

INTERACTION OF ACROLEIN WITH VANADIUM—MOLYBDENUM OXIDE CATALYST SURFACE

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Received January 1st, 1975

Interaction of acrolein with vanadium–molybdenum oxide catalyst surface has been studied by IR spectroscopy. It has been found that character of the surface compounds depends considerably on pretreatment of the catalyst surface. Two surface complexes are formed on absorption of acrolein on the partially reduced surface. One of them, a π -complex, is only stable up to 200°C, i.e. below practical catalysis temperature. The second one is of the type of a surface salt and is highly stable even at the catalysis temperature; the sorbate can be liberated from the surface either by oxygen or by water vapour. In addition to it, absorption bands indicating formation of products of destructive oxidation have been observed in IR spectra of absorption products of acrolein and a catalyst pretreated in oxygen atmosphere.

In the previous work¹ a series of vanadium–molybdenum oxide catalysts were tested in oxidation of acrolein to acrylic acid by air oxygen in gas phase. It was found that a highly active and selective contact for the reaction can be obtained with the use of ethylenediamine and aerosil in the catalyst preparation. Oxidation of acrolein on the mentioned catalyst proceeds most favourably at 270 to 330°C, and its selective course to acrylic acid necessitates the presence of water vapour in the starting gaseous reaction mixture. From the observed change of the catalyst colour in the reaction course and from results of measurements of magnetic susceptibility it was deduced that the catalyst, in the steady state of the reaction, does not contain the both components in their maximum oxidation states. In order to obtain further information and better understand this important reaction we have studied the interaction of acrolein with the surface of vanadium–molybdenum oxide catalyst with the use of IR spectroscopy. The results obtained are presented in this report.

EXPERIMENTAL

Catalyst. The vanadium–molybdenum oxide catalyst coated on aerosil was used¹. With the use of EPR spectra it was found that the catalyst contained six-valent molybdenum and vanadium in the form of vanadyl. Signals of five-valent molybdenum were slight. For the IR spectral studies

of the adsorbed molecules the catalyst was pressed with the pressure 200 kg/cm^2 into rectangular tablets ($3.6 \text{ cm} \times 1.5 \text{ cm}$) weighing 8 mg/cm^2 .

Apparature. IR spectra were registered with a UR-10 spectrometer (Zeiss, Jena) modified for measurements at high temperatures (up to 500°C). The modulator of its sample beam was placed before the sample, and changes in the optical scheme of the apparatus were carried out in such a way that the sample beam was not modulated after passage through the sample, so that the effect of the sample radiation (due to heating of the sample) on its IR spectra might be eliminated. Detailed scheme of the modified apparatus was published². The spectral slot width was 8 cm^{-1} for 1000 cm^{-1} . The catalyst sample was placed in a special evacuated cell which enabled the sample treatment up to the temperature of 500°C and adsorption and desorption of vapours and gases as well as registration of spectra of the adsorbed molecules at elevated temperatures.

RESULTS AND DISCUSSION

First of all acrolein was adsorbed at 0.1 Torr at 20°C on a catalyst sample pretreated at 10^{-4} Torr at 300°C for 1.5 h . In the first moment after introduction of acrolein and its subsequent freezing out from the cell the spectrum contains absorption bands at 1445 , 1570 , 1620 and 1680 cm^{-1} (Fig. 1, curve 1). Increasing of the contact time to 10 – 15 min and subsequent exhaustion of acrolein from the cell causes the formation of further bands at 1490 , 1520 , 1650 and 1710 cm^{-1} (see Fig. 1, curve 2) (Fig. 1 gives spectra in the form related to the basic spectrum of the pretreated catalyst sample). Increasing of desorption temperature causes lowering of transparency of the catalyst sample in the region over 1300 cm^{-1} , which can be due to its reduction³. Desorption at 200°C (Fig. 1, curve 4) causes a practically complete disappearance of the absorption bands at 1490 , 1520 , 1680 cm^{-1} . The absorption bands which disappear due to desorption of acrolein at 200°C can be connected with vibrations of the bonds $\nu(\text{C}=\text{C}) = 1490$, 1520 cm^{-1} and $\nu(\text{C}=\text{O}) = 1680 \text{ cm}^{-1}$ in the surface π -complex of acrolein (I) the formation of which was presumed earlier^{4,5}. The two absorption bands 1490 and 1520 cm^{-1} can characterize the $\text{C}=\text{C}$ bond in two not very different π -complexes of acrolein. It can be presumed that



molybdenum and vanadium (on the basis of their different chemical properties) activate the $\text{C}=\text{C}$ bond in different ways, and, in accord with that, two kinds of π -complexes can be formed from acrolein, each of them being stabilized on a different cation of the catalyst. Increasing desorption temperature to 200°C causes also an increase of the absorption bands at 1710 and 1650 cm^{-1} . Formation of these spectral bands during interaction of acrolein with the catalyst can be connected either with adsorption of acrolein in a slightly distorted form or with formation of acrylic

acid which is characterized by similar values of wave numbers⁶. The absorption bands at 1710 and 1650 cm^{-1} do not appear immediately after introduction of acrolein but first after some time. This fact can make a serious argument for ascribing the absorption bands discussed to vibrations of acrylic acid. According to ref.⁶ the observed absorption bands can be related as it follows: 1710 cm^{-1} to $\nu(\text{C}=\text{O})$, and 1650 cm^{-1} to $\nu(\text{C}=\text{C})$ of acrylic acid. It is to be added that acrylic acid concentration on the catalyst surface increases with increasing temperature, and complete desorption was observed first at 340°C. In accord with refs^{4,7,8} the absorption bands at 1445 and 1570 cm^{-1} can be ascribed to the symmetrical (1445 cm^{-1}) and non-symmetrical (1570 cm^{-1}) valence vibrations of COO^- group in the anion II. Existence of double bond in such a structure is indicated by the absorption band at 1620 cm^{-1} (which appears in the spectrum immediately after introduction of acrolein to the catalyst sample) accompanied by two further bands at 1445 and 1570 cm^{-1} . At 340°C this complex is decomposed only in the presence of oxygen in gas phase, or it is completely liberated from the catalyst surface by water vapour perhaps in the form of acrylic acid. This statement follows from experimental results given in Fig. 2.

Further a catalyst sample was studied which was pretreated in oxygen at 300°C for 1.5 h and pumped off first after cooling of the sample at 20°C. Adsorption of acro-

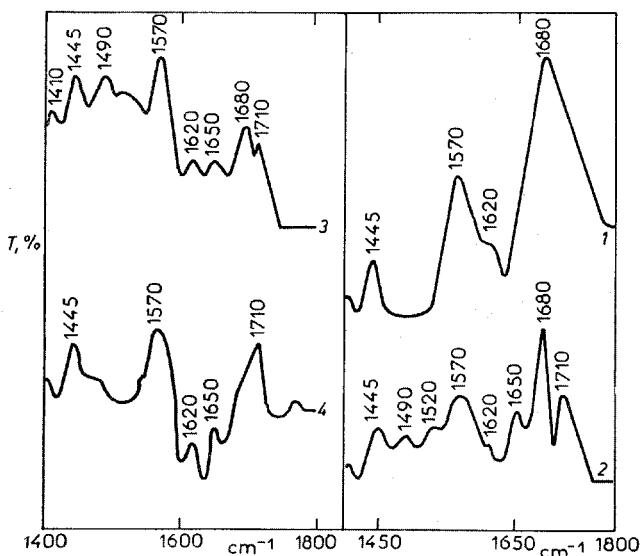


FIG. 1

IR Spectra of Adsorbed Acrolein on Reduced Surface of Mo—V—O Catalyst

1 Adsorption at 20°C with subsequent freezing off of the gas phase by liquid nitrogen; 2 adsorption at 20°C with subsequent evacuation of gas phase at 10^{-4} Torr; 3 desorption at 10^{-4} Torr and temperature 100°C; 4 desorption at 10^{-4} Torr at 200°C.

lein at 20°C on this oxidized catalyst gave a spectrum with the absorption bands presented in the curve 1 (Fig. 3). As it follows from comparison of the spectra of acrolein adsorbed on both the reduced and the oxidized surfaces (Figs 1 and 3), substantially the same surface compounds are formed in the both cases. However, in the case of the oxidized surface the spectrum shows no absorption band at 1490 cm^{-1} ascribed to $\nu(\text{C}=\text{C})$ in the complex I. If we admit the existence of two active centres on the catalyst surface capable of formation of π -complexes with acrolein, then it is possible that the more easily oxidized cation binds oxygen and, therefore, loses its ability of coordination with acrolein as ligand. Besides that the spectrum of oxidized catalyst after interaction with acrolein shows new absorption bands at 1420 and 1590 cm^{-1} which can be connected with formation of a surface complex type II having probably no unsaturated bond. This presumption is supported by the fact that no new absorption bands are observed in the region characteristic for $\nu(\text{C}=\text{C})$ during formation of such structures. From Fig. 3 it is obvious that increasing

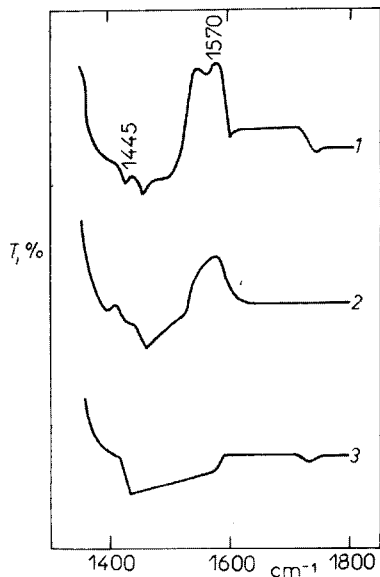


FIG. 2

Effect of Temperature, Oxygen and Water Vapour on Absorption Bands in Spectrum of Adsorbed Acrolein

1 Desorption at 340°C and pressure 10^{-4} Torr; 2 pretreatment in oxygen and evacuation at 340°C; 3 pretreatment in water vapour and evacuation at 340°C.

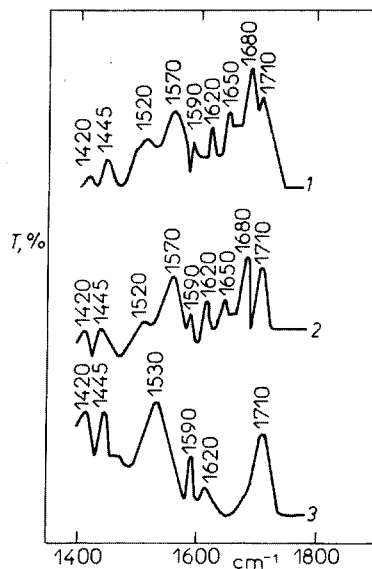


FIG. 3

IR Spectra of Adsorbed Acrolein on Oxidized Surface of Mo—V—O Catalyst

1 Adsorption of acrolein at 20°C with subsequent freezing off of the gas phase; 2 adsorption of acrolein at 100°C with subsequent freezing off of gas phase; 3 adsorption of acrolein at 200°C with subsequent freezing off of gas phase.

temperature from 100 to 200°C leads to diminishing of the absorption bands in the region 1700–1600 cm^{-1} which belongs to the bonds $\nu(\text{C}=\text{C})$ and $\nu(\text{C}=\text{O})$. At the same time a considerable increase in the intensity of the bands which characterize complexes containing COO^- group and a partial increase of the absorption band at 1710 cm^{-1} belonging to acrylic acid are observed. Thus it can be stated that also partial oxidation of acrolein is possible on the oxidized surface of vanadium-molybdenum oxide catalyst, but, compared with the reduced surface, a greater amount of the destructive oxidation products is observed. The superficially bound compounds containing $\text{C}=\text{C}$ bonds are oxidized probably by the loosely bound oxygen as low as at 200°C.

CONCLUSION

On the basis of available experimental results it can be concluded: *a)* Selective oxidation of acrolein to acrylic acid necessitates the catalyst working in its partially reduced form. Therefore, it is advantageous to use weak reducing agents in its preparation (*e.g.* ethylenediamine, triethanolamine). *b)* Formation of acrylic acid from acrolein proceeds through the surface complex type *II* which is strongly bound to the catalyst surface even at 340°C *i.e.* the catalysis temperature. Participation of lattice oxygen of the catalyst in its formation is evident. *c)* The complex *II* can be liberated from the catalyst surface by oxygen and water vapour. In the former case a partial destruction of the complex takes place, as it follows from the results of tests in flow apparatus¹ and the IR spectral data obtained in the case of interaction of acrolein with previously oxidized catalyst surface. *d)* The presence of water vapour is decisive for selective transformation of the complex *II* into acrylic acid and desorption of the latter at the catalysis temperature.

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Translated by J. Panchartek.