STEADY STATE CATALYTIC PROPERTIES
AND OXYGEN BINDING ENERGY
OF CADMIUM-MOLYBDENUM CATALYSTS
IN METHANOL OXIDATION

L. N. Shkuratova, Yu. D. Pankratiev, B. I. Popov
and V. M. Turkov

Institute of Catalysis, Novosibirsk, USSR

Received November 5, 1976
Accepted February 23, 1977

On normal cadmium molybdate the products of methanol oxidation are primarily CO₂ and H₂. After the introduction of excess MoO₃ to reach Mo/Cd = 1.2, methanol is oxidized to formaldehyde and carbon monoxide via a consecutive scheme. The oxygen binding energy in the steady state for the first sample is by 30 kcal/mol higher than that for the second catalyst. The activation energies of methanol conversion are 11.5 and 20 kcal/mol, respectively.

As was shown earlier /1/, after the introduction of excess MoO₃ into normal cadmium molybdate, a significant increase in its activity and selectivity in methanol oxidation to formaldehyde is observed. The objective of the present study is to elucidate whether any correlation exists between these values and oxygen binding energy.

Special purity CdMoO₄ (34.75 wt.% Mo and 40.7 wt.% Cd) and a sample with an atom ratio Mo/Cd = 1.2, prepared by impregnation of normal cadmium molybdate with ammonium paramolybdate were used. The samples were calcined in air (500°C, 4 hrs). The catalytic properties were studied by the flow-circulation method on 0.5-1.0 mm grains and at 3.5-3.7 vol.% initial methanol concentration.
Fig. 1. Catalytic properties of cadmium-molybdenum oxide catalysts in methanol oxidation. a) total degree of methanol conversion vs. selectivity to CH$_2$O for samples Mo/Cd = 1.2 (1) and Mo/Cd = 1.0 (3); the same vs. selectivity to CO$_2$ and CO for samples Mo/Cd = 1.0 (2) and Mo/Cd = 1.2 (4), respectively; b) methanol concentration C$_{\text{MeOH}}$ vs. the overall rate of methanol oxidation (W$_1$) for samples Mo/Cd = 1.2 (2) and Mo/Cd = 1.0 (3). CH$_2$O concentration C$_{\text{CH}_2\text{O}}$ vs. the rate of CH$_2$O oxidation to CO (W$_2$) for the Mo/Cd = 1.2 sample (1); c) temperature dependence of the specific rate constants for (i) oxidation of formaldehyde on the Mo/Cd = 1.2 sample (1) and (ii) oxidation of methanol on the samples Mo/Cd = 1.2 (2) and Mo/Cd = 1.0 (3).

On the sample with Mo/Cd = 1.0 the main reaction products were CO$_2$ and H$_2$. Only insignificant amounts of CH$_2$O and CO were detected. For example, at $350^\circ$C the degree of methanol conversion to CH$_2$O, CO$_2$, CO and H$_2$ is 7.0, 55.0, 2.0 and 59.0%, respectively. As shown by Fig. 1a, the selectivities to CH$_2$O and CO$_2$ change in opposite directions with increasing degree of methanol conversion. Since at conversion degrees close to zero, the selectivities to CH$_2$O and CO$_2$ reach 100% and zero, respectively, it may be concluded that, on this sample, CO$_2$ is formed from the intermediate (CH$_2$O). The overall rate of methanol conversion is first order with respect to methanol (Fig. 1b). The activation energy is $11.5 \pm 1.0$ kcal/mol (Fig. 1c).