Eur. Phys. J. D **34**, 55–58 (2005)
DOI: 10.1140/epjd/e2005-00118-5

THE EUROPEAN PHYSICAL JOURNAL D

Influence of modifying additives on formation of supported copper nanoparticles

A.N. Pestryakov[1,a], V.V. Lunin[2], D.I. Kochubey[3], A.Yu. Stakheev[4], and E. Smolentseva[1]

[1] Tomsk Polytechnic University, Tomsk 634050, Russia
[2] Chemistry Department, Moscow State University, Moscow 119899, Russia
[3] Boreskov Institute of Catalysis, Novosibirsk 630090, Russia
[4] Institute of Organic Chemistry, Moscow, Russia

Received 6 September 2004

Abstract. The influence of modifying additives of Ce, Zr, La and Cs oxides on changes of electronic state of supported copper during the catalytic reaction of butane complete oxidation has been studied by the methods of IR-spectroscopy of adsorbed CO, XPS, EXAFS and XRD. The modifying additions of cerium and zirconium oxides stabilize the ionic state of copper, while lanthanum and cesium oxides decrease the effective charge of copper ions. The observed effects are caused by variation in metal dispersivity in the modified samples and by electron donor-acceptor interaction of the surface atoms and ions of copper with the modifier.

PACS. 36.40.Cg Electronic and magnetic properties of clusters – 82.80.Gk Analytical methods involving vibrational spectroscopy – 82.65.+r Surface and interface chemistry; heterogeneous catalysis at surfaces

1 Introduction

Surface electronic states of copper play an important role as active sites of Cucontaining catalysts for a number of catalytic processes (deep and selective oxidation, dehydrogenation, steam reforming, etc.) [1–5]. In spite of the long-term investigations, the nature of active sites of copper catalysts and the mechanism of interaction of the active component with the supports and modifiers is still under the discussion. Modification of the catalysts by inorganic additions having electron-seeking or electron-releasing properties is a promising method of action on the metal electronic state. Our previous studies revealed significant effect of additives of Zr, Ce, La and Cs oxides on the electronic and catalytic properties of Cu, Ag and Au in the process of alcohol partial oxidation [6–12].

The aim of the present work is to study the changes in electronic states of supported copper under the action of the catalytic process and influence of the modifying additives on these changes.

2 Experimental

1.0 wt.% Cu/support samples were prepared for investigation of catalytic and electronic properties of copper using γ-Al_2O_3 and pumice as supports. Before copper impregnation 1 wt.% of modifying additives of Zr, Ce, La and Cs oxides were deposited on the support from metal nitrate or acetate solutions, followed by thermal decomposition of those salts to oxides in air at 300 °C for 3 hours. Then the metal was deposited by impregnation of the support using $Cu(NO_3)_2$ solution, followed by calcination at 600 °C for 4 hours.

The spectra of the samples were registered before and after using in the processes of complete oxidation of butane. The experiments were carried out in a flow-circulating catalytic apparatus under the following operating conditions: $T = 300$ °C, butane concentration in air 1 vol.%, flow rate — 10000 h^{-1}.

IR-spectra of adsorbed carbon monoxide were recorded on a Specord M80 spectrometers ($P_{CO} = 1.5$ kPa). X-ray diffractograms were recorded in a Philips X'pert diffractometer equipped with a curved graphite monochromator. CuK_α ($\lambda = 0.154$ nm) radiation; HRTEM photomicrographs were obtained on JEOL 2010 electron microscope. Copper K-edge EXAFS data were recorded at room temperature using the EXAFS station of the Siberian Center of Synchrotron Radiation, Novosibirsk, Russia. XPS measurements were carried out using XSAM-800 (monochromatic Al K_α source).

3 Results and discussion

Study of the catalysts by IR spectroscopy, as well as IR spectra of probe molecules can give important information on Cu^+ and $Cu_n^{\delta+}$ states [13]. Within the ranges

---

[a] e-mail: `anp@tspace.ru`

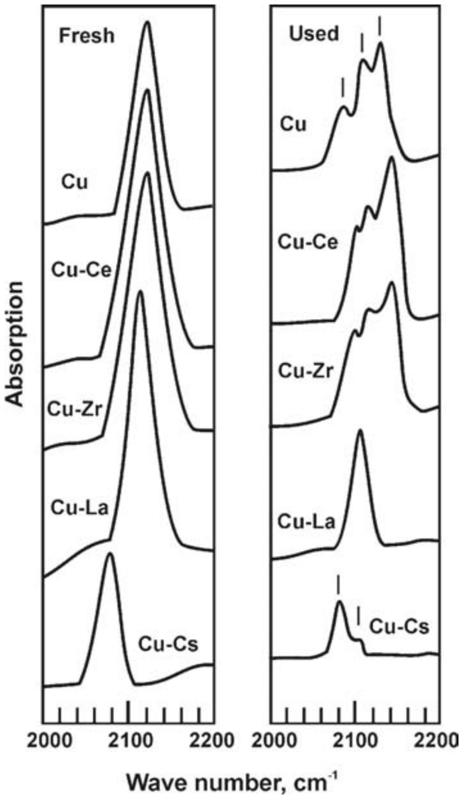

Fig. 1. IR spectra of CO adsorbed on the fresh and used Cu/Al_2O_3 catalysts.

of the $\sigma-\pi$ binding model, the carbon monoxide molecules that adsorb on metal atoms and ions interact with their valence *d*-electrons, and the frequency of the ν_{CO} stretching vibrations in the surface M-CO complexes depends directly on the effective charge of the adsorbent [14]. The system CuO/Al_2O_3 is studied rather well by the method of IR-spectroscopy of adsorbed CO [13–20].

The spectrum of the initial CuO/Al_2O_3 sample exhibits an intensive absorption band at 2120 cm^{-1} attributed to CO stretching vibrations in Cu^+-CO surface complexes (Fig. 1, left). X-ray diffraction analysis shows that most of the copper in this sample is in Cu^{2+} state (oxide and aluminate), but it is obvious that under the conditions of low-temperature reduction with CO a sufficient part of the surface ions is transformed from Cu^{2+} to Cu^+. In this case the formation of surface carbonates is observed (absorption bands at 1350, 1470 and 1550 cm^{-1}). On Cu^{2+} ions CO molecules are not adsorbed under these conditions, which are confirmed by previous data [14–20].

The catalyst performance in the butane oxidation reaction leads to the appearance of three signals of medium intensity at 2135, 2110 and 2090 cm^{-1} in IR spectra (Fig. 1, right). Concurrently, X-ray spectra indicate the metal phase in the catalyst. The low-frequency signal at 2090 cm^{-1} corresponds probably to Cu^o-CO complexes in small clusters of copper. On large three-dimensional particles of copper CO is not adsorbed at room temperature due to weak *s*-*p* interaction of CO with the metal having a completed *d*-electron orbit [14]. According to reference [14] CO absorption bands at 2110 and 2135 cm^{-1} belong to surface carbonyl complexes of singly charged copper in definite oxygen coordination: tetragonal (2110 cm^{-1}), which is ordinary for CuO phase, and tetragonal pyramid (2135 cm^{-1}), which is formed as a result of interaction of CuO and Cu_2O with the support oxygen ions. Evidently, both these states of copper are presented in the initial sample, but the intense band of carbonyl complexes of Cu^+ in tetragonal coordination (2120 cm^{-1}) overlaps completely the other signals. It is obvious that during the catalytic reaction the copper ions are partially reduced under the action of the reaction medium.

Spectra of the samples modified by cerium oxide ($CuO{:}CeO_2/Al_2O_3$) are distinguished by a high intensity of CO absorption bands characterizing ionic state of copper. It may be explained by growth of the metal dispersivity and, accordingly, surface ion concentration. Really, photomicrographs reveal that copper dispersivity in the modified catalysts is higher than that in pure Cu/Al_2O_3. It is apparent that injection of the modifier enhances metalsupport interaction as a great number of sites for copper particle stabilization emerges on the support surface (Ce^{3+} and Ce^{4+} ions).

However not only copper particle size influences the intensity of Cu^+-CO signals. The addition of cerium oxide stabilizes ionic states of copper (Cu^+ and Cu^{2+}). Although Cu^{2+} ions are not identified by the method of IR-spectroscopy of adsorbed CO under our conditions, X-ray diffraction spectra confirm that the modified catalysts contain a greater fraction of ionic copper compounds as compared with the unmodified sample. Copper ions in the modified catalysts are more resistant to reduction under redox treating.

Character of variation in position of absorption bands of Cu^o-CO and Cu^+-CO in IRspectra of Cu-Ce catalyst after run in butane oxidation is approximately analogous to the observed for unmodified Cu/Al_2O_3. We detect three pronounced signals at 2142, 2123 and 2100 cm^{-1}. But as mentioned above, the intensity of these bands are higher and they are shifted to high-frequency range for 5−10 cm^{-1}. The absorption band at 2115 cm^{-1} in the spectra of the reduced samples is absent, perhaps, because of superposition of more intensive neighboring bands. It seems also plausible that in the presence of the modifier Cu^+ coordination close to tetragonal pyramid is more preferable.

Thus, we can conclude that CeO_2 additive stabilizes the ionic states of supported copper. This is also confirmed by XPS of the samples (Fig. 2). Signal at 934 eV is attributed to Cu in CuO [21]. Small shoulder at 936 eV in the spectrum of Cu-Ce catalyst may belong to Cu ions strongly interacted with the modifier.

Similar to Cu-Ce sample the IR spectra of Cu-Zr catalyst are characterized by more intensive signals of oxidized copper and high-frequency shift in the spectrum of the used catalyst (Fig. 1).

Significant shift of the frequency of CO stretching vibrations (ν_{CO}) to lowfrequency range is observed in all spectra of the samples modified by lanthanum oxide

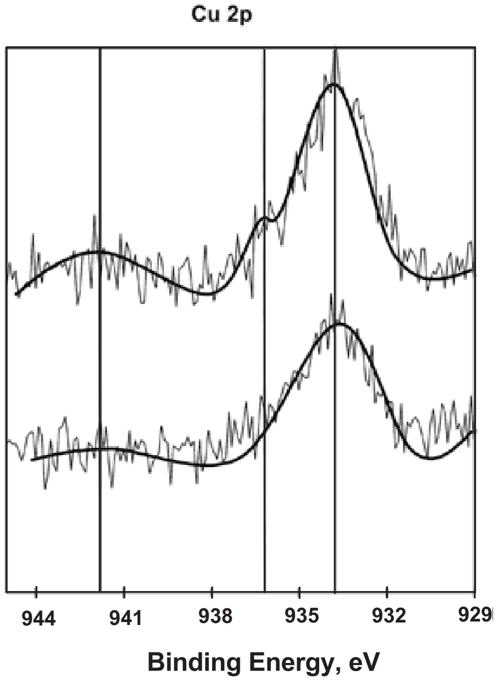

Fig. 2. XPS of the used copper catalysts.

($CuO:La_2O_3/Al_2O_3$). Spectrum of initial CuLa sample exhibits single CO absorption band at 2115 cm^{-1}. After run of Cu-La catalyst in butane oxidation this signal disappears and the band at 2105 cm^{-1} with similar intensity emerges.

Formally, CO absorption bands at 2100 and 2105 cm^{-1} belong to Cu^o-CO complexes. However, symmetry of the signal, as well as absence of any other bands permit to suppose the ionic character of copper state in these carbonyl complexes. Moreover, X-ray diffraction spectra indicate along with metal phase a certain amount of copper oxide in these samples that should be exhibited in IR-spectra of adsorbed CO. Too low ν_{CO} in Cu^+-CO complexes may be caused by electronic donor-acceptor interaction of copper ions with oxygen ions of La_2O_3. Study [20] showed that in CuO/MgO catalyst copper ions due to strong electron-releasing influence of the basic support are transformed to the specific ion state having the decreased effective charge, which corresponds to CO absorption bands at 2080−2100 cm^{-1}. The investigation of surface basic sites of La_2O_3 by IR-spectroscopy method [22] revealed that surface basicity (that is charge density on surface oxygen ions) of lanthanum oxide is very high, close to that of CaO. So it is logical to conclude that modification of the support by La_2O_3 imparts it electron-releasing properties and lowers effective charge of supported copper ions, that results in low-frequency shift of CO absorption bands in IR-spectra of the samples. Decreasing of ν_{CO} after the catalyst run (2115−2105 cm^{-1}) is probably explained by donoracceptor influence on Cu^+ of neighboring Cu^o or Cu^{2+} formed under redox treatment of the catalyst.

This effect is much more pronounced for the catalyst modified by cesium oxide. In the spectra of the fresh Cu-Cs we observed only low-frequency band at 2080 cm^{-1}. In exert sample a small shoulder at 2100 cm^{-1} appeared. Changes in the positions and intensities of these bands under effect of reaction medium, and reasoning mentioned above permit us to attribute the signals to $Cu^{\delta+}$-CO complexes. Low effective charge of copper ions in these catalysts is caused by strong electron-releasing effect of basic modifier.

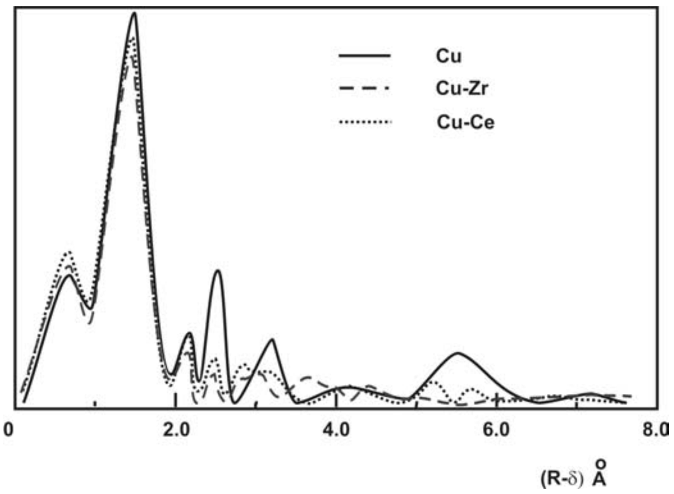

Fig. 3. EXAFS of the used copper catalysts.

All the observed effects may be explained by an increase in the metal dispersivity and surface ion concentration. HRTEM and XRD data reveal that the size of copper particles in the studied catalysts changes within the range 5−40 mn depending on the nature of the modifier and treatment conditions. The metal dispersivity in all the modified catalysts is higher than that in pure Cu/Al_2O_3. It is apparent that injection of the modifier enhances metal-support interaction, since a large number of Lewis acid sites (Ce^{3+}, Ce^{4+}, Zr^{4+}, La^{3+} ions) emerge on the support surface. This increases the dispersivity of the metal particles and slows down the metal surface diffusion under thermal treatments.

However, dispersivity of the metal cannot explain all the observed effects because the samples with close dispersion (Cu-Ce and Cu-La) have different spectral properties and, vice versa, catalysts with different dispersion (Cu-La and Cu-Cs) have similar pattern in IR spectra. The experiments showed that differences in spectral pattern of the catalysts are caused by direct interaction of copper atoms, ions and clusters with Lewis acid sites of the support surface.

EXAFS gives important additional information about the metal-modifier interaction (Fig. 3). Analysis of the spectra of the used catalysts showed that in Cu/Al_2O_3 the most part of Cu ions are in associated state. Signals corresponding to Cu-Cu bonds are not observed (only Cu-O features are presented). It means that band at 2100 cm^{-1} in the IR spectra of the used Cu, Cu-Ce and Cu-Zr samples (Fig. 1) belongs to the carbonyl complexes of ionic copper with low effective charge or to CO adsorbed on the isolated electron-deficient atoms. EXAFS also confirmed the conclusion about ionic character of the carbonyl complexes of copper having absorption band in the range 2080−2110 cm^{-1} in IR spectra of Cu-La and Cu-Cs samples. Thus, in the reaction conditions Cu^{2+} ions are reduced mainly to Cu^{+} state.

EXAFS revealed that in the used Cu-La and Cu-Cs catalysts the most part of copper is in the associate form, although portion of the isolated states increases as compared to the unmodified catalyst. In contrast, in the Cu-Ce and Cu-Zr samples 3/4 of the supported metal is in the isolated form. Signals corresponding to Cu-Cu bonds are not observed.

4 Conclusions

Modifying additives of metal oxides change sufficiently the electronic state of supported copper during the catalytic reaction. These effects are caused by differences in the metal particle dispersivity as well as interaction of copper atoms and ions with Lewis acid sites of the support.

Ce and Zr oxides exert an electron-seeking effect on supported copper, stabilize the oxidized state of the metal and increase the effective charge of copper ions. In contrast, La and Cs oxides lower the effective charge of Cu^{+} and $\mathrm{Cu}_n^{\delta+}$ and favor their fast reduction during catalytic reaction.

This research is supported by Grant No. UR.05.01.413, Program “Universities of Russia”.

References

1. Y. Liu, T. Hayakawa, K. Suzuki, S. Hamakawa, T. Tsunoda, T. Ishii, M. Kumagai, Appl. Catal. A **223**, 137 (2002)
2. T.P. Minyukova, I.I. Simentsova, A.V. Khasin, N.V. Shtertser, N.A. Baronskaya, A.A. Khassin, T.M. Yurieva, Appl. Catal. A **237**, 171 (2002)
3. H. Yahiro, M. Iwamoto, Appl. Catal. A **222**, 163 (2001)
4. A. Santos, P. Yustos, B. Durbán, F. García-Ochoa, Catal. Today **66**, 511 (2001)
5. A. Saadi, Z. Rassoul, M.M. Bettahar, J. Mol. Catal. A **164**, 205 (2000)
6. A.N. Pestryakov, A.A. Davydov, P.G. Tsyrulnikov, Prepr. Am. Chem. Soc., Div. Petr. Chem. **41**, 96 (1996)
7. A.N. Pestryakov, A.A. Davydov, Appl. Surf. Sci. **103**, 479 (1996)
8. A.N. Pestryakov, A.A. Davydov, Kinet. Catal. **37**, 923 (1996)
9. A.N. Pestryakov, A.A. Davydov, Appl. Catal. A **120**, 7 (1994)
10. A.N. Pestryakov, Catal. Today **28**, 239 (1996)
11. A. Pestryakov, V. Lunin, A. Kharlanov, D. Kochubey, N. Bogdanchikova, A.Yu. Stakheev, J. Mol. Struct. **642**, 129 (2002)
12. A. Pestryakov, V. Lunin, A. Kharlanov, N. Bogdanchikova, I. Tuzovskaya, Eur. Phys. J. D **24**, 307 (2003)
13. J. Ryczkowski, Cat. Today **68**, 263 (2001)
14. A.A. Davydov, *Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides* (Wiley, New York, 1990)
15. S. Tikhov, E. Paukshtis, V. Sadykov, Kinet. Catal. **30**, 869 (1989)
16. M. Arai, S. Nishiyama, S. Tsuruya, M. Masai, J. Chem. Soc. Faraday Trans. **92**, 2631 (1996)
17. G. Ghiotti, F. Boccuzzi, A. Chiorino, *Adsorption and Catalysis on Oxide Surfaces* (Elsevier, Amsterdam, 1985), p. 235
18. G. Ghiotti, F. Boccuzzi, Catal. Rev.-Sci. Eng. **29**, 151 (1987)
19. M.A. Kohler, N.W. Cant, M.S. Wainwright, D.L. Trimm, J. Catal. **117**, 188 (1989)
20. M.L. Shepotko, A.A. Davydov, A.A. Budneva, Kinet. Catal. **35**, 612 (1994)
21. *Handbook of X-ray Photoelectron Spectroscopy*, edited by J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben (Publ. Perkin Elmer Corp., Eden Prairie, USA, 1992)
22. A.N. Pestryakov, Dr. Sc. thesis, Moscow State University, Moscow, 1998