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Figure 1: Fig. 1. Change in the specific activity and selectivity of Ag as a function of Cl concentration ($T = 200°$): I —K, II —K_1, III —K_2, IV —E_1, V —E_2, VI —$\lg B_1$, VII —$\lg B_2$, $VIII$ —selectivity

Abstract

Full Text

Chemistry

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EFFECT OF HALIDE IMPURITIES ON THE SPECIFIC ACTIVITY OF SILVER IN THE ETHYLENE OXIDATION REACTION

(Presented by Academician A. A. Balandin, 24 III 1962)

Earlier ([1]) we showed that, with an increase in the chlorine content that may be taken up by silver during its preparation from the starting reagents, the specific activity of the silver catalyst gradually decreases. However, along with chlorine, the silver could also have been contaminated by other microimpurities, the amount of which was not determined. It was therefore of interest to study the effect of concentrations of chlorine, specially introduced into purified silver, on the character of the change in the specific activity of the latter. In addition to chlorine, additions of other halides were also investigated, in order to establish the general regularities of the action of halides on the catalytic properties of silver and to determine the specificity of the action of each halide separately.

Halide impurities were deposited on the surface of Ag in order to avoid migration of the additive from the bulk to the surface of the catalyst grains during activity testing ([2]). The halide concentration was varied from 10^{-5} to 10^{-2} at. % by weight of Ag, which corresponded to a surface coverage fraction $\theta = 10^4$—10^{-1} ([3]). The surface area, measured by low-temperature adsorption of krypton, was 0.44 ± 0.05 m^2/g for the entire series of samples studied.

Fig. 1. Change in the specific activity and selectivity of Ag as a function of Cl concentration ($T = 200°$): I —K, II —K_1, III —K_2, IV —E_1, V —E_2, VI —$\lg B_1$, VII —$\lg B_2$, $VIII$ —selectivity

The activity of the catalyst was characterized by the specific rate constant of the overall ethylene oxidation reaction (K), calculated from equation (1):

$$W = K\frac{C_2H_4}{C_2H_4O}0.5 \tag{1}$$

and by the rate constants for the formation of ethylene oxide $K_1 = K \cdot S$ (S – selectivity) and carbon dioxide $K_2 = K - K_1$. Determination of the activity were carried out in the temperature range 180-230° according to the procedure described in (1).

The change in the catalytic properties of Ag as a function of the halide content is presented in Table 1 and in Figs. 1-2*.

Table 1

Effect of additions of F and I on the activity and selectivity of Ag

Halide	θ	$K \cdot 10^8$	$K_1 \cdot 10^6$	$K_2 \cdot 10^6$	S, %	E_1, kcal/mol	lg B_1	E_2, kcal/mol	lg B_2
F	–	31.0	15.0	16.0	48	23.4	11.7	23.6	11.7
F	0.001	28.0	13.0	15.0	47	23.7	11.6	23.7	11.6
F	0.01	29.8	14.8	15.0	49	23.7	10.7	22.7	11.6
F	0.09	24.0	12.6	11.4	52	22.2	10.7	22.7	11.0
F	0.12	14.8	8.2	6.4	56	21.8	10.5	22.5	10.8
I	0.0001	21.2	10.0	11.2	47	20.5	10.0	20.7	10.3
I	0.001	21.2	10.0	11.2	47	20.7	10.2	20.8	10.3
I	0.006	17.8	8.4	9.4	48	20.0	9.8	20.4	10.0
I	0.02	15.2	7.8	7.4	52	20.2	9.8	20.3	10.0
I	0.09	8.4	5.0	3.4	60	18.5	8.8	19.4	9.1
I	0.12	2.8	1.7	1.1	62	18.0	8.4	19.2	8.7

The results of the study showed that the change in the rate constants for the formation of C_2H_4O and CO_2 (K_1 and K_2), caused by an increase in the halide content in silver, is accompanied by a parallel change in the heats of activation of these reactions (E_1 and E_2) and in the corresponding pre-exponential factors of the Arrhenius equation (B_1 and B_2). Depending on the halide introduced, the character of the change in all the indicated quantities may be different. Thus, the addition of F causes a gradual decrease in the rate constants, heats of activation, and pre-exponential factors (see Table 1). Additions of Cl and Br (and possibly also I) exert a peculiar modifying effect on the surface properties of silver. At low concentrations (for chlorine, θ of the order of 10^{-3}-10^{-2}, see Fig. 1; for bromine, 10^{-4}-10^{-3}, see Fig. 2) they decrease K_1 and K_2, the heats of activation for the formation of C_2H_4O and CO_2, and the pre-exponential factors. With a further increase in coverage (for Cl from 0.05 to 0.09; for Br from 0.001 to 0.005; for I, probably, from 0.0001 to 0.001, see Table 1), the rate constants increase simultaneously with an increase in the heats of activation and pre-exponential factors. An even greater increase in coverage ($\theta \geqslant 0.1$) leads

Fig. 2

Figure 2: Fig. 2

to a sharp fall in K_1 and K_2, a decrease in E_1 and B_1, and a decrease (Table 1) or increase (Fig. 1) in E_2 and B_2. An analogous action of the impurities is observed at all the temperatures investigated.

From the data of Table 1 and the figures it is seen that the effect of halides on the specific activity of silver in the region of low and medium surface coverages ($\theta \sim 10^{-4}$-10^{-2}) cannot be connected with any regularly changing property of the introduced additives. In the region of high coverages ($\theta \geqslant 0.1$), the decrease in specific activity (expressed as K_{hal}/K) is approximately proportional to the magnitude of the ionic radius of the introduced halide (see Fig. 3). From this it may be concluded that the increase in the effect in the series $I > Br > Cl > F$ probably depends on those properties of the halides that are determined by the size of the ionic radius (such as polarizability, ionization potential, etc.).

An increase in the fraction of the silver surface covered by any halide causes an increase in the selectivity of the process. Up to θ approximately equal to 0.01, the selectivity increases very slowly (Fig. 1) or even remains constant (Fig. 2), but when θ exceeds 0.01, the increase in selectivity becomes sharper. In the degree of increase in selectivity at the same–

* The data in Table 1 and in the figures are average values from determination of the activity of 2-3 samples.

at the same fraction of surface coverage of silver by the additive ($\theta = 0.1$), the halides can be arranged in the following order: Cl > Br > J > F (Fig. 3). This order is preserved over the entire temperature range studied, since in the interval 180-230° the selectivity of silver with halide impurities in our experiments did not depend on temperature.

Fig. 2. Change in the specific activity and selectivity of Ag as a function of Br concentration ($T = 200°$): I –K, II –K_1, III –K_2, IV –E_1, V –E_2, VI –$\lg B_1$, VII –$\lg B_2$, $VIII$ –selectivity

The character of the change in the specific activity of silver as a function of the content of halide additives in it, established in the present work, differs from the data of other authors who studied the effect of electron-withdrawing impurities on the specific activity of Ag. When modified with S (4), Se (3), and P (5), the specific activity of silver gradually increased, reached a maximum, and then decreased. Addition of Cl (4,5) only poisoned the catalyst. It should be noted, however, that in the cited works the silver was not subjected to special purification from microcontaminants that enter it during preparation. These small amounts of "biographical" microimpurities could have distorted the picture of the influence of the introduced additives.

Although a number of works have been devoted to modification (6) of the sil-

Figure 3

Figure 3: Figure 3

ver catalyst for ethylene oxidation, the mechanism of this phenomenon has not yet been sufficiently studied. Some authors (^{7}) believe that metalloid additives change the form of the kinetic equation for the rate of the process. Special experiments showed that equation (1) is well applicable for describing the kinetics of ethylene oxidation both on pure silver and on silver promoted with chlorine. Therefore, the assumption that the reaction orders with respect to oxygen and ethylene change upon modification of Ag is insufficiently substantiated. More convincing is the view that impurities affect the bond energy of oxygen (^{3}), or of both reactants, with the catalyst surface, facilitating or hindering the oxidation reaction. Such an influence

can occur only if the interaction of the additive with the catalyst is electronic in character (^{8}). It has been established (^{7}, ^{9}) that metalloid impurities increase the electron work function (φ) from Ag. But the relation between φ and the heat of activation of ethylene oxidation on modified silver has not been investigated. It is believed (^{7}) that modification should not appreciably affect the heat of activation of C_2H_4 oxidation. In our experiments it has been shown that, with increasing content of halides in silver, a

Fig. 3. Change in the specific activity and selectivity of silver as a function of the ionic radius of the introduced halide at $\theta = 0.1$ and $T = 200^\circ$:
$I - K_{\text{hal}}/K$; II –selectivity

symbatic change occurs in the heats of activation of the formation of C_2H_4O and CO_2 and in the corresponding pre-exponential factors of the Arrhenius equation. This is yet another proof of the electronic nature of the action of halides on the surface properties of Ag. By lowering the electron density at the catalyst surface, electronegative impurities should decrease the bond energy of oxygen and increase the bond energy of ethylene with silver. In this case, the attainment of the optimum (^{10}) bond strength for both components may not be simultaneous, and therefore the modification curve will have a minimum and a maximum of activity.

The action of F on the specific activity of silver is different from the action of the other halides. It is very probable that, owing to the closeness of the ionic radii of F and Ag, fluorine can penetrate into the near-surface layers of silver and its influence on the surface properties of silver is weakened.

Particular attention should be paid to the fact that the selectivity of silver with halide additives begins to increase appreciably only at significant ($\theta \sim 0.01$) fractions of coverage of the catalyst surface by the impurity (see table and Figs. 1, 2). The value of the selectivity in the oxidation of C_2H_4 has usually been associated with the ratio of molecularly and atomically adsorbed oxygen on the Ag surface (^{11}). Apparently, a sharp change in this ratio upon introduction of electronegative additives (^{12}) occurs only at high impurity concentrations ($\theta \sim 0.01$), and then the increase in selectivity becomes more noticeable.

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