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CuO–CeO_2 composites: Synthesis from mixed sols

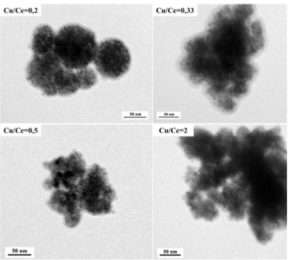
I.V. Zagaynov[a,*], S.V. Kutsev[a], E.V. Shelekhov[a,b], A.V. Naumkin[c]

[a] *A.A. Baikov Institute of Metallurgy and Materials Science, Leninskii pr. 49, Moscow, Russia*
[b] *National University of Science and Technology "MISIS", Leninskii pr. 4, Moscow, Russia*
[c] *A.N. Nesmeyanov Institute of Organoelement Compounds, Vavilova st. 28, Moscow, Russia*

HIGHLIGHTS

- The main contribution to the formation of specific surface makes CeO_2.
- Samples have a mesoporous structure with narrow pore size distribution.
- The smaller particle size of ceria in CuO–CeO_2 composite is due to the presence of a protective shell on the ceria surface of CuO particles in sols by hetero-coagulation behavior.

GRAPHICAL ABSTRACT



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ABSTRACT

The new modified sol–gel method of obtaining copper oxide–ceria composites was developed. The use of mixed sols for a uniform distribution of the components in the resulting composite was demonstrated for the first time. The impact of acetylacetone, which was as the complexing agent and stabilizer of particles, was demonstrated. It was shown that all samples have two-phase systems consisting of CeO_2 and CuO, thus the size of the individual particles of 5–20 nm, which are organized into aggregates with size of 40–80 nm. All samples have a mesoporous structure with a narrow pore size distribution, and the main contribution to the formation of surface made CeO_2.

1. Introduction

Copper–cerium oxides are used as catalysts for CO and CH_4 oxidation, CO preferential oxidation (COPROX). In recent years these systems have promising application as cathode in SOFC. However, this industry makes high technological demands of morphology of intermediate products; the major requirement is high dispersity and phase quality of these composites.

The next methods are applied to synthesis CuO–CeO_2 composites: co-precipitation [1–6], impregnation [4,7–10], sol–gel [3,11–13], homogenous hydrolysis [4,13,14], template method [5,15], hydrothermal method [4,16], Pechini method [17].

It is known that the products obtained by different methods have different physico-chemical characteristics: particle size, specific surface, electronic state of copper on ceria. The charge state of copper in composites is a key factor of the effectivity of these systems in catalysis. It is known that the addition of copper oxide to ceria increases of catalytic activity—the synergetic effect. The most significant synergetic effect occurs with adding copper in amount up to 10 mol% [18].

So using XPS can be registered the charge of copper [19,20]. In freshly prepared catalysts obtained by impregnation as well as co-precipitation, copper is present in the form of Cu^{2+} and Cu^{+}. A significant portion of the copper is in the form of CuO phase, the

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* Corresponding author. Tel.: +7 499 1352060.
E-mail address: igorscience@gmail.com (I.V. Zagaynov).

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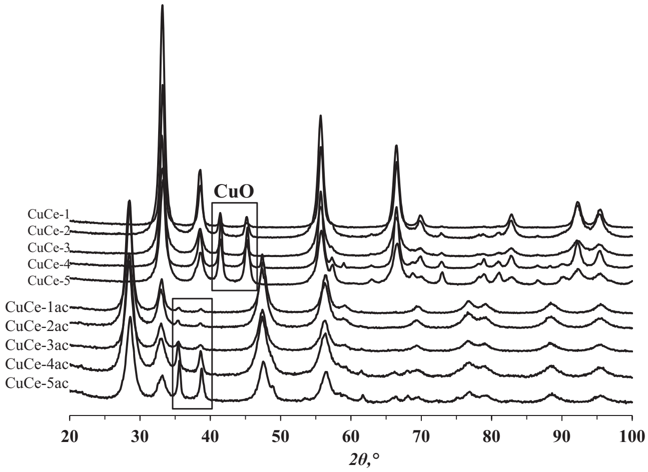

Fig. 1. XRD patterns of CuO–CeO_2 powders with Co K_α (samples CuCe-1–CuCe-5) or Cu K_α (samples CuCe-1ac–CuCe-5ac) radiation.

remainder, which is not observed by XRD, is in highly dispersed state in the form of Cu^+. This confirmed that the amount of copper oxide in a highly dispersed state in a composite prepared by impregnation is greater than prepared by co-precipitation. In either case CuO mainly segregates on the surface of ceria.

Therefore we have developed the method, based on the modified sol–gel technique using two mixed sols [21]. In previous publications copper oxide was deposited from sol on calcined ceria or combine sol/gel formation occurred.

2. Material and methods

2.1. Synthesis

Cerium(III) nitrate was dissolved in deionized water (0.05 M solution) and then after stirring ethanol ($H_2O/C_2H_5OH = 10$ vol), dimethyloctylamine (DMOA) and acetylacetone (AcAc) were added. Then resulting solutions were mixed, thus obtaining water-organic phase, and were stirred to form sol. A similar procedure was carried out with copper oxide (from copper nitrate). The amount of taken copper and the concentration were varied at a constant initial volume of the solvent. The Cu/Ce molar ratio was varied from 0.2 to 2, wherein AcAc was used in one series of syntheses. All procedures were carried out at 80 °C. These individual as-prepared sols were combined, the solvents from sols were evaporated at 95 °C until the mixture has thickened and a gel was formed. After drying at 100 °C for 12 h the xerogels obtained were stepwise calcined at 500 °C during 4 h. The initial molar ratio was AcAc/Ce = AcAc/Cu = 2.4 and DMOA/Ce = DMOA/Cu = 1. DMOA was used as sol stabilizer and AcAc as complexing agent and stabilizer of particles [21–23].

2.2. Characterization

Powders XRD data were collected at room temperature (DRON-3M, Russia) with Cu K_α or Co K_α radiation. Particle size (d_{XRD}) measurements were made by applying the Scherrer equation to the full-width at half maximum after accounting for instrumental broadening using germanium as reference [24]. Quantitative phase analysis was calculated by the Rietveld method.

Specific surface area (S_{BET}) of the powders was measured by a conventional (BET method) nitrogen sorption method at 77 K (Tri Star 3000 Micromeritics). Pore-size distributions were calculated from desorption isotherm data using BJH method. Samples were degassed at 120 °C for 5 h prior to measurement.

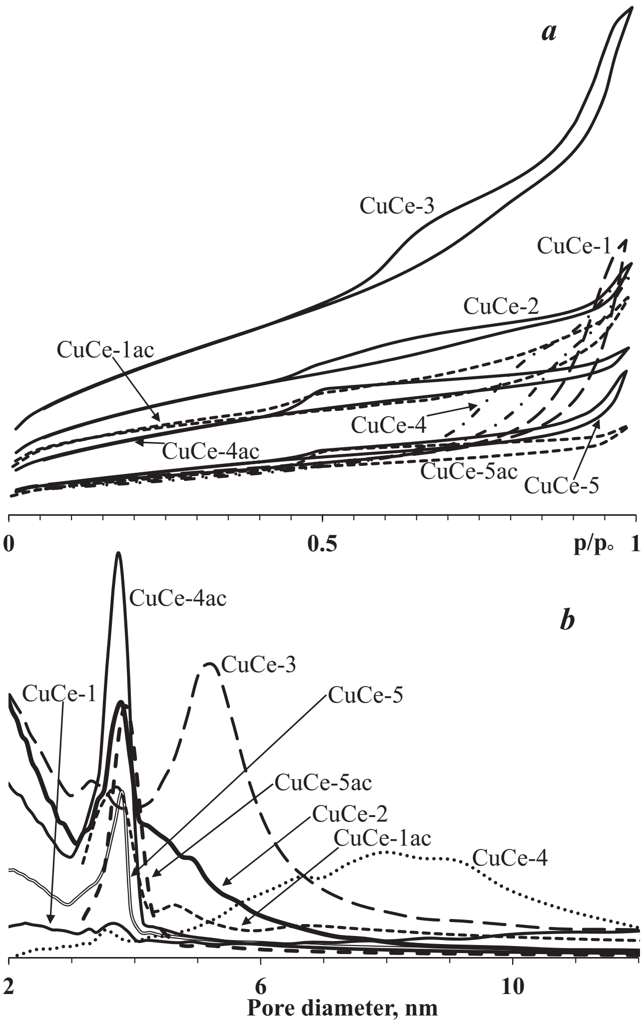

Fig. 2. Adsorption–desorption isotherms (a) and pore size distributions (b).

TEM analyses were conducted on Philips EM-301 transmission electron microscope with accelerating voltage of 100 kV.

SEM was obtained with TescanVEGAII LEO 1420 scanning electron microscope with accelerating voltage of 20 kV, equipped energy-dispersive X-ray spectrometer (EDS) INCA Energy 300.

X-ray photoelectron spectra were recorded on Kratos XSAM-800 with Mg K_α radiation (1253.6 eV). Background caused by secondary electrons and photoelectrons lost energy was approximated by a straight line. Measurements were carried out at a pressure of about 5×10^{-8} Pa. The spectra were recorded at room temperature. The calibration of the spectrometer was carried out by peaks Au 4f7/2 (84.0 eV) and Ni 2p3/2 (852.7 eV). The Ce 3d line at 916.7 eV was used as an internal standard for correction of binding energies [25].

3. Results and discussion

According to XRD (Fig. 1), all samples have two phase consisting of CeO_2 with a cubic fluorite structure (cF12) and monoclinic CuO (mC8). The copper content by XRD (Table 1) was lower than the initial defined composition. This means that a part of copper oxide is in a highly dispersed state (particle size less than 2 nm).

When comparing the mean crystallite size of ceria and copper oxide, the specific surface area of powders (Table 1), the patterns of relationship were as follows.

1) CeO_2 crystallite size in the samples obtained using AcAc as additional stabilizer is less than without use of AcAc. Thus, the