

CATALYTIC REACTION MECHANISMS

Role of the Surface Acid–Base Properties of Silver Catalysts in the Partial Oxidation of Ethylene Glycol

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Abstract—The acid–base properties of a bulk silver catalyst and silver catalysts supported on various carriers for the partial oxidation of ethylene glycol were studied. A relationship between the catalytic activity and the concentration of surface acid sites in the catalysts was found. A mechanism was proposed for the participation of Lewis acid sites in the reaction of partial ethylene glycol oxidation to glyoxal.

INTRODUCTION

In previous studies of the oxidation of methanol into formaldehyde [1, 2], it was found that the yield of formaldehyde increased with increasing surface concentration of acid sites in supported silver catalysts. There is no information on a relationship between the acid–base characteristics and the catalytic activity of bulk and supported silver catalysts in the oxidation of ethylene glycol. A similarity between the oxidation mechanisms of monohydric and dihydric alcohols [3] suggests such a relationship. The occurrence of Brønsted acid sites on the surface of supported silver catalysts for the partial oxidation of methanol was assumed previously [4, 5]. At the same time, Pestryakov *et al.* [6] expressed an opinion that the Lewis acid sites $\text{Ag}^{\delta+}$ are the active centers of catalyst surfaces in this process. Note that the correlation dependence of the activity of catalysts for methanol oxidation on the concentration of acid sites was demonstrated in the cited publications; however, a reaction scheme with the participation of acid sites was not given.

To understand the mechanism of a complex heterogeneous catalytic process of the partial oxidation of ethylene glycol to glyoxal, it is necessary to study the role of the surface acid properties of silver catalysts.

EXPERIMENTAL

Silver catalysts supported on oxide carriers and a polycrystalline bulk silver catalyst were used in this study. The bulk catalyst was prepared by electrolysis in accordance with a published procedure [7]. The purity of the test material was checked using X-ray spectrum analysis. The supported silver catalysts were prepared by the fractional chemical reduction of silver nitrate with hydrazine sulphate [8]. Natural pumice stone and synthetic aluminosilicates were used as the supports.

Table 1 summarizes the composition and properties of the supports.

The catalytic activity of samples was studied by a flow method in a quartz fixed-bed reactor [9] under the following conditions: oxygen/ethylene glycol (O_2/EG) molar ratio of 1.0, $\text{N}_2/\text{EG} = 7.0$, and $T = 600^\circ\text{C}$. The liquid products of the reaction were analyzed on a Tsvet-500 chromatograph in accordance with the procedure in [10]. Gas analysis was performed on an LKhM-80 chromatograph with 1-m silica gel and 3-m CaA columns; argon was used as a carrier gas.

The total concentration of acid sites, which was determined by nonaqueous potentiometric titration with potassium ethylate ($\text{C}_2\text{H}_5\text{OK}$) in dimethylformamide [4], was used for characterizing the surface acid properties of the bulk and supported Ag catalysts. A saturated calomel electrode and a platinum electrode were used as reference and indicator electrodes, respectively.

RESULTS AND DISCUSSION

The procedure published for the nonaqueous potentiometric titration of the surface of heterogeneous catalysts implies the use of ground sample suspensions [4]. However, the mechanical grinding of a supported silver catalyst disturbed the structure of grains and resulted in the removal of active component particles from the surface of the support. Consequently, the support surface, which has its own acid sites, exerted an interfering effect. For samples with a small specific surface area, its value changed, and this change could be reflected in the calculations of the surface concentration of acid sites. In this work, grains of a fraction of 1–2 mm were used to obtain data on the acid properties of silver catalyst surfaces.

Tables 1 and 2 summarize experimental data on the acid and catalytic properties of the samples. As can be seen in Table 1, the surfaces of the test supports exhib-

Table 1. Structural and acidic properties of the surfaces of individual supports

No.	S_{sp} , m ² /g	SiO ₂ content, %	Support	Concentration of acid sites, $\mu\text{mol}/\text{cm}^2$			
				type I	type II	type III	Σ^*
1	2	70	Pumice	0.80	2.50	3.2	6.50
2	3.4	40	Aluminosilicate 1	0.04	0.60	–	0.64
3	12	88	Aluminosilicate 2	0.18	0.35	–	0.53
4	10	88	Aluminosilicate 3	0.25	0.61	–	0.86
5	3.5	100	Cristobalite	0.10	0.40	0.2	0.70
6	0.5	0	Corundum 1	4.70	4.90	–	9.60
7	0.6	0	Corundum 2	0.70	1.30	1.5	3.50
8	2.2	0	Corundum 3	–	1.40	2.7	4.10

Note: Sample nos. 2–8 were synthesized at the Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences (Novosibirsk).

* Σ is the total surface acidity.

Table 2. Catalytic and acidic properties of the surfaces of freshly prepared silver catalysts and the catalysts treated with a reaction mixture ($\text{O}_2/\text{EG} = 1$, $\text{N}_2/\text{EG} = 7$, and $T = 600^\circ\text{C}$) for 10 h

No.	Sample		Concentration of acid sites, $\mu\text{mol}/\text{cm}^2$					Yield of glyoxal, wt %
			type I	type II	type III	type IV	Σ^*	
1	Electrolytic Ag	Fresh	6.30	8.50	4.90	8.60	28.30	65.5
		Treated	4.30	7.30	7.50	–	19.00	59.3
2	Ag/pumice	Fresh	0.42	0.99	0.99	1.06	3.48	36.5
		Treated	0.58	5.45	2.23	–	8.24	42.3
3	Ag/aluminosilicate 1	Fresh	0.63	2.14	2.13	–	4.90	48.6
		Treated	0.56	2.99	2.43	–	5.80	55.3
4	Ag/corundum 1	Fresh	4.40	–	–	–	4.40	16.2
		Treated	0.06	–	–	–	0.06	–
5	Ag/corundum 2	Fresh	1.90	–	–	–	1.90	27.4
		Treated	0.09	0.35	–	–	0.45	12.0
6	Ag/corundum 3	Fresh	0.33	1.19	–	–	1.52	36.2
		Treated	0.05	0.27	–	–	0.32	15.6
7	Ag/cristobalite	Fresh	0.037	–	–	–	0.037	28.6
		Treated	0.016	0.02	–	–	0.036	18.0

* Σ is the total surface acidity.

ited acid properties, and three types of acid sites were detected. The supporting of silver onto the carrier surfaces changed the pattern: the concentration and amount of acid sites changed. The supported Ag catalysts were characterized by higher surface concentrations of acid sites as compared with the individual supports. A comparison with catalytic data indicates that in the selective oxidation of ethylene glycol the most active catalysts (Table 2, sample nos. 1–3) exhibited high concentrations of surface acid sites. The highest concentration of surface acid sites was detected in bulk silver (Table 2, sample no. 1); this is consistent with high selectivity for the target product, as compared with

the supported catalysts. The surfaces of Ag catalysts supported on aluminosilicate carriers (Table 2, sample nos. 2, 3) are also characterized by sufficiently high concentrations of acid sites. Sample nos. 4–7, which were prepared based on the individual oxides Al_2O_3 (corundum) and SiO_2 (cristobalite), exhibited the lowest total concentrations of surface acid sites.

The concentration of acid sites on catalyst surfaces changed after a 10-h treatment of the samples in a reaction mixture (Table 2). Both the concentration of acid sites on catalyst surfaces and the activity in the selective oxidation of ethylene glycol decreased in the samples

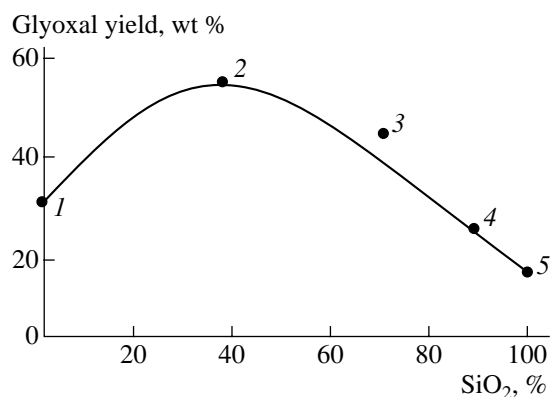


Fig. 1. Effect of the chemical composition of supports on the activity of Ag catalysts supported on (1) corundum, (2) aluminosilicate 1, (3) pumice, (4) aluminosilicate 2, and (5) cristobalite.

prepared based on individual oxides (nos. 4–7). At the same time, the total concentration of surface acid sites and the catalytic activity in the selective conversion of ethylene glycol into glyoxal increased in Ag catalysts supported on aluminosilicates (nos. 2 and 3) after exposure to a reaction mixture. That is, the catalyst was activated under the action of a reaction mixture.

Batyan *et al.* [11] found that the catalytic activity of Ag catalysts supported on carriers different in nature changed in the course of the partial oxidation of methanol into formaldehyde because of differences in the stabilization of a highly dispersed state of silver on the surface of carrier grains. As the SiO₂ content increased, the concentration and stabilization of disperse silver particles were observed at the sites of formation of a mullite phase.

Figure 1 demonstrates that the chemical composition of supports in supported Ag systems has a considerable effect on the selectivity of ethylene glycol oxidation. A maximum yield of glyoxal was obtained when the process of ethylene glycol oxidation was performed on Ag catalysts supported on aluminosilicate carriers containing ~40% SiO₂ (Fig. 1). Of the tested group of catalytic systems, a support in which the silicon oxide content was as high as 40% was the most efficient. Note that the comparison was performed with samples pre-

pared by fractional chemical reduction onto supports with close specific surface areas. Consequently, the stabilization of the active component in a highly dispersed state is a necessary condition for preparing an efficient catalytic system.

Based on the experimental data, we can propose the following order of changes in the total concentration of acid sites on the surfaces of the tested catalysts, which coincides with the order of activity in the selective conversion of ethylene glycol into glyoxal:

Electrolytic Ag > Ag/pumice, Ag/aluminosilicate > Ag/corundum > Ag/cristobalite.

The relation between the selectivity of catalysts and the concentration of acid sites on the surface of samples allowed us to assume the participation of acid sites on the catalyst surfaces in the selective conversion of ethylene glycol into glyoxal.

Supported silver occurs as crystallites of 50–90 nm on the surface of supports [3]. In this case, 30–50% of the support surface remains bare and can interact with reactants to decrease the selectivity of the process. The individual supports exhibited activity in the nonselective conversion of the alcohol (Table 3). All the supports exhibited significant ethylene glycol conversions. Formaldehyde was the main reaction product; CO, CO₂, acetaldehyde, glycolaldehyde, and carboxylic acids (acetic and formic acids) were also found; glyoxal was not detected.

This can be due to the structure peculiarities of ethylene glycol. Taking into account the preferred adsorption of ethylene glycol with the participation of paired surface sites of an Ag catalyst [12], we can assume that, at a precatalytic step, ethylene glycol and its carbonyl derivatives are adsorbed at two hydroxyl and aldehyde groups to cause stresses at the C–C bond, whose length is 1.54 or 1.47 Å for ethylene glycol or glyoxal, respectively (for Ag, the distance between neighboring atoms is 1.4 Å [13]). This cyclic structure on the surface of individual supports (oxide systems) is stabilized by C–C bond cleavage and the formation of formaldehyde as the main product of vapor-phase ethylene glycol oxidation. Thus, the surface acid sites of individual supports take no part in the selective conversion of ethylene glycol into glyoxal because they participate in the non-

Table 3. Catalytic activity of individual supports in the oxidation of ethylene glycol ($T = 550^\circ\text{C}$; $\text{O}_2/\text{EG} = 0.8$, and $\text{N}_2/\text{EG} = 7$)

Support	SiO ₂ content, %	Ethylene glycol conversion, %	Product yields, wt %				
			H ₂ CO	CO	CO ₂	aldehydes*	acids**
Corundum	–	57.3	40.2	3.7	6.4	10.0	0.2
Cristobalite	100	45.1	20.3	4.8	3.8	5.9	0.1
Aluminosilicate 1	40	52.6	36.0	3.4	1.8	9.8	0.2

* Acetaldehyde and glycolaldehyde.

** Glycolic, glyoxalic, and formic acids.

selective oxidation of ethylene glycol with the predominant formation of formaldehyde.

Pestryakov *et al.* [6] studied the adsorption of CO on supported Ag catalysts using IR spectroscopy and found that the interaction of alcohols with the surface of silver occurs via a donor-acceptor mechanism at active Lewis sites of the $\text{Ag}^{\delta+}$ type. These sites can be formed by a reaction with gas-phase oxygen or under the action of lattice oxygen from the support in the case of supported systems.

Note that the potentiometric titration curves of bulk and supported Ag catalysts differ from the titration curves of the supports (Fig. 2). On the titration of the surfaces of individual supports with potassium ethylate, the K^+ ion is exchanged for the surface proton H^+ ; this was supported by the normal positive run of the titration curve. Thus, the determined surface acid sites of individual supports are Brønsted sites. The experimental data demonstrated that the support surfaces are characterized by the occurrence of up to three types of acid sites (Table 1).

However, the process was more complicated on bulk silver and supported Ag catalysts. It is well known that the oxygen-free reduced surface of silver does not exhibit acid properties [14]. The preadsorption of oxygen on the surface of silver results in that a number of molecules that can dissociate to form a proton (such as formic acid, acetylene, ethanol, etc. [15]) react as Brønsted acids with oxygen atoms adsorbed on the $\text{Ag}(110)$ single-crystal surface with proton transfer and the formation of OH_{ads} and then water. Oxygen adsorbed on silver (O_{ads}), which is a strong surface base, exhibits the properties of a strong nucleophile in reactions with carbonyl compounds [14]. Thus, the Lewis acid-base pair $\text{Ag}^{\delta+} \cdots \text{Ag}-\text{O}^{\delta-}$ occurs on the oxidized surface of silver.

On the titration of this catalyst with potassium ethylate in a nonaqueous solution, the surface base $\text{O}^{\delta-}$ (protonated in a real solution) is replaced by the ethylate anion $\text{C}_2\text{H}_5\text{O}^-$, which is preferable because the nucleophilicity of $\text{C}_2\text{H}_5\text{O}^-$ is higher than that of OH^- [14]. The concentration of hydroxyl anions OH^- increases in the titrated solution. A change in the state of the solution is detected as a decrease in the potential of the indicator platinum electrode. In this case, the positive run of the potentiometric titration curve is reached by changing the polarity of electrodes. A similar effect of changing the polarity of electrodes was observed for bulk and all the freshly prepared Ag catalysts.

After a 10-h treatment of the samples with a reaction mixture, the initial polarity of the electrodes remained unchanged for sample nos. 1–3 (Table 2) or changed for sample nos. 4–7. As demonstrated above, the reaction mixture had analogous effects on changes in the catalytic activity of the samples (Table 2). An analysis of the above factors allowed us to assume that, in the study of all the freshly prepared samples and sample nos. 1–3 treated with the reaction mixture, the potential jumps observed were due to the titration of Lewis acid sites of

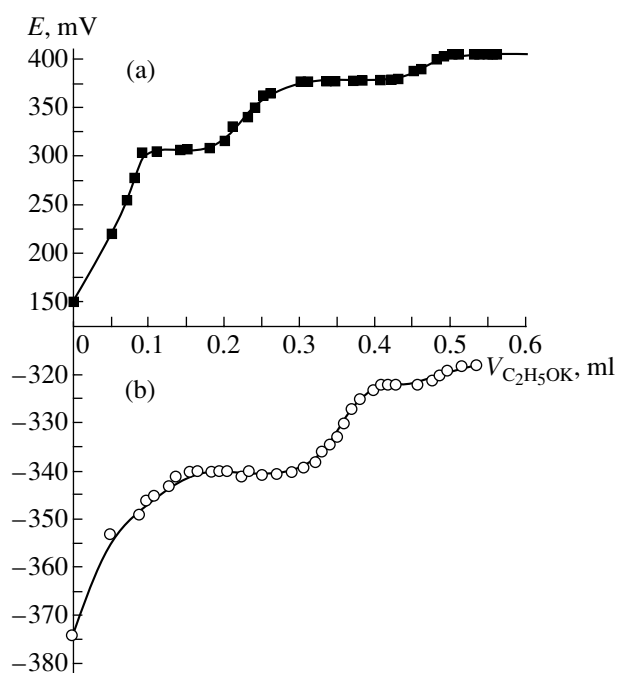
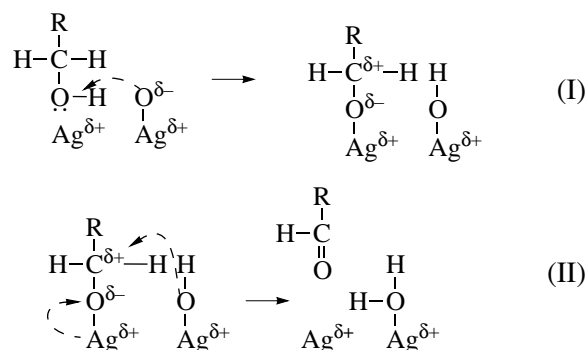


Fig. 2. Potentiometric titration curves for the surfaces of (a) pumice and (b) a supported silver-pumice catalyst (10 wt % Ag).

the active component—silver. The treatment of catalyst nos. 4–7, which are based on corundum and cristobalite, with the reaction mixture resulted in the agglomeration of supported metal particles. In this case, the shapes of titration curves for supported Ag catalysts and individual supports were practically identical because acid properties depend on the bare surface of the support containing Brønsted acid sites.

Based on the data on the occurrence of Lewis acid sites on the surface of silver, the selective conversion of alcohols with the participation of these sites can be schematically represented as follows:



Initial step (I) is associated with the reaction of a Lewis base (an alcohol molecule) with a surface Lewis acid site ($\text{Ag}^{\delta+}$). As a result, a long-lived alkoxy intermediate and OH_{ads} are formed on the catalyst surface. Capote and Madix [13] demonstrated the existence of an alkoxy intermediate using the EELS method.

At step (II), the selective oxidation of the intermediate takes place with the formation of an aldehyde and a water molecule adsorbed on the catalyst surface. In the case of a dihydric alcohol (ethylene glycol), when the two-center adsorption of the reactant takes place on the surface of an Ag catalyst [12], it is believed that the partial oxidation of ethylene glycol to glyoxal occurs analogously to reaction schemes (I) and (II), where R is the CH₂OH group, which interacts with the neighboring conjugated Lewis acid–base pair Ag^{δ+}...Ag–O^{δ-} on the surface of a silver catalyst.

Thus, as a result of the studies, we found that the surface acidity of silver catalysts affects the activity of the catalysts. Lewis acid sites can serve as active centers for the conversion of ethylene glycol into glyoxal on the surface of silver catalysts.

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