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Abstract

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Study of the Photocatalytic Oxidation of Organic Compounds on ZnO, TiO_2, Al_2O_3, and SiO_2 from the Absorption Spectra of Adsorbed Molecules in the Infrared Region

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In a previous work ([1]), in order to elucidate the mechanism of the photocatalytic oxidation of alcohols on metal oxides, we investigated the kinetic regularities of the reaction converting gaseous isopropanol into acetone on ZnO and TiO_2 upon illumination of these oxides with near-ultraviolet light in the presence of oxygen. At the same time it was shown that the photooxidation of isopropanol can be sensitized to near-UV light not only by ZnO and TiO_2, but also by WO_3, SnO_2, and ZrO_2. The rate and products of the reaction were determined by analyzing the composition of the gas above the photocatalyst layer from absorption spectra in the IR region. The aim of the present work was to investigate photocatalytic oxidation directly on the catalyst surface from changes in the IR spectra of adsorbed molecules. This made it possible to observe photooxidation on silica gel and γ-Al_2O_3, where the reaction products are strongly adsorbed on the catalyst surface, and also made it possible to detect surface compounds formed on ZnO, TiO_2, and Al_2O_3 during the photooxidation of organic compounds.

Molecules of isopropanol, methanol, heptane, and methane were subjected to photooxidation. The experiments were carried out in a vacuum cell intended for the study of IR spectra of adsorbed molecules, described in ([2]). An oxide layer (in the form of a powder) 5–25 mg/cm^2 thick, after calcination in air at 450–500°, was clamped between NaCl plates, placed in the cell, and evacuated at 350°. Adsorption of the organic compounds was carried out at a pressure of 10–30 torr and room temperature; the excess substance was removed by brief evacuation. In the experiments with methane, the latter was not removed from the volume of the cell during illumination. The samples were illuminated in the presence of O_2 at pressures of 100–200 torr with the light of an SVDSh-500 mercury lamp through glass and water filters transmitting the ultraviolet region of the spectrum with wavelength $\lambda > 320$ mμ, where absorption by the organic molecules subjected to photooxidation themselves is absent. The temperature of the samples during illumination did not exceed 35°. The spectra were recorded on an IKS-14 IR spectrometer with a NaCl prism in the region 1000–2000 cm^{-1}.

In order to compensate for the scattering of light by the sample, which increases sharply with increasing frequency, a diaphragm was placed in the comparison beam of the spectrometer and moved synchronously with the change in the recorded frequency. The diaphragm profile and the degree of diaphragming were selected beforehand for each sample. In the spectrograms presented, where the transmittance of the initial samples is taken as 100%, the transmittance scale refers to the upper curves; the remaining curves have been shifted vertically for clarity. To identify the products of photooxidation, spectra of the gas above the oxide surface were also investigated. In these experiments the reaction was carried out in a gas cell described in (1), and the oxide layer was illuminated with the light of a PRK-2 mercury lamp with $\lambda > 320$ mμ.

Figure 1 shows the change in the spectrum of isopropanol adsorbed on γ-Al_2O_3 upon irradiation with ultraviolet light. The absorption maxima near 1125, 1162, 1298, 1382, and 1465 cm^{-1} in curves 2, 3, and 4 belong to adsorbed alcohol molecules. Irradiation in the absence of O_2 leads to the appearance of weak absorption bands at 1700 and 1605 cm^{-1}. Upon irradiation in O_2 these bands rapidly increase in intensity, a new band appears at 1234 cm^{-1}, and the maxima in the region 1300-1465 cm^{-1} are somewhat shifted because of the superposition of new bands. Pumping at room temperature causes some weakening of a number of bands, but does not substantially change the form of the spectrum.

Fig. 1 Fig. 2 Fig. 3

Fig. 1. Photooxidation of isopropanol on γ-Al_2O_3. **1** –initial sample, **2** –sample with adsorbed isopropanol, **3** –irradiation for 4 h in the absence of O_2, **4** –irradiation for 4 h in O_2 (200 torr) and pumping at 20°, **5** –pumping at 200°, **6** –admission and pumping of acetone vapors

Fig. 2. Photooxidation of methane on γ-Al_2O_3. **1** –initial sample, **2** –irradiation for 4 h in an atmosphere of CH_4 (50 torr) and O_2 (100 torr), **3** –pumping at 100°, **4** –pumping at 350°

Fig. 3. Photooxidation of isopropanol on silica gel. **1** –sample with adsorbed alcohol, **2** –irradiation for 4 h in O_2 (100 torr)

Pumping at 200° leads to the disappearance of the bands of adsorbed alcohol and of part of the bands formed upon irradiation. Comparison of the spectra of the sample before and after pumping with the spectrum of a pumped sample on which acetone had additionally been adsorbed shows that the absorption bands arising upon irradiation and removed by pumping at 200° belong to adsorbed acetone molecules formed as a result of the photooxidation of isopropanol. Upon prolonged irradiation of γ-Al_2O_3 in the presence of isopropanol and O_2, the formation of acetone can also be observed from the change in the spectrum of the gas beneath the oxide layer. The narrowing of the 1605 cm^{-1} band observed during pumping and its shift to 1590 cm^{-1} are apparently associated with removal of the superposed band of adsorbed water at 1635 cm^{-1}, formed during oxidation of the alcohol. The bands at 1590, 1465, and 1382 cm^{-1} remaining after pumping the sample at elevated temperature, as will be shown

Fig. 4

Figure 1: Fig. 4

below, belong to surface compounds arising as a result of deeper oxidation of isopropanol.

In order to determine whether the photooxidation of isopropanol is caused by absorption of light by surface alkoxide groups formed during chemisorption of alcohols on Al_2O_3 ([3,4]), we also studied the photooxidation on γ-Al_2O_3 of heptane and methane, which are not chemisorbed at room temperature. After irradiation of Al_2O_3 in the presence of methane and O_2 (Fig. 2), an absorption maximum at 1685 cm^{-1}, a broad intense band near 1610 cm^{-1}, and weaker ⋯

bands at 1457 and 1370 cm^{-1}. The first maximum may be assigned to the C=O group of a methane oxidation product, which could not be identified. (The absorption spectrum of the gas above Al_2O_3 does not change upon illumination, which is evidently due to strong adsorption of the reaction product.) The band at 1610 cm^{-1} after evacuation at 100° narrows and shifts to 1597 cm^{-1}, apparently as a result of desorption of the water formed. The bands at 1597, 1457, and 1370 cm^{-1} change little when the sample is heated in vacuum to 200° and may be assigned to surface compounds formed during methane oxidation. On illumination of heptane adsorbed on Al_2O_3, the appearance of a band of the carbonyl group at 1700 cm^{-1} and a number of other bands is also observed, indicating oxidation of heptane.

Fig. 4. Spectra of adsorbed oxidation products: **1** –methanol on TiO_2, **2** –methanol on ZnO, **3** –isopropanol on ZnO, **4** –isopropanol on ZnO after evacuation at 350°.

Illumination of silica gel in the presence of isopropanol and O_2 does not cause any noticeable change in the spectrum of the gas phase; however, in the spectrum of the adsorbate (Fig. 3) a new band appears at 1700 cm^{-1}. This band disappears after evacuation of the sample at 200° and probably belongs to acetone, formed as a result of photooxidation and strongly adsorbed on the surface. No products of deeper oxidation of isopropanol on silica gel were detected. Thus SiO_2, like Al_2O_3, sensitizes the photooxidation of organic molecules to near ultraviolet light. This conclusion agrees with the data of Weil and Forland (5), who noted that SiO_2 and Al_2O_3 exhibit oxidizing ability when illuminated with sunlight, owing to absorption of light by the surface layer of the oxide, which, unlike the bulk of the crystal, has absorption in the near ultraviolet region, and to the liberation of atomic oxygen. It should be noted, however, that we did not observe photooxidation on Aerosil. It is possible, therefore, that silica gel sensitizes oxidation because of the presence in it of foreign impurities (for example, Al_2O_3).

In the case of ZnO and TiO_2, photooxidation of all the organic compounds we studied, with the exception of methane, can readily be followed from the change in the infrared spectrum of the gas phase. Analysis of the spectra shows that during oxidation on TiO_2 of heptane, as well as of isopropanol, acetone is formed, while during oxidation of methanol methyl formate is formed. The latter is apparently formed as a result of reaction of the primary oxidation product with excess alcohol. On the surface of ZnO and TiO_2, in the adsorbed state these reaction products give absorption bands of low intensity, which is explained by the small specific surface area of the oxides, and also by the fact that the compounds formed are readily desorbed from the surface. In addition to these bands, which disappear when the sample is evacuated at 20°, upon illumination of ZnO and TiO_2 with molecules of methanol, isopropanol, and heptane adsorbed on them in the presence of O_2, and also upon illumination of these oxides in an atmosphere of CH_4 and O_2, strong absorption bands appear in the spectrum, belonging to surface compounds that can be removed by evacuation only at 350°. Figure 4 shows spectra of the compounds formed during photooxidation of alcohols. The maxima near 1700 cm^{-1} belong to carbonyl groups of reaction products removed upon evacuation. The band near 1130 cm^{-1} on curve 3 belongs to adsorbed isopropanol; it completely disappears upon further illumination of the sample.

The remaining bands are associated with strongly adsorbed surface compounds. In the case of methanol these bands are located at 1600, 1360, 1310 cm^{-1} for ZnO and at 1618, 1320 cm^{-1} for TiO_2. During the oxidation of isopropanol the surface compounds have bands at 1603, 1435, 1370 cm^{-1} for ZnO and at 1625, 1430 cm^{-1} for TiO_2; during the oxidation of methane, bands at 1525, 1365 cm^{-1} for ZnO and 1600, 1380 cm^{-1} for TiO_2; during the oxidation of heptane on TiO_2, bands at 1618, 1450, 1375 cm^{-1}.

As a result of the photooxidation of CH_4 and CH_3OH, bands generally appear in the spectrum in the regions of 1600 and 1350 cm^{-1}, while upon oxidation of C_3H_7OH and C_7H_{16}, in addition to these bands, absorption is also observed in the region of 1450 cm^{-1}. Comparison of the spectra of strongly adsorbed compounds with the spectra of metal formates and acetates (^{6}) makes it possible to conclude that, during the oxidation of methane and methanol on Al_2O_3, ZnO, and TiO_2, compounds of the type

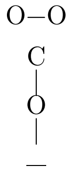
$$\mathrm{H{-}C(=O)O{-}}$$

are formed, whereas in the case of isopropanol and heptane the observed spectrum is a superposition of the spectrum of this compound and that of a compound of the type

$$\mathrm{CH_3{-}C(=O)O{-}}.$$

For the first of these compounds the frequencies of the asymmetric and symmetric stretching vibrations of the COO^- group should lie in the regions of 1600 and 1350 cm^{-1}, and for the second, near 1600 and 1450 cm^{-1}. An additional confirmation of this assignment of the frequencies is provided by the data of Greenler (^{4}), who observed the appearance of analogous bands upon adsorption of methanol and ethanol on Al_2O_3 at 170° and showed that they belong to formate- and acetate-like surface compounds.

When the samples are heated in vacuum to 350°, the bands in the region of 1350 cm^{-1} disappear, while the bands at 1600 and 1450 cm^{-1} become less intense and shift to 1550 and 1470 cm^{-1}, regardless of which compound had been subjected to photooxidation (see Figs. 2 and 4). These bands, not observed earlier because of overlap by stronger bands and disappearing upon prolonged pumping at 350°, apparently belong to surface groups



$$\begin{array}{c} O{-}O \\ C \\ | \\ O \\ | \\ - \end{array}$$

which are products of still deeper oxidation of organic molecules. The band in the region of 1450 cm^{-1} may, moreover, be due to CO_3^{2-} ions. The presence of these compounds apparently explains the appearance of the band at 1457 cm^{-1} during the photooxidation of methane on Al_2O_3. The band at 1300 cm^{-1}, arising after the photooxidation of isopropanol on ZnO and evacuation of the sample (Fig. 4), can be explained by the formation of surface oxalate upon heating.

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