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Electronic state of gold in supported clusters

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Abstract. The electronic states of gold in gold supported nanoparticles modified by Ce, Zr, La and Cs oxides have been studied by the methods of IR spectroscopy of adsorbed CO, UV-visible spectroscopy of diffuse reflectance, XRD and electron microscopy. The additives of Ce and Zr oxides stabilize the ionic states of supported gold and increase the effective charge of the ions. In contrast, La and Cs oxides lower the ion effective charge and favour their fast reduction under redox treatments and reaction medium. It is explained by electron donor-acceptor interaction of the supported metal nanoparticles with the modifiers.

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

1 Introduction

Physicochemical and catalytic properties of gold-containing systems attract a great interest of scientists due to high catalytic activity of gold in low-temperature CO oxidation and partial oxidation of alcohols to aldehydes [1–5]. To study supported gold nanoparticles by spectroscopic methods is important for understanding the nature of the active site of gold catalysts in oxidation processes. Our previous studies showed specific ionic states of silver and copper (neighbours of gold on subgroup) to be the active sites of the catalysts in selective and deep oxidation processes [5–10]. So, it is of great interest to study the electronic states of supported gold nanoparticles and their changes under the action of different factors. Previous studies showed that electronic state of Ag, Au and Cu and their catalytic properties can be efficiently regulated by modifiers [4–10].

The aim of the present study is to investigate the nature and mechanism of the modifying action of La, Ce, Zr and Cs oxides on electronic state of supported gold nanoparticles.

2 Experimental

Samples of 3 wt.% $Au/\tilde{\gamma}$-Al_2O_3 were prepared for studying electronic states of gold. Before gold impregnation, 3 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 $HAuCl_4$ solution, followed by a treatment with H_2 at 200 °C for 2 hours. A number of catalysts were used in CO oxidation process at 150 °C for 3 hours (CO concentration in air was 1%).

IR-spectra of adsorbed carbon monoxide were recorded on a Specord M80 spectrometers ($P_{\mathrm{CO}} = 1.5$ kPa). UV-visible spectra of diffuse reflectance were measured on a Specord M40. Dispersity of the metals was studied using DRON-3 X-ray diffractometer and JEOL JSM electron microscope.

3 Results and discussion

A representative IR-spectrum of CO adsorbed on $Au/\tilde{\gamma}$-Al_2O_3 sample, shown in Figure 1, contains a number of absorption bands (a.b.) corresponding to different surface states of gold. Signal at 2170 cm^{-1} is attributed to surface monocarbonyls of isolated Au^+ ions [6,11–15]. Absorption band at 2140 cm^{-1} belongs to $Au^{\delta+}$-CO complexes formed on Au_n^{m+} clusters ($m < n$), where $Au^{\delta+}$ ions are a part of Au_n^{m+} clusters and have effective charge ($\delta+$) less than 1+. Intensive signal at 2118 cm^{-1} some authors attribute to monocarbonyls of reduced gold Au^0-CO [12,13], but relatively high ν_{CO} indicates sufficient electron deficiency of those states of gold, perhaps due to metal-support interaction. Double band at 2050–2060 cm^{-1} and weak signal at 2090 cm^{-1} belongs to atomic Au^0-CO complexes in Au_n clusters [6,11–15]. Differences in the band positions

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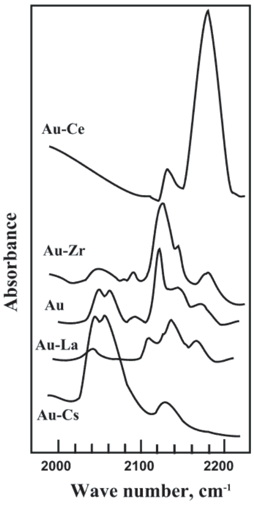

Fig. 1. IR spectra of CO adsorbed on the initial Au/Al_2O_3 samples.

are caused by variations in the metal cluster sizes. Adsorption of CO on large gold metal particles as well as on the modified supports was not observed. Lateral interaction of the adsorbed CO molecules does not influence a position of a.b. at high CO pressure [16].

Spectrum of Au-Zr sample, in general, is similar to the one of unmodified catalyst. However, intensity of the signals corresponding to ionic and electron-deficient states is higher and a shift of the high-frequency band to 2180 cm^{-1} is observed. Within the model of $\sigma-\pi$ binding in M-CO complexes, these changes mean an increase of the effective charge of Au^+ ions.

Spectrum of CO adsorbed on Au-Ce sample presents several differences as compared with an unmodified catalyst. Firstly, a high-frequency shift of the band at 2180 cm^{-1} is observed. This signal has high intensity after any redox treatment of the sample. The band at 2140 cm^{-1} is not displayed, probably, due to superposition of intensive signal at 2180 cm^{-1}. The band belonging to electron-deficient Au-CO complexes is also shifted to 2125 cm^{-1} indicating a rise of the electron-seeking metal-support interaction.

The opposite effects are observed in the IR-spectrum of CO adsorbed on Au-La sample. The bands at 2165 and 2115 cm^{-1} present low intensity and a shift to lower frequency, although signal at 2140 cm^{-1} is relatively stable. Bands in the range 2050−2090 cm^{-1} are also very weak, as expected by the absence of metal clusters.

The electron-releasing effects of the additives are more pronounced for the catalyst modified by Cs oxide. Signal at 2170−2180 cm^{-1} is absent in the IR spectrum and the band at 2130 cm^{-1} is shifted to low-frequency range. In contrast, signals attributed to Au^0-CO are more intensive. It is evident that under the strong electron-releasing action of the modifier, the isolated gold ions are rapidly reduced under H_2 treatment. Caesium oxide changes electron properties of gold clusters that results in low-frequency shift of absorption band to 2130 cm^{-1}.

All observed effects may be explained by an increase in the metal dispersion and surface ion concentration. Micrographs, and XRD data reveal that all studied catalysts have different average size of gold particles: unmodified Au–26 nm, Au-Ce–11 nm, Au-Zr–18 nm, Au-La–16 nm, Au-Cs–28 nm. Smallest nanoparticles (< 5 nm) form 25−40% of total gold. The metal dispersion in the modified catalysts is higher than that in pure Au/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) emerges on the support surface. This increases the dispersity of the metal particles and slows down the metal surface diffusion under thermal treatments. It is known that metal dispersion influences strongly the position of M^0-CO absorption bands in IR spectra, whereas for ionic M^{n+}-CO complexes this effect is not so pronounced [16]. However, in our work, dispersion of the metal can not explain all observed effects because the samples with close dispersion (Au-Zr and Au-La) have different spectral properties and, *vice versa*, catalysts with different dispersion (Au-La and Au-Cs) have similar pattern in IR spectra. As mentioned above, the metal dispersion in Au-Ce, Au-Zr and Au-La samples is higher than that one in unmodified catalyst, whereas intensity of CO absorption band corresponding to Au^+-CO in IR-spectra of Au-La sample is lower. Probably, the additives of Ce and Zr oxides stabilize the ionic and electron-deficient states of gold and increase the effective charge of the ions. Additives of La_2O_3, in spite of increasing the metal dispersion, exert an electron-releasing effect on the supported gold ions and lower their effective charge. This results in a low-frequency shift of CO absorption bands in IR-spectra of the sample. Similar effect was observed earlier, when studying the modified silver and copper catalysts [5,6].

These arguments are confirmed by the behaviour of other Au^+-CO absorption band at 2140 cm^{-1}. This signal has a relatively stable position and intensity in all analysed spectra. Au^+ ions included in Au_n^{m+} nanoparticles are not so susceptible to the influence of the modifiers as compared with isolated gold ions. The modifiers can not change sufficiently the collective electronic properties of the metal particles. So, noticeable shifts in the position of the band at 2140 cm^{-1} are not observed.

IR spectra of the modified catalysts used in CO oxidation process show that the portion of ionic states of gold in these samples is higher as compared with the initial catalysts (Fig. 2). Used Au-Ce and Au-Zr catalysts have maximal share of ionic gold. However, in the spectrum of Au-Cs sample, the high-frequency band is shifted to 2120 cm^{-1}. It means that gold ions in this catalyst have very low effective charge.

Electron spectrum of diffuse reflectance of the fresh $HAuCl_4/Al_2O_3$ sample contains four pronounced signals in UV-visible range – 16000, 25000, 31000 and 41000 cm^{-1} (Fig. 3). XRD and ESR data show that on the support surface, gold is mainly in the form of Au^+ and partly Au^{3+} included in the oxides and chlorides. So, the signal at 25000 cm^{-1} may be attributed to a charge transfer band of $AuCl_4^-$ [17], and a band at 16000 cm^{-1} is in the traditional range of *d-d* electron transitions and corresponds to Au^{3+} as well. Interpretation of the bands at 31000 and

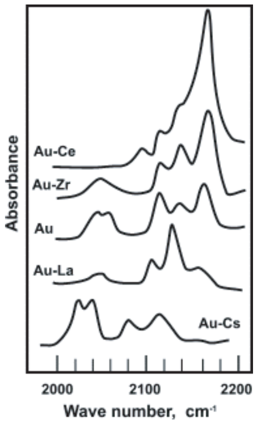

Fig. 2. IR spectra of CO adsorbed on the used Au/Al_2O_3 catalysts.

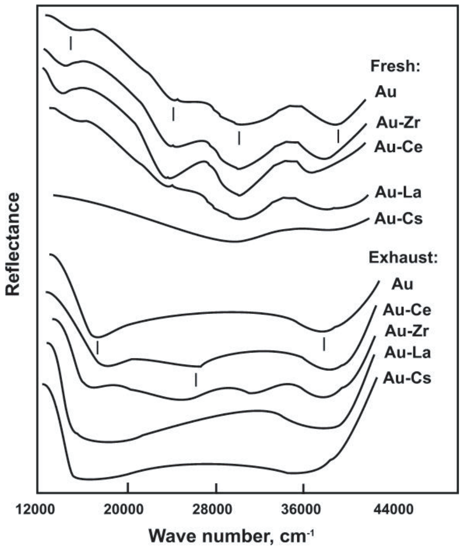

Fig. 3. UV-visible spectra of the modified Au/Al_2O_3 catalysts.

41000 cm^{-1} is more difficult as the literary data on UV-visible spectra of gold catalysts are very poor. By analogy with the electron spectra of supported silver [18,19], the signals in this range may be attributed to ionic states of gold – Au^+ and $Au_n^{\delta+}$.

UV-vis spectra of the catalysts modified by Ce and Zr oxides have a similar view. However, the spectrum of Au-Cs shows several differences – the signals corresponding to Au^{3+} are absent and the absorption bands at 31000 and 41000 cm^{-1} are very weak. This is clearly caused by a fast reduction of gold on the step of impregnation under the action of an electron-releasing modifier.

After studying the catalysts in CO oxidation process all electron spectra seem to be changed. The signals at 16000−17000 cm^{-1} are in the range of *d-d* electron transitions of Au^{3+} cations. Other methods (XRD, ESR) do not indicate such states in the exhaust catalysts. Moreover, this band presents the highest intensity in the spectrum of Au-Cs sample, where the formation of high-charged gold ions is improbable. So, according to the previous study [6] this signal may be attributed to Au_n particles (plasmon resonance). Bands corresponding to oxidized states of gold (Au^+ and $Au_n^{\delta+}$) are much less intensive. This indicates the significant extent of gold reduction during the catalytic reactions. It is necessary to note that in the exhaust Au-Ce and Au-Zr catalysts the contribution of the oxidized states of gold (bands at 26000 and 40000 cm^{-1}) is much higher than in the original.

Thus, the modifying additives change significantly the electronic state of supported gold. The additives of Ce and Zr oxides stabilize the ionic states of supported gold (Au^+ and $Au_n^{\delta+}$) and increase the effective charge of the ions. In contrast, La and Cs oxides lower the ion effective charge and favour their fast reduction. The modifiers change also size of gold nanoparticles due to the intensification of metal-support interaction. The modifying additives play an important role in formation of active surface of gold catalysts.

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References

1. R.M.T. Sanchez, A. Ueda, K. Tanaka, M. Haruta, J. Catal. **168**, 125 (1997)
2. Y. Iizuka *et al.*, Catal. Today **36**, 115 (1997)
3. A.I. Kozlov, A.P. Kozlova, H. Liu, Y. Iwasawa, Appl. Catal. **182**, 9 (1999)
4. M.L. Kaliya, V.I. Moskovko, S.M. Braylovskii, Kinet. Catal. **20**, 1055 (1979)
5. A.N. Pestryakov, Dr. Sc. thesis, Moscow State University, 1998
6. A.N. Pestryakov, V.V. Lunin, A.N. Kharlanov, D.I. Kochubey, N.E. Bogdanchikova, A.Yu. Stakheev, J. Mol. Struct. **642**, 129 (2002)
7. A.N. Pestryakov, Catal. Today **28**, 239 (1996)
8. A.N. Pestryakov, A.A. Davydov, Appl. Surf. Sci. **103**, 479 (1996)
9. A.N. Pestryakov, A.A. Davydov, Appl. Catal. A **120**, 7 (1994)
10. A.N. Pestryakov, V.V. Lunin, J. Mol. Catal. **158**, 325 (2000)
11. E.I. Kochetkova, N.P. Sokolova, Rus. J. Phys. Chem. **66**, 1667 (1992)
12. F. Boccuzzi, A. Chiorino, S. Tsubota, M. Haruta, J. Phys. Chem. **100**, 3625 (1996)
13. C. Ruggiero, P. Hollins, J. Chem. Soc., Faraday Trans. **92**, 4829 (1996)
14. T.M. Salama, R. Ohnishi, M. Ichikawa, J. Chem. Soc., Faraday Trans. **92**, 301 (1996)
15. Q. Xu, Y. Imamura, M. Fujiwara, Y. Souma, J. Org. Chem. **62**, 1594 (1997)
16. A.A. Davydov, *Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides* (Wiley, New York, 1990)
17. E. Liver, *Electron Spectroscopy of Inorganic Compounds* (Mir, Moscow, 1987), p. 491
18. A.N. Pestryakov, A.A. Davydov, J. Electron Spectr. **74**, 195 (1995)
19. A.N. Devochkin, A.N. Pestryakov, L.N. Kurina, React. Kinet. Catal. Lett. **47**, 13 (1992)