Structural properties of CuAu nanoparticles with different type. Molecular dynamic simulations

I V Chepkasov, V S Baidyshev, A Y Baev

Katanov Khakas State University, Lenina Av., 90, Abakan, 655000, Russia

E-mail: ilya_cheokasov@mail.ru

Abstract. The paper is devoted to the thermal stability of a CuAu nanoparticles structure (D=5 nm) of various type (binary alloy, core-shell, "Janus" type) and of various percentage of copper atoms. The simulation was carried out with molecular dynamics, using the embedded atom potential. The authors defined the most preferable structural options from the standpoint of thermodynamics, as well as studied in detail the influence of different temperatures on the structural stability of CuAu nanoparticles.

1. Introduction

The metal nanoparticles have been recently used actively in the heterogeneous catalysis due to the fact that the regulation of the particle surface composition is possible with proper selectivity of the catalyst. The copper nanoparticles are widely used in various chemical reactions of CO₂ hydrogenation and recovery as well as of CO oxidation. However, copper is easily oxidized, which jeopardizes the catalytic activity. One of the solutions to this problem is the copper alloy with a stabilizing metal, such as gold that is resistant to corrosion and oxidation. The copper-gold bimetal alloys are also known to be more effective in the low oxidation of CO than their single-component analogues are [1]. Thus, it is possible to effectively configure catalytic properties of these nanoparticles by combining two metals - Cu and Au. However, to comprehend the structural and thermal stability of these nanoparticles is a complicated task. The molecular dynamics method is an ideal tool for the study of the thermal-physical properties of such small clusters [2-5].

It is obvious that the catalytic activity of nanoparticles defined, first of all, through the superficial properties strongly depends on the structural features of the nanoparticle [6-8]. Basically, it is possible to distinguish four different patterns of the internal structure of CuAu bimetal nanoparticles: Cu-core/Au-shell (Cu@Au), Au-core/Cu-shell (Au@Cu), "Janus" structure (Cu|Au) and a homogeneous particle of bimetal alloy (Cu-Au) (see Figure 1).

The chemical activity of Cu-Au nanoparticles is well known as strongly dependent not only on the size, but also on the ratio of gold and copper. Thus, in order to develop high-reactive nanocatalysts, it is essential to consider all the structural peculiarities of such nanoparticles: the size of the nucleus and the shell, the ratio of copper and gold atoms and the structure of the surface. Moreover, as catalysts are usually used at elevated temperature, another important issue is the thermal stability of the nanoparticle structure. Up to now a large number of experimental and theoretical works were mainly devoted to various methods of synthesis for CuAu bimetal nanoparticles of various patterns as well as to the study of their catalytic activity. However, in the authors’ opinion, there is still no complete vision to understanding the structural evolution and thermal stability of such nanoparticles. Thus, the
main purpose of this work is to study the structural stability of CuAu nanoparticles of various types using the molecular dynamics method.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{CuAu_nanostructures.png}
\caption{CuAu nanoparticles with different structures}
\end{figure}

2. Computer simulation

The computer simulation was performed with the software package LAMMPS (Large-scale Atomic/Molecular Massively Parallel Simulator). The molecular dynamics method used in the research allows calculating the dynamic characteristics of the simulated system and has recently been widely used to study structural phase transitions in metals and alloys [2, 9]. To determine the binding energy of copper and gold atoms this research used EAM-potential which was quite successfully implemented when simulating various nanoobjects from CuAu alloy [10].

In order to study the kinetics of the possible thermally activated structural transformations and to determine the thermal stability limits, Cu-Au nanoparticles have been exposed to thermal influence at different temperature ranges (T=300, 500, 700, 900 K) for t=5 ns. Heating between these temperatures was achieved for t=1 ns. The ratio of Cu atoms changed from 10 % to 70 % with the Cu@Au particles of nucleus-shell type. In the particles with Au atoms as nucleus and Cu as shells (Au@Cu), the ratio of Cu atoms ranged from 30 % to 90 %. In Cu-Au bimetal nanoparticles and "Janus" particles, the number of Cu atoms was 10-90 %.

To estimate the thermal dynamic stability of nanoparticles of various structure this paper gives a calculation of energies difference $\Delta E$, showing the particle energy peculiarity as compared to the volume energy:

$$
\Delta E = \sum_{i=1}^{N} E_i - E_{Cu} \cdot N_{Cu} - E_{Au} \cdot N_{Au},
$$

where $E_i$ – the potential energy of the $i$ atom in the cluster, N – the total number of atoms in the particle, $N_{Cu}$, $N_{Au}$ – the number of Cu and Au atoms, $E_{Cu}$ and $E_{Au}$ – the potential binding energy for bulk samples of copper and gold.

3. Results and Discussion

Figure 2 shows $\Delta E$ values after t=5 ns molecular dynamic simulation of nanoparticles with D=5 nm, with different percentage ratio of copper and gold atoms, with four structural types and at different temperature ranges. The presented graphs clearly visualize that the smallest difference of nanoparticles binding energies and volume is seen with Cu-Au bimetal nanoparticles containing from 40 % to 60 % of copper on the average. When comparing two types of nucleus-shell structures of nanoparticles, it is possible to clearly see the difference in binding energies for Cu@Au and Au@Cu nanoparticles, which makes from 200 up to 350 eV according to the copper concentration. Obtained experimentally, the values of the "average" surface energies (1.83 J/m$^2$ for Cu [11] and 1.5 J/m$^2$ for Au [12]) indicate that the coating of the nanoparticle surface with gold atoms is thermodynamically more preferable than the coating with copper atoms. Moreover, this fact agrees properly with the authors’ values $\Delta E$ calculated for the nanoparticles of pure copper and gold ($\Delta E=817$ eV for Cu, $\Delta E=654$ eV for Au).
Figure 2. Dependence of the energy $\Delta E$ difference on the percentage of Cu atoms in Cu-Au nanoparticles with four configurations of the structure after annealing during $t=5$ ns at different temperatures.

Figure 3. The structures (slice) of nanoparticles of Cu|Au (a,b), Au@Cu (c,d), Cu@Au (e,f) containing 50 % Cu atoms; a, c, d – T=300 K, b, d, f – T=900 K.
The temperature increase causes slight structural transformations of both internal morphology and external form of nanoparticles, with active processes of copper and gold atoms diffusion, and with an alloy formation. The most active processes are observed at temperature 900 K (see figure 3.), which is clearly seen in Figure 2, where the curves showing the binding energy difference for the nucleus-shell nanoparticles and "Janus" particles are close to the bimetal alloy values.

As an example, figure 3 shows the initial state and state at a temperature of \( T = 900 \) K for nanoparticles of different types. In the case of Janus particles, mainly surface diffusion of Au atoms is observed with the tendency of formation of the core-shell particle.

4. Conclusion

As a result, the research of thermal dynamic properties of CuAu nanoparticles of various patterns defines that coating of the nanoparticle surface with gold atoms is thermodynamically a more preferable option of the particle structure. Moreover, the study of the nanoparticles at different temperatures makes certain the fact that CuAu nanoparticles of all the four patterns keep a relatively stable structure at approximately to \( T=700 \) K, while higher temperatures demonstrate active diffusion processes with copper and gold atoms, which results in the formation of the copper-gold alloy of a mixed surface composition.

5. Acknowledgments

The reported study was funded by the Russian Foundation for Basic Research (RFBR ), according to research project No. 17-42-190308 r_a. The research is carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University and resources of the Center for the Information and Computing of Novosibirsk State University.

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