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# Oxygen diffusion at surface reduction in catalysts for selective oxidation

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The coefficient of oxygen diffusion and the activation energy for diffusion have been measured for the series of oxide catalysts of selective oxidation of organic compounds (Sm–Mg–O, Sm–O; V–P–O, Sn–Sb–O, Sn–Bi–O, Fe–Sb–O, Bi–Sb–O). The rates of oxygen diffusion under catalytic conditions have been compared with the reaction rates. For all studied systems (except Sm–O and Sm–Mg–O) at optimal operative temperatures the maximum rate of oxygen diffusion is sufficient to carry out the reactions of selective oxidation through rapid oxygen diffusion in the surface layers.

**Keywords:** Oxygen diffusion; oxide catalysts; reduced surface

## 1. Introduction

Recently, we have measured the effective coefficient of oxygen diffusion at the surface reduction for the series of oxide catalysts for selective oxidation of organic compounds (V–Mo–O, Bi–Mo–O, Ga–Sb–O and Mg–O) [1,2]. The effective coefficients of oxygen diffusion in these catalysts defined at optimal operative temperatures were found to be similar in magnitude. Based on these results and some general considerations [3] we proposed that the possibility of using oxide systems as catalysts for selective oxidation was determined by their ability to achieve sufficiently large oxygen diffusion coefficients at the reaction temperature [1].

In this work the validity of these statements is verified on the series of oxide catalysts, including the different types of oxide catalyst for selective conversion of organic compounds. We have determined the coefficient of oxygen diffusion in Sm–O and Sm–Mg–O catalysts for oxidative dimerization of methane and in Bi–Sn–O catalyst for oxidative dimerization of propene. Oxygen diffusion in the V–P–O catalyst for butane oxidation to maleic anhydride and in Sn–Sb–O catalyst for propene oxidation has also been studied. In addition, the Fe–Sb–O and Bi–Sn–O catalysts, which were effective for oxidative dehydrogenation of butane and for propene ammoxidation, were used for the measurements.

It was of great interest to compare the reaction rate with the rate of oxygen diffusion under catalytic conditions and to determine the activation energy for oxygen diffusion.

## 2. Experimental

$Sm_2O_3$ ($S_{spec.} = 4$ m$^2$/g) was obtained by the calcination of $Sm(NO_3)_3$ at 800°C for 4 h.

1%(at) $Sm_2O_3/MgO$ ($S_{spec.} = 9.2$ m$^2$/g) catalyst (Sm–Mg–O-1) was obtained by impregnation of MgO with the solution of $Sm(NO_3)_3$ followed by calcination at 800°C for 4 h.

5%(at) $Sm_2O_3 * MgO$ ($S_{spec.} = 14$ m$^2$/g) catalyst (Sm–Mg–O-2) was obtained by the evaporation of the solution of Sm and Mg nitrates followed by calcination at 800°C for 4 h.

The preparation of the V–P–O catalyst ($(VO)_2P_2O_7$), ($S_{spec.} = 7.5$ m$^2$/g) can be found in ref. [4].

The preparation and catalytic properties of the Sn–Sb–O (1 : 1) ($S_{spec.} = 61$ m$^2$/g) and Sn–Bi–O (1 : 1) ($S_{spec.} = 33$ m$^2$/g) are described in ref. [5].

The preparation of the Fe–Sb–O (1 : 2) ($S_{spec.} = 35$ m$^2$/g) and Bi–Sb–O (2 : 1) ($S_{spec.} = 10$ m$^2$/g) are given in refs. [6] and [7], respectively.

The method used for determining 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. The details of the experimental procedure and the treatment of results have been described previously [2]. In the present study this method was developed. The effective coefficient of oxygen diffusion was calculated from the oxygen diffusion rates at different degrees of surface reduction,

$$D^0_{ef} = \frac{\Delta W_{dif}}{\Delta \Theta N_m},$$

where $W_{dif}$ is the rate of oxygen diffusion at the degree of surface reduction $\Theta$, $N_m$ the oxygen quantity in 1 m$^2$ of the surface monolayer.

This value of $D^0_{ef}$ was used as a first approximation. In order to obtain more accurate value of $D_{ef}$ a computer program was written to account for the fact that even during reduction (not only during keeping in vacuum) the oxygen diffusion takes place and the degree of surface reduction (more precisely, the degree of the reduction of the sites of oxygen removal) actually was slightly less,

$$\Theta' = \Theta - N_d,$$

where $\Theta'$ is the corrected value of the degree of surface reduction, $N_d$ the quantity of the oxygen diffused during reduction. $N_d$, in a first approximation, was calculated from $D^0_{ef}$.

From the new value of the degree of surface reduction the corrected value $D'_{ef}$ was calculated. Then calculations were repeated, using $D'_{ef}$, and after some iterations the accurate value of $D_{ef}$ was obtained.

It should be noted, that such correction for the catalysts with low oxygen mobility and at low temperatures was not important, but in order to obtain a correct value of the activation energy for diffusion we should take this correction into account.

$H_2$ was used for the reduction of Sm–Mg–O and V–Mo–O systems, CO was used for reduction of the others.

The degree of surface reduction during measurements of $D_{ef}$ in Sm–Mg–O catalysts achieved 30% of monolayer, for other systems it did not exceed 7% of monolayer.

## 3. Results and discussion

Table 1 presents the results of measurements of the effective coefficient of oxygen diffusion for the investigated systems at the operative temperatures. It is clear from this table that the effective coefficients for oxygen diffusion for the wide series of oxide catalysts, including the catalysts for oxidative dimerization, ammoxidation, oxidation and oxidative dehydrogenation of saturated and unsaturated hydrocarbon, measured at the optimal operative temperatures are similar.

It was of interest to compare the reaction rate with the rate of oxygen diffusion under catalytic conditions for the systems studied. Let us make the estimation, proceeding from the redox mechanism, that was shown for the majority of studied systems [17–21], except high-temperature ones.

According to the literature [22,23], the catalyst reduction sites and the oxygen insertion sites are not the same, so for the effective regeneration of the reduction sites the rapid oxygen diffusion in oxide catalyst is needed [22]. Thus the rate of the oxygen diffusion under catalytic conditions should be equal or more than the rate of the reaction of selective conversion of organic compounds.

Let us estimate the oxygen diffusion rate under reaction condition. Assume that oxygen insertion sites are completely full (the fast process) $\Theta_{ox} \to 1$, and the sites of oxygen removal (into products) are empty ($\Theta_{red} \to 0$). Then the upper limit of the oxygen diffusion rate is

$$W^m_{dif} = D_{ef} N_m, \tag{1}$$

Table 1
Comparison of the effective coefficients of oxygen diffusion, the oxygen diffusion rates and the rates of selective oxidation for oxide catalysts

| Catalyst | Reaction | $T$ (°C) | $D_{ef} \times 10^3$ ($s^{-1}$) | $E_a$(dif) (kcal/mol) | $W^m_{dif}$ ($10^{11}$ atoms/ $cm^2$ s) | $W_{select.}$ ($10^{11}$ molecules/$cm^2$ s) | Ref. |
|---|---|---|---|---|---|---|---|
| Mg-O | $CH_4 \rightarrow C_2H_4 + C_2H_6$ | 800 | 4.0 | 41 | 52 | 90 | [15] |
| Sm-O | | 750 | 5.7 | 27 | 74 | 1200 | [16] |
| Sm-Mg-O-1 | | 750 | 3.0 | 26 | 40 | 830 | [16] |
| Sm-Mg-O-2 | | 750 | 3.5 | 22 | 45 | 1070 | [16] |
| Ga-Sb-Ni-P-O | $C_3H_8 \rightarrow C_3H_3N$ | 550 | 25 | 22 | 330 | 1.8 | [12] |
| Ga-Sb-O | | 550 | 12 | 18 | 160 | 0.6 | [11] |
| | $C_3H_6 \rightarrow C_3H_3N$ | 450 | 1.9 | 18 | 25 | 1.1 | [14] |
| Bi-Sn-O | $C_6H_{10} \rightarrow C_6H_8 + C_6H_6$ | 500 | 2.0 | 20 | 26 | 21 | [5] |
| Sn-Sb-O | $C_3H_6 \rightarrow C_3H_4O$ | 500 | 4.0 | 24 | 52 | 9.0 | [5] |
| Fe-Sb-O | $C_4H_8 \rightarrow C_4H_6$ | 425 | 1.0 | 19 | 13 | 10 | [6] |
| V-P-O | $C_4H_{10} \rightarrow C_4H_4O_3$ | 480 | 4.3 | 18 | 56 | 39 | [4] |
| Bi-Sb-O | $C_4H_{10} \rightarrow C_4H_8$ | 450 | 2.0 | 21 | 26 | 6.0 | [7] |
| | $C_3H_6 \rightarrow C_3H_3N$ | 450 | 2.0 | 21 | 26 | 0.8 | [7] |
| Bi-Mo-Fe- | $C_3H_6 \rightarrow C_3H_4O$ | 330 | 2.5 | 14 | 33 | 12 | [9] |
| V-Mo-O | $C_3H_4O \rightarrow C_3H_4O_2$ | 260 | 3.4 | 12 | 44 | 11 | [10] |
| V-Mo-Cu-O | $C_3H_4O \rightarrow C_3H_4O_2$ | 260 | 2.2 | 9 | 29 | 14 | [13] |

where $N_m$ denotes the oxygen quantity in 1 $cm^2$ of the surface monolayer. Considering, that $N_m = 1.3 \times 10^{15}$ atoms/$cm^2$ and taking into account the interval of $D_{ef}$ at catalytic conditions [1], the maximum rate of diffusion can be

$$W_{dif}^{m} = (10^{-2}\text{–}10^{-3}) \times (1.3 \times 10^{15}) = 10^{12}\text{–}10^{13} \text{ atoms/cm}^2 \text{ s}.$$

The value of the maximum diffusion rate calculated according to formula (1) are given in table 1. The reaction rates (to products of selective oxidation) are also given there. It should be noted that effective coefficients of oxygen diffusion were defined on the same samples for which the values of reaction rate are given.

As one can see from table 1 for all studied systems (except Sm–O and Sm–Mg–O high-temperature catalysts for oxidative coupling of methane) the maximum rate of oxygen diffusion is sufficient to carry out the selective oxidation reaction through rapid oxygen diffusion. For the Bi–Mo–O systems this was studied and proved [21] but as one can see from the table other systems could also have the same oxygen mobility in surface layers at other temperatures, whereas the number of oxygen monolayers taking part in the reaction may be less by orders of magnitude than in Bi–Mo–O catalysts [18,8].

For high-temperature catalysts the homogeneous–heterogeneous processes were possible. It is interesting to note, that in this case the effective coefficients of oxygen diffusion defined at optimal operative temperatures for oxidative dimerization of methane were also close to the effective coefficient of oxygen diffusion in other catalysts defined at optimal operative temperatures.

In conclusion, the presented results are the valid evidence for the possibility of carrying out the majority of the selective oxidation reactions of organic compounds through rapid oxygen diffusion in the surface layers. In order to prove this mechanism further research on molecular scale is needed. However, our results clearly indicate, that oxygen mobility is the essential, important factor determining the possibility of using the oxide system as a catalyst for selective oxidation.

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