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Figure 1

Figure 1: Figure 1

Abstract

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PHOTOCATALYTIC OXIDATION OF GASEOUS ISOPROPANOL ON ZnO AND TiO_2

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The ability of ZnO, TiO_2, and several other oxides, upon illumination with ultraviolet light, to oxidize organic and inorganic compounds in the presence of oxygen is well known. However, little data are available on the mechanism of these reactions and on the very nature of the photocatalytic activity of solids. In this connection, the study of the kinetic regularities of these reactions is of considerable interest in particular. As the object of investigation we chose isopropanol, the photooxidation of which on ZnO in the gas phase had been observed earlier by Myasnikov (1). In the liquid phase this reaction was studied in (2, 3), where it was shown that under these conditions the only products of photooxidation are acetone and H_2O_2:

$$(CH_3)_2CHOH + O_2 = (CH_3)_2CO + H_2O_2$$

and the quantum yield of the reaction varies from 0.25 to 1.50.

Fig. 1. Increase in acetone pressure upon illumination of isopropanol on ZnO (solid curves) and TiO_2 (dashed curves) in the absence of H_2O *(1)* and at water-vapor pressures of 7 mm Hg *(2)*, 10 *(3)*, 13 *(4)*, and 20 mm Hg *(5)*. Initial isopropanol pressure on ZnO, 9; on TiO_2, 11 mm Hg; $p_{O2} = 200$ mm Hg.

Photooxidation of isopropanol vapor was carried out by us at 30° in a closed cylindrical glass vessel 12 cm long and 200 cm^3 in volume. The side walls of the vessel were NaCl plates, which made it possible to analyze the composition of the gas mixture in the reactor from the absorption spectra in the infrared region. A layer of the oxide photocatalyst, about 5 mg/cm^2 thick, was applied from an alcoholic suspension to the lower half of the inner surface of the cylinder. After introducing isopropanol vapor and oxygen at the specified pressure, the reactor was disconnected from the vacuum system and placed in front of a PRK-2 mercury lamp. To reduce heating, illumination was carried out through a glass

Figure 2

Figure 2: Figure 2

filter. The illumination intensity was varied by means of wire-mesh attenuators. The change in the partial pressure of isopropanol and acetone as a result of the reaction was determined from the intensity of the absorption bands of these compounds at 960 and 1740 cm^{-1}, respectively. The absorption spectrum was recorded on an IKS-14 infrared spectrometer either during illumination (at fixed wavelength) or immediately after the end of exposure. Quantitative determination of other reaction products was not carried out. After each experiment the reactor was subjected to prolonged evacuation at room temperature and a pressure of 10^{-4} mm Hg.

Preliminary experiments with various samples of ZnO and TiO_2, as well as WO_3, SnO_2, and ZrO_2, showed that on all these oxides, when they are irradiated with near-ultraviolet light in the presence of O_2, isopropanol is converted into acetone. The reaction was studied in greater detail on an industrial sample of ZnO M-1 and a sample of TiO_2—anatase with a specific surface area of 70 m^2/g, obtained by the method described in (^{4}).

Figure 1 shows the increase in the pressure of acetone upon illumination of ZnO and TiO_2 in the presence of isopropanol and oxygen, and also the effect of water vapor on the reaction rate. In the absence of H_2O, the rate of photooxidation on ZnO increases as the amount of alcohol that has reacted increases, until its pressure falls to 1-2 mm Hg. The increase in the reaction rate with time is not the result of the formation and subsequent decomposition of a stable intermediate compound, since the curves for the change in the pressure of isopropanol are of an analogous character, but is apparently caused by the appearance and gradual increase during the reaction of the amount of H_2O_2 or of the product of its decomposition, H_2O. This is indicated, in particular, by the sharp increase in the oxidation rate in the presence of water vapor, and also by the absence of any increase in the reaction rate with time at a sufficiently high pressure of water vapor.

Fig. 2. Effect of isopropanol pressure on the rate of acetone formation.
1 –ZnO. $p_{O_2} = 70$ mm Hg, $\tau = 3$ h; 2 –ZnO. $p_{O_2} = 250$ mm Hg, $\tau = 2$ h; 3 – TiO_2. $p_{O_2} = 200$ mm Hg, $\tau = 4$ min.

As can be seen from Fig. 1, the pressure of acetone in the reaction vessel, after reaching a certain maximum value, begins to fall. The fall in pressure is evidently connected with the gradual oxidation of the acetone itself that has formed. The oxidation of acetone is also indicated by the fact that the maximum acetone pressure is considerably lower than the initial pressure of the alcohol.

Unlike ZnO, in the photooxidation of isopropanol on TiO_2 no increase in the rate of acetone formation with time is observed, and the addition of water vapor somewhat decreases the reaction rate. Decomposition of the acetone itself on

Figure 3

Figure 3: Figure 3

TiO_2 apparently does not occur. The initial reaction rate in the absence of water on the samples we used was approximately 35 times greater for TiO_2 than for ZnO.

Fig. 3. Effect of O_2 pressure on the reaction rate.
1 –ZnO, $p_{C_3H_7OH} = 20$ mm Hg, $\tau = 2$ h; 2 –TiO_2, $p_{C_3H_7OH} = 16$ mm Hg, $\tau = 6$ min.

Figures 2, 3, and 4 show the dependence of the initial reaction rate on the pressures of isopropanol and oxygen and on the light intensity. Along the ordinate is plotted the pressure of acetone formed during the exposure time (τ), constant for each curve and chosen so that the pressures of isopropanol and O_2 changed little during the reaction. Under these conditions the pressure of the acetone formed was proportional to τ.

The rate of acetone formation changes little when the vapor pressure of isopropanol over ZnO and TiO_2 is varied. When the alcohol pressure is reduced to several mm Hg, the reaction rate falls; at pressures close to the saturated vapor pressure of isopropanol, the rate increases somewhat, which may be associated with capillary condensation of the alcohol on the oxide surface. If, after the admission of isopropanol vapor, it was removed by pumping, no formation of acetone on ZnO was observed; on TiO_2, formation of a certain amount of acetone was observed at the expense of irreversibly adsorbed alcohol (see Fig. 2). In considering the effect of isopropanol pressure on the reaction rate, it should be borne in mind that the concentration of alcohol on the catalyst surface may depend on its vapor pressure in a complex manner.

The rate of photooxidation at low oxygen pressures increases proportionally to p_{O2} on ZnO and approximately proportionally to $p_{O2}^{1/2}$ on TiO_2. At relatively high O_2 pressures the reaction rate on both catalysts is independent of p_{O2}. The oxygen pressure above which the reaction rate remains constant, as experiments with ZnO showed, is practically independent of the alcohol pressure. In the absence of O_2, no acetone formation is observed on ZnO; on TiO_2 acetone is formed even in the absence of oxygen (see Fig. 3), and under these conditions the acetone pressure increases proportionally to $\tau^{1/2}$. When TiO_2 is illuminated in an atmosphere of alcohol without O_2, the sample becomes gray-blue in color and, at the same time, the transmission of TiO_2 decreases over a broad region of the infrared spectrum, analogous to that observed by us in work (^{5}). The appearance of coloration and infrared absorption indicates partial reduction of TiO_2 during the reaction. Admission of O_2 restores the original color and transmission of the sample.

Fig. 4. Effect of illumination intensity on the reaction rate.
1 –ZnO, $p_{O2} = 200$, $p_{C_3H_7OH} = 20$ mm Hg, $\tau = 4$ h;

Fig. 4

Figure 4: Fig. 4

2 $-\mathrm{TiO_2}$, $p_{\mathrm{O2}} = 200$, $p_{\mathrm{C_3H_7OH}} = 16$ mm Hg, $\tau = 6$ min.

The dependence of the rate of acetone formation on the illumination intensity (I) is also different for ZnO and $\mathrm{TiO_2}$. For ZnO the reaction rate is proportional to $I^{0.6}$. This dependence does not change when p_{O2} is varied from 70 to 200 mm Hg. The reaction rate on $\mathrm{TiO_2}$ increases approximately linearly with increasing light intensity.

The data obtained indicate that the mechanism of acetone formation on ZnO and $\mathrm{TiO_2}$ is different. It may be assumed that the overall reaction of photocatalytic oxidation of gaseous isopropanol on ZnO is the same as for the photooxidation of liquid isopropanol, i.e., in both cases $\mathrm{H_2O_2}$ is formed simultaneously with acetone. The presence of peroxide among the reaction products on ZnO was established by us by the iodometric method. In the case of $\mathrm{TiO_2}$, peroxide was not detected by us, which agrees with the data of Merckx and Laidler (^{6}), who showed that peroxide is not formed upon illumination of an aqueous suspension of $\mathrm{TiO_2}$ either in the absence or in the presence of phenolic compounds. Thus, the overall reaction on $\mathrm{TiO_2}$ apparently has the following form:

$$(\mathrm{CH_3})_2\mathrm{CHOH} + \tfrac{1}{2}\mathrm{O_2} \rightarrow (\mathrm{CH_3})_2\mathrm{CO} + \mathrm{H_2O}.$$

The kinetic regularities obtained by us are satisfied by the following simple reaction scheme:

$$\mathrm{TiO_2} + h\nu \xrightarrow{k_1} \mathrm{TiO_2^*},$$

$$\mathrm{TiO_2^*} \xrightarrow{k_2} \mathrm{TiO_2},$$

$$\mathrm{TiO_2} + (\mathrm{CH_3})_2\mathrm{CHOH} \xrightarrow{R_3} (\mathrm{CH_3})_2\mathrm{CO} + \mathrm{H_2O} + \mathrm{TiO},$$

$$\mathrm{TiO} + \frac{1}{2}\mathrm{O_2} \xrightarrow{k_4} \mathrm{TiO_2},$$

where $\mathrm{TiO_2}$ and $\mathrm{TiO_2^*}$ denote, respectively, unexcited and excited elements of the crystal lattice, and the symbol TiO denotes a lattice element containing an oxygen vacancy. According to this scheme, after absorption of a light quantum in the near-surface layer of the oxide, an oxygen atom located on the surface can react with the organic compound. The oxygen vacancies thereby formed are filled at the expense of gaseous O_2, which dissociates on the surface of TiO_2. The rate of acetone formation according to this scheme will depend on the light intensity, the concentration of isopropanol $[C_3H_7OH]$, and oxygen $[O_2]$ as follows:

$$v = \frac{k_3 k_4 \cdot S \cdot I \cdot [C_3H_7OH] \cdot [O_2]^{1/2}}{k_3 I [C_3H_7OH] + k_3 k_4 [C_3H_7OH] \cdot [O_2]^{1/2} + k_2 k_4 [O_2]^{1/2}}.$$

Here k_i are the rate constants of the corresponding elementary stages of the reaction, and $S = [TiO_2] + [TiO]$ is the concentration, in the absence of illumination, of the photocatalyst participating in the reaction.

The reaction scheme given above is a simplified one. It should be borne in mind, in particular, that light absorption may occur in the bulk of the crystal, whereas only the oxygen on the surface of the oxide participates in the reaction. However, additional reaction stages that take into account transfer of excitation from the bulk to the surface of the crystal and deactivation of excited centers within the crystal, under certain assumptions, do not substantially change the expressions for the reaction rate.

The mechanism proposed here for the photocatalytic oxidation of isopropanol on TiO_2 is consistent with the data of works ([7],[8]), according to which, in the presence of oxidizable substances, TiO_2 undergoes photolysis, while the Ti_2O_3 formed in the process is again oxidized in air in the dark to TiO_2. The photooxidation of isopropanol on ZnO obeys different kinetic regularities. The formation of H_2O_2 that occurs in this case, the linear dependence of the reaction rate on p_{O_2} at low O_2 pressures, and also the absence, as was shown by Korsunovskii ([9]), of photolysis of ZnO indicate that the mechanism of oxygen activation in this case is substantially different and, apparently, does not include dissociation of the O_2 molecule.

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REFERENCES

1. I. A. Myasnikov, ZhFKh, **31**, 2005 (1957).

2. I. Komure, Y. Fujita, T. Kwan, J. Res. Inst. Catalysis, Hokkaido Univ., **7**, 73 (1959).
3. J. S. Kuriacose, M. C. Markham, J. Catalysia, **1**, 498 (1962).
4. Yu. M. Shvetsun, V. N. Filimonov, N. P. Keier, A. N. Terenin, Kinetics and Catalysis, **5**, No. 1 (1964).
5. V. N. Filimonov, Optics and Spectroscopy, **8**, 270 (1960).
6. M. C. Markham, K. J. Laidler, J. Phys. Chem., **57**, 363 (1953).
7. A. E. Jacobson, Ind. and Eng. Chem., **41**, 523 (1949).
8. W. A. Weyl, T. Förland, Ind. and Eng. Chem., **42**, 257 (1950).
9. G. A. Korsunovskii, Fiz. tverd. tela, **4**, 968 (1962).

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