BINDING ENERGY OF OXYGEN WITH A VANADIUM-MOLYBDENUM OXIDE ON SILICA CATALYST

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Received August 5, 1974

The binding energy of oxygen with the surface of a vanadium-molybdenum oxide catalyst brought to the steady state in the oxidation of acrolein is 68–70 kcal/mol O_2. Oxygen of a lower binding energy is adsorbed on the catalyst at a lower rate and its steady-state concentration under conditions of the catalytic reaction is small.

Энергия связи кислорода с поверхностью ванадиймолибденового окисного катализатора, доведенного до стационарного состояния в реакции окисления акролеина, составляет 68–70 ккал/моль O_2. Кислород, имеющий меньшую энергию связи, поглощается катализатором с меньшей скоростью, и его стационарная концентрация в условиях протекания каталитической реакции невелика.

The binding energy of oxygen with the surface of oxide catalysts is one of the most important characteristics which determines the activity and selectivity in catalytic oxidation reactions. In this connection, in the Institute of Catalysis, measurements of this characteristic of oxide catalysts are systematically carried out using a calorimetric method /1/. The present work gives data on a vanadium-molybdenum oxide on silica catalyst having a high activity and selectivity in the oxidation of acrolein to acrylic acid.

The catalyst was prepared by co-precipitation from ammonium paramolybdate and ammonium metavanadate solutions at pH = 7 and addition of an aqueous aerosil suspension. Then it was dried in succession at 20, 100, 150 and 180 °C and calcined in air for 6 hrs /2/. The catalyst obtained was X-ray amorphus. Its BET surface area was 57 m^2/g, the molybdenum-vanadium atom ratio was equal to 4.

Before calorimetric measurements, the catalyst was brought to a steady state in a reaction mixture (acrolein 4%, oxygen 70%, H_2O 20%, N_2 6%) at 300 °C in a flow circulation system. The kinetic law can be given by the equation $W = k\ p_{O_2}^{1/2}$ /3/. The catalyst color changed from yellow to blue-black. After stopping the feed of the reaction mixture, the catalyst was cooled down to room temperature, then transferred from the reactor into the calorimetric ampoule, which was pumped out for 1 hr at room temperature and for 1 hr at 300 °C. After this treatment no noticeable gas evolution from the catalyst surface was observed.

Judging from the change in color and the form of the kinetic equation, the amount of reduction of the catalyst in the steady state was appreciable.

The heats of oxygen adsorption were measured at 300 °C with a calorimeter described in Ref. /4/. Oxygen was passed over the catalyst in portions every 30–40 min. After several portions, there was a pause, during which the sample was kept at the experimental temperature. Durations of these pauses are given in the figure.

It is seen that with continuous feed of oxygen portions to the catalyst, the heat of adsorption on the catalyst decreases substantially, but after a pause increases again to the initial value (68–70 kcal/mol O_2). Such changes in the heat of oxygen adsorption as the surface is covered may be due to the following reasons:

1) The adsorption process may be accompained by penetration of oxygen into the layers near the surface of the catalyst (chemical diffusion). This should reduce the actual degree of surface coverage by oxygen and retard the fall in the heat of adsorption. This effect should be most pronounced for a freshly reduced catalyst be-

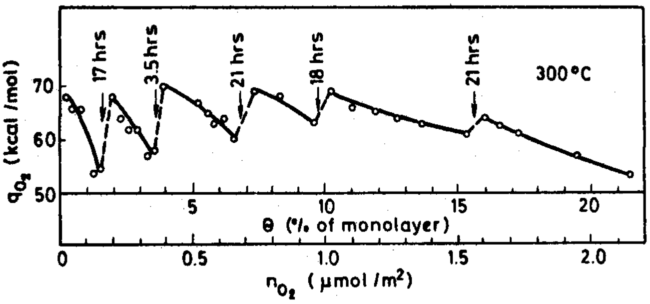

Fig. 1. Variation of the heat of oxygen adsorption with the coverage of the surface of a vanadium-molybdenum oxide catalyst

cause oxygen diffusion in such a catalyst is the fastest. However, the experiments indicate the opposite: the sharpest reduction in the heat of oxygen adsorption is observed near the steady state of the catalyst (see Figure 1).

2) The oxidation process of the steady-state catalyst surface may be localized near the most active regions. In this case, oxygen adsorption would sharply fall at the lowest surface coverages. During the pauses the active surface regions may be freed and again become oxidation conters owing to the migration of adsorbed oxygen over the surface or its penetration into the bulk of the catalyst. However, additional information is necessary to judge unambiguously the nature of the phenomenon observed.

All this evidence indicates conclusively that on the surface of a vanadium-molybdenum oxide catalyst in the steady state, oxygen is mainly present having a binding energy of 68–70 kcal/mol. A more weakly bound oxygen is adsorbed by the catalyst more slowly. Its steady-state concentration under the conditions of the catalytic reaction is small, therefore, the rate of formation of completely oxidized products is low.

REFERENCES

1. Yu. D. Pankratyev, G. K. Boreskov, V. I. Solovyev, V. V. Popovskii, V. A. Sazonov: Dokl. AN SSSR, 184, 611 (1969); Yu. D. Pankratyev, N. P. Keyer, V. I. Solovyev, G. V. Gridasova: Kinetika i kataliz, 11, 1279 (1970); G. K. Boreskov, S. A. Venyaminov, Yu. D. Pankratyev: Dokl. AN SSSR, 196, 621 (1971); B. I. Popov, K. D. Osipova, Yu. D. Pankratyev: Kinetika i kataliz, 12, 1234 (1971); A. L. Tsailingold, N. A. Komarovskii, Ye. Ye. Chekhov, G. A. Stepanov, L. S. Tuktarova, Yu. D. Pankratyev, M. G. Slinko: Kinetika i kataliz, 13, 1181 (1972); Yu. D. Pankratyev, V. V. Popovskii, G. K. Boreskov: Kinetika i kataliz, 13, 1230 (1972); A. G. Anshits, V. D. Sokolovskii, G. K. Boreskov, Yu. D. Pankratyev, V. F. Malakhov, A. M. Kolchin: Kinetika i kataliz, 14, 1209 (1973)
2. J. Tichy, J. Kustka, J. Vencl: Coll. Czech. Chem. Comm., 39, 1797 (1974)
3. J. Tichy, J. Kustka: J. Catal. (to be published)
4. A. P. Karnaukhov, M. I. Krivousov, G. G. Muttik, Yu. D. Pankratyev: Kinetika i kataliz, 9, 1369 (1968)