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STUDY BY IR SPECTROSCOPY OF THE INTERACTION OF A VANADIUM OXIDE CATALYST WITH A NAPHTHALENE-AIR MIXTURE IN THE COURSE OF CATALYSIS

(Presented by Academician A. N. Terenin, 3 XI 1964)

In the process of catalytic oxidation of naphthalene on V_2O_5, its partial reduction takes place ([1,2]), and organic substances accumulate on its surface ([2,3]). It may be assumed that these substances block the surface, which leads to a decrease in activity and makes it necessary periodically to regenerate the catalyst by treatment with air at 420—435°.

Experimental procedure. To record the spectra of individual organic substances, they were pelleted with KBr. The content of the substance being analyzed in the pellet was about 0.05 mg/cm^2. The initial vanadium oxides were studied as suspensions in Vaseline oil and as films obtained by vacuum evaporation of V_2O_5 onto NaCl plates measuring $1 \times 10 \times 30$ mm, followed by oxidation or reduction. Samples of these films were used both to study the interaction of the surface of the vanadium oxide catalyst with the naphthalene-air mixture during catalysis and to study the adsorption of naphthalene and the products of its oxidation: 1,4-naphthoquinone, phthalic and maleic anhydrides. The spectra were studied mainly in the region 700—2000 cm^{-1} on a double-beam UR-10 spectrophotometer with a spectral slit width of $3 \div 7$ cm^{-1} and a recording speed of 150 cm^{-1}/min. To study adsorption, NaCl plates with V_2O_5 films and adsorbates were sealed in ampoules in an atmosphere of air or in a vacuum of 10^{-3} mm Hg and kept at 99° for 24 hours or at 400° for 6 hours. When studying the interaction of the contact with the reaction mixture, the samples were placed in a gradientless reactor ([4]) and treated with the reaction mixture. For treatment of the films under conditions of high degrees of naphthalene conversion (50–60%), in addition to the films, which contained negligible amounts of V_2O_5 (2–5 mg), 1 g of pelleted V_2O_5 in the form of pieces 1–2 mm in size (forkontakt) was placed in the reactor.

To distinguish between the processes of reduction of the contact and accumulation of organic substances on its surface, the spectra of individual oxides were studied. In the IR spectrum of V_2O_5 ([5]) there are strong and narrow absorption bands at 1020 cm^{-1} and a weaker and broader one at 825 cm^{-1}. They

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

are assigned, respectively, to the valence vibrations of the groups $V = O$ and $V—O—V$. The spectrum of V_2O_5 obtained by us (Fig. 1, 1) coincides with that given in (^{5}). When V_2O_5 is evaporated onto an NaCl plate, owing to thermal dissociation of V_2O_5 (^{6}), the films are depleted in oxygen and a mixture of V_2O_5 with lower oxides is formed. In the spectra of the films after evaporation there is an absorption band at 980—1000 cm^{-1}, whose intensity and position are determined by the ratio $V_2O_5 : V_2O_4$, which we did not control during evaporation, and by the dispersion (cf., for example, curves 2 and 4 in Fig. 1). The absorption bands present in the spectra of evaporated films in the region 1420—1630 cm^{-1} (Fig. 1; 2, 4), and also at 2860 and 2985 cm^{-1}, should be attributed to impurities of organic substances.

to the initial V_2O_5. All these bands disappear both upon oxidation and reduction of the samples, and upon evacuation. To obtain spectra of films of the individual oxides, the deposited samples were oxidized with air at 500° (Fig. 1, 3) and reduced with hydrogen at 400-450° (Fig. 1, 5).

To elucidate the structure and the bond with the surface of the compounds formed in the course of catalysis, V_2O_5 films, heated in an atmosphere of air at 400-410° to remove impurities and oxidize V_2O_4, were treated at the same temperature with a naphthalene-air mixture; as a result, one absorption band appears in the spectrum in the region 1140-1160 cm^{-1} (Fig. 2, 1). As the treatment time is increased, its intensity increases (Fig. 2, 2, 3). Since the film contains a negligible amount of oxides, the degree

Fig. 1

Fig. 2

Fig. 1. Spectra of the initial oxides. 1 –V_2O_5, chemically pure, in vaseline oil; 2, 4 –V_2O_5 films after deposition; 3 –the same after treatment with air at 500°; 5 –the same after treatment with hydrogen at 400-450°.

Fig. 2. Spectra of the compounds formed on the surface of the contact during catalytic oxidation of naphthalene: 1 –V_2O_5 film treated in the reactor with air at 400-410°, and then at the same temperature with a naphthalene-air mixture for 85 min; 2 –the same film treated with a naphthalene-air mixture for 170 min; 3 –the same V_2O_5 film treated with a naphthalene-air mixture for 320 min; 4 –the same V_2O_5 film treated with a naphthalene-air mixture for 170 min in the presence of formcontact; 5 –the same V_2O_5 film after evacuation at 350-360° for 7.5 h; 6 –the same V_2O_5 film after treatment with air at 350-360° for

5.5 h.

conversion of naphthalene is very small; therefore, in the reaction space there is naphthalene with only traces of the products of its oxidation. Consequently, the band in the region 1140-1160 cm^{-1} is formed through interaction of the contact with naphthalene. Further treatment of the oxide film at the same temperature, but already with formcontact, at naphthalene conversions of 50-60%, leads, in addition to some increase in the intensity of the 1140-1160 cm^{-1} band, to the appearance of bands in the region 1300-1600 cm^{-1} (Fig. 2, 4). Therefore these absorption bands should be assigned to compounds formed through interaction of the naphthalene oxidation products with the surface of the contact. Thus, on the surface of the contact, compounds are formed both as a result of interaction directly with naphthalene and with the products of its oxidation, i.e., a mixture of substances, and not one individual compound, as Pontratz assumed ([3]).

Evacuation of the film to $2 \cdot 10^{-5}$ mm Hg at 350-360° for 7.5 h does not lead to a change in the spectrum; curves 4 and 5 coincide completely. Consequently, desorption of these surface compounds does not occur; it is not possible to destroy these compounds completely by oxidation with air oxygen at 350-360° either (Fig. 2, 6). In the latter case a significant decrease is observed in the intensity of the bands in the region 1300-1600 cm^{-1}, while the band 1140-1150 cm^{-1} remains unchanged. Thus, both the order

the removal of these bands indicates that on the surface there is a mixture, and not a single individual substance; moreover, the most stable of these compounds is formed through the interaction of naphthalene itself with the surface.

It could be assumed that these compounds are chemisorbed naphthalene and the products of its oxidation. To clarify the nature of the sorption of these substances by the catalyst, oxide films were treated under static conditions with vapors of these substances in the absence of oxygen at 99 and 400°. Treatment with vapors at 400° in the absence of oxygen leads to the formation of resinous products giving a spectrum completely different from the spectrum of the compounds obtained during catalysis. In the case of vapor treatment at 99°, chemisorption of naphthalene, 1,4-naphthoquinone, phthalic and maleic anhydrides occurs, with the formation of surface compounds of different stability, as shown by studying their spectra before and after evacuation for 8-10 h at 350-360°. Analysis of the spectra obtained makes it possible to assert that not merely chemisorption of the components of the reaction mixture occurs, but also oxidation of these chemisorbed substances, with the formation of stable surface oxygen-containing compounds.

Fig. 3. Spectra recorded to clarify the structure of the surface compounds formed during catalysis: **1** —potassium salt of phthalic acid; **2** —barium salt of maleic acid; **3** —V_2O_5 films after treatment with a naphthalene-air mixture at 400-410° in the presence of fluorocontact; **4** —oxide films after treatment with a naphthoquinone-air mixture at 400-410°; **3a, 4a** —spectra of the initial films.

To determine at the expense of which product or products the surface com-

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pounds having absorption bands in the region 1300-1600 cm^{-1} are formed, a V_2O_5 film was treated at 400° under static conditions with a mixture of air and each of the oxidation products of naphthalene. Treatment with a mixture of phthalic and maleic anhydrides with air leads to the formation of compounds giving spectra different from the spectrum of the compound obtained on the contact surface during catalysis at naphthalene conversions of 50-60%, which is also connected with resin formation. Treatment of the oxide film with a mixture of 1,4-naphthoquinone and air, however, leads to the formation of a compound giving a spectrum (Fig. 3, 4) that practically coincides with the spectrum of the compound formed during catalysis with fluorocontact, i.e., at the expense of the products of naphthalene oxidation. Apparently, the formation of intense absorption bands in the region 1300-1600 cm^{-1} occurs due to interaction with the surface of 1,4-naphthoquinone.

The presence of absorption bands in the regions 1550-1610 and 1300-1400 cm^{-1}, characteristic of the carboxyl ion in salts of organic acids ([7]), makes it possible to suppose that, upon interaction of 1,4-naphthoquinone with the catalyst surface, a salt-like compound is formed. It is known that in the catalytic oxidation of 1,4-naphthoquinone, phthalic and maleic anhydrides are formed ([8]); in this process the 1-2, 3-4 and 1-9, 4-10 bonds in the naphthoquinone molecule are broken. It could be assumed that, upon interaction of the 1,4-naphthoquinone molecule with surface oxygen atoms, precisely these bonds are also broken, which should lead to the formation of vanadium salts of phthalic and maleic acids.

A quantum-mechanical calculation of the 1,4-naphthoquinone molecule, carried out by the LCAO MO method in the Hückel approximation on an M-20 digital computer by means of the "Hückel" program developed by the quantum-chemistry group of the Institute of Physical Chemistry of the Academy of Sciences of the Ukrainian SSR, gives the distribution of the π-electron density in this molecule (Fig. 4). It follows from the diagram that in the 1,4-naphthoquinone molecule the least strong bonds are 1—9 and 4—10. Consequently, taking into account the homolytic character of the process, it may be assumed that, upon interaction of naphthoquinone with the surface of the con-

Fig. 4. Molecular diagram of 1,4-naphthoquinone

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tact, a compound of the type of the vanadium salt of maleic acid is formed. The latter apparently indicates a fairly deep reduction of the surface layers of V_2O_5. The conclusion that a surface compound of the salt type, namely of maleic acid, is formed is confirmed by comparison of the absorption spectrum of this compound (Fig. 3, 3) with the spectrum obtained by us (Fig. 3, 2) of the barium salt of maleic acid, and also by the fact that the spectrum obtained by us of the potassium salt of phthalic acid (Fig. 3, 1), which would be formed in the event of rupture in the 1,4-naphthoquinone molecule of the bonds 1—2 and 3—4, and not 1—9 and 4—10, differs from the spectrum of our surface vanadium salt. The probability of formation on the surface of other vanadium salts is considerably lower, since they can be formed only at the expense of a more profound oxidation of 1,4-naphthoquinone; nevertheless, we studied the spectra of the salts of those organic acids whose formation could still be considered possible, namely: salts of benzoic, oxalic, and carbonic acids. The spectra of these salts differ substantially from the spectrum of the surface compound obtained by us. In addition, formation of a carbonic-acid salt is unlikely also because of the instability at high temperatures (above 150°) of the surface carboxyl ion, as shown by Eischens (^{9}).

Fig. 4. Molecular diagram of 1,4-naphthoquinone

All this permits us to assert that one of the products of the interaction of the contact with a naphthalene–air mixture is a surface compound of the type of the vanadium salt of maleic acid. It should be noted that surface salt-like compounds were also detected in the photocatalytic oxidation of alcohols on ZnO, TiO_2, and Al_2O_3 (^{10}). Because of the high stability of the surface compounds formed, they evidently cannot be intermediate products of the catalytic reaction.

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