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Methanol partial oxidation over gold catalysts

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Resumen

Se han estudiado las características del proceso de oxidación parcial del metanol en los catalizadores soportados de oro comparando con respecto a catalizadores de Ag y de Cu. La influencia del estado electrónico del oro soportado fué investigada por los métodos de espectroscopia de reflectancia difusa UV-Visible, de XRD, y de microscopía electrónica. La comparación de los datos catalíticos y espectroscópicos lleva a concluir que los iones mono-valentes de Au^+ son los sitios activos en los catalizadores de oro para la oxidación parcial del alcohol. Los modificantes que estabilizan los estados iónicos del oro (óxidos de Ce y de Zr) aumentan la selectividad del catalizador, mientras que la adición de donadores de electrones (óxidos de La y de Cs) deteriora las características del catalizador.

Keywords: catalizadores de oro, oxidación del metanol, sitios activos, espectros UV-visibles

Abstract

Features of the process of methanol partial oxidation on supported gold catalysts as compared with Ag and Cu catalysts have been studied. The influence of electronic states of supported gold was investigated by the methods of diffuse reflectance electron spectroscopy, XRD and electron microscopy. By comparison of catalytic and spectroscopic data it was concluded that univalent Au^+ ions are the active sites of the gold catalysts in alcohol partial oxidation. Modifiers stabilizing the ionic states of gold (Ce and Zr oxides) increase the selectivity of the catalyst, whereas electron-releasing additions (La and Cs oxides) impair the catalyst properties.

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

Introduction

Processes of alcohol partial oxidation are widely used for production of aldehydes and ketones [1]. Metals of 1B group - Ag and Cu - are traditional catalysts for these processes, whereas catalytic properties of gold have not been studied much. Literature data are scarce and are presented mainly as patents concerning mixed Ag-Au catalysts (alloys or two-layer systems) [2-7]. According to these patents, additions of gold to silver catalyst raise the selectivity of the process. For a better understanding of the mechanism of gold action on the alcohol oxidation process it is important to study the nature of the active sites of gold catalysts as well as influence the of different factors on the catalyst characteristics. However, to our best knowledge, systematical comparative studies of gold catalyst properties in these processes have not being published.

The aim of the present study is to investigate the features of catalytic and electronic properties of supported gold in methanol oxidation under the action of some factors - modifying additives, reaction medium and operating conditions.

Experimental

10 wt.% Au/pumice samples were prepared for investigation of catalytic and electronic properties of gold. Before gold impregnation an amount of 1 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 in air at 300°C for 3 hours. Then the metal was deposited by impregnation of the support using $HAuCl_4$ solution, followed by

calcination at 600°C for 4 hours. Specific surface area of the pumice is 1.8 m^2/g.

UV-visible spectra of diffuse reflectance (ESDR) were recorded on Specord M40 spectrometer. Dispersity of the metals was studied using using DRON-3 X-ray diffractometer and JEOL JSM electron microscope.

The samples were tested in the processes of partial oxidation of methanol to formaldehyde. The experiments were carried out in a flow catalytic apparatus under the following operating conditions: T = 600-700°C (hot zone is 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 measurements were carried out when the catalysts were in steady state (after 2 hours of work). The process was controlled in autothermal mode (without any heating). These are usual conditions for commercial process of aldehyde synthesis on metal catalysts.

Abbreviations of the sample titles are given as Au for Au/pumice, Au-Ce for Au/CeO_2/pumice, Au-La for Au/La_2O_3/pumice, Au-Zr for Au/ZrO_2/pumice and Au-Cs for Au/Cs_2O/pumice.

Results and discussion

Results of the catalytic testing the modified gold catalysts are presented in the Figure 1. Comparison of these data with data of Refs [8-11] shows that the activity of gold is inferior to the one of silver or copper catalysts (yield of formaldehyde is small) (Table 1.). However, selectivity of gold catalysts is rather high, in fact it is close to Ag sample and exceeds sufficiently the characteristics of Cu catalyst due to less intensity of deep oxidation reactions.

Percentage of CO_2 in the reaction gases on Au catalysts is 2-3 vol.% as compared with 10-14 vol.% for Cu samples [10-11]. It is necessary to note the higher content of CO in exhaust gases – 2-3 vol.% as compared with 0.5-1.5 vol.% for Ag. As formaldehyde decomposition (CH_2O = CO + H_2) is the main source of CO in this process, we can suppose that gold may catalyze this reaction to a certain extent. The samples were not sintered, did not lose activity for 120 hours of work (usual period of service of commercial supported Ag and Cu catalysts under these conditions is 3-6 months).

The experiments show that additions of Ce and Zr oxides increase the formaldehyde selectivity of gold catalyst whereas La and Cs oxides impair the process indices. Thus, character of the modifier influences on the gold catalyst is similar to the one of silver samples [8-9]. Tests of the modified pumice (without gold supporting) under the comparable conditions show that all modifiers raise slightly the formaldehyde yield as compared with a pure support (Table 2). Hence, intrinsic catalytic properties of the modifiers can not explain the differences in selectivity of the modified gold catalysts.

Table 1. Catalytic properties of 10 wt.% Me/pumice in methanol oxidation (T = 650°C)

Catalyst	Formaldehyde yield, mol.%	Selectivity, mol.%
Cu	58.4	71.1
Ag	72.0	88.2
Au	45.8	84.7

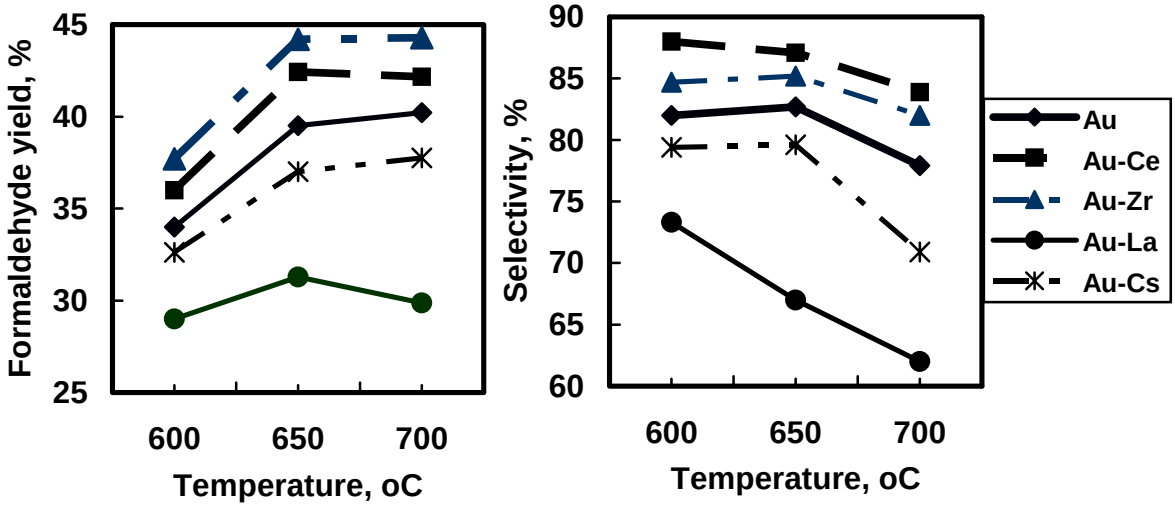

Fig. 1. Catalytic properties of the modified gold catalysts in methanol partial oxidation.

Table 2. Catalytic properties of the modified pumice in methanol oxidation (650°C)

No	Modifier	Exhaust gases, vol.%			Formaldehyde yield, mol. %
		CO_2	CO	H_2	
1.	-	0,3	2,2	3,9	3,8
2.	CeO_2	0,6	1,8	3,1	7,6
3.	La_2O_3	0,6	3,2	4,6	6,8
4.	ZrO_2	0,3	1,6	1,1	7,0
5.	Cs_2O	0,1	1,0	1,2	7,3

A great effect of gold dispersivity on its catalytic activity in different processes is well known [12-13]. However, micrographs and XRD data show that variations in gold dispersivity on the surface of the modified supports are not sufficient – average size of gold particles is 700-800 nm for all samples. Due to low specific surface area of pumice and high percentage of the metal the most part of gold (70-80 %) is in the form of big particles.

In our opinion, the observed effects of the modifier influence on catalytic properties of supported gold are concerned with features of electronic states of the metal. In our previous studies we suggested that one-charged

Ag^+ cations are the active sites of silver catalysts in alcohol oxidation [8-11]. By the analogy, we may suppose Au^+ ions to be the active sites of gold catalysts in this process. Like silver, gold has a stable ionic state Au^+, and these cations are detected by spectral methods on the surface of the catalysts.

The electron spectra of 10 wt.% Au/pumice catalyst used in methanol oxidation process indicate three pronounced absorption bands – 21000, 28000 and 36000 cm^{-1} (Fig. 2). Literature data on UV-visible spectra of supported gold are very scarce. However, using the analogy with the spectra of Ag samples [14-15], literature data [16-19] and our previous results [20-24], the signal at 21000 cm^{-1} is attributed to the absorption of the metal Au_m particles (plasmon resonance). The other two bands correspond to partly charged $Au_n^{\delta+}$ clusters. Electron spectrum of the crystal gold catalyst (bulk gold sample prepared by electrolysis method) indicates the similar structures of the metal – Au_m (24000 cm^{-1}), $Au_n^{\delta+}$ (38000 cm^{-1}); band at 33000 cm^{-1} is attributed to absorption of bulk gold (intrinsic photoeffect). On the catalyst surface gold is in the form of Au^o and Au^+, as is confirmed by XRD and XPS methods. High-charge Au^{3+} ions are not observed in the studied catalysts. The electron spectra indicate that in the catalysts modified by Ce and Zr oxides the portion of ionic states (ions and charged clusters) of gold is higher as compared with pure Au/pumice, whereas in Au-La and Au-Cs samples the amount of Au^+ is much lower. These results are qualitative but differences in comparative intensities of signals are evident.

Thus, UV-visible spectroscopy as well as the other physicochemical methods (IR-spectroscopy, XRD, EXAFS

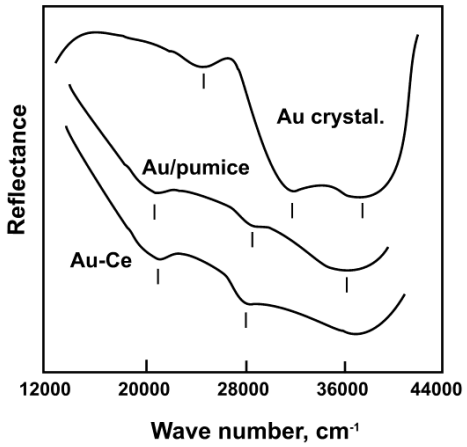

Fig. 2. UV-visible spectra of diffuse reflectance of exhaust gold catalysts.

[20-21]) revealed that the additions of Ce and Zr oxides stabilize the ionic states of supported gold. In contrast, La and Cs oxides lower the concentration of the charged states of the metal and favour their fast reduction. In agreement with our hypothesis on the nature of active sites of gold catalysts it is in a good correlation with the catalytic properties of the modified gold samples in methanol oxidation. Electron-seeking modifiers (Ce and Zr oxides) raise the concentration of active sites (Au^+) and increase the activity and selectivity of the catalyst. Electron-releasing additions (La and Cs oxides), in contrast, decrease Au^+ ion number and impair catalytic properties of the modified samples.

As expected, the modifiers can not change sufficiently the electronic properties of big gold particles. However, our experiments showed that part of the support surface (20-30 %) is not covered by big metal particles and contains high-dispersed Au^+ and $Au_n^{\delta+}$ states. As our previous studies showed [8-11, 20-26] the modifiers exert a great effect on electronic properties of these dispersed states of supported metals (Ag, Cu, Au) by the interaction of the supported metal with the Lewis acid sites (Ce^{3+}, Ce^{4+}, La^{3+}, Zr^{4+}) of the modified support surface. This interaction is carried out by the formation of the bonds of $M^{\delta+} \rightarrow Mod^{n+}$ (electron-acceptor) or $M^{\delta+} \leftarrow O^{2-} \leftarrow Mod^{n+}$ (electron-donor) type. In the last case electron-donor effect occurs through oxygen ions with the high charge density.

Gold cations on the surface of bulk metal and big particles are active in this process as well but the modifiers can not influence sufficiently the electronic properties of these states.

Although the conditions and the main tendencies of the alcohol oxidation on gold and silver catalysts are similar, there are some clear differences. The exhaust gases of the process on Au catalysts contain a significant amount of oxygen – 6-9 vol.%, while in the case of Ag and Cu catalysts only traces of O_2 are observed, i.e., part of oxygen does not react on the Au catalyst surface. It is known that partial oxidation of the alcohols on Ag and Cu catalysts occurs in the diffusion mode [1, 8-9]. As the experiments were carried out under the comparable conditions and, therefore, diffusion characteristics were the same, we can suppose that under the traditional operating conditions the process of methanol oxidation on gold catalyst occurs in the kinetic mode.

A direct dependence of the formaldehyde yield on the oxygen/alcohol ratio for Ag and Cu catalysts is well known [1, 8-9]. Under the conditions of diffusion mode of the catalytic process this is due to the injection of additional amount of the reagent into the reaction zone (oxygen is in deficiency relative to the alcohol). Our experiments showed that under the traditional condition formaldehyde yield on gold catalyst does not depend on the O_2/CH_3OH ratio. Increasing oxygen concentration in the initial gas mixture leads only to the rise of oxygen content in the exhaust gases. This indicates directly the kinetic character of the methanol oxidation process on gold catalysts. The tests also revealed that at low gas flow rate (50 h^{-1}) the rate of formaldehyde formation depends directly on the oxygen concentration in the alcohol-air mixture (Fig. 3) and is described by the equation: $W = kP_{O2}$.

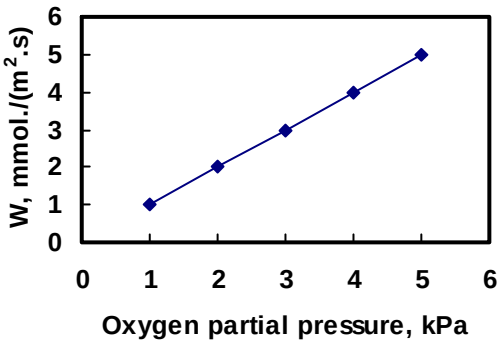

Fig. 3. Dependence of formaldehyde formation rate on oxygen partial pressure.

Conclusions

1. One-charged Au^+ ions are the active sites of the gold catalysts in alcohol partial oxidation. Modifiers stabilizing the ionic states of gold (Ce and Zr oxides) increase the selectivity of the catalyst. Electron-releasing additions (La and Cs oxides) impair the catalyst properties.
2. Contrary to Ag and Cu catalysts, methanol oxidation process on Au catalysts occurs in kinetic mode described by the equation: $W = kP_{O2}$.

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