ELSEVIER

Catalysis Today 28 (1996) 239-244

CATALYSIS TODAY

Modification of silver catalysts for oxidation of methanol to formaldehyde

A.N. Pestryakov

Department of Chemistry, State Academy of Civil Engineering, Solanaya sq. 2, Tomsk 634003, Russia

Abstract

Physico-chemical and catalytic properties of silver catalysts modified by Zr, Ce, La, Rb and Cs oxides have been studied in the process of the selective oxidation of methanol. Modifying additions in amounts of 1-10 wt.% change the effective charge and redox properties of supported silver, the metal dispersivity and its surface diffusion, surface acidity of the catalyst and degree of coking in the process of oxidation of methanol to formaldehyde. The influence of the modifier on the electronic state of the catalyst active sites (Ag^+, $Ag_n^{\delta+}$) is of primary importance when varying the catalytic properties of silver.

Keywords: Silver catalysts; Methanol to formaldehyde oxidation

1. Introduction

Bulk and supported silver catalysts are widely used for selective oxidation of methanol to formaldehyde [1-3]. Modification of a catalyst by different inorganic additions is one of the most promising methods for improving its characteristics. Almost immediately after the discovery of the silver catalyst efforts were mounted to promote the catalyst for the purpose of increasing its activity and service life, lowering the noble metal content and extending the range of the process operating conditions. Supports widely used to decrease the specific load of silver into the reactor and preventing the silver catalyst sintering under 'hard' conditions (600-700°C) can be considered as modifiers as well. But the collection of supports is limited, so small modifying additions of different compounds (0.1-10 wt.%) permit to achieve greater variety of changeable properties.

In scientific and patent literature a lot of different additives have been described both improving and impairing the silver catalyst characteristics [3-14]. The researchers suggest various mechanisms for the modifying action: change of the electronic work function of a metal and electron density in silver [7-9], variations in O_2 adsorption [3,10], the catalyst surface acidity [11], mechanical block of the catalyst surface [12], intrinsic catalytic properties of the additions [13,14]. However, all these models describe only separate aspects of modifications and do not embrace the variety of the modifying effects of the additions on the silver catalyst. The influence of the modifiers on the electronic state of the active sites of the catalyst is not considered either.

SSDI 0920-5861(95)00239-1

In previous studies we dealt with separate aspects of the modifier effect on some properties of silver [15–18]. The aim of the present study is a comprehensive investigation of the reaction of rare and rare-earth metal oxides and electronic, physico-chemical and catalytic properties of silver catalysts in the process of oxidation of methanol to formaldehyde. As is known, oxides of Zr, Rb, Cs, Ce, La and other lanthanides display a strong interaction of metal and support. So these additives are a convenient subject for the study of the mechanisms of silver catalysts.

2. Experimental

10 wt.% Ag/support samples were prepared by chemical (with hydrazine sulfate) or thermal (at 650°C) reduction of silver from an aqueous solution of $AgNO_3$. The modifiers in amounts of 1–10 wt.% were coated onto a support (pumice or Al_2O_3) of aqueous solutions of nitrates and acetates with the subsequent thermal decomposition of nitrates to oxides at 400°C.

Catalytic tests were carried out in a flow catalytic plant under the following operating conditions: $T = 600\text{–}700°C$; $O_2/CH_3OH = 0.35$; concentration of aqueous alcohol = 70%; methanol load on reactor = 100 g/(cm^2 h); thickness of catalyst layer = 10 cm. IR-spectra of adsorbed CO were registered using a SPECORD-75IR spectrometer, electron spectra of diffuse reflectance were recorded on a Shimadzu UV-300 at 200–800 nm wavelength (MgO reference sample). The catalyst samples were pretreated with O_2 at 100–500°C and with H_2 at 100–400°C. The metal dispersivity was determined using a Digisorb-2500 and JEOL JSM-35C electron microscope with a 35DDS X-ray microsonde. X-ray diffraction spectra were registered on a DRON-3 diffractometer (Cu-K_a) irradiation. Bronsted acidity of the catalyst surface was determined using the method of nonaqueous potentiometric titration with potassium ethylate in dimethyl formamide.

3. Results and discussion

For a long time silver was the leading catalyst for high-temperature synthesis of formaldehyde. Therefore, on addition of a foreign component into the balanced catalytic system it is necessary to take into account all potential aspects of the modifying action of the additions including the factors of long duration exposure during prolonged service of the catalyst in the reactor: aggregation, sintering, coking. Catalytic tests of the modified silver catalyst carried out in a number of our studies [15–17] and integrated on Fig. 1 indicated that additions of 1–5

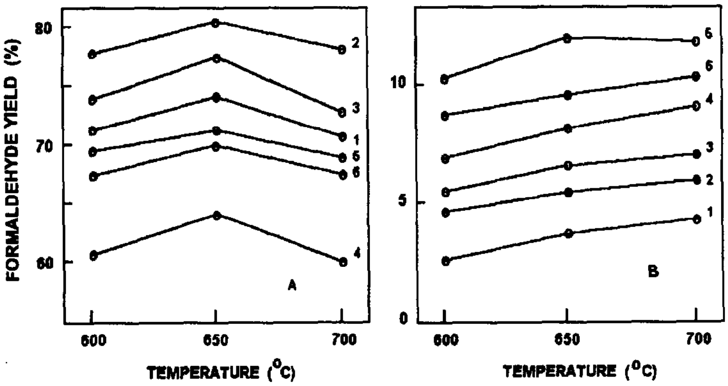

Fig. 1. Catalytic behavior of 15 wt.% Ag/pumice (a) and pumice (b) modified by 1 wt.% oxides: (1) unmodified; (2) ZrO_2; (3) CeO_2; (4) La_2O_3; (5) Rb_2O; (6) Cs_2O.

wt.% Zr and Ce oxides improve the catalyst performance, oxides of La, Pr, Sm and other lanthanides (except Ce), lower yield of formaldehyde, but additions of Rb and Cs oxides only slightly affect the process (Fig. 1a). Variations in selectivity of these catalysts have similar differences.

The observed effects are not explained by the intrinsic catalytic properties of the modifiers, as all these additions raise formaldehyde yield over the modified support (Fig. 1b). Certainly, the intrinsic catalytic activity of the modifiers makes some contribution to the total mechanism of the process. But it is obvious that this contribution is not principal as it does not explain the decline of selectivity of the catalyst modified by rare-earth metal oxides.

X-ray diffraction spectra exhibit the differences in modifier–support interaction. Contrary to lanthanide oxides, Cs_2O readily combined with the support to form silicates and aluminates with changing composition. Variations in chemical properties of supports under the effect of modifiers influence many important characteristics of supported metals. Dispersivity is one of such characteristics. Photomicrographs and oxygen adsorption measurements show that degree of silver dispersion on the supports modified by Zr and Ln oxides is 1.5–3 times higher than in unmodified samples. This is associated with the strong metal–support interaction. High-charged Zr^{4+}, Ce^{4+}, Ce^{3+}, La^{3+}, Sm^{3+} ions generate a large amount of sites for silver stabilization on the support surface. Also these sites retard the surface diffusion and aggregation of the metal during the process of methanol oxidation. Rb and Cs oxides do not have these properties, so silver dispersivity in Ag–Rb and Ag–Cs samples is similar or less than in unmodified catalyst.

However, tests of the catalysts with different percentages of silver intimated that the metal dispersivity does not play an important part in the formaldehyde synthesis process (Fig. 2). Formaldehyde yield reaches a maximal value at 3–5 wt.% Ag. Further rise of silver percentage does not lead to yield increasing, although the average size of the metal particles increases monotonically from 30–50 nm at 4–5 wt.% Ag to 500 nm and more at 40–50 wt.% Ag. Quieter growth of Ag–La activity is explained by easier accessibility of the modifier with negative effect (La_2O_3) for the reaction mixture at low silver content. The observed effects are caused by the external diffuse mechanism of the methanol oxidation process. At high temperatures (500–700°C) the diffusion of gas molecules controls the rate of the process, whereas the metal particle size influences only the rate of surface reaction at kinetic ranges of temperature ($< 300°C$). So the silver particle size slightly affects the process mechanism and cannot explain the differences in catalytic properties of the modified samples.

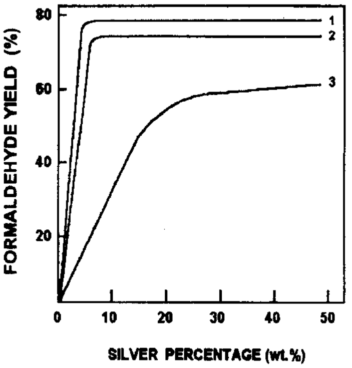

Fig. 2. Catalytic behavior of Ag/pumice samples modified by 1 wt.% oxides: (1) ZrO_2; (2) unmodified; (3) La_2O_3.

In our opinion, influence on electronic and redox properties of silver is the leading factor of the modifying action of the additives. The investigations [16–18] of the modified silver catalysts by the method of IR-spectroscopy of adsorbed CO demonstrated that ν_{CO} of surface Ag^+–CO complexes in Ag–Ce and Ag–Zr samples is higher than in the unmodified catalyst (Fig. 3). According to the model of σ–π binding of M–CO the frequency of C–O stretching vibrations in the surface complexes of M–CO depends directly on the effective charge of the adsorbent [19]. So it may be assumed that Zr and Ce oxides raise positive effective charge of Ag^+ ions. Moreover, the reducing treatments of the samples with H_2 and CO points to the fact that these modifiers stabilize the oxidized state of silver. Addition of La, Rb, Cs oxides, in contrast, abruptly decreases the effective charge of silver ions and favours their easy reduction when heating with H_2 or CO.

The observed effects concern the electronic donor–acceptor M^{n+}–Ag^+ and $O^{\delta-}$–Ag^+ interaction. High-charged Zr^{4+} and Ce^{4+} ions draw off the electron density from silver atoms and ions directly or through the intermediary of M^{n+}–O–$Ag^{\delta+}$ bridges. Cs_2O and Rb_2O are basic oxides with high negative charge density on oxygen ions. So at the expense of the electron-releasing $O^{\delta-}$–$Ag^{\delta+}$ interaction the effective charge of silver decreases sharply. Lanthanum has chemical properties closer to Ce and Zr than to Rb and Cs. But IR-spectroscopic investigation presented in Ref. [20] revealed that La and Sm oxides have strong basic sites similar to the ones in CaO. That is why the La_2O_3 action on the electronic state of silver is analogous with Rb_2O and Cs_2O.

The obtained results are confirmed by diffuse reflectance electron spectroscopy. According to the identification of signals of supported silver at UV-visible wavelength carried out preliminary in Refs. [21–23], the absorption band at 310–315 nm corresponds to the film and large particles of silver (intrinsic photoeffect), bands at 240–250 nm to Ag^+ ions (s–p, d–p electron transitions), signals at 280–290 nm and 370–390 nm to charged $Ag_n^{\delta+}$ clusters (n–σ^*, σ–σ^* transitions), and bands at 420–460 nm to silver big clusters (plasma resonance absorption). As Fig. 4 demonstrates, injection of Ce and Zr oxides raises the share of the oxidized states of silver (bands at 240, 280 and 370–390 nm). La, Rb and Cs oxides, in contrast, lower the part of these states.

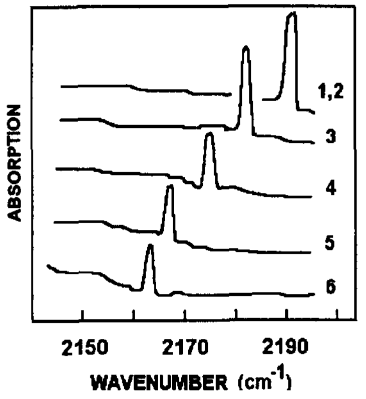

Fig. 3. IR-spectra of 15 wt.% Ag/Al_2O_3 modified by: (1) ZrO_2; (2) CeO_2; (3) unmodified; (4) La_2O_3; (5) Rb_2O; (6) Cs_2O.

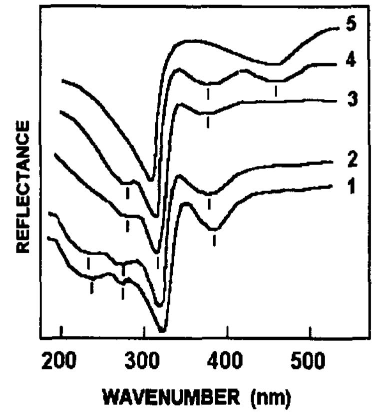

Fig. 4. Diffuse reflectance electron spectra of 15% Ag/pumice modified by: (1) ZrO_2; (2) CeO_2; (3) unmodified; (4) La_2O_2; (5) Rb_2O, Cs_2O.

Thus, the obtained data correlate well with the catalytic properties of the modified silver catalysts (Fig. 1a). In some studies [16,17] we suggested the hypothesis that Ag ions with maximal effective charge are active sites of silver catalyst for selective oxidation of methanol. Hence, modifiers raising the effective charge of silver and stabilizing its oxidized state promote the catalyst (Zr and Ce oxides). Oxides of lanthanum and other lanthanides (except Ce) favour Ag^+ reduction and so impair the catalyst performance. Rb and Cs oxides lower the Ag^+ effective charge as well, but their intrinsic catalytic properties (Fig. 1b) and depression of the coke deposition process on the catalyst partially neutralize the negative effect.

Of course, at high silver content in the catalyst (20–40 wt.%) the greatest part of the modifier is blocked by the metal cover. But our studies [22] disclosed that even at high silver content a major portion of support surface (10–30%) is not covered with the metal film but contains high-dispersed Ag^+ and $Ag_n^{\delta+}$ particles. It is the electronic state of these dispersed particles which is subjected directly to the modifiers. At prolonged working at high temperature silver partially aggregates and uncovers the modified support, but part of the modifier can recover from the support surface on the surface of the metal, as these substances have higher oxygen affinity than silver.

However, the modifier action is not limited by the effects mentioned above. The investigations [24,25] showed that applying the additions notably changes the Bronsted acidity of the support surface. Thus, Zr, Ce and La oxides raise concentration and strength of Bronsted acid sites (B.a.s.) (Table 1). Rb and Cs oxides do not influence the Bronsted acidity significantly since natural pumice contains some quantity of alkali metal compounds (Na and K). But on the surface of synthetic supports Rb and Cs oxides depress the catalyst acidity appreciably [11]. As is known, coke deposition process takes place on B.a.s., but it appreciably displays in prolonged service of the catalyst. For the evaluation of long-term action of the additions the catalyst samples were tested in a commercial reactor for methanol oxidation during 2 months. The degree of carbonization of the samples modified by Zr, Ce and La oxides were higher, which correlates well with the surface acidity of the catalysts.

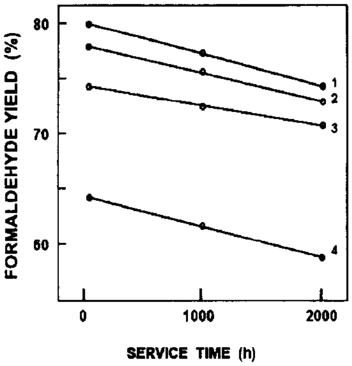

Fig. 5. Catalytic behavior of the modified 15% Ag/pumice samples after exposure in commercial reactor (650°C): (1) ZrO_2; (2) CeO_2; (3) unmodified; (4) La_2O_3.

Catalytic tests of the used up samples in flow catalytic plant demonstrate that with time the activity of all samples decreases, but the differences in their catalytic properties remains (Fig. 5). Hence, coke does not depress the positive effect of Zr and Ce oxide additions. Photomicrographs exhibit that coke in these samples is concentrated on the sections of the support surface uncovered with silver film. At the same time, degree of silver aggregation in the modified samples is less than in commercial Ag/pumice catalyst due to deceleration of surface diffusion of the metal. So in the samples modified by Ce and Zr oxides the larger part of the support surface is covered with silver, that has a wholesome effect on the catalyst properties. Study of the exhausted samples by the method of diffuse reflectance electron spectroscopy indicates that part of the oxidized states of silver in the catalysts modified by Ce and Zr oxides rises more than in unmodified Ag/pumice (Fig. 6). Hence, growth of acidity and degree of carbonization of the catalyst on addition of Zr and Ce oxides does not depress

Table 1

Bronsted acidity and degree of carbonization of 15 wt.% Ag/pumice catalysts modified by 1 wt.% oxides (reprinted from Ref. [25])

No.	Modifier	pH of B.a.s.	B.a.s. concentration ($mmol/cm^2$)	Coke content [a] (wt.%)
1	–	4.6; 5.5; 6.2	0.42	2.81
2	ZrO_2	1.6; 3.6; 4.7; 5.5; 5.83.	0.53	3.24
3	CeO_2	1.9; 3.7; 5.5; 6.4	0.49	3.11
4	La_2O_3	2.5; 3.9; 5.0; 5.6	0.48	3.04
5	RbO	4.0; 5.2; 6.5	0.41	2.78
6	CsO	4.8; 5.3; 5.8	0.41	2.80

[a] After 2000 h exposure in a commercial reactor.

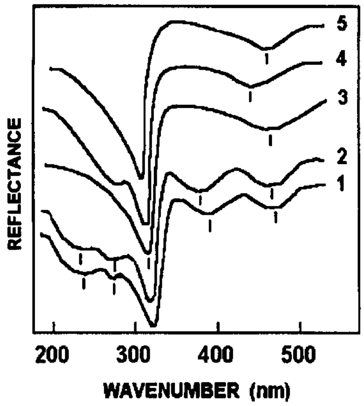

Fig. 6. Electron spectra of the used up catalysts modified by: (1) ZrO_2; (2) CeO_2; (3) unmodified; (4) La_2O_3; (5) Cs_2O.

the wholesome effect of these additions on electronic and redox properties of active sites of the silver catalyst.

4. Conclusions

The investigations revealed that the effect of modifying additions on silver catalyst is versatile and includes variations in effective charge and redox properties of silver, change of the metal dispersivity, surface diffusion, surface acidity, degree of coking and aggregation of silver during the prolonged service, and display of intrinsic catalytic properties of the modifiers. However, the influence of the modifier on the electronic state of active sites of silver catalyst is a leading contribution to the change of activity and selectivity of the catalyst.

References

[1] J.K. Walker, Formaldehyde, 3rd edn., Reinhold, New York, 1964.

[2] M.A. Barteau and R.J. Madix, The Surface Reactivity of Silver Oxidation Reactions, The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis, ESPC, vol. 4, 1982, pp. 96–142.

[3] S.M. Braylovskiy, O.N. Tiomkin and I.V. Trofimova, Probl. Kinet. Catal. (Russ), 19 (1985) 146.

[4] P.F. Carcia and V.N. Rao, Production of Formaldehyde, US Patent No 4474996 (1984).

[5] D.E. Vebster and I.M. Rouse, Improvements in and Relating into Catalysts for the Production of Formaldehyde, UK Patent No 1 603 821 (1981).

[6] H.R. Gerberich and E.T. Smith, Catalyst of Supported Silver and Lead, US Patent No 4386014 (1983).

[7] B.V. Suvorov and N.R. Vukeyhanov, Oxidation Reactions in Organic Synthesis, Khimia, Moscow, 1978.

[8] R.M. Flid, I.V. Trofimova, S.M. Braylovskiy et al., Khim. Prom. (Russ), 10 (1980) 589.

[9] B.D. Yagodovskiy and S.K. Rey, Rus. J. Phys. Chem., 60 (1986) 10.

[10] M.L. Kalia, G.U. Nechaeva and N.V.Kulkova, Kinet. Catal., 23 (1982) 1287.

[11] M.L. Kalia, I.V. Trofimova, C.M. Braylovskiy et al., Khim. Prom. (Russ), 4 (1982) 201.

[12] J. Schroeder, A. Jakubowich, M. Szustakowski et al., Prz. Chem., 59 (1980) 11.

[13] R.M. Flid and A.E. Krasotkin, Kinet. Catal., 3 (1962) 282.

[14] R.Iede, E. Mansko and O. Ganschow, J. Vac. Sci. Technol., 3 (1985) 1983.

[15] A.N. Pestryakov and M.I. Roznina, Izv. VUZ. Khim. and Khim. Technol. (Russ), 6 (1993) 92.

[16] A.N. Pestryakov and A.A. Davydov, Appl. Catal. A, 120 (1994) 7.

[17] A.N. Pestryakov and A.A. Davydov, Kinet. Catal., 35 (1994) 273.

[18] A.N. Pestryakov, A.A. Davydov and L.N. Kurina, Rus. J. Phys. Chem., 61 (1987) 2381.

[19] A.A. Davydov, Infrared Spectroscopy of Adsorbed Species on Surface of Transition Metal Oxides, Wiley, New York, 1990.

[20] A.A. Davydov, M.L. Shepotko and A.A. Budneva, Kinet. Catal., 35 (1994) 299.

[21] A.N. Pestryakov, A.A. Davydov and L.N. Kurina, Rus. J. Phys. Chem., 60 (1986) 2081.

[22] S.P. Noskova, A.A. Davydov, A.N. Pestryakov et al., Rus. J. Appl. Chem., 61 (1988) 2021.

[23] A.N. Pestryakov and A.A. Davydov, J. Electron Spectr., in press.

[24] A.N. Pestryakov, V.N. Belousova and M.I. Roznina, Rus. J. Appl. Chem., 66 (1993) 1148.

[25] A.N. Pestryakov, M.I. Roznina and V.N. Belousova, Rus. J. Appl. Chem., 66 (1993) 2285.