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Application of polyethyleneimine to obtain a mesoporous CuO–Al_2O_3 composite

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An organized mesoporous CuO–Al_2O_3 composite was synthesized using a sol-gel based self-assembly technique; unfolded polyethyleneimine supramolecular formations were employed as a structure-directing agent. The formation mechanism of a well-organized composite structure is explained.

Since the first successful synthesis of well-ordered, periodically organized mesoporous silica materials, such as the members of the M41S family[1] and SBA-15,[2] efforts have been directed toward extending the group of mesoporous materials to other inorganic systems[3] including their composites. Copper-based alumina catalysts are active in large-scale industrial processes.[4,5] These materials are generally prepared by the impregnation of commercial γ-Al_2O_3 having microporous and mesoporous structures. Valange *et al.*[6] used mesoporous alumina as a support.

Here, we report the synthesis of an organized mesoporous CuO–Al_2O_3 composite in one stage with a designed loading of 2.5 wt% Cu, which is an interesting and attractive material because of its application as a catalyst or catalytic membrane in heterogeneous catalytic reactions.[5,7]

Polyethyleneimine $M_n = 10000$ $(NHCH_2CH_2)_x[N(CH_2CH_2NH_2)CH_2CH_2]_y$ (2 g) was dissolved in double-distilled water (100 ml). The mixture was stirred for 15 min, and then copper nitrate (1.2 g) was added to the resulting solution. The system was kept for 1 h at 75 °C. After that, aluminum isopropoxide (16.4 g) was slowly added with permanent stirring; the mixture was kept for 2 h, and then concentrated nitric acid (2 ml) was added to reach pH 4. The molar ratio of the components $[Al(PrOH)_3]$:$[Cu(NO_3)_2]$:$[H_2O]$:$[HNO_3]$ was [0.08]:[0.006]:[5.6]:[0.03]. After that, the homogeneous gel was dried in air at 50 °C in a Teflon cup and the resulting dark-blue xerogel was calcined for 3 h at 500 °C in a tube furnace in order to remove the organic polymer from the pores. Addition of nitric acid results, on the one hand, in transition of the aluminum hydroxide precipitate to a sol and thus formation of positively charged micelles, and on the other hand, in uncoiling of polyethyleneimine macromolecules.[6] Donor–acceptor bonds are formed between imine groups and copper ions, and, as a result, a polymer-colloid complex is formed. Subsequently, aluminium oxide precursor particles are adsorbed on its surface. As we believe, this approach should produce a mesoporous material under conditions of layer-by-layer self-assembly, where first copper oxide precursor layers and then aluminum oxide precursor layers are formed in succession on the surface of supramolecular polyethyleneimine. According to the results of elementary analysis,† calcined samples contain insignificant amounts of C, N and H (less than 0.1 wt%). γ-Al_2O_3 is the main phase present in the composite. It is impossible to identify copper compounds from X-ray diffraction data due to the low content of these compounds. Most likely, the major part of copper is in the form of CuO and a small fraction is in the form of $CuAl_2O_4$.[5]

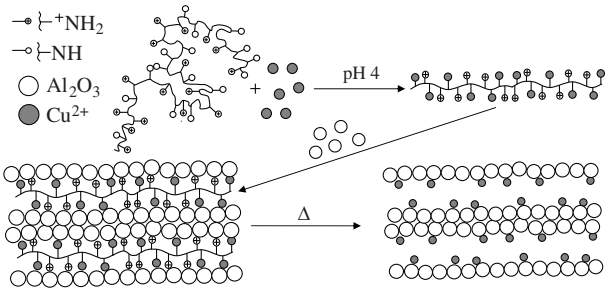

Figure 1 Scheme of CuO–Al_2O_3 formation.

Small-angle X-ray measurements were employed for detecting mesoporous structure in synthesized materials.[10] The presence of reflexes in low angle field explains the presence of long range ordering in systems.[11] The SAXS pattern of the uncalcinated CuO–Al_2O_3 composite exhibits only a single reflection having a maximum at $2\theta = 2.35°$ (Figure 2). In this case, the peak appears due to the presence of high organized periodic areas in the structure of composite, which generate polyethyleneimine supramolecular formations. The position of a

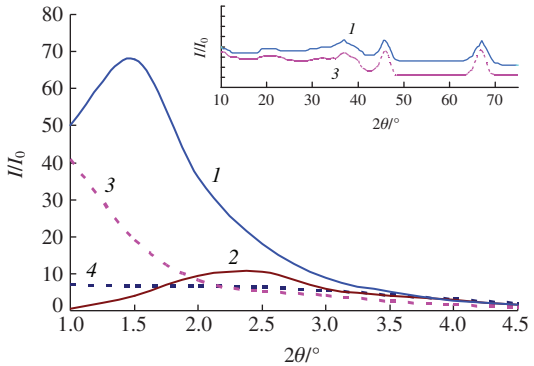

Figure 2 X-ray diffractograms of CuO–Al_2O_3 samples (*1*), (*3*) after calcination and (*2*), (*4*) before calcination; (*1*), (*2*) using polyethyleneimine, (*3*), (*4*) without template.

† *Characterization of the samples*. Atomic force microscope (AFM) studies were carried out using a SPM Solver P47H-PRO microscope. Mesoporous CuO–Al_2O_3 composite was applied on a glass plate having clean surface. X-ray scattering measurements were performed on a DRON-2 diffractometer using CuKα radiation (1.54 Å). The C, N, H content was measured on a Flash EA 1112 elemental analyzer. A Saturn-2 atomic absorption spectrophotometer was employed for determining copper concentrations in samples.

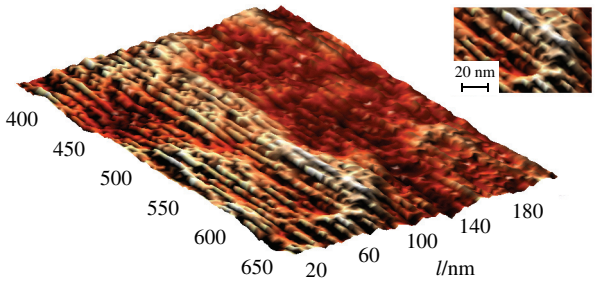

Figure 3 AFM image of mesoporous $CuO–Al_2O_3$ composite after calcination.

maximum after calcination is displaced into smaller value $2\theta = 1.55°$ because of increasing pore diameter in the samples at burning of the organic substance. Increase in intensity of reflex signifies to structurization of a material at calcination, leading to the formation of the organized mesoporous structure. Correlation length for calcined and uncalcined materials was calculated using the Bragg equation (5.7 and 3.8 nm, respectively). The SAXS patterns obtained without templates contained no peaks at a lower angle field.

The surface image of the synthesized sample of $CuO–Al_2O_3$ was obtained using an atomic force microscope (Figure 3). As the AFM image indicates, the surface of $CuO–Al_2O_3$ composite consists of highly organized channels of mesopores with an external diameter of the channel from 5 to 12 nm, which is in a good agreement with the data obtained by the small-angle X-ray measurements.

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