adsorption was carried out immediately after heating, the calculated value of the active surface was 540 cm². Immediately after heating, hydrogen adsorption was carried out; the calculated value of the active surface was 65 cm². Thus, heating the sample in a hydrogen atmosphere allows us to restore the active surface to the initial value. However, after 4 days, active surface degradation to 55 cm² was again noted. Reheating in hydrogen again restored the surface to its original values. Given the analysis of particle sizes (TEM), the phenomenon of a decrease in the active surface is not associated with particle agglomeration. Copper nanoparticles are extremely sensitive to any impurities in the reaction medium and are subject to rapid oxidation. We assume that the particles could interact with the support material (Al₂O₃), or with the residual gases in the installation.

2.4. Catalytic activity

The reactions were studied under static conditions without gas circulation at an operating 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).

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 ($S_{H_2}$):

$$K_{sp} = \frac{k_0 N_T}{S_{H_2}}$$

(2)

The catalytic activity of the samples was measured in the reaction of the ortho-vapor conversion of protium at the boiling point of liquid nitrogen (77 K). The main results and a comparison of the specific catalytic activities of the nanoparticles of the studied metals are given in table 1 and in fig. 7.
**Table 1.** A summary table of the results of a study of the catalytic properties of copper, silver, and gold nanoparticles in the reaction of ortho-para conversion of protium at 77 K.

| Metal nanoparticles | $S_{\text{H-P}}^{77}$, cm²·g⁻¹ | $K_{\text{H-P}}^{77}$, molecules ·s⁻¹·cm⁻² |
|---------------------|---------------------------------|----------------------------------------|
| Cu                  | 470                             | (1.48±0.028)·10^{14}                   |
| Ag                  | 700                             | (1.84±0.24)·10^{14}                    |
| Au                  | 900                             | (3.00±0.19)·10^{14}                    |

All nanoparticles, in contrast to bulk metals, showed a “surprisingly” high catalytic activity in the reaction of ortho-para conversion of protium. The activity of metal nanoparticles increases in the group with an increase in the element serial number. Perhaps this is due to a decrease in the ionization potential and the ease of electron transfer to localized surface plasmon resonance (LSPR) of nanoparticles. This, in turn, contributes to an increase in the amount of the chemisorbed form of protium in the form of $\text{Н}_2\delta^+$, which can lead to an increase in the processing speed. Gold nanoparticles have the highest specific catalytic activity.

To explain the results obtained, it is necessary to understand the mechanism of the conversion reaction. As is known, ortho-para conversion of protium can proceed by the chemical mechanism through dissociative adsorption of hydrogen or by the physical magnetic mechanism with a flip of the spins of the nuclei of the protium molecule on the magnetic centers of the catalyst. To understand this issue, the specific catalytic activity of the same nanoparticles in the deuterio-hydrogen exchange reaction was measured under the same conditions. Since the isotope exchange reaction in molecular hydrogen proceeds according to the chemical mechanism with bond breaking in the protium and deuterium molecules, if we assume that the protium conversion reaction proceeds by the same mechanism, then the reaction rates may differ by a factor of 2-5 due to the kinetic isotope effect. Table 2 presents a comparison of the specific catalytic activities of copper, silver, and gold nanoparticles with respect to homo-molecular reactions.

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**Figure 7.** Comparison diagram of specific catalytic activity of metal nanoparticles.
**Table 2.** Comparison of the results of a study of the catalytic properties of copper, silver and gold in the reaction of ortho-vapor conversion of protium and isotopic exchange of hydrogen at 77 K.

| NP Metal | $K_{77}^{\text{sp}}$, molecules $\cdot s^{-1} \cdot cm^{-2}$ ortho-para conversion | $K_{77}^{\text{sp}}$, molecules $\cdot s^{-1} \cdot cm^{-2}$ H$_2$-D$_2$ exchange | $K_{o-p}^{\text{sp}} / K_{H-D}^{\text{sp}}$ |
|----------|---------------------------------------------------------------------------------|---------------------------------------------------------------------------------|-----------------|
| Cu       | $148 \cdot 10^{12}$                                                             | $0,2 \cdot 10^{12}$                                                            | 740              |
| Ag       | $184 \cdot 10^{12}$                                                             | $11,9 \cdot 10^{12}$                                                           | 16               |
| Au       | $300 \cdot 10^{12}$                                                             | $2,37 \cdot 10^{12}$                                                           | 127              |

The difference in the ratio of reaction rates far exceeds the kinetic isotope effect. It follows that the reactions proceed according to various mechanisms. Thus, it can be stated that the ortho-para conversion proceeds not by the chemical mechanism, but by the magnetic mechanism, in which the mutual orientation of the spins of the hydrogen nuclei occurs on the surface magnetic centers of the catalytic system, namely, on metal nanoparticles. Investigation of the reaction of the ortho-vapor conversion of protium shows the presence of magnetic properties in nanoparticles of copper, silver and gold. It can be assumed that the emerging magnetic properties of nanoparticles depend on the nature of the metal because they exhibit different catalytic activities in the conversion reaction.

### 3. Conclusion

1) It is shown that nanoparticles of copper, silver, and gold have a high specific catalytic activity in the reaction of ortho-vapor conversion of hydrogen. According to the catalytic activity, metal nanoparticles are arranged in the following order: Au → Ag → Cu.
2) It is shown that the o-p protium conversion reaction flows through the magnetic mechanism, and, therefore, Au, Ag, Cu particles acquire magnetic properties in contrast to diamagnetic massive metal.

### References

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