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STUDY OF OXYGEN DIFFUSION IN MgO IN THE PROCESS OF SURFACE REDUCTION

O.Yu. OVSITSER, K.S. GULJAEV and V.D. SOKOLOVSKII

Institute of Catalysis, Siberian Branch of the USSR Academy of Sciences, Prosp. Akad. Lavrentieva 5, Novosibirsk 630090, USSR

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We have defined the coefficient of oxygen diffusion in MgO ($S_{spec.} = 55$ m^2/g) at 750° and 780°C, the activation energy for diffusion by measuring oxygen diffusion rates at different degrees of surface reduction. The method used for defining the oxygen diffusion rate is based on the increase in the rate of oxide catalyst reduction (CO or H_2) after keeping the sample in vacuum.

Keywords: Oxygen diffusion, oxide catalysts, reduced surface

1. Introduction

As has been shown in a great number of publication [1,2], the majority of the reactions of selective hydrocarbon oxidation proceeds with the participation of the oxygen of the catalyst. One of the main factors, defining the activity and selectivity of an oxide catalyst, according to references [3,4], is the diffusion of the catalyst oxygen. The state of the oxygen on the catalyst surface depends greatly on the rate of oxygen diffusion.

At the same time only a few investigations dedicated to the study of oxygen diffusion in oxide catalysts have been made, and most of these were not carried out under real catalytic conditions. These studies were mainly oxygen self-diffusion by isotope oxygen exchange. This self-diffusion deals with the redistribution of oxygen isotopes in oxide that is in equilibrium with gas-phase oxygen [5], though, for the processes of selective catalytic oxidation, the surface of the oxide catalyst is, as a rule, significantly reduced [1]. The concentration of oxygen vacancies in surface layers may be substantially higher than in the bulk, and the rate of diffusion may change by orders of magnitude on varying the vacancy concentration.

Therefore, the study of oxygen diffusion at different degrees of surface reduction and at temperatures approaching the optimal temperatures of catalytic reaction, is of great interest. The aim of this work is to investigate the method for defining the rate of oxygen diffusion over partially reduced samples and to study oxygen diffusion in MgO, which is a major component in a number of catalysts for the oxidative dimerization of methane.

2. Experimental

MgO was obtained by the calcination of $MgCO_3$ (analytic grade) at 800 °C for 4 hours. Then the samples were tabletted, ground and the fraction of 0.25–1 mm was taken. The method for defining the rate of oxygen diffusion was based on the increase of the rate of oxide catalyst reduction after the sample was kept in vacuum. The study was carried out in the vacuum static installation with the mass-spectrometer (IPDO-2A), connected on line with the reaction volume.

CO and H_2 were used for the reduction. CO was obtained by the decomposition of formic acid and H_2 was purified over the nickel-chromium catalyst and NaA zeolite. The purity of the gases was controlled by mass-spectrometer.

1 g of MgO ($S_{\text{spec.}} = 55$ m^2/g) was calcined in vacuum at 800 °C for one hour and then was kept in oxygen (30 Torr) for 2 hours. The temperature was decreased to the temperature of the experiment, and the sample was evacuated at 10^{-4} Torr for the definite time. Then 1–2 Torr of the reductant (CO or H_2) was added and the reaction was observed by continuous scanning in the mass-spectrometer. The mixture was rapidly pumped out and then, if necessary, the experiment was repeated to obtain the required degree of the surface reduction of the catalyst.

It was found that, while studying the MgO reduction by CO at 750 °C, reaction was inhibited by the adsorption of CO_2. Thus the reduction rate was defined from the initial stage of CO addition or under the freezing out of the products. In both cases the balance in CO and CO_2 quantity was observed. It indicates the absence of irreversible interaction of the reactant and product with the catalyst surface.

The dependence of the reduction rate on the quantity of oxygen taken off was obtained by measuring reduction rate at the different degrees of the surface reduction (fig. 1).

The quantity of the oxygen, taken off from the catalyst (N_O) was defined by the quantity of the reductant used or the product accumulated. The degree of surface reduction (θ) was calculated from equation:

$$\theta = \frac{N_O \times 100\%}{S \times N_m},$$

where N_m–oxygen quantity in 1 m^2 of the surface monolayer It was assumed that $N_m = 1.27 \times 10^{19}$ at/m^2.

The rate of the oxygen diffusion was defined as follows. The reduction rate was measured for the sample with defined degree of the surface reduction, after that the sample was kept in vacuum and the reduction rate was measured once more.

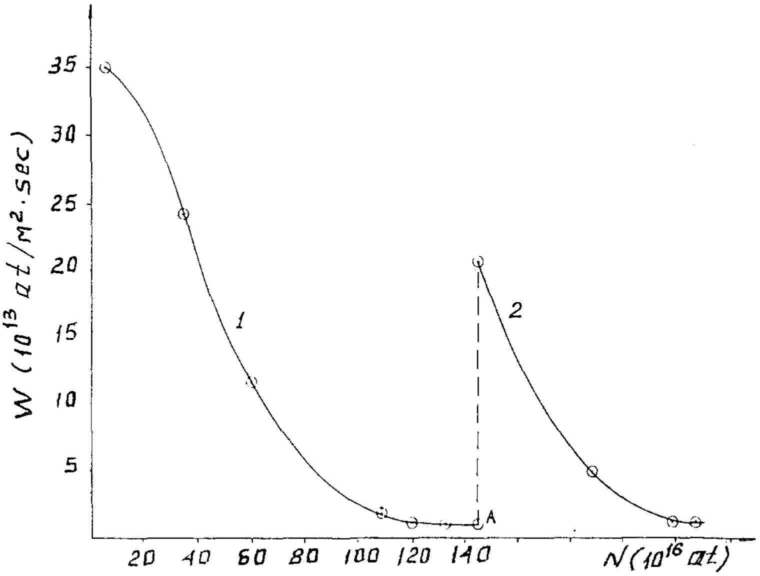

Fig. 1. The reduction rate of MgO at 750 °C as a function of the quantity of the oxygen taken off (1). 2–keeping for 1 hour at point A.

Observed was the increase of the reduction rate in comparison with its value before keeping in vacuum (fig. 1). From the reduction calibration curve the quantity of the oxygen diffused was obtained. The rate of the oxygen diffusion was calculated according to the formula:

$$W_{д}(\theta^*) = \frac{\Delta^N}{\Delta^\tau},$$

$$\Delta^N = (\theta_1 - \theta_2) \times N,$$

$$\theta^* = \frac{\theta_1 + \theta_2}{2},$$

where θ_1–degree of the surface reduction before keeping in vacuum, θ_2–degree of the surface reduction after keeping in vacuum, Δ^τ–time of keeping, N_m–quantity of oxygen atoms in 1 m^2 of the monolayer.

3. Results and discussion

Fig. 2 shows the oxygen diffusion rate and the surface reduction rate as a function of the degree of the surface reduction at 750 °C. After taking off ~ 0.18% of monolayer we observed the approximately constant rate of the surface reduction, which was 1×10^{13} at/m^2 × s and which was close to the oxygen diffusion rate at the same degree of the surface reduction. Therefore, one can admit, that the degree of the surface reduction was not changed during the further proceeding of the reduction.

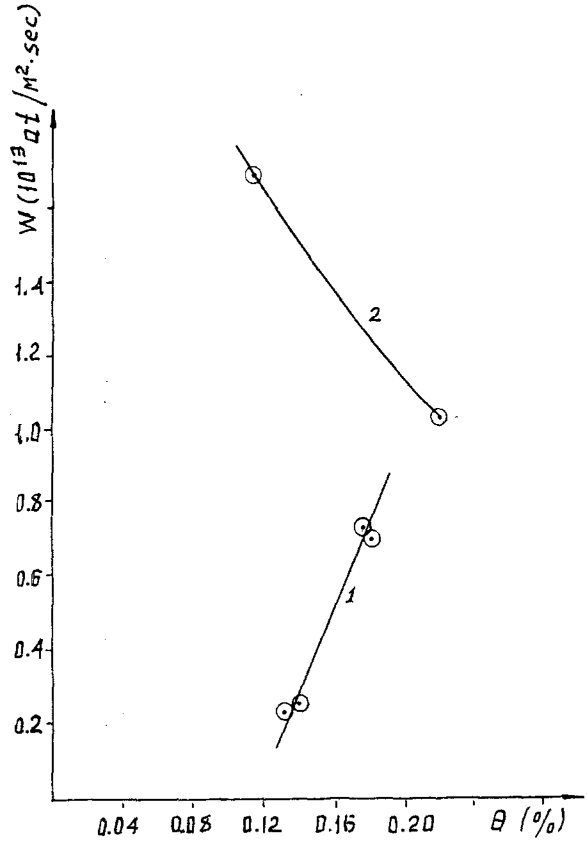

Fig. 2. The oxygen diffusion rate (1) and the rate of MgO reduction by CO (2) at 750 °C as a function of the degree of surface reduction.

The linear extrapolation of the plot of the diffusion rate versus the degree of reduction according to Fick's law in fig. 2 did not pass through the origin. This fact can be explained by the presence of a few of the residual oxygens on the catalyst surface (~ 0.11% of monolayer, when the time of evacuation before the experiment is 5 min.). The removal of this oxygen did not lead to the formation of oxygen vacancies. At the increase of the evacuation time before the experiments the concentration of the residual oxygen should decrease. For the verification of this assumption we increased the time of evacuation up to the hour. As one can see from fig. 3 the increase of the evacuation time leads to shifts of the curve to the origin, but the line slope remains unchanged. From this line slope the effective coefficient of diffusion was calculated from the Fick's law:

$$D_{\text{ef.}} = \frac{\Delta^{W}_{\text{д}}}{\Delta^{\theta} \times N_{\text{m}}},$$

$$D_{\text{ef.}} = 1.1 \times 10^{-3}\ \text{s}^{-1}\ (\text{at } 750\,^{\circ}\text{C}).$$

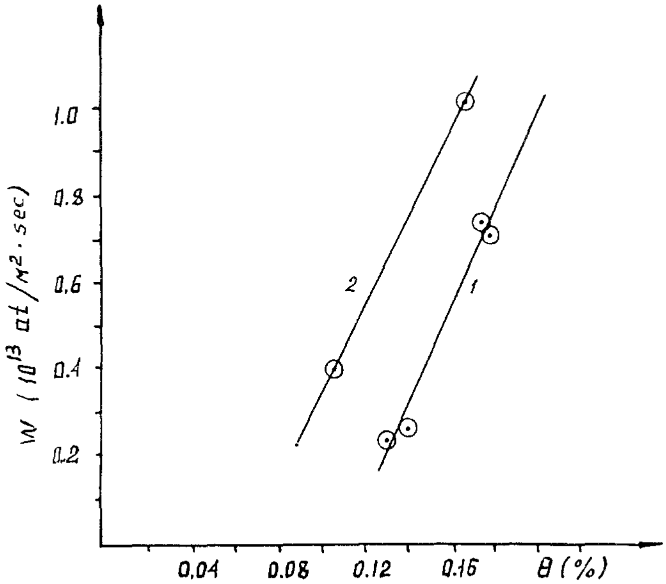

Fig. 3. The oxygen diffusion rate in MgO at 750 °C as a function of the degree of the surface reduction at different evacuation times before the experiments. 1–the evacuation time is 1 hour. 2–the evacuation time is 5 min.

For the verification of this method for the definition of the diffusion coefficient additional experiments were carried out with hydrogen as the reductant. The stationary rate of the reduction by hydrogen was equal 0.93×10^{13} at/m^2 × s and was close to the stationary rate of the reduction by CO. The diffusion coefficient defined at the reduction by hydrogen was 0.9×10^{-3} s^{-1}, which was in a good agreement with the value, obtained at the process of reduction by CO.

The diffusion coefficient at the reduction process by CO at 780 °C was 2.03×10^{-3} s^{-1}. The activation energy for diffusion was 170 kJ/mole. In the literature a wide range of values has been observed for the activation energies for diffusion in MgO. For extrinsic lattice oxygen diffusion at lower temperatures ($T < 1300$ °C) the values 120–340 kJ/mole have been given in reviews [6,7]. The same range of values for the activation energy corresponded to grain boundary diffusion and for surface diffusion in MgO [6,7]. In current experiments it is not possible to distinguish between these types of diffusion. We can correspond our results to the surface diffusion, considering diffusion through the surface layer rather than diffusion along the surface [8].

Thus, the suggested method allows us to define the effective coefficients of the oxygen diffusion with considerable reliability. These methods will be used for the study of the oxygen diffusion in catalysts for selective oxidation.

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