- 13. A. A. Davydov, IR Spectroscopy in the Chemistry of Surface Oxides [in Russian], Novosibirsk (1984).
- 14. L. A. Denisenko, A. A. Tsyganenko, and V. N. Filimonov, React. Kinet. Catal. Lett, <u>25</u>, No. 1-2, 23-26 (1984).
- 15. L. N. Kurina, N. A. Osipova, and A. A. Davydov, Kinet. Katal., <u>28</u>, No. 5, 1277 (1987).
- 16. S. Pinchas, Spectrochim. Acta, <u>28A</u>, No. 3-4, 801-802 (1972).

ADSORPTION OF METHANOL ON ORTHOVANADATES

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The industrial catalytic oxidation of methanol into formaldehyde on an iron-molybdenum oxide catalyst, by which a methanol-free formaldehyde can be obtained, is one of a number of large scale processes. The search for other systems is presently being carried out. Most of the publications deal with the study of molybdates while orthovanadates have been little studied in this process.

We studied Fe, Co, Cu, Cr, Sb orthovanadates [1] and showed that in the oxidation of methanol, Sb and Co orthovanadates catalyze a total oxidation of methanol, while Fe, Cr, and Cu orthovanadates, its partial oxidation. The reason for the low selectivity of Sb and Co orthovanadates is the strong interaction of methanol with the surface, which predominates with the formation of a strongly adsorbed methanol. At higher temperatures this converts into products of extensive oxidation [2]. On Cr, Fe, Cu orthovanadates the ratio between the weakly and strongly bound forms of methanol is reversed, and this leads to increase in the selectivity with respect to the partial oxidation product.

To obtain a more definite information on the nature of the reversible and irreversible forms of the adsorbed methanol that we have observed, we used IR spectroscopy to identify the detected forms on an activated and oxidized surface of chromium orthovadate, which is one of the active catalysts of partial oxidation of methanol under close to catalytic conditions.

The adsorption of methanol was studied under static conditions in the temperature range of 20-300°C, with further evacuation of the sample successively at 20, 100, 200, 300, 400, 500°C at each adsorption temperature.

The adsorption of methanol on an activated surface of $CrVO_4$ at 20°C, with its subsequent evacuation under the same conditions, leads to the appearance in the spectrum of several absorption bands (Fig. 1, curve 3), which in accordance with the literature data [3-8] characterize structures of the formate type, where the absorption band at 1370 cm⁻¹ corresponds to $v_{\rm SOCO}$, 1565 cm⁻¹ $-v_{\rm aSOCO}$, 2935 cm⁻¹ $v_{\rm CH}$ (compound of type 1), and also absorption bands at 1450, 2835, 2965 cm⁻¹, belonging, according to [9-13], to $\delta_{\rm CH_3}$ and $v_{\rm CH_3}$ of the surface compounds of a methoxyl type (compound of type II). Increase in the evacuation temperature leads to increase in the concentration of formates on the surface, as indicated by increase in the intensity of the absorption bands at 1370, 1565 cm⁻¹ (Fig. 1, curves 4-6). The number of structures of type II thus decreases, i.e., there is a transition from type II structures into structures of type I. At 300°C, the formate structures begin to decompose, and at 400°C they have a minimal intensity (Fig. 1, curves 7, 8). By comparing the intensities and the decomposition temperature of the above structures with the data on adsorption [2], we can interpret the reversibly adsorbed methanol as methoxyl and the strongly bound methanol as formate structures.

Increase in the temperature of the reaction of methanol with $CrVO_4$ to increase in the band intensity of both the formate and the methoxyl structures and to the appearance of an absorption band at 1740 cm⁻¹ belonging to the stretching vibrations of the surface compounds with a structure similar to that of formaldehyde. The presence of formaldehyde as a partial oxidation product, as well as the oxidized structures of both the methoxyl and formate types, which can be intermediates in the total oxidation reaction of methanol, indicates that the oxidation of methanol may occur at the expense of lattice oxygen in the sample.

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Fig. 1. IR spectra of methanol adsorbed on an activated surface of $CrVO_4$ at 20°C: initial spectrum of $CrVO_4$ (1), adsorption of methanol at 20°C (2), desorption of methanol at 20 (3), 100 (4), 200 (5), 250 (6), 300 (7), and 400°C (8).



Fig. 2. IR spectra of methanol adsorbed on an oxidized surface of $CrVO_4$: initial spectrum of $CrVO_4$ (1), adsorption of methanol at 300°C (2), subsequent desorption of methanol at 20 (3), 100 (4), 200 (5), 250 (6), 300 (7), 400°C (8), 500°C (9).

Preliminary treatment of the surface with oxygen and also the presence of oxygen in the reaction medium substantially influence the formation of surface compounds during the absorption of alcohol. The adsorption of methanol on the oxidized surface is shown in Fig. 2. Besides the previously indicated structures, the formation on the oxidized surface was noted of totally oxidized structures of type Me $\langle {}_{O} \rangle$ C=O, characterized by absorption bands at 1310 and 1610 cm⁻¹ and Me $\langle {}_{O} \rangle$ C=O, characterized by absorption bands at 1280 and 1670 cm⁻¹ [13] (Fig. 2, curve 3). The presence of an intense absorption band at 1450 cm⁻¹ may



Fig. 3. Desorption spectra of methanol adsorbed on $CrVO_4$ (a) and $SbVO_4$ (b) at 25 (1),75(2), and 110°C (3). On the right - chromatographic analysis of desorption products.

indicate the formation of the $(CO_3)^{2^-}$ ion [14], i.e., new acidic centers appear on the oxidized surface, which may further oxidize the formate structures into carbonate structures.

In the reaction of a mixture of an alcohol and oxygen with an activated surface of $CrVO_4$ at 20-100°C, spectra are observed, which are similar to the spectra obtained in the reaction of the alcohol with an activated surface of chromium orthovanadate. Increase in the reaction temperature to 300°C leads to decrease in the band intensity of the oxidized structures, while in the absence of oxygen, the maxima characterizing these structures have a low intensity, which indicates decomposition of these structures in the presence of oxygen and the possibility of formation of total oxidation products from the formates or other oxidized structures by an associative mechanism. We believe that these structures, which are formed during the adsorption of alcohol, are intermediate surface compounds before complete oxidation of methanol into CO_2 .

In separate experiments it was shown that on the oxidized surface of $CrVO_4$ further oxidation of the methoxyl structures formed to formate structures takes place, while with increase in the degree of reduction of the surface, an increase in the band intensity of the surface methoxyl structures was observed on the reduced centers on the surface according to the scheme

At the same time, with increase in the absorption temperature, the amount of the desorbed formaldehyde increases. From this, and taking into account the desorption temperature of the methoxyl structures, it can be assumed that the methoxyl structures are intermediate surface compounds in the partial oxidation reaction of methanol to formaldehyde. A favorable condition for the occurrence of the reaction in this direction is the removal of a certain proportion of oxygen from the surface. Since the presence of a weakly bound oxygen on the CrVO₄ surface ensures the occurrence of a competing further oxidation of the surface methoxyl structures to the formate structures, and further to CO_2 , it can be assumed that in a stationary state, CrVO₄ is present in a reduced state, and this ensures a preferential occurrence of the surface methoxyl structures into formaldehyde.



Fig. 4. Desorption spectrum of methanol adsorbed on $CrVO_4$ at 25°C (a). The same with a preliminary desorption of a reversibly chemisorbed methanol (b). On the right – chromatographic analysis of the desorption products.

Thus, it has been IR spectroscopically shown that the main structures in the oxidation of methanol on $CrVO_4$ are the methoxyl structures, which with increase in temperature, convert into a partial oxidation product, formaldehyde, and the formate structures which are responsible for the total oxidation products.

To specify the paths of formation of the oxidation products of methanol more accurately, we studied the thermodesorption of methanol adsorbed at 20, 75, and 100°C, from the surface of orthovanadates, which sharply differ in the catalytic properties: $CrVO_4 - a$ catalyst of a preferentially partial, and SbVO₄ of total oxidation.

By comparing the thermodesorptional curves for $CrVO_4$ (Fig. 3a) and $SbVO_4$ (Fig. 3b) it was shown that the fraction of methanol strongly adsorbed on $SbVO_4$ is much larger than on $CrVO_4$, while by chromatographic analysis it was confirmed that on $SbVO_4$, in contrast to $CrVO_4$, a considerably larger amount of CO_2 is liberated than that of formaldehyde, i.e., the ratio of the weakly and strongly bound forms of methanol adsorbed on the surface of the samples is a decisive factor determining the course of the reaction in the direction of formation of products of an extensive or selective oxidation.

With increase in the temperature of adsorption of methanol on the $SbVO_4$ surface, in contrast to the case of $CrVO_4$, the amount of the desorbed formaldehyde and the amount of CO_2 increases, which indicates a preferentially further oxidation of the surface oxidized structures.

To additionally clarify the participation of the forms of the adsorbed methanol in the formation of the oxidation products, we studied separately the oxidation of the adsorbed forms, followed by desorption and chromatographic analysis of the compounds formed. For this purpose, oxygen was adsorbed on $CrVO_4$ containing the two forms of adsorbed methanol. The desorption spectrum of methanol did not differ from the spectrum of methanol without the subsequent adsorption of oxygen. In the desorption products, formaldehyde and considerable amounts of CO_2 were present (Fig. 4a).

The adsorption of oxygen on the $CrVO_4$ surface from which the reversible form of the adsorbed methanol was removed by heating the sample in a helium current to 160-190°C led to the disappearance of formaldehyde in the desorption products (Fig. 4b), which unequivocally indicates that the weakly bound form of adsorbed methanol is responsible for the formation of the partial oxidation product. Comparison of the amounts of liberated CO_2 in experiments with and without the removal of the weakly bound form of the adsorbed methanol showed that the strongly bound form of adsorbed methanol is responsible for the occurrence of total oxidation.

Thus the above data show that formaldehyde, the product of the selective oxidation, is formed from the weakly bound form of the adsorbed methanol, which according to the IR spectroscopic data comprises methoxyl structures. The formation of extensive oxidation products occurs during further oxidation of the strongly bound form of adsorbed methanol, identified as formate structures.

Based on the IR spectroscopic and thermodesorption investigations, the scheme of oxidation of methanol on samples with different catalytic properties is as follows:



On $CrVO_4$, the oxidation of methanol proceeds by stages $1 \rightarrow 2 \rightarrow 3 \rightarrow 5$, and on $SbVO_4$ by stages $1, 2 \rightarrow 4 \rightarrow 5$, i.e., on the partial oxidation catalyst $CrVO_4$, the process proceeds by a consecutive scheme, while on the total oxidation catalyst $SbVO_4$, it proceeds by a parallel-consecutive scheme. The main difference in the catalytic action consists in that $CrVO_4$ acts in a reduced state, i.e., on the surface of a stationarily working partial oxidation catalyst there is no oxygen which would be free to further oxidize the methoxyl structures, while on the total oxidation catalyst $SbVO_4$, such oxygen is present under all conditions.

LITERATURE CITED

- 1. L. M. Potalitsyna, Candidate of Chemical Sciences Dissertation, Tomsk (1979).
- L. N. Kurina and L. M. Potalitsyna, Izv. Vyssh. Uchebn. Zaved SSSR, Khim. Khim. Tekhnol., 21, No. 12, 1765-1767 (1978).
- 3. L. M. Shevchenko, Ukr. Khim. Zh., 29, No. 12, 1247-1250 (1963).
- 4. A. A. Babushkin and A. V. Uvarov, Dokl. Akad. Nauk SSSR, <u>110</u>, No. 4, 581-584 (1956).
- 5. L. M. Roev and A. N. Terenin, Dokl. Akad. Nauk SSSR, <u>124</u>, No. 2, 373-376 (1959).
- 6. V. N. Filimonov, Kinet. Katal., 7, No. 3, 512-515 (1966).
- 7. V. M. Shchekochikhin, A. A. Davydov, and Yu. M. Shchekochikhin, Zh. Prikl. Spektrosk., 14, No. 5, 884-889 (1971).
- 8. V. N. Filimonov, Dokl. Akad. Nauk SSSR, 158, No. 6, 1408-1411 (1964).
- 9. A. N. Sidorov, Dokl. Akad. Nauk SSSR, 95, No. 6, 1235-1237 (1954).
- A. V. Alekseev, Yu. N. Lopatin, and A. A. Tsyganenko, Soobshch. Kinet. Katal., <u>1</u>, No. 4, 443-445 (1974).
- 11. L. I. Lafer, V. I. Yakerson, and A. M. Rubinshtein, Dokl. Akad. Nauk SSSR, <u>174</u>, No. 1, 111-114 (1967).
- 12. I. S. Ignat'ev and V. N. Filimonov, Dokl. Akad. Nauk SSSR, 183, No. 3, 621-624 (1968).
- 13. K. Nakomoto, Infrared Spectra of Inorganic and Coordination Compounds [Russian translation], Moscow (1966), pp. 268-270.
- 14. L. Little, Infrared Spectra of Adsorbed Molecules [Russian translation], Moscow (1969), pp. 224-228.