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Abstract

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CATALYTIC PROPERTIES OF COBALT-MANGANESE SPINELS

Compounds with a spinel structure are used rather widely in industrial catalysis as catalysts for oxidation, hydrogenation, and carbon monoxide conversion (^{1}). The structure and the magnetic and electrical properties of complex spinels used in technology under the name "ferrites" have been studied comprehensively. At the same time, the literature contains only a limited number of works devoted to elucidating the specific features of the catalytic action of spinels and to establishing the relationship between the catalytic activity of these compounds and the physical characteristics of the solid ($^{2-5}$).

In the present work we studied the influence of structure on the catalytic properties of the normal—$CoMn_2O_4$—and inverse—$MnCo_2O_4$—cobalt-manganese spinels. The catalytic activity was evaluated for the reaction of deep oxidation of propylene.

The preparation of the normal and inverse spinels has been described previously (^{6}). The catalytic activity was determined from the rate of oxidation of propylene by oxygen taken in the stoichiometric ratio $C_3H_6 : O_2 = 2 : 9$. The reaction products were carbon dioxide and water. The values of the specific surface areas of the catalysts, determined by the BET method from equilibrium isotherms of low-temperature krypton sorption, were: 0.70 m^2/g ($CoMn_2O_4$) and 0.25 m^2/g ($MnCo_2O_4$). The reaction was carried out under static conditions at a constant initial pressure of the mixture (0.450 mm Hg) in the temperature range 200–350°C. The catalyst samples were trained in vacuum, 10^{-6} mm Hg, at 550° for 4 h. The water formed was continuously frozen out during the reaction. Repeated experiments on the same catalyst charge showed good reproducibility of the results.

If the oxidation reaction of propylene is carried out with continuous absorption of the CO_2 formed during the reaction and freezing out of water, then its kinetics follows a monomolecular law: in the coordinates $\lg P - \tau$ a strict linearity is observed, whereas the quadratic law is distorted (Fig. 1). The specific rate constant $K^{\mathrm{I}}_{\mathrm{sp}}$, calculated from the equation for a first-order reaction, remains constant (Fig. 2).

Figures 3 and 4 present kinetic curves for the oxidation of the mixture ($2C_3H_6 + 9O_2$) at different temperatures when the reaction is conducted without removal of carbon dioxide from the reaction space. The overall rate of the oxidation process under these conditions is described approximately by the equation for a second-order reaction, from which the values of the rate constants referred to unit surface area (1 m^2) of the catalyst (K^{II}_{sp}) were calculated. Experiments on oxidation of the mixture at different initial pressures showed that K^{II}_{sp}, calculated from the equation for a second-order reaction, depends on the initial pressure (Fig. 2). Earlier, one of the authors ([7]) showed that an increase in the observed reaction order as compared with the true one may be due to self-inhibition of the process as a result of blocking of the active centers of the catalyst by reaction products. In the present case such an effect may be exerted by CO_2 molecules, which probably form on the catalyst surface a complex of the type CO_3^- ([14]).

The specific nature of the reaction conditions (the possibility of reduction of the catalyst surface by propylene when its content in the mixture is high, and the decrease in measurement accuracy when the oxygen content is high) did not make it possible to vary widely the composition of the initial mixture.

Table 1

$P^0_{C_3H_6}$: $P^0_{O_2}$	$P^0_{C_3H_6}$ at $P^0_{O_2}$ = const = 0.320	$K^I_{u\text{–}d}$ at $P^0_{O_2}$ = const = 0.320	$P^2_{O_2}$ at $P^0_{C_3H_6}$ = const = 0.048	$K^I_{u\text{–}d}$ at $P^0_{C_3H_6}$ = const = 0.048
1 : 9	0.036	0.105	0.433	0.105
1 : 4.5	0.072	0.105	0.217	0.090
1 : 2	0.160	0.105	0.096	0.030

Note: Pressures are given in mm Hg.

Table 1 presents the results of experiments on the oxidation of propylene over $MnCo_2O_4$ at 250°.

From Table 1 it is seen that changing the propylene concentration by a factor of 4.5 does not affect the rate constant, whereas increasing the oxygen content from 0.096 to 0.433 mm Hg leads to an increase in the rate constant; i.e., the reaction rate does not depend on the propylene concentration and is determined by the oxygen concentration according to the equation:

$$W = K^I_{u\text{–}d}[P_{O_2}]^1[P_{C_3H_6}]^0.$$

Fig. 1. Kinetic isotherm of oxidation of the mixture $2C_3H_6 + 9O_2$ over $MnCo_2O_4$ at $t = 250°$ with continuous absorption of CO_2 during the reaction. $P^0_{\text{mixture}} = 0.522$ mm.

Earlier (6) it was shown that oxygen is chemisorbed chemically irreversibly on both spinels, and the kinetics of chemisorption follows the laws:

$$\theta = A\tau^{1/n} \text{ —for } \mathrm{MnCo_2O_4} \quad \text{and} \quad \theta = a + b \lg \tau \text{ for } \mathrm{CoMn_2O_4},$$

where θ is the surface coverage and τ is time. According to additional measurements of oxygen chemisorption on both spinels in the temperature interval 200–350°, the following values of the activation energies of chemisorption were found: 18 kcal/mole for $CoMn_2O_4$ and 14 kcal/mole for $MnCo_2O_4$ (at coverage $\theta = 0.03$ cm^3/m^2).

Propylene on these catalysts, as on a number of other oxides, is adsorbed reversibly, "quasi-equilibrially," with small values of coverage and activation energies. Preliminary sorption of oxygen on the spinels (at temperatures below 200°) does not affect the rate of propylene sorption or the final surface coverages. Special experiments showed the absence of CO_2 chemisorption by the normal and inverse spinels in the temperature interval 100–350°.

It has been shown by the work of other authors (2, 8) that the reaction of hydrocarbon oxidation on spinel catalysts may have a bulk pro-

position. To clarify the question of the possibility of a heterogeneous-homogeneous mechanism for the propylene oxidation reaction on $CoMn_2O_4$ and $MnCo_2O_4$, we applied the separate-calorimetry method of Koval' skii—Bogoyavlenskaya (9). The diameter of the reaction vessel was 50 mm; to measure the temperature difference, a nichrome-constantan differential thermocouple made of wires 0.05 mm in diameter was used. The sensitivity for measuring the temperature difference was $\Delta t = 0.05°$.

Fig. 2. Dependence of the rate constants K_{ud}^{II} and K_{ud}^{I} for the oxidation reaction of the mixture $2C_3H_6 + 9O_2$ on the initial pressure of the mixture.

For calibration of the instrument, the following were used: a purely heterogeneous reaction of oxidation by oxygen of fine copper powder treated with propylene at 450° for 4 h; the reaction of propylene oxidation on platinized asbestos, which has a homogeneous component (10); and homogeneous oxidation of acetaldehyde at 200° (11). It was established that the oxidation reaction of a stoichiometric mixture of propylene with oxygen on both spinels at a temperature of 300° and initial pressures of 0.5 and 40.0 mm Hg proceeds by a purely heterogeneous mechanism.

Table 2

Reaction temperature or chemisorption of O_2, °C	$CoMn_2O_4$ K^I_{ud}	$CoMn_2O_4$ θ_{O_2}, cm^3/m^2	$MnCo_2O_4$ K^I_{ud}	$MnCo_2O_4$ θ_{O_2}, cm^3/m^2	$K^I_{ud, dir.}/t_{O_2, dir.}$	$K^I_{ud, rev.}/t_{O_2, rev.}$	Activation energy of the reaction, kcal/mol $CoMn_2O_4$	Activation energy of the reaction, kcal/mol $MnCo_2O_4$
200	0.019	0.026	0.0124	0.017*	1.52	1.53		
250	0.150	0.052	0.075	0.026	2.00	2.00	19.4	17.0
300	0.690	0.083	0.300	0.039	2.30	2.13		
350	2.74	0.138	0.975	0.054	2.70	2.56		

* Extrapolated value.

The occurrence of the propylene oxidation reaction only on the catalyst surface and the absence of a noticeable amount of products of incomplete oxidation are apparently due to the presence, on the catalyst surface, of fixed chains (12).

Table 2 gives the values of the specific rate constants (K^I_{ud}) for the oxidation reaction of the mixture $2C_3H_6 + 9O_2$ and the specific coverages of the catalyst surface with oxygen, taken from the oxygen chemisorption isotherms for one value of the time (30 min) at temperatures corresponding to the reaction temperatures.

Fig. 3. Kinetic isotherms of oxidation of the mixture $2C_3H_6 + 9O_2$ on $CoMn_2O_4$.
$1 - t = 350°$, $S = 0.14$ m^2; $2 - t = 300°$, $S = 0.25$ m^2; $3 - t = 250°$, $S = 0.50$ m^2; $4 - t = 200°$, $S = 0.50$ m^2.

From the data of Table 2 it is evident that there is a direct relationship between the rate constant of the propylene oxidation reaction on spinels and the rate of oxygen chemisorption.

It was noted above that the chemisorption of oxygen on the normal and inverse spinels is described by different kinetic laws, characteristic of a heterogeneous surface with a different character of the distribution of active sites by activation energies (exponential for $MnCo_2O_4$ and linear for $CoMn_2O_4$). At the same time, the different statistics of the heterogeneity of the surfaces of the normal and inverse spinels is not manifested in the kinetics of propylene oxidation on these catalysts.

The oxidation reaction probably proceeds in both cases on a limited number of active sites, which may be regarded as homogeneous. Confirmation of this may be provided by the identity of the kinetic law, the closeness of the activation-energy values of the oxidation reaction, and the proportionality between the

Fig. 4. Kinetic isotherms of oxidation of a mixture $2C_3H_6 + 9O_2$ on $MnCo_2O_4$. $S = 0.5$ m^2. 1–$t = 350°$, 2–$t = 300°$, 3–$t = 250°$, 4–$t = 200°$.

Figure 1: Fig. 4. Kinetic isotherms of oxidation of a mixture $2C_3H_6 + 9O_2$ on $MnCo_2O_4$. $S = 0.5$ m^2. 1–$t = 350°$, 2–$t = 300°$, 3–$t = 250°$, 4–$t = 200°$.

values of the reaction-rate constants and the rate of oxygen chemisorption.

Fig. 4. Kinetic isotherms of oxidation of a mixture $2C_3H_6 + 9O_2$ on $MnCo_2O_4$. $S = 0.5$ m^2. 1–$t = 350°$, 2–$t = 300°$, 3–$t = 250°$, 4–$t = 200°$.

The kinetic laws for the normal and inverse spinels are the same, but their catalytic activity is different. Consequently, the lattice structure does not affect the character of the limiting stage and the activation energy, but changes the preexponential factor, which is probably connected with the number of active centers.

From consideration of the structural formulas of the normal –$Co^{2+}[Mn^{3+}Mn^{3+}]O_4{}^{2-}$ –and inverse –$Co^{3+}[Mn^{2+}Co^{3+}]O_4{}^{2-}$ –spinels, it is seen that manganese cations located on the surface, to a greater extent than cobalt cations, can become electron donors for chemisorbed oxygen atoms. Owing to the considerable dispersity of the catalyst powders, one may probably, without great error, assume proportionality between the number of manganese cations in the bulk and on the surface of the grains.

The higher chemisorption capacity and catalytic activity of the normal spinel is possibly connected with the higher concentration in it of manganese cations, which exert the main influence on the formation of active surface centers.

Since the rate of propylene oxidation is proportional to the rate of oxygen chemisorption, one may hope, by introducing into the spinel lattice modifying additives that regulate oxygen chemisorption, to change the catalytic properties of the normal and inverse spinels.

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