Infrared Study of the Oxidation of 2-Propanol on TiO_2

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Synopsis. Oxidation of 2-propanol on TiO_2 was studied by infrared spectroscopy as well as analysis of reaction products. Propene and acetone are formed from isopropoxide species on TiO_2. Only adsorbed acetone is oxidized to carbon dioxide *via* carboxylate species. Propene undergoes no oxidation.

We previously studied surface species formed in oxidation of alcohols on metal oxides such as MgO,[1] NiO,[1] and ZnO[2,3] and concluded that secondary alcohols are dehydrogenated to ketones, which are in turn oxidized to carboxylate species *via* enolate complexes of ketones. However, Walker *et al.*[4] reported that over a UV-irradiated TiO_2 secondary alcohols are oxidized *via* alkenes which have been formed by dehydration. In order to decide to what extent the conclusion obtained with MgO and ZnO is applicable, in the present research similar experiments were extended to the 2-propanol/TiO_2 system for which propene formation is expected to be predominant.

The titanium dioxide used was obtained from Japan Aerosil Co. The details of the apparatus and procedures were as reported previously.[1-3,5] A sample disk was degassed, oxidized at 673 K for several hours, degassed for a short period at the same temperature, and cooled to room temperature. After introduction of 1 cm^3/g of the reactant into an IR cell, an oxygen of 2 kPa was circulated over the TiO_2, the temperature of which was raised in steps. Each of stepwise heat-treatments of the sample was followed by recording infrared spectra at ambient temperature on a JASCO IR-G infrared spectrometer, no reference disk being used.

The infrared spectrum of 2-propanol adsorbed on TiO_2 (1.0 cm^3/g) exhibits a number of bands (Fig. 1a), which does not change significantly on evacuation at 353 K. All the bands except for the one at 3430 cm^{-1} agree with those due to the surface isopropoxide formed on metal oxides,[1,2,6] confirming the formation of the surface isopropoxide species on TiO_2.

The temperature of the disk containing isopropoxide was raised in steps under circulation of oxygen. The bands due to isopropoxide were slightly reduced in intensity at 423 K (Fig. 1b) and disappeared at 523 K (Fig. 1c). The band appearing at 1690 cm^{-1} at 423 K can be attributed to a coordinately adsorbed acetone as will be described later. As regards the new bands appearing at 523 K, the following assignments are possible from comparison of surface carboxylate species on metal oxides.[1-3,7,8] The bands at 1560 and 1360 cm^{-1} are due to the formate species,[7] while those at 1530 and 1440 cm^{-1} are due to the acetate species.[8]

Figure 2 shows the amount of oxygen taken up as well as the amount of reaction products, measured at each step in the stepwise heating in oxygen. At 523 K, formation of water occurs together with uptake of oxygen in an appreciable amount, as expected from the formation of carboxylate species described above.

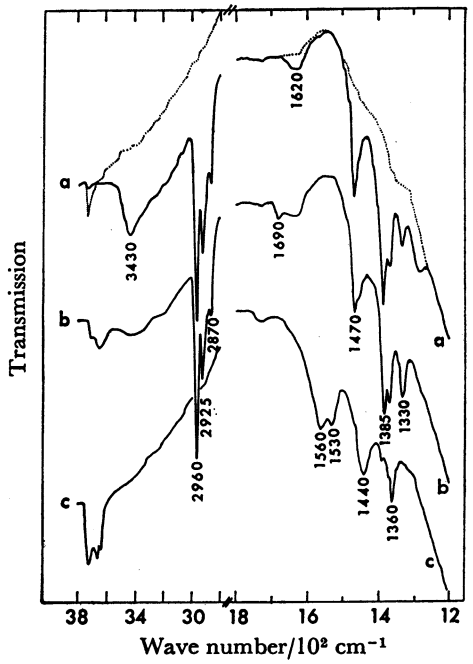

Fig. 1. Interaction of oxygen with 2-propanol adsorbed on TiO_2.
(a): After 1 h adsorption of 2-propanol (1.0 cm^3/g) at 293 K, (b): followed by 1 h at 423 K in oxygen (2.0 kPa), (c): 1 h at 523 K in oxygen.

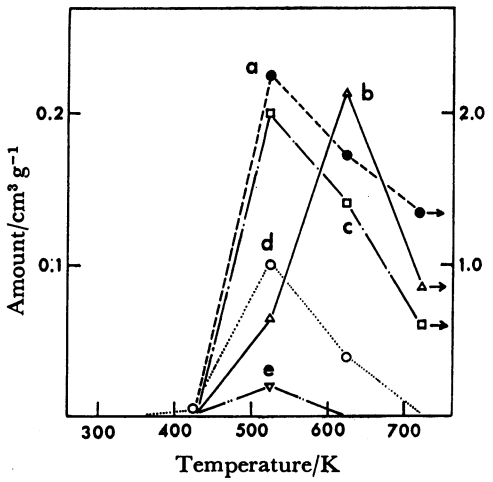

Fig. 2. Reaction of oxygen with 2-propanol adsorbed on TiO_2.
(a): Oxygen uptake or consumed by the reactions, (b): CO_2 formed, (c): H_2O formed, (d): propene formed, (e): acetone formed. Amount of 2-propanol adsorbed at 293 K was 1.1 cm^3/g.

CO_2 is formed above 523 K. In addition, propene and a small amount of acetone are also formed, providing information on intermediates for the oxidation.

In order to obtain information on the pathway of the

oxidation, similar experiments were carried out with propene or acetone adsorbed on TiO_2. When a small amount of propene (500 Pa) was introduced to the TiO_2 at ambient temperature, bands appeared at 2950, 2920, 1635, and 1460 cm^{-1}. Evacuation of the sample at ambient temperature reduced the intensity of the bands, suggesting that propene is weakly adsorbed on TiO_2. On raising the temperature of the sample containing propene in oxygen, few carboxylate bands could be observed. On the other hand, the acetone adsorption was found to be strong. The adsorbed acetone shows bands at 1700, 1620, and 1590 cm^{-1} in the carbonyl stretching region (Fig. 3a). Their corresponding bands were observed at 1690, 1600, and 1570 cm^{-1} with acetone-d_6. The 1700- or 1690-cm^{-1} band of acetone or acetone-d_6 can be assigned to CO-stretching vibrations of coordinately adsorbed species on Lewis acidic sites.[9] The same assignment appears applicable to the bands at 1620 and 1590 cm^{-1}, as proposed by Kiselev and Uvarov.[10] The possibility that these bands arise from mesityl oxide as proposed by Griffiths and Rochester,[9] may be excluded since no mesityl oxide

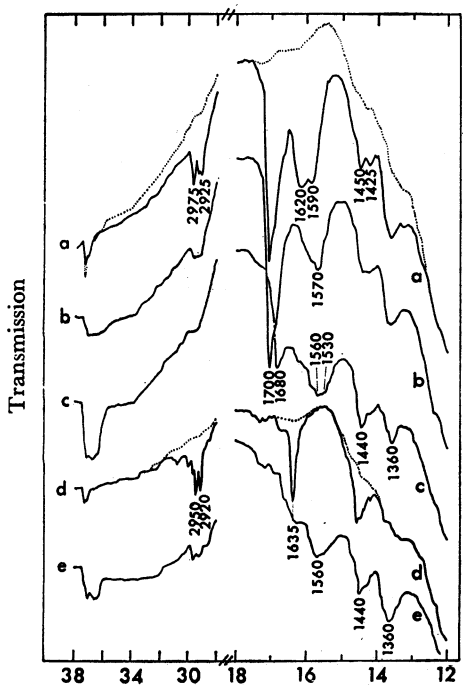

Fig. 3. Interaction of oxygen with acetone or propene on TiO_2.
(a): After 2 h adsorption of acetone (1.0 cm^3/g) at 293 K, (b): followed by 1 h at 353 K in oxygen (1.0 kPa), (c): 1 h at 423 K in oxygen, (d): after introduction of propene (500 Pa) at 293 K, (e): after 1 h reaction at 423 K in a mixture of propene (500 Pa) and oxygen (2.0 kPa). In Figs. 1 and 3, the dotted lines show background spectra.

was detected in the present system. Although at present it is not decided whether or not the band at 1570 cm^{-1} appearing at 353 K is attributable to the enolate species, its formation is supported by the occurrence of hydrogen isotopic exchange between acetone-d_6 and surface OH groups, which proceeds *via* the enolate intermediate.[11] The spectral behavior of adsorbed acetone upon raising the temperature was similar to that of adsorbed 2-propanol in that the carbonyl bands were reduced in intensity, while the carboxylate bands appeared (Fig. 3c).

Contribution of the weakly adsorbed propene to the oxidation was examined by allowing a mixture of propene (500 Pa) and oxygen (2 kPa) to circulate over the TiO_2 at 423 K. The results were compared with those of similar experiments using acetone instead of propene. The amount of carbon dioxide formed in the acetone/oxygen system was found to be more than ten times that in the propene/oxygen system, where carboxylate bands were observed as shown in Fig. 3e.

Figure 2 shows that about 12% of the 2-propanol adsorbed on TiO_2 is converted to propene, in contrast to the negligible formation of propene observed with MgO[1] and ZnO.[2] Such a difference may by expected from acid-base properties of metal oxides. From the results described above, it is concluded that the propene formed on TiO_2 makes no contribution to the formation of oxidation products. It appears that the acetone formed by dehydrogenation is oxidized to carboxylate species, from which CO_2 is formed. About 88% of the 2-propanol adsorbed on TiO_2 was oxidized *via* this reaction pathway. Thus, the same conclusion as that with MgO and ZnO is also applicable to TiO_2.

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