Copper-containing nanocomposites in catalytic systems

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Abstract. Nanostructured systems, including the products of copper ions recovery – nanoparticles of copper, copper(I) oxide or complex copper particles and copper oxides, have been obtained. Copper ions were reduced by tert-butylamine borane in aqueous solutions of poly(N-vinylpyrrolidone) at room temperature under air. Different synthesis conditions allowed controlling both the size of the resulting particles and the final product of the synthesis. The composition, morphology and size characteristics of nanocomposites were studied by methods of electron microscopy and XRD. The efficiency of the Cu/CeO₂ catalytic system in the purification of hydrogen from CO was shown.

1. Introduction

The synthesis of copper sols by reducing Cu²⁺ ions in aqueous media, polymers or surfactants is used as size regulators of the forming metal nanoparticles. These compounds protect the nanoparticles from aggregation and oxidation [1-3]. The manufacturing procedure allows controlling the size of particles containing Cu, and to choose parameters for an optimal particle range of 2-15 nm.

The properties of a nanostructured system strongly depend on their dimensional characteristics. In our earlier work [4, 5], the formation of copper(I) oxide nanoparticles protected from aggregation by macromolecular screens polymeric protector of poly(N-vinylpyrrolidone) (PVP) was investigated. Nanosized copper or copper(I) oxide are promising in many applications: solar energy conversion, catalysis and photocatalysis, the development of photovoltaic cells and nanofluids, etc. [6, 7]. They could also be effective substitutes for gold due to the abundance of copper and relatively low cost in catalytic systems.

For commercially and ecologically important processes, various Cu-containing catalysts are used, among which there is hydrogen purification from CO [8]. However, their preparation techniques are not very environmentally friendly due to the waste of water and energy expenditure. The main disadvantages are high costs and strict requirements for use and production. On the contrary, the mechanochemical synthesis applied for this purpose is fast and ecologically friendly. This article focuses on the preparation and morphology of nanosized particles of Cu/Cu₂O, as well as the redox properties of the composite Cu-CeO₂ manufactured by mechanochemical synthesis.

2. Experimental

Copper(II) sulfate pentahydrate (reagent grade, Reakhim, Russia), tert-butylamine borane (TBAB) (98% Aviabor, Russia) and PVP (BASF, Mn = 3.6×10⁵) were used as the initial materials. The water
was distilled twice. Cu nanoparticles were obtained via the reduction of copper ions with TBAB at room temperature in air. The calculated amount of a freshly prepared reducing agent solution was added to an aqueous solution containing a salt of copper (0.01 mol/L) and PVP (0.01 base-mol/L). The concentration of the reducing agent in the reaction mixture varied from 0.01 to 0.03 mol/L.

TEM images of the particles were obtained using a JEM-1011 microscope equipped with a side-mounted digital camera Gatan Erlangshen ES500W. The size distribution histograms were constructed from the obtained TEM images.

XRD analysis was performed using a DRON-3 diffractometer (Russia) with Cu-Kα radiation. The composition of the powder phase was determined using JCPDS files provided by the International Center for Diffraction Data.

The morphology of the samples was examined in a dual beam scanning electron microscope/focused ion beam (SEM/FIB) Versa 3D (FEI, USA), equipped with a concentric backscatter detector (CBS). The microstructure of thin cross-sections of specimens prepared by Ga+ FIB was studied in a Titan 80-300 TEM/STEM (FEI, USA).

Nanocomposite catalysts were prepared by mechanochemical synthesis. Meanwhile, the mass ratio of Cu /CeO$_2$ was 8:92. Catalysts can be prepared for 0.5–1.5 hours at room temperature in air. Nanocomposite redox properties towards CO and H$_2$ were studied by temperature-programmed reduction (CO-TPR and H$_2$-TPR, respectively), which are given in detail. Earlier this method was tested on the system of CuO/CeO$_2$ and Cu/CeO$_2$[9].

3. Results and Discussion

The formation of transparent stable dispersions of Cu$_2$O, Cu$_0$ in the presence of PVP indicates the small size of the particles of the dispersed phase and the shielding thereof by macromolecules. Figure 1 depicts the TEM image and the particle size distribution histogram of the particles. They have a spherical shape and a narrow size distribution with an average diameter of about 6.5 nm.

![Figure 1](image)

**Figure 1.** (a) TEM image and (b) histogram of numerical size distribution of particles in the Cu sol obtained by the reduction of copper ions in solution of PVP.

Weak cooperative non-covalent interactions with the participation of macromolecules and other macromolecules or the surface of species such as nanoparticles result in the formation of products the stability of which depends on the size of the smallest component of the complex formed. In particular, in the case of interaction between a long macromolecule and a nanoparticle, the stability of corresponding complex (MNC) representing a nanoparticle screened by the polymer chain increases exponentially with the surface area of nanoparticle. This explains the reason of essential consequences such as:

- In dilute MNC dispersions (sols), a very low polymer – nanoparticle interaction energy (ΔG of order $10^{-3}$ - $10^{-4}$ J/m$^2$) is sufficient to ensure the stability of MNC, including nanoparticles with a diameter from 2 to 12 nm.
- A small size and a narrow size distribution of nanoparticles are typical of the soles obtained in processes of new phase formation proceeding in solutions of appropriate polymers (pseudo-template processes).

Figure 2 shows the XRD pattern of the final product obtained after reduction of CuSO₄. The phase composition is identified as metal Cu (~75 mass%) and Cu₂O (~25 mass%).

![XRD patterns of CuSO₄. Characteristic peaks of Cu and Cu₂O, are marked in (a) and (b), respectively. The corresponding JCPDS phase numbers are given at the top of the figures.](image)

The calculation of the lattice spacing indicates the presence of CeO₂ and Cu₅O₄, Cu⁴⁺ nanofragments. At the same time, the crystal lattice of the original Cu₂O and Cu metal contains defects and their particles are porous due to the special features of the synthesis.

Figure 3 shows images of BF STEM and HR TEM of Cu/CeO₂ particles. The characteristic structures of CeO₂ and Cu₂O, Cu⁰ are shown by direct measurements of the lattice spacing.

![Figure 3. (a) TEM and (b) STEM images of Cu/CeO₂.](image)

Nano-sized copper powder was used as an active component of the Cu-CeO₂ composite catalyst prepared by intermixing and mechanical activation of both components in a ball mill. High energy impact during the processing by ball-milling results in the adhesion of Cu particles to the surface of CeO₂. Figure 4 shows CO-TPR and H₂-TPR MS profiles (m/e = 44, CO₂ and m/e = 18, H₂O, respectively) recorded for 30 minute milled powder. In accordance with [9], low-temperature peaks were attributed to the reaction of both CO and H₂ with oxygen localized in the Cu/CeO₂ interface. This is “active” oxygen participating in the oxidation of CO in an excess of H₂. A large temperature loop between Tmax of low-temperature peaks of CO- and H₂-TPR point to the possibility of successful purification of H₂ from CO. Especially important are two features. (1) – Both CO- and H₂-TPR profiles are virtually identical for 30- and 60-minute milled powders (not shown) which indicate the extremely effective and rapid incorporation of nano-sized Cu particles in the CeO₂ matrix. (2) – The low-temperature peak fraction corresponding to the “active” oxygen fraction in the composite is ~ 40% after 30 minutes of milling instead of ~ 16.5% measured for a catalyst prepared from electrolytic (dendrite) Cu powder and CeO₂ [10] which also points to a significant effect of the size of Cu powder on the formation of the Cu/CeO₂ interface (figure 5).
4. Conclusions

A new manufacturing procedure, including the reduction of copper ions by tert-butylamine borane in aqueous solutions of poly(N-vinylpyrrolidone) at room temperature under air is applied to synthesize copper, copper(I) oxide or complex copper nanoparticles. The size of Cu-containing particles of 2-15 nm is controlled by preparation parameters. The nanoscale particles obtained allow one to create new highly reactive oxygen states for CO oxidation in Cu-CeO$_2$ nanocomposites during a short time of joint mechanochemical treatment. This point on the promising potential of these systems in purification of hydrogen from CO.

Acknowledgment

This work was supported by the Ministry of Education and Science of the Russian Federation within the framework of the state assignment (project No. 16.11777.2018/11.12) and partially (XRD and DSC-DTG-MS measurements) by RFBR through research project No. 16-03-00330.

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