



Modified copper catalysts in methanol oxidation

A. Pestryakov^{a,*}, V. Petranovskii^b, O. Temkin^c, V. Belousova^d

^a Fritz Haber Institute, Berlin 14195, Germany;

^b Centro de Ciencias de la Materia Condensada, UNAM, Ensenada 22800, México

^c Lomonosov Fine Chemical Technology Institute, Moscow 117571, Russia

^d Tomsk State University, Tomsk 634050, Russia.

* Corresponding author: e-mail alex@fhi-berlin.mpg.de,

Resumen

Se estudiaron las características del proceso de la oxidación parcial y profunda del metanol en los catalizadores de cobre soportados con referencia a las muestras de plata. La influencia de los soportes de diversa naturaleza de ácido-base y de aditivos de modificación de los óxidos de Zr, Ce, La y Cs sobre estados electrónicos del cobre soportado fue investigada por los métodos de espectroscopia de reflectancia difusa, difracción de rayos X y microscopia electrónica. Comparando datos catalíticos y espectroscópicos las conclusiones en la naturaleza de los sitios activos de los catalizadores de cobre en este proceso ha sido hecha.

Abstract

Features of the process of methanol partial and deep oxidation on supported copper catalysts as compared with silver samples have been studied. The influence of supports of different acid-base nature and modifying additives of Zr, Ce, La and Cs oxides on electronic states of supported copper was investigated by the methods of diffuse reflectance electron spectroscopy, XRD and electron microscopy. By comparison of catalytic and spectroscopic data a conclusion on the nature of active sites of copper catalysts in this process has been made.

Keywords: copper catalysts, methanol oxidation, active sites, UV-visible spectra

Introduction

The processes of partial oxidation of alcohols on metal catalysts are widely used in organic synthesis for production of aldehydes and ketones [1]. Historically copper was the first catalyst of selective oxidation of alcohols. Later more effective silver catalyst everywhere has superseded copper from this process. Now on some companies producing formaldehyde in "soft" conditions, the copper grids are placed in bottom of the reactor after a layer of crystalline silver and silver grids, forming thus multilayer Ag-Cu catalyst. For many years the interest of the researchers to copper catalysts for alcohol oxidation does not decay, and in the literature (mainly, patent one) the different versions of copper and complex Ag-Cu contacts are permanently offered purposing to lower the consumption of the noble metal [2-18].

Practically all authors of published studies note, that, despite of different attempts to update copper catalyst, its

selectivity is inferior to Ag-containing systems. It is explained, as a rule, by formation of CuO oxide under the conditions of the process; it is known that Cu(II) intensifies complete oxidation of alcohols. So, the authors of Refs [8-9] explain promoting effect of the additives of alkali metal oxides to copper catalyst in analogous process of conversion of benzalcohol to benzaldehyde by decreasing CuO quantity. At the same time, the high selectivity of uncharged copper (Cu₂O) in partial oxidation of hydrocarbons (for example, acrolein) is well known [19].

Thus, in spite of the long-term investigations, the question on 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 discussion. This investigation aimed at finding the influence of different factors (supports, modifiers, operating conditions) on the formation of active surface of supported copper in partial and deep oxidation of methanol.

Experimental

10 wt.% Cu/support samples were prepared using corundum ($\alpha\text{-Al}_2\text{O}_3$), MgO and pumice as supports (0.5-2.0 m^2/g). 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 h. Then the metal was deposited by impregnation of the modified supports using $\text{Cu}(\text{NO}_3)_2$ solution, followed by calcination at 600 °C for 4 h.

Copper supported on mordenite was used with a purpose to obtain reference spectra of different copper species in UV-Vis range. 1 wt % Cu-mordenite was prepared by ion exchange from aqueous 0.1 M $\text{Cu}(\text{NO}_3)_2$ solution, followed by reduction in hydrogen flow at 200 and 450 °C. CuO/mordenite was obtained by fast oxidation in air of hydrogen-reduced Cu particles in Cu/Mor with air at 450 °C.

Electronic spectra of diffuse reflectance (ESDR) were recorded on CARY 300 SCAN. X-ray diffraction (XRD) measurements were done using a DRON-3 diffractometer. Micrographs of the catalysts were obtained using JEOL JSM-35C electron microscopes. Brønsted acidity of the catalyst surface was studied using the method of non-aqueous potentiometric titration by $\text{C}_2\text{H}_5\text{OK}$ in dimethylformamide medium.

The samples were tested in the processes of partial oxidation of methanol. The experiments were carried out in a flow catalytic apparatus under the following operating conditions: $T = 600\text{-}700^\circ\text{C}$, $\text{O}_2/\text{alcohol}$ ratio = 0.3, catalyst layer thickness = 10 cm, gas flow volume rate = 1000 h^{-1} . The processes were conducted in auto-thermal mode.

Results and discussion

The nature of the support is one of the most relevant factors influencing the physicochemical and catalytic characteristics of metal catalysts. In our previous studies of the supported silver catalysts of alcohol oxidation it was revealed that, depending on the acid-base nature of the support, the electronic and oxidation-reduction properties of the metal, its dispersivity, a surface diffusion, Brønsted acidity and number of other characteristics are considerably changed [20-22]. All these factors exert a direct effect on formation of active surface of silver catalysts and, accordingly, on their catalytic properties.

The results of tests of different copper/support catalysts in oxidation of a methanol are shown in the Figure 1. It can be observed that the changes of catalytic properties of copper catalysts depend on the nature of the support in the way different from similar parameters of silver contacts studied earlier [20-23]. Thus, for getting a maximum formaldehyde yield on copper catalyst the greater content of metal (6-8 wt.%) is necessary than on Ag ones (*ca.* 5 wt.%), that in recalculation on an atomic weight twice exceeds a similar index for silver. The activities of the Cu/pumice and Cu/corundum samples differ a little. The selectivity of the

sample Cu/MgO is lower than the other catalysts; however, appearance of a curve differs from that one obtained for Ag/MgO sample as well.

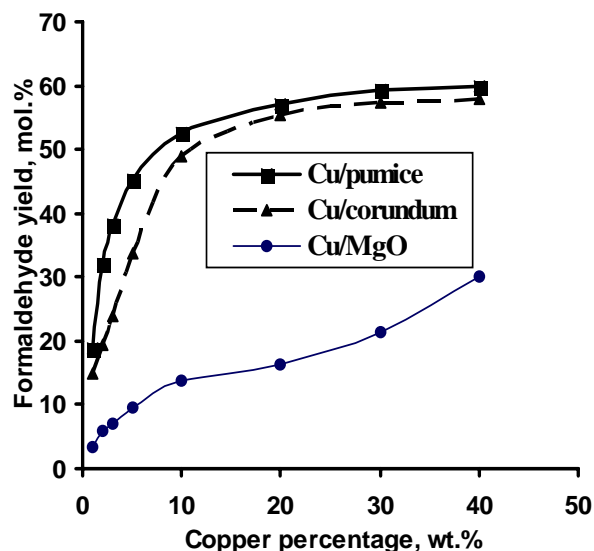


Figure 1. Catalytic properties of supported copper catalysts in methanol partial oxidation (650°C).

Preliminary studies demonstrated that: 1) the intrinsic catalytic properties of supports exert a minor effect on the parameters of the metal catalysts; 2) the dispersivity of the metal under the diffusion conditions of alcohol oxidation practically does not influence its catalytic characteristics.

Apparently, the observed influence of the support on catalytic properties of supported copper is caused by the features of electronic properties of copper. Earlier [21-26] we put forward the supposition, that active sites of silver catalysts in oxidation of alcohols are the one-charged cations Ag^+ . In the studied process, copper forms two ionic states - Cu^+ and Cu^{2+} , those are registered by XRD method as Cu_2O and CuO phases. While the first ion, according to our hypothesis, is active site of partial oxidation, the divalent ion catalyzes deep oxidation that agrees with the literary data [19]. Hence, catalytic properties of copper depend on a ratio of these states on the catalyst surface. When Cu content in the sample is low, the metal on the support surface is in the form of high-dispersed particles those are oxidized easily. Earlier we showed that the aluminosilicate supports stabilize the oxidized states of silver and increase their effective charge [20]. In the case of copper the aluminosilicate supports (including pumice) stabilize both univalent ions (that increases selectivity), and the divalent states (that raises the proportion of deep oxidation). As the XRD data demonstrate, under reducing conditions of aldehyde synthesis process, ionic copper is mainly in Cu^+ state that determines the priority of selective oxidation reactions. Nevertheless, the aluminosilicates (including pumice) stabilize also some Cu^{2+} ions those lower the efficiency of the aluminosilicates in a series of other supports for copper catalysts as compared with the analogous silver contacts. Support with the basic properties (MgO) decreases the oxidizability of metal copper

(quantity of active sites) and effective charge of ions. So the selectivity of the catalyst in oxidation of alcohols decreases, but as on MgO the portion of Cu^{2+} drops as well, the effect of impairing the catalytic properties of Cu/MgO is less expressed as compared with the Ag/MgO sample.

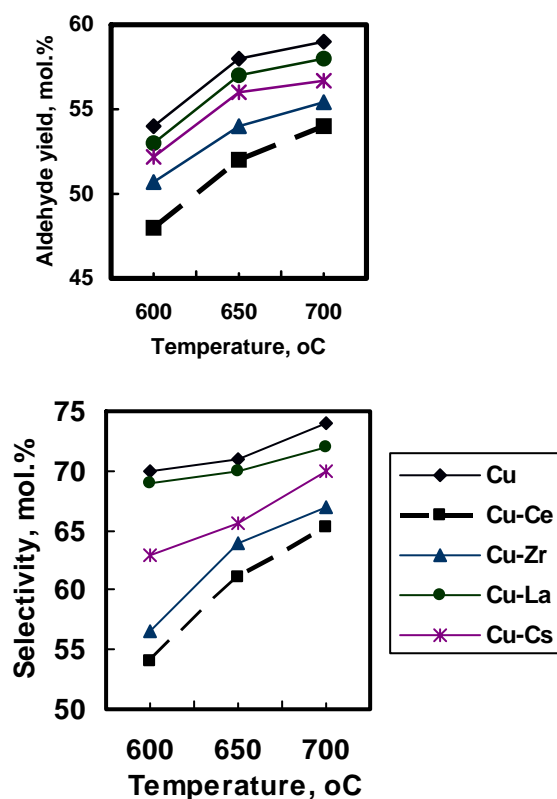


Figure 2. Catalytic properties of modified Cu/pumice catalysts in methanol partial oxidation

Results of the tests of modified 10 wt. % Cu/pumice catalysts confirm these conclusions. As the Figure 2 demonstrates, Ce and Zr oxides considerably degrade the selectivity of copper catalysts, increasing a contribution of deep oxidation reaction. La and Cs oxides do not produce the promoting effect, but characteristics of Cu-La and Cu-Cs samples exceed the parameters of Cu-Ce and Cu-Zr. Thus, the effects of modifying agents on catalytic properties of copper have an inverse character as contrasted to silver samples [22-25].

The tests of modified pumice (without deposition of copper) under the same conditions showed that all the modifiers increase formaldehyde yield as compared with sample of the unmodified support.

Thus, the intrinsic catalytic properties of modifying additives in this process cannot explain the observed effects. The changes in specific surface area of copper at the introducing of modifying agents are insignificant (according to the data of electron microscopy) because of low surface area of the support and high contents of the metal. Moreover, the dispersivity of the metal does not play a noticeable role under the diffusion conditions of the process.

The modifiers change Brønsted acidity of the catalysts as well. The experiments show that all additives (except of Cs_2O) increase the concentration and strength of proton acid sites of the support surface (Table 1). As it is known from the previous studies [27-29] the reactions of alcohol destruction occur on strong proton sites, so Brønsted acidity is the main cause of the catalyst carbonization in this process. However, these effects are notably expressed only after prolonged run of the catalysts, whereas in short-time laboratory experiments the catalyst coking is not observed. Hence, changes in surface acidity cannot explain the character of the modifying action of the additives on the catalytic properties of the samples.

The obtained results could be concerned with electronic factors. According to the earlier obtained spectral data [30-31], the addition of Ce and Zr oxides increases concentration of active states of Cu^+ in the catalyst, but at the same time raises sufficiently a portion of Cu^{2+} states that gives in total negative effect. In contrast, La_2O_3 and Cs_2O lower quantity of divalent ions, that gives a positive effect for the process. However these agents decrease oxidizability of copper and effective charge of ions and degrade selectivity of the catalyst as compared with the unmodified sample, though not in such degree, as Ce and Zr oxides.

Thus, the tests of copper catalysts confirm the supposition about the univalent ionic nature of active sites of metal catalysts in selective oxidation of alcohols. Distinctive feature of copper catalysts is the formation of some Cu^{2+} states, catalyzing reaction of deep oxidation. Our studies have shown also that in absence of oxygen no noticeable formation of aldehydes on copper catalysts is observed, despite of controversial reports available in the literature [7].

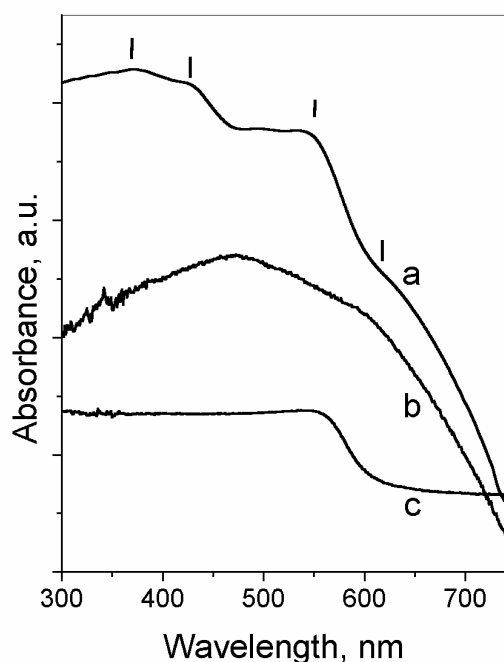
The selectivity of the catalysts in partial oxidation of alcohols is determined mainly by the ratio of reactions of formation of aldehydes and deep oxidation of the reagents. Therefore, it is necessary to determine how an electronic state of supported copper influences the processes of complete oxidation of alcohols and the other products of the reaction (CO , hydrocarbons, etc.). Copper-containing catalysts are widely used in deep oxidation of different organic compounds [19]. Practically in all catalysts, the copper is present as CuO or mixed oxides of a different structure. Catalytic processes on metals and oxides occur through different mechanisms. Studies of catalytic properties of metal copper are much less presented in the literature as compared with copper oxide systems.

The easy transition into a divalent state, catalyzing deep oxidation processes, is the main difference of copper unlike its neighbors on a subgroup. Some amount of Cu^{2+} ions is always formed on a surface of copper at the presence of oxygen. The Cu^{2+} ions are registered on a surface of these catalysts by method of electronic spectroscopy of diffuse reflectance (Figure 3). Electronic spectra of fresh Cu/pumice samples display only unstructured absorption corresponding to large metal particles. After run of Cu/pumice catalyst in catalytic reactor noticeable signals at

Table 1. Brønsted acidity of the modified pumice surface

No	Modifier	pH of Brønsted acid sites	Brønsted acid sites concentration, mmol/m ²
1	-	2.1; 4.5; 5.0	0.44
2	ZrO ₂	1.6; 3.6; 4.7; 5.5; 5.8	0.53
3	La ₂ O ₃	2.5; 3.9; 5.0; 5.6	0.48
4	CeO ₂	1.9; 3.7; 5.5; 6.4	0.49
5	Cs ₂ O	3.8; 5.3; 5.8	0.41

370, 440, 550 nm and wide absorption in 620-660 range are observed in the electronic spectrum (Figure 3a). According to the literature data [32-35] the first two signals belong to O-Cu-O and Cu-O-Cu complexes (charge transfer bands).

**Figure 3.** UV-visible spectra of the used Cu/pumice catalysts:

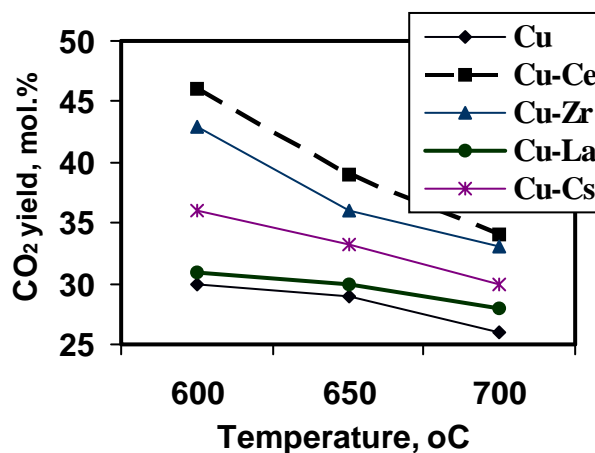
- a) 10 wt.% Cu/pumice, exhaust;
- b) 1 wt.% CuO/mordenite;
- c) 1 wt.% Cu/mordenite

Absorption at 620-660 nm is attributed to electronic d-d transitions of Cu²⁺ ions octahedrally surrounded by oxygen in CuO particles. This is confirmed by the spectra of reference CuO/zeolite (Figure 3b). Absorption bands in the range of 520-550 nm some authors attribute to CuAl₂O₃ [34]. However, formation of copper aluminate structures is not typical for pumice, so this signal can belong to plasmon resonance of Cu_n small particles. This attribution is confirmed by investigation of reference Cu/zeolite sample (Figure 3c) and calculations carried out in our previous work [35]. Thus, the prolonged run of the sample in catalytic reactor favors the formation of some amount of Cu²⁺ states and small metal particles. It is one of the reasons of lower selectivity of copper in alcohol oxidation as com-

pared with silver, as CuO is well-known catalyst for deep oxidation of organic compounds.

However, XRD data demonstrate that under reduction conditions of the process of aldehyde synthesis on Cu/pumice catalysts copper is mainly in Cu⁰ and Cu⁺ states, while amount of CuO is small. Due to primary formation of Cu⁺ states, instead of Cu²⁺ ones, these catalysts have high enough selectivity.

Yield of product of deep oxidation (CO₂) on the modified 10 wt.% Cu/pumice samples is presented in Figure 4. The yield of CO₂ changes antitabately to the yield of aldehyde (Figures 2 and 4). I.e., the predominate secondary process of partial oxidation of alcohols on copper is the deep oxidation, whereas all other reactions (dehydrogenation, formaldehyde decomposing, coking, etc.) produce the minor contribution to the total mechanism of the process.

**Figure 4.** Yield of the product of deep oxidation of methanol on the modified Cu/pumice catalysts.

As evident from the Figure 4, all modifiers intensify deep oxidation of the alcohol on the surface of copper catalysts. In the case of Ce and Zr oxides it is caused, apparently, by the increase of an amount of surface Cu²⁺ ions, as these additives stabilize the oxidized states of the metal [30-31]. Quantity of Cu⁺ ions also grows, however, ratio of rates of the reactions of selective and complete oxidation shifts to the benefit of the last one.

The addition of La and Cs oxides lowers the formation of Cu²⁺ states in the catalyst [30-31]. Nevertheless, the selectivity of aldehyde formation decreases a little, and CO₂ yield grows, though not in such degree, as on Cu-Ce and Cu-Zr samples. Perhaps, deep oxidation of alcohol on copper catalysts surface is catalyzed not only by Cu²⁺ states, but also by

univalent Cu^+ ions having low effective charge. Opinions concerning this problem vary significantly in the literature. It is generally assumed that the ions Cu^{2+} are most active in deep oxidation, both isolated ones (in zeolites) [36], and in a structure of a bulk or dispersed phase of CuO oxide [19,37]. However, there are reports in the literature about activity of Cu^+ and Cu^0 states in deep oxidation also [38]. Thus, univalent ions of copper may be also considered as active sites of processes of deep oxidation. Consequently, as in the case of silver catalysts [22-26], the decrease of an effective charge of Cu^+ ions under the action of electron-donating modifying agents intensifies deep oxidation of alcohol. Hence, it is possible to assume that on the surface of copper under the studied conditions there are two types of sites of deep oxidation – Cu^{2+} states and univalent Cu^+ ions having low effective charge.

On supports with low specific surface area (pumice, corundum) and high contents of the metal the most part of the active phase is in the form of large aggregates of metal. Of course, the supports and modifiers cannot change sufficiently the electronic properties of big copper particles. According to the results of in-situ XPS and XAS measurements the main role in methanol oxidation over bulk copper belongs to special states of surface and subsurface oxygen [39-43]. However, our previous studies of Ag/pumice catalysts by the methods of ESDR, XRD, electron microscopy and O_2 - H_2 titration revealed, that part of the support surface (20-40 %) is not covered by big metal particles and contains high-dispersed M^+ and $\text{M}_n^{\delta+}$ states [44]. The supports and modifiers exert direct action upon the electronic properties of these dispersed species by the way of interaction of the supported metal with the Lewis acid sites (Ce^{3+} , Ce^{4+} , La^{3+} , Zr^{4+}) of the modified support surface [20-26,30-

31]. This interaction is realized by the formation of the bonds of M-Mod^{n+} (electron-acceptor) or $\text{M}^{\delta+}\text{-O}^{2-}\text{-Mod}^{n+}$ (electron-donor) type.

Conclusions

1. Univalent Cu^+ ions having high effective charge are the active states of supported copper catalysts in alcohol partial oxidation.
2. Cu^{2+} states and Cu^+ ions with low effective charge catalyze deep oxidation of alcohols and other products of the reaction.
3. Supports and modifiers stabilizing two-charged states of copper (aluminosilicates, Zr and Ce oxides) or lowering the effective charge of Cu^+ ions (MgO support, La and Cs oxide additives) favor the reaction of deep oxidation on copper catalysts.

Acknowledgements

We have benefited greatly from many discussions and collaborations with Drs. Sergio Fuentes, Yoshihiro Sugi and Evgeny Stoyanov. Thanks are given to Juan Peralta and Eric Flores for valuable technical support. This research was supported by grant of President of Russian Federation No. MD-344.2003.03; CONACYT, Mexico through grant No. 32118-E and UNAM-PAPIIT through grant IN114603-3.

References

- [1] J.K. Walker, Formaldehyde, 3d ed., Reinhold, New York, 1964.
- [2] Pat. 33460, Bulgaria.
- [3] Pat. 2939883, USA.
- [4] Pat. 49-24889, Japan.
- [5] M. Bowker, Top. Catal. 3 (1996) 461.
- [6] A.F. Carley, A.W. Owens, M.K. Rajumon, M.W. Roberts, S.D. Jackson, Catal. Lett. 37 (1996) 79.
- [7] A.K. Chen, R. Masel, Surf. Sci. 343 (1995) 17.
- [8] M. Arai, S. Nishiyama, S. Tsuruya, M. Masai, J. Chem. Soc. Faraday Trans. 92 (1996) 2631.
- [9] S. Sueto, S. Nishiyama, S. Tsuruya, M. Masai, J. Chem. Soc. Faraday Trans. 93 (1997) 659.
- [10] A.F. Carley, P.R. Davies, G.G. Mariotti, S. Read, Surf. Sci. 364 (1996) 219.
- [11] A.J. Marchi, J.L.G. Fierro, J. Santamaria, A. Monzon, Appl. Catal., A. 142 (1996) 375.
- [12] P.R. Davies, G.G. Mariotti, Catal. Lett. 43 (1997) 261.
- [13] P.R. Davies, G.G. Mariotti, J. Phys. Chem. 100 (1996) 19975.
- [14] M. Bowker, S. Poulston, R.A. Bennett, A.H. Jones, Catal. Lett. 43 (1997) 267.
- [15] S. Poulston, A.H. Jones, R.A. Bennett, M. Bowker, J. Phys.: Condens. Matter. 8 (1996) L765.
- [16] S.M. Francis, F.M. Leibsle, S. Haq, N. Xiang, M. Bowker, Surf. Sci. 315 (1994) 284.
- [17] M.A. Newton, M. Bowker, Catal. Lett. 21 (1993) 139.
- [18] L. Prati, M. Rossi, J. Mol. Catal. A: Chem. 110 (1996) 221.
- [19] T.G. Alkhozov, L.Ya. Margolis, Catalytic Deep Oxidation of Organic Substances, Moscow, Khimia, 1985.
- [20] A.N. Pestryakov, A.A. Davydov, L.N. Kurina, Rus. J. Phys. Chem. 62 (1988) 1813.
- [21] A.N. Pestryakov, O.D. Filicheva, Formation of active sites of supported silver catalysts, in: Problems of Kinetics and Catalysis, Ivanovo, 1988, p. 72.
- [22] A.N. Pestryakov, A.A. Davydov, Appl. Catal. A 120 (1994) 7.
- [23] A.N. Pestryakov, A.A. Davydov, Kinet. Catal. 37 (1996) 923.
- [24] A.N. Pestryakov, Catal. Today 28 (1996) 239.
- [25] A.N. Pestryakov, A. Davydov, P. Tsyrlunikov, Prepr. Am. Chem. Soc., Div. Petr. Chem. 41 (1996) 96.
- [26] A.N. Pestryakov, V.V. Lunin, J. Mol. Catal. 158 (2000) 325.
- [27] A.N. Pestryakov, V.N. Belousova, M.I. Roznina, Rus. J. Appl. Chem. 66 (1993) 1148.
- [28] A.N. Pestryakov, M.I. Roznina, V.N. Belousova, Rus. J. Appl. Chem. 66 (1993) 2285.
- [29] A.N. Pestryakov, Formation of active surface of the catalysts based on d^{n-1} metals in alcohol oxidation, Dr Sc Thesis, Moscow State University, Moscow, 1998.
- [30] A.N. Pestryakov, A.A. Davydov, Appl. Surface Sci. 103 (1996) 479.
- [31] A.N. Pestryakov, A.A. Davydov, Kinet. Catal. 37 (1996) 923.

- [32] G.A. Dergaleva, N.A. Pakhomov, V.N. Bendurin, V.F. Anufrienko, *Kinet. Catal.* 32 (1991) 490.
- [33] M. Arai, S. Nishiyama, S. Tsuruya, M. Masai, *J. Chem. Soc. Faraday Trans.* 92 (1996) 2631.
- [34] M.C. Marion, E. Garbovski, M. Primet, *J. Chem. Soc. Faraday Trans.* 86 (1990) 3027.
- [35] V. Petranovskii, V. Gurin, N. Bogdanchikova, A. Licea-Claverie, Y. Sugi, E. Stoyanov, *Mat. Sci. Eng. A* 332 (2002) 174.
- [36] A.V. Kucherov, T.N. Kucherova, A.A. Slinkin, *Kinet. Catal.* 33 (1992) 618.
- [37] L.P. Davydova, V.B. Fenelonov, V.A. Sadykov, *Kinet. Catal.* 34 (1993) 99.
- [38] M.A. Ismailov, R.B. Akhverdiev, B.S. Gadzhi-Kasumov, *Kinet. Catal.* 34 (1993) 117.
- [39] Th. Schedel-Niedrig, M. Hävecker, A. Knop-Gericke, R. Schlögl, *Phys. Chem. Chem. Phys.*, 2 (2000) 3473.
- [40] A. Knop-Gericke, M. Hävecker, T. Schedel-Niedrig, R. Schlögl, *Catal. Lett.*, 66 (2000) 215.
- [41] A. Knop-Gericke, M. Hävecker, T. Schedel-Niedrig, R. Schlögl, *Topics in Catalysis*, 15 (2001) 27.
- [42] I. Böttger, T. Schedel-Niedrig, O. Timpe, M. Hävecker, R. Gottschall, G. Weinberg, R. Schlögl, *Chem. Europ. J.*, 6 (2000) 1870.
- [43] T. Schedel-Niedrig, T. Neisius, I. Böttger, E. Kitzelmann, D. Demuth, G. Weinberg, R. Schlögl, *Phys. Chem. Chem. Phys.*, 2 (2000) 2407.
- [44] S.P. Noskova, A.A. Davydov, A.N. Petryakov, *J. Appl. Chem. USSR (Engl. Trans.)* 61 (1988) 2051.