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Physicochemical study of active sites of metal catalysts for alcohol partial oxidation

A.N. Pestryakov [a,*], V.V. Lunin [b]

[a] *Tomsk State University of Civil Engineering, Tomsk 634003, Russia*
[b] *Chemistry Department, Moscow State University, Moscow 119899, Russia*

Abstract

The active electronic states of the supported metal catalysts (Ag, Cu, Au) in the processes of alcohol partial oxidation were studied by the methods of IR spectroscopy of adsorbed CO, electron spectroscopy of diffuse reflectance, X-ray diffraction, XPS, EXAFS, ESR and electron microscopy. Comparison of the obtained catalytic and spectroscopic data revealed that one-charged cations M^+ are the active sites of the local interaction on the metal catalyst surface in the processes of alcohol oxidation. The catalyst selectivity strongly depends on the effective charge of the surface active sites. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalysts based on the metals of the Cu subgroup are widely used for the processes of oxidation of alcohols to aldehydes. Silver catalysts are the most used, but in some cases, the complex Ag−Cu and Ag−Au systems are applied as well. In spite of long-standing studies, the question of the mechanism of alcohol oxidation and of the nature of the active sites is still under discussion. As a rule, active sites on silver catalysts are considered in terms of M−O binding energy or to be different form of oxygen adsorbed on metal surface, i.e. O^{2-}, O^-, O_2^-, while the electronic states of the metals are not adequately investigated [1,2].

The aim of the present paper was to study the nature of the active sites of the metal catalysts in alcohol partial oxidation.

2. Experimental

Samples in the range of 1–10 wt.% Me/support were prepared for investigation of electronic and catalytic properties of silver, copper and gold. The metals was deposited by impregnation of the support using $AgNO_3$, $Cu(NO_3)_2$ and H_3AuCl_6, followed by thermal decompositions of these substances. An amount of 1–10 wt.% of modifying additions 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. Aluminosilicate, aerosil SiO_2, γ- and α-Al_2O_3, MgO and pumice were used as supports.

* Corresponding author. Fax: +7-3822-753-362.
E-mail address: anp@tspace.ru (A.N. Pestryakov).

The IR spectra of adsorbed carbon monoxide were recorded on Specord-75IR and Specord M80 spectrometers, electron spectra of diffuse reflectance (ESDR) on a Shimadzu UV-300 and Specord M40. Investigation of the samples by the method of X-ray diffraction was carried out using DRON-3 diffractometer. XPS spectra were recorded on XSAM-800 spectrometer, EXAFS spectra on EXAFS station of Siberian Center of Synchrotronic Radiation. Dispersivity of the metals was studied using Digisorb-2500 and JEOL JSM-35C electron microscope with X-ray microsonde 35-DDS.

Samples with low specific surface area (1–3 m^2/g: pumice, a-Al_2O_3, D-53 aluminosilicate and MgO supports) were tested in the processes of partial oxidation of methanol and ethanol. The experiments were carried out in a flow catalytic apparatus under the following operating conditions: $T = 600–700°C$ (hot zone — upper 1–2 cm of the catalyst layer), O_2/alcohol ratio = 0.3, catalyst layer thickness = 10 cm, catalyst volume = 10 cm^3, volume rate = 1000 h^{-1}. The processes were passed in external diffusion field and in autothermal regime.

3. Results and discussion

In our previous studies on the base of comparison of spectroscopic and catalytic data, we suggested one-charged $Ag^{\delta+}$ cations to be active sites of silver catalysts in methanol oxidation [3–5]. Factors raising the effective charge of the cations (supports, modifiers, redox, treatments) increase the selectivity of aldehyde formation, whereas reduction of $\delta +$ favours the reactions of deep oxidation and destruction of the alcohols. With the aim of obtaining comparative data, the investigations of electronic states and catalytic properties of copper and gold catalysts were carried out using the same procedure.

The data of the methods of IR spectroscopy of adsorbed CO, electron spectroscopy, XPS, EXAFS and ESR show that the electronic state of Au in the supported samples is close to the one of Ag. The Au^+ cations are the main ionic states of Au in oxidized samples (absorption bands at 2140 and 2175 cm^{-1} in IR spectra, 31,000 and 41,000 cm^{-1} in electron spectra). Highly-charged Au^{3+} ions were determined in some species stabilized by chlorine (bands at 16,000 and 25,000 cm^{-1} in ESDR, signals in ESR). However, after using the samples in catalytic process for 30 min, these signals disappear and in all spectra only Au^0 and Au^+ states are observed. All spectroscopic methods show that on aluminosilicate support and in the presence of CeO_2 and ZrO_2 modifying additions, fraction of ionic state of Au rises as compared with the control Au/Al_2O_3 sample. Basic supports (MgO, CaO) and additions of La and Cs oxides reduce abruptly the number of Au^+ ions, and low-frequency shifts (10–15 cm^{-1}) of Au^+−CO signals in the IR spectra of adsorbed CO point to decreasing of the effective charge of the ions.

Study of the metal dispersivity by the methods of X-ray diffraction and electron spectroscopy indicates that the observed effects are due not only to variations in the metal particles size on the surface of the modified support, but mainly to direct electron-seeking and electron-releasing interaction between the Lewis acid sites of the support surface and Au atoms and ions. The EXAFS data of the modified Au samples show that on high-surface supports (γ-Al_2O_3, aluminosilicate) portion of ionic state of gold (Au−O bonds, $R − \delta$ near 1.8 A) after a run in the CO oxidation process, accounts for 8–15% depending on the modifier type. On low-surface pumice and α-Al_2O_3, only weak signals of gold ions are observed (1–2%). These characteristics are significantly below the values exhibited by Ag catalysts. The poor oxidizability of gold causes low activity of Au catalysts in the oxidizing processes.

Contrary to neighbours in its subgroup, copper easily form Cu^{2+} ions. Literary data as well as our investigations [5] on supported copper catalysts show that this state of copper is the main factor in the processes of deep oxidation

of substances on Cu catalysts. But under the conditions of alcohol partial oxidation, one-charged ions constitute the major portion of oxidized copper. X-ray diffraction spectra, ESDR (14,000, 19,000 and 25,000 cm^{-1}) and XPS (signals at 936–943 eV) indicate the signals of Cu^{2+} in exhaust catalysts as well, but their portion constitutes to not more than $1/10$ of all ionic states of copper.

Previously, through the IR spectroscopy of adsorbed CO, we revealed that modifying additions of Ce and Zr oxides raise the portion of oxidized states of supported copper and effective charge of the ions, while La and Cs oxides reduce the number of ions and their effective charge [6,7]. These effects are analogous to the behaviour observed for Ag and Au catalysts. The EXAFS spectra indicate that the electron-seeking action of Ce and Zr oxides on supported Cu^+ and Cu^{2+} ions occurs through the direct interaction of these ions with Lewis acid sites with forming Cu−Ce and Cu−Zr bonds. At the same time, the electron-releasing effect of La and Cs oxides occurs by formation of the oxygen-bridging bonds of the $Cu^{\delta+}$−O^{δ}−M^{n+} type.

Spectroscopic methods show that donor–acceptor coupling the supports and modifiers with the metals occurs mainly by local interaction of the metal atoms and ions with Lewis acid sites of the support. IR spectroscopic data indicate the dependence of the modifiers on the collective electron properties of small, partly charged metal clusters (absorption bands of M−CO complexes at 2100 cm^{-1} for Cu, and 2118 cm^{-1} for Au). However, this effect is slightly pronounced, and only agents with very strong electron-releasing properties (e.g., MgO, CaO, Cs_2O) are able to prominently change the effective charge of such metal clusters.

Catalytic tests of the supported metals in the process of oxidation of ethanol to acetaldehyde show that Ag catalysts are the most effective (Fig. 1). In our previous studies, we suggested that it is related to the unique electronic properties of silver — the only existing stable ion state Ag^+ (active sites, according to our hypothesis), maximal effective charge of these ions among the number of the metals-analogs [3]. The catalytic characteristics of the Cu samples are sufficiently worse. This is caused by the formation of some numbers of Cu^{2+} ions favouring deep oxidation of alcohols. But according to spectroscopic data, one-charged ions Cu^+ constitute the major portion of copper ionic states under the conditions of aldehyde synthesis. This causes rather high selectivity of Cu samples, which allows the use of copper in some complex Ag−Cu catalysts.

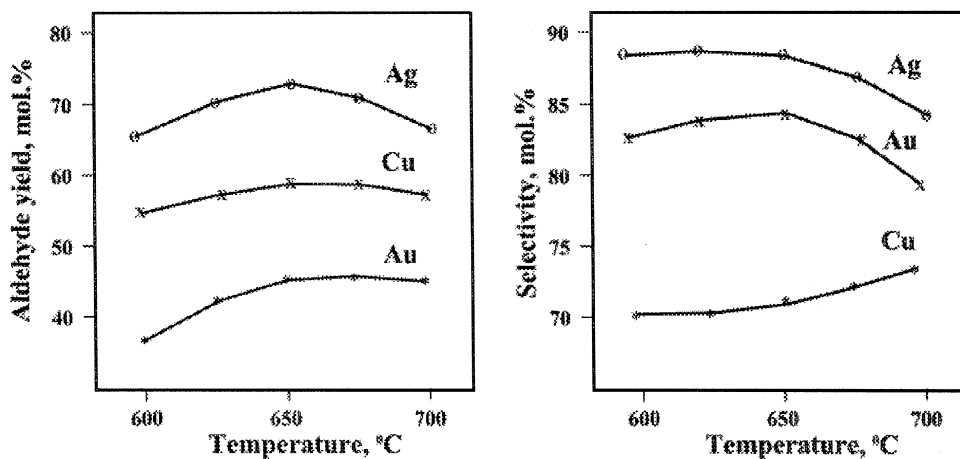The activity of gold catalysts (alcohol conversion, aldehyde yield) is substantially lower

Fig. 1. Catalytic properties of the 10 wt.% Me/pumice samples in ethanol oxidation.

than those of Ag and Cu samples. This is caused by the poor oxidizability of gold and small number of the active sites (Au$^+$). However, according to spectroscopic data, gold does not form highly-charged ion states under these conditions and the effective charge of Au$^+$ ions is close to Ag$^+$. So, the selectivity of Au catalysts exceeds that of Cu samples (Fig. 1). In the diffuse regime of our process, alcohol conversion depends on oxygen concentration (100% of oxygen conversion corresponds to 80–85% of alcohol conversion).

Tests of the catalysts on the different supports indicate that the metals supported on aluminosilicates (including pumice) have the best characteristics, whereas on the basic carriers of MgO type, the efficiency of their performance is minimal (Fig. 2). Within the range of our hypothesis on the nature of the active sites, the observed effects are caused by the fact that, on aluminosilicates, the number of ion states of metals and their effective charge are maximal (according to spectroscopic data). In contrast, on MgO — as a result of strong electron-releasing interaction — the effective charge of M$^+$ cations decreases abruptly, which favours their fast reduction under the action of reaction environment. The parameters of the process of alde-
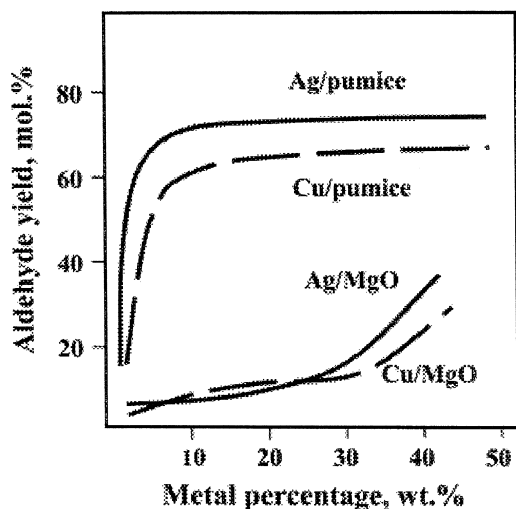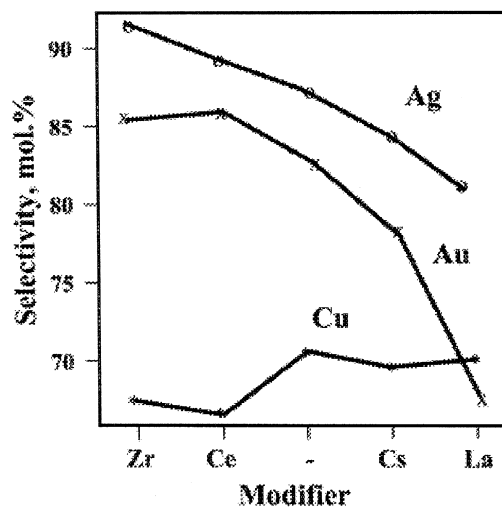

Fig. 3. Catalytic properties of the modified 10 wt.% Me/pumice samples in methanol oxidation ($T = 650°C$).

hyde synthesis only rise when there is a high content of metal because the support could significantly change the electronic properties of thick metal films.

Tests of the modified samples showed that additions of Ce and Zr oxides increase the selectivity of Ag and Au catalysts, whereas La and Cs oxides impair their characteristics (Fig. 3). This is caused by the stabilization of ionic states of these metals in Me–Ce and Me–Zr samples, and the electron-seeking influence of CeO$_2$ and ZrO$_2$ on active sites (M$^+$). For the modified copper catalysts, the opposite effects are observed — CeO$_2$ and ZrO$_2$ additions significantly impair the selectivity of the samples. This is involved by stabilization in these catalysts not only Cu$^+$ states but Cu^{2+} ions (active sites of deep oxidation) as well. Electron-releasing modifiers (La and Cs oxides) lower the number of Cu^{2+} states, so Cu–La and Cu–Cs catalysts have better catalytic properties as compared with Cu–Ce and Cu–Zr samples. However, these modifiers do not exert a positive effect relative to unmodified catalyst, and the yield of deep oxidation product (CO$_2$) increases somewhat. It is probable that not only the Cu^{2+} states are responsible for complete oxidation reactions on copper catalysts, but Cu$^+$ ions with

Fig. 2. Catalytic properties of the metals on different supports in methanol oxidation ($T = 650°C$).

low effective charge as well (as in the case of Ag and Au catalysts).

Physicochemical studies showed that the supports and modifiers change not only electron states of the metals, but other properties as well — the metal dispersivity, surface diffusion, Brönsted acidity of the catalyst surface, degree of its carbonization during the catalytic process, etc. However, special investigations revealed that all of these factors exert a minor effect on the process of aldehyde synthesis. Variations in electronic states and redox properties of the catalyst active sites are the main factors that determine the selectivity of metal catalysts in the studied processes.

4. Conclusions

Comparing the spectroscopic and catalytic data allows us to suggest that M^+ cations with maximal effective charge are the active sites of catalysts based on the Cu subgroup metals in the processes of alcohol partial oxidation. Shift of the metals to the highly-charged state (Cu^{2+}) or reducing the effective charge of M^+ cations decreases the selectivity of aldehyde synthesis.

Acknowledgements

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