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Abstract

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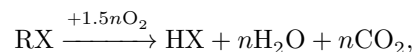
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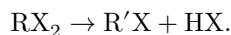
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MODIFICATION OF A SILVER CATALYST WITH HALOORGANIC COMPOUNDS

It was shown by us earlier that metalloids introduced into silver and increasing the selectivity of the process of oxidation of ethylene to ethylene oxide are partly removed from the catalyst as a result of their interaction with ethylene (¹). Therefore, a more rational method of controlling selectivity is modification of the catalyst with volatile organic metalloid additives introduced into the gaseous reaction mixture. Data on the action of various organic halide compounds on the selectivity of the reaction of oxidation of ethylene to ethylene oxide have been published in the literature (²⁻⁵), but the mechanism of the action of the additives has not been investigated. The purpose of this work is to elucidate the behavior of these additives on the surface of silver. Under the conditions of the catalytic process, organic metalloid additives may be oxidized:



where R is the radical $\text{C}_n\text{H}_{2n+1}$, X is a halogen: Cl, Br, I, S, etc. It is also possible for halogen-containing molecules to split:



The nature of their adsorption on silver may play a substantial role in these reactions.

The oxidation of the additives was studied as follows. Air, purified from carbon dioxide, was saturated with volatile organic additives in various concentrations and passed through a layer of silver catalyst in the temperature range 150-350° under dynamic conditions. As a result of oxidation of the additive, carbon dioxide is liberated, which is absorbed by a solution of $\text{Ba}(\text{OH})_2$ with subsequent titration. After each experiment, the concentration of chloride ion in the silver was determined nephelometrically or by the gravimetric method. If only the

oxidation reaction of the haloorganic substance proceeds, then the amount of carbon dioxide must be equivalent to the chlorine content in the silver. Therefore, establishing the balance with respect to CO_2 and chlorine in the silver makes it possible to determine the ratio of the oxidation and decomposition reactions of the additives. Table 1 gives data on the oxidation of a number of haloorganic compounds on silver. At a temperature of 180–200°, carbon tetrachloride and pentachloroethane are oxidized by more than 50%. Dichloroethane, chlorobenzene, and others are oxidized to a considerably smaller extent. The silver after oxidation of these additives on it was examined by the X-ray diffraction method (by reflection from a pellet with an area of 0.78 cm^2). A considerable concentration of silver chloride was found on the surface of the pellet. After removal of the surface layer 0.2 mm thick, no silver chloride was found in the sample. It should be noted that with this method of modification there is observed not only a gradient of the concentration of AgCl through the thickness of the pellet, but also along the length of the catalyst layer. Thus, examination of a silver contact for the content of chloride ion in it after treatment with dichloroethane ($10^{-5}\%$) showed that, along with a considerable increase in the selectivity of the oxidation process—

Table 1

Oxidation of organic additives on silver at 180–200°

Additive	Conc. of additive in air, vol. %	Catalyst temp., °C	CO content in gas, vol. %	Conc. of Cl in silver, wt. %	Degree of oxidation of additive, %, by CO	Degree of oxidation of additive, %, by halide
CCl_4	$5,5 \cdot 10^{-2}$	200	0,34	0,2–0,7	62,0	68,0
CH_2Cl_2	$3,2 \cdot 10^{-2}$	180	Traces	$3 \cdot 10^{-3}$ – $6 \cdot 10^{-3}$	—	3,0
$\text{ClCH}_2\text{—CH}_2\text{Cl}$	10^{-2}	180	Traces	$3 \cdot 10^{-3}$ – $5 \cdot 10^{-3}$	—	4,0
$\text{C}_2\text{H}_4\text{Cl}_2$	$2,3 \cdot 10^{-2}$	200	0,0033	$1,3 \cdot 10^{-2}$	7,0	5,0
$\text{HOCH}_2\text{—CH}_2\text{Cl}$	10^{-2}	180	Traces	$4 \cdot 10^{-3}$ – $1 \cdot 10^{-2}$	—	9,0
$\text{HCCl}_2\text{—CCl}_3$	10^{-2}	200	0,0109	$1,4 \cdot 10^{-1}$	59,0	52,0
$\text{Cl}_2\text{CF—CF}_2$	10^{-2}	180	Traces	$1 \cdot 10^{-2}$ – $3 \cdot 10^{-2}$	—	4,0*
FCl_2CF_2	10^{-2}	180	Traces	$4 \cdot 10^{-3}$ – $2 \cdot 10^{-2}$	—	3,0*
$\text{C}_6\text{H}_5\text{Cl}$	$3,3 \cdot 10^{-2}$	180	0,0224	$4 \cdot 10^{-3}$ – $1 \cdot 10^{-2}$	11,0	7,0
$\text{C}_6\text{H}_5\text{Br}$	$3,3 \cdot 10^{-2}$	180	0,0079	$7 \cdot 10^{-3}$ – $1 \cdot 10^{-2}$	4,0	4,0**

Note. The degree of oxidation by halide was calculated from the average concentration of chlorine in the silver.

* Calculation of the degree of oxidation of the additive was carried out only for the Cl ion; the F ion was not included in the calculation.

** The calculation was carried out for the Br ion.

Table 2

Distribution of the modifying additive over the catalyst layer

Catalyst temp., °C	Yield of C ₂ H ₄ O, %, based on passed C ₂ H ₄	Yield of C ₂ H ₄ O, %, based on converted C ₂ H ₄	Conc. of Cl, wt. %, layer I, 20 mm	Conc. of Cl, wt. %, layer II, 30 mm	Conc. of Cl, wt. %, layer III, 30 mm
220	33,0	45,5	$8,6 \cdot 10^{-3}$	$6,5 \cdot 10^{-3}$	$4,1 \cdot 10^{-3}$
255	35,0	70,5	$8,6 \cdot 10^{-3}$	$6,5 \cdot 10^{-3}$	$4,1 \cdot 10^{-3}$
265	37,0	68,5	$8,6 \cdot 10^{-3}$	$6,5 \cdot 10^{-3}$	$4,1 \cdot 10^{-3}$

of ethylene to ethylene oxide, a nonuniform distribution of the halide over the layer is observed (see Table 2). The results of analysis of the layers of the silver catalyst, presented in Table 2, show that in the head layer the concentration of chlorine ion is considerably greater than in the subsequent layers.

Table 3

Decomposition of organic halogen additives on silver in the absence of oxygen at 250°

Type of additive	Conc. of additive in nitrogen, vol. %	Decomp. of additive, calculated from Cl data, %	Cl content in silver, %
Without additive	—	—	0,0012
CCl ₄	$9,7 \cdot 10^{-2}$	27,0	0,3
CH ₃ \CHCl/CH ₃	$5,4 \cdot 10^{-1}$	15,0	0,18
C ₂ HCl ₅	$2,8 \cdot 10^{-2}$	42,0	0,14
ClCH ₂ -CH ₂ Cl	$1,4 \cdot 10^{-1}$	16,5	0,12
FCl ₂ C-CFCl ₂ *	$1 \cdot 10^{-1}$	32,0	0,366
C ₆ H ₅ Cl*	$3,4 \cdot 10^{-2}$	8,0	0,0055

* Calculation only for Cl .

In the absence of oxygen in the reaction mixture, the additives decompose on silver (see Table 3). At 250°, the greatest depth of decomposition is observed for pentachloroethane (~42%) and the smallest for chlorobenzene (~8%).

Figure 1 shows the oxidation curves of 1,2-dichloroethane and chlorobenzene. When the initial concentration of the organic additives is changed by almost a factor of 2, the degree of oxidation does not change, and the rate of this process is practically independent of the initial concentration of the additive.

It should be noted that during this process a sharp decrease in the oxidation rate is observed. Thus, 30 min after the start of the experiment,

Fig. 1. Change in the degree of oxidation during the experiment. Volumetric rate 4000 h^{-1} , $t = 250^\circ$. 1 –initial concentration of chlorobenzene $1.7 \cdot 10^{-2}$ vol.%; 2 –the same, $9.2 \cdot 10^{-3}$ vol.%; 3 –initial concentration of dichloroethane $3.8 \cdot 10^{-2}$ vol.%; 4 –the same, $5.9 \cdot 10^{-2}$ vol.%.

Fig. 2. Degree of reduction of AgCl on the surface of silver by a 3% ethylene-air mixture at $t = 200^\circ$. Chlorine concentration in silver: 1 –0.005, 2 –0.01, 3 –0.02 wt.%.

the rate of oxidation of 1,2-dichloroethane is three times greater than after 2 h. The decrease in the rate of oxidation of organohalogen substances on silver is probably explained by the formation of a film of silver chloride on the surface of the pellet. Experiments carried out by us on pure AgCl under the same conditions showed that organohalogen substances are not oxidized. The activation energies of oxidation on Ag, determined from the initial rates, are: for pentachloroethane 3 kcal/mol, for chlorobenzene 4 kcal/mol, and for dichloroethane 6 kcal/mol.

The rate of reduction of the chloride ion introduced into the silver during its preparation is considerably lower than the oxidation rates. Determination of the rate of reduction of silver chloride formed during oxidation of organic additives by a 3% ethylene-air mixture showed that in this case the process rates are considerably higher than in the reduction of chloride ion introduced into silver from solutions of inorganic salts during its preparation, and are close in magnitude to the oxidation rates of the organic additives. Figure 2 shows the kinetic curves for reduction by a 3% ethylene-air mixture of three silver samples containing AgCl only on the surface (the chloride-ion concentration, calculated per volume, is 0.005, 0.01, and 0.02 wt.%). The rate of reduction of AgCl from the surface of silver is proportional to the chloride-ion concentration. Thus, at a content of 0.005% Cl, the initial rate in arbitrary units is 17.5, while for samples with 0.02% Cl the rate decreased by a factor of 3. Figure 3 shows the dependences of the logarithms of the initial oxidation rates of organohalogen additives (C_2HCl_5 , $\text{C}_6\text{H}_5\text{Cl}$, and $\text{C}_2\text{H}_4\text{Cl}_2$) and of AgCl reduction (chlorine concentration ~0.01 wt.%) on reciprocal temperature.

The difference in the activation energies of oxidation of organic halide additives ($E = 4\text{--}6$ kcal/mole) and reduction of AgCl ($E = 15$ kcal/mole) shows that in

the temperature range 200–230° (at which the catalytic process proceeds) the oxidation rate for chlorobenzene is greater than the reduction rate, and in this case accumulation of chloride ion on the surface and poisoning of the catalyst are possible. Raising the temperature to 240° leads to an increase in the reduction rate, and in order to maintain the necessary concentration of chloride ion on the surface it is necessary to increase the amount of additive introduced. For dichloroethane, which is oxidized at a considerably lower rate than C_6H_5Cl in the temperature range 200–250°, the reduction rate is greater than the oxidation rate, and therefore modification of silver is regulated only by supplying a definite concentration of $C_2H_4Cl_2$. The rates of the oxidation and reduction processes may vary for different silver samples, owing to the different content of chloride ion on their surfaces. For each volatile organic additive, the ratio of the rates of its oxidation and reduction of AgCl will determine the modification regime (concentration, temperature) that provides the greatest selectivity of the process of ethylene oxidation to ethylene oxide.

Fig. 3. Dependence of the logarithm of the initial rates on reciprocal temperature.

1 –oxidation of C_2HCl_5 , 2 –oxidation of C_6H_5Cl , 3 –oxidation of $C_2H_4Cl_2$, 4 –reduction of AgCl on the surface of silver (0.01 wt.% Cl relative to the weight of silver) in a 3% ethylene-air mixture.

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