Full Length Article

The decomposition of mixed oxide $Ag_2Cu_2O_3$: Structural features and the catalytic properties in CO and C_2H_4 oxidation

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ABSTRACT

The mixed silver-copper oxide $Ag_2Cu_2O_3$ with a paramelaconite crystal structure is a promising material for catalytic applications. The as-prepared sample of $Ag_2Cu_2O_3$ consisted of brick-like particles extended along the [001] direction. A combination of physicochemical techniques such as TEM, XPS and XRD was applied to investigate the structural features of this mixed silver-copper oxide. The thermal stability of $Ag_2Cu_2O_3$ was investigated using *in situ* XRD under different reaction conditions, including a catalytic $CO + O_2$ mixture. The first step of $Ag_2Cu_2O_3$ decomposition was accompanied by the appearance of ensembles consisting of silver nanoparticles with sizes of 5–15 nm. Silver nanoparticles were strongly oriented to each other and to the surface of the initial $Ag_2Cu_2O_3$ bricks. Based on the XRD data, it was shown that the release of silver occurred along the *a* and *b* axes of the paramelaconite structure. Partial decomposition of $Ag_2Cu_2O_3$ accompanied by the formation of silver nanoparticles was observed during prolonged air storage under ambient conditions. The high reactivity is discussed as a reason for spontaneous decomposition during $Ag_2Cu_2O_3$ storage. The full decomposition of the mixed oxide into metallic silver and copper (II) oxide took place at temperatures higher than 300 °C regardless of the nature of the reaction medium (helium, air, $CO + O_2$). Catalytic properties of partially and fully decomposed samples of mixed silver-copper oxide were measured in low-temperature CO oxidation and C_2H_4 epoxidation reactions.

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1. Introduction

Mixed silver-copper oxide $Ag_2Cu_2O_3$ with a paramelaconite crystal structure is a novel and little-studied material. The unique structural features of $Ag_2Cu_2O_3$ are the following: (a) the presence of two non-equivalent oxygen species; (b) the rhomboid distortion of square planar CuO_4 fragments; and (c) the enhanced value of the Ag—O bond length in comparison with individual silver oxides [1–3]. Such structural features may be responsible for the high-profile electronic [4], electrochemical [5,6], magnetic [1,7], and catalytic properties of this material [8–10]. Mixed silver-copper oxides have excellent potential for various applications.

It has been shown that the mixed oxide $Ag_2Cu_2O_3$ demonstrated high catalytic activity in CO oxidation at near room tempera-
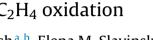
ture [8–10]. The specific activity of $Ag_2Cu_2O_3$ is similar to that of a hopcalite-type catalyst [9]. Moreover, the mixed silver-copper oxide is active in the partial oxidation of alcohols [11]. Therefore, a detailed study of $Ag_2Cu_2O_3$ is important not only from a fundamental point of view, but also for catalytic applications.

The oxide $Ag^{1+}_2Cu^{2+}_2O_3$ is a structural analog of another mixed oxide, $Cu_4O_3 \equiv Cu^{1+}_2Cu^{2+}_2O_3$, in which monovalent copper ions occupy silver positions [12]. The oxide Cu_4O_3 is metastable [13]. So, the synthesis of pure Cu_4O_3 oxide is rather problematic [14]. The influence of different factors on crystal structure stability is a key question for the application of $Ag_2Cu_2O_3$ in various fields, including heterogeneous catalysis. Taylor and Rhodes prepared a $Ag_2Cu_2O_3$-based catalyst by a co-precipitation method in alkaline solution [10]. The authors observed different phase composition of the synthesized catalyst depending on the aging time of the precipitate. However, the pure $Ag_2Cu_2O_3$ oxide was not obtained. Moreover, Tejada-Rosales et al. found the presence of a ~2 wt.% CuO admixture during the refinement of neutron diffraction data for the $Ag_2Cu_2O_3$ structure [2]. Prolonged exposure of $Ag_2Cu_2O_3$ to the reaction

mixture $CO + O_2 = 1:5$ at 150 °C resulted in the appearance of a small amount of metallic silver (~2.4 wt.%) [8]. According to thermogravimetry data, the mixed oxide $Ag_2Cu_2O_3$, preliminarily dried at 170 °C, was characterized by a 1% weight loss during heating in an H_2 flow below 100 °C [3]. Full reduction occurred at ~260 °C. Hydrogen consumption by $Ag_2Cu_2O_3$ in the range from 25 to 200 °C has also been observed elsewhere [9]. Therefore, the mixed silver-copper oxide, prepared by precipitation in alkali medium, either contains some amount of admixture (Ag^0 or CuO) initially or can be partially decomposed under reaction conditions with preservation of the paramelaconite structure. This could be caused by the metastability of $Ag_2Cu_2O_3$ (similarly to Cu_4O_3) or by some other features of the mixed oxide decomposition/reduction. Tejada-Rosales et al. showed that the thermal stability of $Ag_2Cu_2O_3$ in H_2 flow depended on the temperature of sample drying [3]. The reasons for this are still unclear. Also, the high reactivity of $Ag_2Cu_2O_3$ at near room temperature emphasizes the importance of a detailed investigation into this mixed silver-copper oxide under various conditions, including inert, oxidative or reductive medium [8–10].

Other important area of investigation is the product of $Ag_2Cu_2O_3$ decomposition. It is well-known that $Ag_2Cu_2O_3$ decomposes into mixture of Ag^0 and CuO [1]. This mixture can be considered a promising metal-oxide composite material. For example, Ag/CuO nanoparticles, obtained during the decomposition of a trinuclear complex compound, have demonstrated antibacterial activity [15]. Also, nanocomposites of Ag/CuO are characterized by a surface-enhanced Raman scattering (SERS) effect in solutions [16]. This can be very useful for the analytical detection of low concentration substances. Furthermore, such nanocomposites can be applied in heterogeneous catalysis [17,18]. Therefore, the process of $Ag_2Cu_2O_3$ decomposition is interesting from two points of view: (a) the determination of conditions for the existence of the mixed oxide and (b) the properties of the Ag/CuO composite formed during decomposition.

This work is devoted to the study of the $Ag_2Cu_2O_3$ decomposition process under various conditions, including air storage. X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) were applied to study the phase composition, structural features and electronic states of the elements, respectively. It was shown that the first step of $Ag_2Cu_2O_3$ decomposition results in the appearance of an ensemble consisting of oriented metallic silver nanoparticles.

2. Experimental part

2.1. Sample preparation

The mixed silver-copper oxide $Ag_2Cu_2O_3$ was prepared by a co-precipitation method as described elsewhere [1]. Approximately 0.01 mol of $AgNO_3$ and 0.01 mol $Cu(NO_3)_2 \cdot 3H_2O$ were dissolved in 50 ml of distilled water. Then, 50 ml of 5 M NaOH solution was added drop-by-drop with vigorous stirring of the metal salt solution. The obtained precipitate was washed with distilled water to a neutral pH. After filtration, the precipitate was dried at 90–120 °C for 4.5 h. Dried samples were placed in a glass or plastic transparent box for storage without vacuumization.

2.2. Physicochemical characterization

Diffraction data were measured using a Bruker D8 Advance diffractometer (CuKα radiation, λ = 0.154184 nm) with a Bregg-Brentano focusing scheme: primary slit 0.26°; receiving slit 2.2°. The Ni filter on the reflected beam was used for subtraction of the CuKβ-component. The aperture of the Soller slits was 2.5° for the primary and reflection beams. A multistrip LynxEye detector (Bruker) with a 2.9° 2θ angle range was applied for signal acquisition. The patterns were measured in the 2θ range from 15 to 70° with a step of 0.05° and collection time of 1 s per point. A collection time of 3 s per point was used during the structure refinement experiments. In situ experiments were carried out using an Anton Paar XRK900 reaction chamber. The volume rate of the reaction mixture (100% He, 1%CO/5%O₂/He) was 70 ml/min. Before heating, the reaction mixture was blown through the reaction chamber with the sample. The interaction of the sample with the air medium during the corresponding in situ study was provided by the removal of the chamber cap. The heating rate was 12 °C/min. The acquisition of X-ray patterns was started when the given temperature had been reached. Sample cooling was immediately performed in the reaction flow. The PDF-2 Release 2009 database of the International Centre for Diffraction Data (ICDD PDF-2) was used for phase composition analysis. Structural data were extracted from ICSD (Inorganic Crystal Structure Database). Profile analysis and structural refinement by the Rietveld method were performed using the TOPAS v. 4.3 program [19]. The diffraction line profile was analyzed by the fundamental parameter approach. The lengths of the coherent scattering domain were calculated using LVol-IB values (*i.e.* volume weighted mean column lengths based on integral breadth).

The TEM study was performed using JEM-2010 and JEM-2200FS (JEOL, Japan) microscopes with an accelerating voltage of 200 kV. A lattice resolution of the JEM-2010 apparatus was 1.4 Å. The JEM-2200FS microscope can provide high resolution TEM mode as scanning STEM mode with a lattice resolution of 1 Å. The presence of a Ω-filter allows for using electron energy loss spectroscopy (EELS) for EFTEM mapping with energy filtration. EFTEM mapping was done using the three-window technique. The crystal-lattice images were analyzed using the Fourier method (in Digital Micrograph™ Gatan, Inc.). Carbon films with a network of holes fixed on standard aluminum and nickel grids (sieve diameter of 3 mm) were used as substrates. The samples were deposited from alcohol suspensions dispersed via ultrasound with a frequency of 35 kHz.

The X-ray photoelectron spectroscopy experiments were performed using a VG ESCALAB HP photoelectron spectrometer, equipped with the measurement and the preparation chambers. An MgKα (hν = 1253.6 eV) X-ray source with 50–150 W of power was used to record the spectra. Spectrometer calibration was performed using bulk gold ($Au4f_{7/2}$) and copper ($Cu2p_{3/2}$) photoelectron lines with BE values of 84.0 and 932.7 eV, respectively. Exposure to X-rays with a power of 50 W for no more than 20 min was applied to avoid X-ray induced reduction of $Ag_2Cu_2O_3$. A sample of $Ag_2Cu_2O_3$ was pressed into a pellet with a thickness of 0.5–1 mm. The sample pellet was fixed to a holder using tantalum foil. A K-type thermocouple was immediately welded onto the foil under the sample pellet. The heating of $Ag_2Cu_2O_3$ was performed in preparation chamber of photoelectron spectrometer. Then, sample was transferred in measurement chamber under ultra-high vacuum conditions. No charging effect was observed for the $Ag_2Cu_2O_3$ pellet during spectrum acquisition. The chemical composition of the surface was determined from the integral peak areas using standard atomic sensitivity factors (ASFs) [20]. Processing of spectral data (curve fitting, area calculation, difference spectra, *etc.*) was performed using the homemade XPS-Calc program, which has been tested on a number of systems [21–25]. The procedure of curve fitting was performed using an approximation based on a combination of the Gaussian and Lorentzian functions with the subtraction of Shirley-type background. Before curve fitting, all experimental spectra were smoothed using a Fourier filter. No considerable differences between the smoothed and experimental curves were observed; the mean-square deviation was less than 1%.

Calorimetric analysis was performed using a NETZSCH DSC 204 Fl Phoenix differential scanning calorimeter. The measurements