ISOTOPIC EXCHANGE OF OXYGEN ON OXIDATION CATALYSTS

1960

SovietRxiv

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Fig. 2. Kinetic curves of homoatomic isotopic oxygen exchange on porous silver with AgCl additives: 1—0.0015%, 2—0.002%, 3—0.004%, 4—0.015%

Figure 2: Fig. 2. Kinetic curves of homoatomic isotopic oxygen exchange on porous silver with AgCl additives: 1—0.0015%, 2—0.002%, 3—0.004%, 4—0.015%

Abstract

Full Text

PHYSICAL CHEMISTRY

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ISOTOPIC EXCHANGE OF OXYGEN ON OXIDATION CATALYSTS

(Presented by Academician V. I. Spitsyn, July 9, 1959)

A number of studies on isotopic oxygen exchange on metal oxides—semiconductors [1]—have been published in the literature, while there are almost no data on oxygen exchange on metallic oxidation catalysts—platinum and silver [2]. The influence of additives on the rate of oxygen isotopic exchange has not been investigated; there are only data by G. K. Boreskov and co-workers on the acceleration of exchange on vanadium pentoxide with an admixture of potassium sulfate [1]. The activity and selectivity of oxidation catalysts change upon the introduction of additives. The mobility of oxygen adsorbed on the surface of contacts plays an essential role in the course of the catalytic oxidation of various substances [3]. Isotopic oxygen exchange is a method for establishing such mobility. Therefore, it was of great interest to investigate the influence of additives introduced into a catalyst on the rate of isotopic oxygen exchange, which is the aim of the present study.

Fig. 1. Kinetic curves of isotopic oxygen exchange at 232° on porous silver with AgCl additives:
1—0.0015%, 2—0.002%, 3—0.004%, 4—0.015%.

Fig. 2. Kinetic curves of homoatomic isotopic oxygen exchange on porous silver with AgCl additives:
1—0.0015%, 2—0.002%, 3—0.004%, 4—0.015%.

As typical oxidation contacts, metallic silver was selected—the catalyst for the oxidation of ethylene to ethylene oxide with an addition of halides in the form of AgCl, AgI—and copper oxide—the catalyst for the oxidation of propylene to acrolein with an addition of the oxides of lithium, chromium, bismuth, and cupric sulfate. The halides were introduced into the silver by applying AgCl and AgI solutions to silver powder with vigorous stirring, ensuring their uniform distribution over the surface, monitored radiometrically by the isotopes Cl^{36} and I^{131}. Into the copper oxide, oxides of various metals were introduced by mixing or coprecipitating nitrate and carbonate salts, followed by calcination at 700°. To introduce the SO_4^{2-} ion, solutions of ammonium sulfate and copper nitrate were mixed, followed by drying and calcination at 700°. The experiments were carried out in a static system at low pressures (up to 1 mm Hg). The content of the oxygen isotope O^{18} was determined mass-spectrometrically by masses

36, 34, and 32. The initial heavy oxygen contained 15-20 at.% O^{18}. From the change in the concentrations in the gas of O_2^{18} (mass 36) and $O^{16}O^{18}$ (mass 34), the rate of the homolytic oxygen isotope-exchange reaction

$$O_2^{18} + O_2^{16} \rightleftarrows 2O^{16}O^{18}$$

was monitored. The rate of isotope exchange was calculated from the equation

$$(1 - F) = -Kt,$$

where

$$F = \frac{C_0' - C}{C_0 - C_\infty}$$

is the relative exchange, K is the exchange rate constant, C_∞ is the concentration of O^{18} at equilibrium, C_0 is the initial concentration of O^{18}, C is the concentration of O^{18} at the given time t, and t is time.

Table 1

Additive	Additive concentration, wt.%	K_{exch}, min/m^2	K_{hom}, min/m^2
Chlorine in the form of silver chloride	0.0015	$7.8 \cdot 10^{-4}$	$3 \cdot 10^{-4}$
Chlorine in the form of silver chloride	0.0020	$7.5 \cdot 10^{-4}$	$2.8 \cdot 10^{-4}$

Additive	Additive concentration, wt.%	K_{exch}, min/m^2	K_{hom}, min/m^2
Chlorine in the form of silver chloride	0.0040	$6.6 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$
Chlorine in the form of silver chloride	0.015	$5.5 \cdot 10^{-4}$	$1.1 \cdot 10^{-4}$

Table 2

Additive	Concentration, at.%	Surface area, m^2/g	Initial rate of isotope exchange per 1 m^2
–	0	0.25	0.066
Cr_2O_3	2	0.40	0.063
Bi_2O_3	2	0.40	0.025
Li_2O	2	0.2	0.172
$CuSO_4$	2	1.0	0.01

Figure 1 shows the kinetic curves of oxygen isotope exchange on silver containing different concentrations of the chlorine ion. In the time interval of 150 min, the reaction is monomolecular. Figure 2 shows the kinetic curves of homomolecular isotope exchange on the same silver samples with the additive (α—the mass ratio equal to 36/34).

Table 1 gives the values of the oxygen isotope-exchange rate constants at 232° on silver with an added chlorine ion.

The isotope-exchange rate constant changes monotonically with increasing concentration. When the chlorine content in silver is increased tenfold, the exchange rate constant decreases by a factor of 1.5. The rate constant of homolytic exchange, i.e., the reaction associated with dissociation of the oxygen molecule into atoms, decreases by a factor of 3 when the chlorine concentration in silver is increased tenfold.

The addition of iodine modifies the silver catalyst; at some iodine concentration an increase in the yield of ethylene oxide is observed ([3]). A study of isotope exchange on this catalyst sample showed that the addition of iodine sharply increases the rate constant of homolytic oxygen exchange and almost does not change the rate of molecular isotope exchange. The addition of halides to silver changes the ratio of molecular and atomic oxygen on the surface and its mobility. The effect of these additives on the exchange rate is probably connected with

Fig. 3

Figure 3: Fig. 3

Fig. 4. Kinetic curves of homolytic isotopic exchange of oxygen at 412° on copper oxide with additions: 1—CuO; 2—CuO + 2% Bi_2O_3; 3—CuO + 2% Cr_2O_3; 4—CuO + 2% Li_2O

Figure 4: Fig. 4. Kinetic curves of homolytic isotopic exchange of oxygen at 412° on copper oxide with additions: 1—CuO; 2—CuO + 2% Bi_2O_3; 3—CuO + 2% Cr_2O_3; 4—CuO + 2% Li_2O

a change in the charge of the silver surface and, consequently, in the heat and activation energy of oxygen adsorption and desorption.

Fig. 3. Kinetic curves of oxygen isotope exchange at 412° on copper oxide with additives: *I*—CuO; *II*—CuO + 2% Bi_2O_3; *III*—CuO + 2% Cr_2O_3; *IV*—CuO + 2% Li_2O.

It was of interest to determine the effect of additives on the rate of oxygen isotope exchange not only for silver catalysts but also for semi-

conductors—metal oxides. Figure 3 gives kinetic curves of isotopic exchange of copper oxide with additions of Cr_2O_3, Bi_2O_3, Li_2O. The rate of the isotopic-exchange reaction for these oxides does not obey a monomolecular law, while the experimental data for pure copper oxide and CuO with an addition of Bi_2O_3 and Cr_2O_3 are expressed by the Roginskii—Zel' dovich equation $dF/dt = al^{\alpha F}$ (see Figs. 3 and 4). The deviation of the isotopic-exchange rate from first order is probably caused by the inhomogeneity of the CuO surface. The same law for the course of the reaction of oxygen isotopic exchange was observed by Kasatkina and Boreskov on MnO_2 (^{1}).

For CuO preparations containing Li_2O, the rate of isotopic exchange follows a bilogarithmic law, which also indicates inhomogeneity of the CuO surface and should correspond to an exponential distribution of sites with respect to the activation energies of exchange.

In Table 2 are shown the initial rates of oxygen isotopic exchange at 412°, calculated per 1 m^2 of the surface of copper oxide with additions.

Chromium oxide introduced into CuO changes the rate of oxygen isotopic exchange hardly at all. Addition of Bi_2O_3 lowers the exchange rate by a factor of 3, while introduction of Li_2O increases the rate by a factor of 3. The presence of the ion SO_4^{2-} on the surface of copper oxide sharply inhibits the rate of oxygen isotopic exchange. It is interesting to note that the rate of isotopic exchange is determined by the charge of the surface of semiconducting oxidation catalysts (^{4}).

Fig. 4. Kinetic curves of homolytic isotopic exchange of oxygen at 412° on

copper oxide with additions: 1—CuO; 2—CuO + 2% Bi_2O_3; 3—CuO + 2% Cr_2O_3; 4—CuO + 2% Li_2O

Thus, by introducing additions into oxidation catalysts, both metallic (silver) and oxide–semiconducting (CuO), it is possible to regulate the rate of oxygen isotopic exchange and, consequently, its mobility on the surface of catalysts.

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Received
6 VII 1959

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Note: Figure translations are in progress. See original paper for figures.