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REACTIONS OF ISOPROPANOL AND n-HEXANE WITH O^- HOLE SITES ON UV-IRRADIATED V/SiO_2

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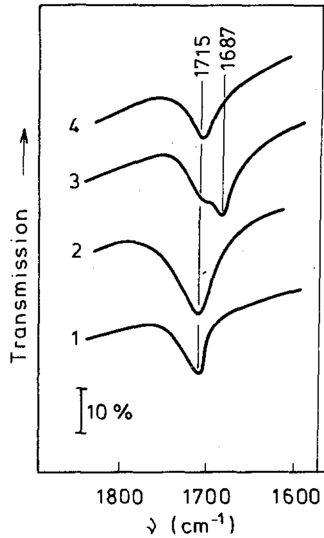
IR spectra of surface species formed in the reaction of isopropanol and n-hexane with UV-irradiated V/SiO_2 in the presence of $^{16}O_2$ or $^{18}O_2$ and in the absence of gaseous O_2 have been examined. Photoactivation of the lattice oxygen is shown to account for the oxidation of adsorbed molecules.

Метод ИК-спектроскопии применён для обнаружения поверхностных комплексов, образующихся в результате реакций изопропанола и н-гексана с V/SiO_2 при УФ облучении в присутствии $^{16}O_2$, $^{18}O_2$ и в отсутствие газообразного кислорода. Обнаружено, что фотоактивация решёточного кислорода приводит к окислению адсорбированных молекул.

It has been shown previously /1/ that due to a reversible electron transfer from lattice oxygen to metal ion, during the UV irradiation of SiO_2 with supported isolated V^{5+} ions, unstable O^- hole sites are formed. These sites participate directly in the CO photocatalytic oxidation /1, 2/ and are suggested to be active for the photooxidation of methane, ethane /3/, and propylene /4/ on V/SiO_2 catalysts. In our prèvious study /5/ we have established a possibility to detect the surface species formed by the photoactivation of lattice oxygen in the presence of H_2 and CO by using IR spectroscopy. The aim of the present study was to elucidate the role of O^- hole sites in the photocatalytic oxidation. For this purpose, we have studied the surface species formed in the reactions of isopropanol and n-hexane on UV-irradiated V/SiO_2.

The V/SiO_2 catalyst (C_V = 0.5 wt. %) was prepared via impregnation of aerosil with an aqueous solution of NH_4VO_3. Then it was dried, heated in O_2 at 300 K and evacuated at the same temperature. After evacuation the catalyst was retreated by O_2 and after cooling to 300 K it was evacuated. A high-pressure mercury lamp (SVD-120A) was used for irradiation.

1



2

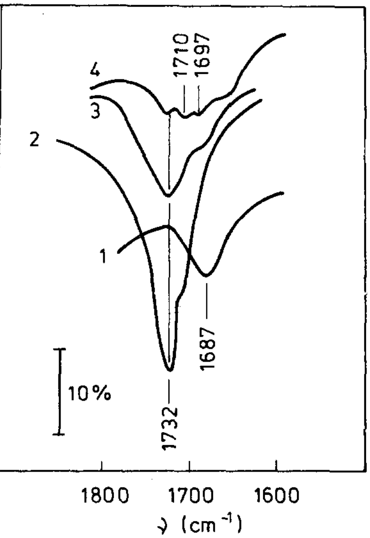


Fig. 1. IR spectra of V/SiO$_2$ with adsorbed isopropanol in the νC=O region after irradiation at $\lambda \geqslant 300$ nm for 2 h: 1) without oxygen; 2) upon admitting 1.3×10^3 Pa $^{16}O_2$; 3) after irradiation in 4×10^2 Pa $^{16}O_2$; 4) the same in 4×10^2 Pa $^{18}O_2$

Fig. 2. IR spectra of V/SiO$_2$ in the νC=O region after irradiation by unfiltered light (for 3 h) in the presence of n-hexane vapor (2×10^3 Pa): 1) in the absence of O$_2$; in the presence of: 2) 4×10^3 Pa $^{16}O_2$; 3) 4×10^2 Pa $^{16}O_2$ and 4) 4×10^2 Pa $^{18}O_2$

The preliminary experiments indicate that the irradiation of aerosil containing no vanadium in the presence of isopropanol does not lead to the appearance of new absorption bands in the examined spectral range (4000–1350 cm^{-1}). After the irradiation of aerosil in the mixture of isopropanol vapor and oxygen by the unfiltered light of the mercury lamp, the spectrum exhibits a weak absorption band at 1715 cm^{-1} identical to the νC=O band of adsorbed acetone.

The IR spectrum of isopropanol adsorbed on the V/SiO$_2$ catalyst does not differ from that of isopropanol adsorbed on silica. Irradiation ($\lambda \geqslant 300$ nm) of the catalyst with adsorbed isopropanol after evacuation of the isopropanol vapor at 300 K leads to a decrease in the intensity of the isopropanol bands and to the appearance of a strong band at 1687 cm^{-1} (Fig. 1). In order to identify this band, we have recorded spectra of acetone adsorbed on unreduced V/SiO$_2$ and on the catalyst samples prereduced by irradiation in H$_2$ or CO. According to Ref. /6/, irradiation of V/SiO$_2$ in H$_2$ at $\lambda \geqslant 340$ nm promotes the photoreduction of V^{5+} to V^{4+}, whereas during the irradiation in CO at $\lambda < 340$ nm V^{5+} reduces to V^{3+}. Spectra of the acetone adsorbed on both unreduced and photoreduced ($\lambda \geqslant 340$

nm) samples in H_2, exhibit a band ($\nu C = 0$) at 1715 cm^{-1} coinciding with that of acetone adsorbed on SiO_2. Beside this band, the spectra of acetone adsorbed on the catalyst photoreduced in CO or H_2 by the unfiltered light, exhibit a second band of $\nu C = 0$ at 1687 cm^{-1}. This band should be ascribed to the acetone bonded to V^{3+} ions. Unlike the band at 1715 cm^{-1} attributed to the weak-bound acetone which disappears after evacuation of the sample at 300 K, the band at 1687 cm^{-1} can be removed only by an evacuation of the catalyst at 500 K.

Thus the irradiation of the catalyst leads to the abstraction of hydrogen atoms from adsorbed isopropanol molecules and the formation of acetone coordinatively bonded to the photoreduced vanadium ions:

$$V^{5+}O^{2-} \overset{h\nu}{\rightleftharpoons} V^{4+}O^{-};$$

$$V^{4+}O^{-} + (CH_3)_2HCOH \rightarrow V^{3+} : O{=}C(CH_3)_2 + H_2O$$

This reaction mechanism is supported by experiments with deuterium-labelled isopropanol $(CD_3)_2DCOH$. In this case beside the band $C{=}O(CD_3)_2CO$ at 1677 cm^{-1} after irradiation, the spectrum also exhibits a band of the Si–OD groups at 2760 cm^{-1}. This result can be naturally explained by isotope exchange between the Si–OH groups of the support and HDO or D_2O molecules formed due to the abstraction of deuterium atoms by O^- sites. No formation of either V–OH or V–OD groups was observed after irradiation. On the contrary, whereas the spectrum of the catalyst before irradiation exhibits the bands of V–OH and V–OD groups at 3675 and 2710 cm^{-1}, respectively (e.g., after partial desorption of $(CD_3)_2DCOH$ at 500 K) the intensity of these bands after irradiation decreases with a simultaneous increase of the $\nu C{=}O$ band. One can suggest that irradiation produces a charge transfer: $V^{4+}OH^{-} \overset{h\nu}{\rightleftharpoons} V^{3+}OH^{\bullet}$ followed by the reaction of OH groups with isopropanol to form water molecules.

Upon admitting O_2 or isopropanol vapors, the absorption band $\nu C{=}O$ at 1687 cm^{-1} of acetone coordinatively bonded to V^{3+} ions disappears and simultaneously, the spectrum exhibits the $\nu C{=}O$ band at 1715 cm^{-1}, which evidences the displacement of acetone molecules from vanadium ions to the support. A similar band appears upon irradiating the catalyst with adsorbed isopropanol in the presence of $^{16}O_2$ or $^{18}O_2$ (Fig. 1).

The absence of an isotopic shift for the $\nu C{=}O$ band indicates that gaseous O_2 does not enter into the product acetone. But in the case of the irradiation of the catalyst by unfiltered light, beside the band $\nu C{=}O$, the spectrum exhibits bands at about 1600 and 1400 cm^{-1} belonging to surface carboxylates being the products of deeper oxidation of isopropanol.

Photooxidation of CH_4 over V/SiO$_2$ in the presence of oxygen containing 85% ^{18}O indicates that according to mass-spectroscopic data, the rate of $C^{16}O_2$ formation is much higher than that of $C^{16}O^{18}O$. The amount of $C^{18}O_2$ formed in these conditions is negligible. However, the IR spectra of V/SiO$_2$ irradiated both in CH_4 and in a mixture of CH_4 and O_2, exhibit no absorption bands of the adsorbed oxidation products of CH_4.

When V/SiO$_2$ is irradiated (either by unfiltered light or at $\lambda \geqslant 300$ nm) in the presence of n-hexane vapors, the band at 1687 cm^{-1} typical for the coordinatively bonded carbonyl groups is observed. (Fig. 2). After admitting O_2 this band disappears, apparently due to the displacement of the carbonyl-containing product compound from photoreduced V^{3+} ions like in the case of acetone. The spectrum of the catalyst irradiated in the presence of n-hexane vapor and $^{16}O_2$, exhibits a band at 1732 cm^{-1} and a weak band at about 1700 cm^{-1} in the νC=O region. After evacuation of the catalyst, the intensity of these bands decreases and an additional band at 1742 cm^{-1} is observed. Irradiation also leads to the appearance of the bands at about 1600 and 1400 cm^{-1} due to the formation of surface carboxylates. The spectrum of the catalyst irradiated in a mixture of n-hexane and oxygen (85% $^{18}O_2$) exhibits a complex absorption band with maxima at 1732, 1710 and 1697 cm^{-1} in the νC=O region (Fig. 2). It can be attributed to the superposition of the bands appearing after V/SiO$_2$ irradiation in a mixture of n-hexane and $^{16}O_2$ and of similar but more intense bands displaced to by 30–35 cm^{-1} lower frequencies due to the substitution of ^{16}O by ^{18}O in the carbonyl group.

The results indicate that the UV irradiation of V/SiO$_2$ leads to the partial oxidation of n-hexane both in the presence and in the absence of O_2. Phase compositions of the oxidation products are, however, different.

Hence, it can be suggested that the surface O^- sites photogenerated on V/SiO$_2$, oxidize isopropanol and n-hexane in the absence of O_2. Labelled oxygen from the gas phase is not incorporated into the acetone molecules formed due to the hydrogenation of isopropanol but can be detected in the products of n-hexane photooxidation.

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