Study of copper nanoparticles formation on supports of different nature by UV-visible diffuse reflectance spectroscopy

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Abstract

Supported copper particles are widely used in heterogeneous catalysis. Influence of supports of different nature on the Cu particles formation is studied by the methods of UV-Visible spectroscopy of diffuse reflectance, XRD and electron microscopy. Different states of supported copper have been identified by UV-Vis spectroscopy: absorption bands at 250 (Cu^+), 320-370 and 400-440 (charge transfer bands of O-Cu-O and Cu-O-Cu complexes), 520-580 (Cu_n plasmon resonance) and 620-850 nm (d-d transitions in Cu^{2+} ions). The size of Cu clusters and $Cu_n/Cu_n^{\delta+}$ ratio strongly depends on the support nature.

Introduction

Copper "supported on" or "incorporated into" solid matrices is widely used for preparation of catalysts and nanocomposites with unusual optical, electrical and magnetic properties [1-3]; those are generated by properties of clusters and nanoparticles. The nature of the support is one of the most relevant factors influencing the physicochemical characteristics of metal particles [4-9]. Our previous studies of the supported copper species revealed that under the action of acid-base nature of support the electronic and oxidation-reduction properties of the supported metal, its degree of dispersion, a surface diffusion, proton acidity and a number of other characteristics are considerably changed [10-14]. All these factors exert a direct effect on formation of active surface of copper and, accordingly, on their catalytic properties.

The aim of the present work is the screening of the influence of supports of different nature on Cu particle formation by the methods of UV-Visible spectroscopy of diffuse reflectance.

Experimental

Crystalline Cu, 5 wt % Cu/corundum and 1 wt % Cu/zeolite (zeolites are mordenites with variable ratio in the range 5 < Si/Al < 103, erionite and clinoptilolite) samples were prepared for investigation of electronic states of supported Cu species. The metal was deposited by impregnation of the corundum support using $Cu(NO_3)_2$ solution, followed by calcination at 600°C for 4 hours. Cu-mordenites, Cu-clinoptilolite and Cu-erionite were prepared by ion exchange and reduced in hydrogen flow under fixed temperatures 150, 250, 350 and 450 °C. Crystalline Cu was prepared by electrolysis of $Cu(NO_3)_2$ solution. Crystalline Cu and Cu/corundum samples were applied to the processes of partial oxidation of methanol in a flow catalytic apparatus at 650°C for 76 h; their UV-Vis spectra were taken before and after reaction run.

UV-visible spectra of diffuse reflectance (DRS) were measured by means of a CARY 300 SCAN and Shimadzu UV-300 spectrometers (supports were used as reference samples). Characterization by X-ray diffraction was carried out using a Philips X'Pert diffractometer with CuK_α radiation. SEM characterization was carried out using JEOL

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JSM microscope, TEM micrographs were obtained on Philips CM 200 LaB6.

Results and Discussion

UV-visible spectra of fresh-prepared crystalline copper and Cu/corundum (Fig. 2) samples display only unstructured absorption corresponding to large metal particles. XRD and SEM show that the major part of copper in 5 %-wt. Cu/corundum sample is in the form of big particles (> 1000 nm). These aggregates do not have specific signals in electronic spectra in accordance with the literary data. According to Refs [15-18] only highly dispersed copper particles possess discrete signals in UV-visible range. However, after the long-term catalyst run in the reactor the spectroscopic pattern of the catalysts was changed sufficiently. XRD and SEM measurements revealed that part of big particles of copper was aggregated into larger ones (> 3000-5000 nm). However, 30-40 % of the support surface was not covered by large aggregates, but contained metal in highly dispersed states (2-10 nm) (Fig. 1a,b). These copper nanoparticles display a number of characteristic signals in UV-Vis range.
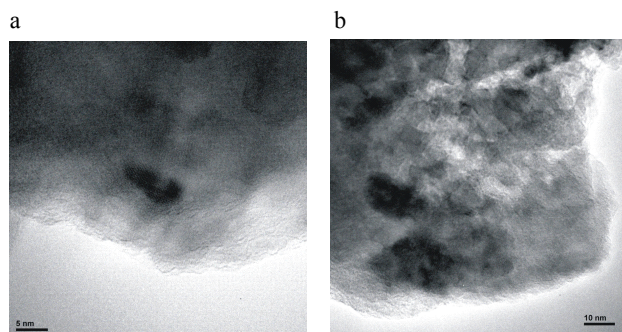

a b

Fig. 1. TEM micrographs of the used Cu/corundum samples.

Thus, in the spectrum of the used Cu/corundum catalyst noticeable signals at 360, 430, 550 nm and wide absorption in 630-660 range are observed (Fig. 2). According to literary data [15-18] the first two signals belong to O-Cu-O (1) and Cu-O-Cu (2) complexes (charge transfer bands). Absorption at 620-660 nm (4) is attributed to electron d-d transitions in Cu^{2+} in distorted octahedral surrounding by oxygen in CuO particles. Absorption bands in the range of 520-540 nm some authors attribute to $CuAl_2O_4$ [15, 17]. However, formation of aluminate structures is not typical for corundum, so this signal can belong to plasmon resonance (3) of Cu_n nanoparticles. This conclusion is confirmed by investigation of crystalline copper (Fig. 2) and Cu/zeolite samples (Fig. 3) as well as by calculations carried out in our previous work [19]. Thus, the prolonged run of the sample in catalytic reactor favors the formation of some amount of Cu^{2+} states and the metal nanoparticles.

The portion of dispersed copper particles increases if the support surface is modified by some metal oxides. Our previous studies of $Cu/\gamma-Al_2O_3$ samples [12] showed that additives of Zr, Ce and La oxides enhance metal-support interaction, since a large number of Lewis acid sites (Ce^{3+},

Ce^{4+}, Zr^{4+}, La^{3+} ions) emerges on the support surface. This increases the dispersity of the metal particles and slows down the metal surface diffusion under thermal treatments. In the case of corundum this effect is not so pronounced because of low surface area of the support. However, in the spectra of $Cu/ZrO_2/corundum$ and $Cu/CeO_2/corundum$ samples the signals attributed to charged copper particles are more intensive (Fig. 2).
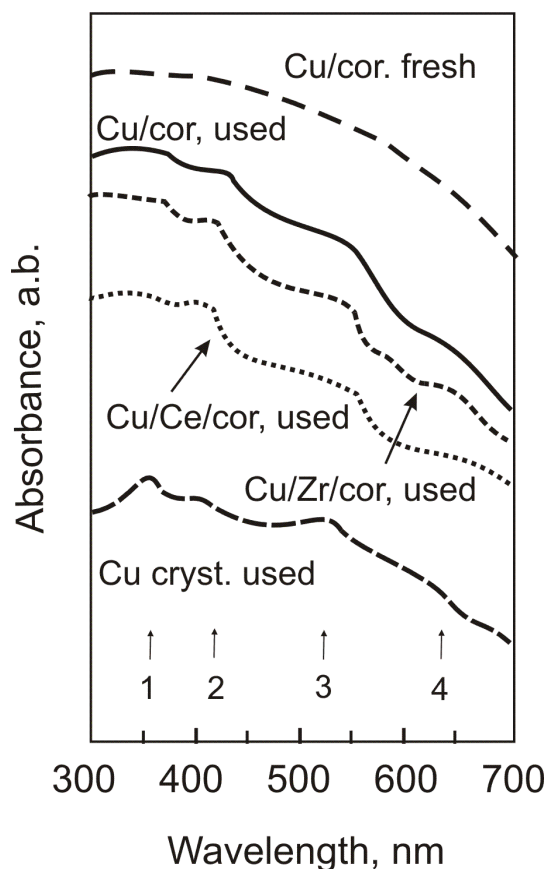

Fig. 2. DRS spectra of copper catalysts. Arrows mark positions of bands belonging to Cu-O-Cu (1), O-Cu-O (2), Cu_n (3), Cu^{2+} (4).

Unexpected signals are observed in the spectra of exhaust crystalline copper catalyst, namely, two pronounced bands at 350 nm (1) (O-Cu-O) and 540 nm (3) (Cu_n plasmon resonance) (Fig. 1). Bands at 420 (2) and 620 nm (4) are very weak. In this case we observe the formation of copper particles with separate electronic properties on the surface of bulk metal, because absorption bands in the range of 540-580 nm (3) belong to plasmon resonance bands of Cu_n particles. Thus, catalytic reaction accompanied by oxidation-reduction cycles of metal Cu favors the formation of small metal particles. For Cu/corundum it can be explain as Cu dispersion, but for crystalline copper appearance of plasmon resonance band can be only due to formation of nanoparticles with distinct electronic properties on the surface of bulk metal during the catalytic process. It is worthy of note that anodized electrodes developing surfaces with characteristic nano-roughness and active in SERS have fractal properties.

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This harsh surface forms so-called hot areas, in which the electromagnetic radiation concentrates; those are responsible for strengthening of an electromagnetic field and enhancing of Raman spectra [20]. This unusual at first glance process is also observed on the clean metal surfaces. In the nucleation of a new layer on a crystal, the properties of the small clusters formed initially on the surface play a significant role in the overall kinetics. When a Pt wire is evaporated in vacuum over Pt single crystal, Pt atoms arrive at the (111) plane and forms clusters of different size on the bulk Pt metal surface [21-22]. These platinum clusters on Pt(111) have been examined to provide atomistic information about their stability and mobility. It was shown from the STM experiments that dimers and all other small clusters are stable nuclei up to 400 K, i.e. they do not dissociate on a time scale relevant to island formation. Detailed data were obtained also on the properties of Ir clusters containing from two to eight atoms stabilized on the Ir surface [23]. Similar mechanism can explain the development of catalytically active centers on the surface of bulk metals, but in this case it takes place in the atmosphere of reaction. So, not only small metal clusters and particles are formed, but their oxidized forms too.

In contrast with matrices like corundum and alumina, the crystallinity of zeolites *a priori* provides the special organization of the composite material due to highly regular porous system. Variation of zeolite structure, acidity of zeolites (regulated via Si/Al ratio) and reduction temperature are the main factors influencing metal reducibility and appearance of copper reduced forms. In the recent publication [19] we have shown the leading role of SiO_2/Al_2O_3 molar ratio (MR) in mordenite (from 10 through 206) on the optical appearance of reduced copper species. Changing the chemical composition of mordenite framework leads to a non-monotonous dependence of the copper reducibility upon MR (Fig. 3). Zeolite structure type is another factor to con-

the low-acidity matrices that are distinguished from mordenite by the geometry of intracrystalline voids and dielectric properties. It was shown earlier [4, 24-25] that coordination, localization and stabilization of copper ions in the zeolitic materials depend strongly on the structure and composition of zeolite matrix. The *redox* behavior of the system $Cu^{2+}/Cu^+/Cu^0$ is known to be very sensitive to medium and complexation of copper by different ligands. For copper within zeolites this role is played by the solid matrix. DRS spectra of selected mordenite samples (Fig. 2) demonstrate that the same zeolite structure but with different MR change products of copper reduction drastically. Copper is easily reduced to small copper particles in mordenites with high MR=206. According to estimations made by us recently from the spectral appearance [26], such shape of spectra has copper particles with size of order of several nanometers. Copper reduced under intermediate acidity of the matrix (mordenite with SiO_2/Al_2O_3=30) reveals an optical absorption feature in the form of a shoulder associated with the particles of less size. High-acid mordenites with SiO_2/Al_2O_3=15 prevent the particle formation (Fig. 3). The three types of zeolites under consideration (Cu/Mordenite, Cu/Erionite, and Cu/Clinoptilolite) provide similar temperature range of the process (at 450°C the reduction can be considered as complete). But even at the beginning of reduction the shape of plasmon resonance peak is the same. It means that copper particles have approximately the same size as at the higher temperatures. That is to say, the size of particles is controlled by the matrix properties. Detailed calculations of the influence of these parameters upon the optical appearance of reduced copper were done in our previous studies [19,25].

Conclusions

1. Spectroscopic experiments identified different copper particles in the oxide matrices – ions, charged clusters, crystallites. These features depend strongly on the nature of the support.

2. Low-acid mordenites with highest SiO_2/Al_2O_3 molar ratios, as well as clinoptilolite and erionite, favor efficient copper reduction with the formation of particles with an approximate radius of a few nanometers. This produces a pronounced plasmon resonance band in the visible range (550-600 nm).

3. During the catalytic process the portion of highly dispersed copper particles increases sufficiently as a result of surface diffusion of the metal. Modifying additives of metal oxides increases part of charged copper particles on the support surface. These effects are caused not only by the difference in the metal particle dispersivity, but also by interaction of copper atoms and ions with Lewis acid sites of the support. Copper ions, neutral and partly charged clusters (Cu_n and $Cu_n^{\delta+}$) play a great role in formation of the catalyst active surface.

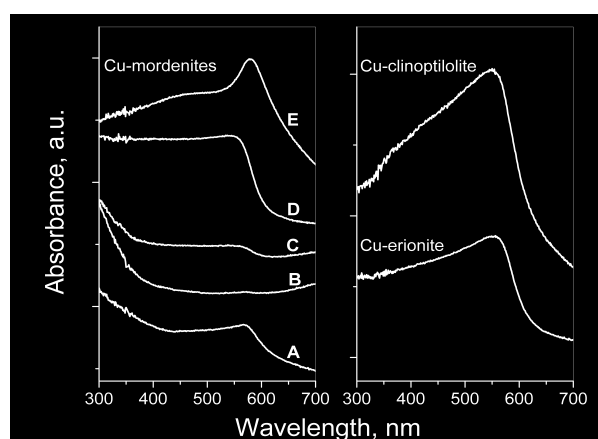**Fig. 3.** DRS spectra of Cu-zeolites reduced at 450 °C. For Cu-mordenites SiO_2/Al_2O_3 molar ratios are: 10 (A), 15 (B), 20 (C), 31 (D) and 206 (E).

trol copper reducibility and state of final products. Properties of mordenites are controlled by MR from 10 through 206, while erionite and clinoptilolite were chosen as examples of

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