

KINETICS OF OXIDATION OF METHANOL
WITH AIR ON A CHROMIUM-MOLYBDENUM OXIDE
CATALYST SUPPORTED ON POROUS α -Al₂O₃

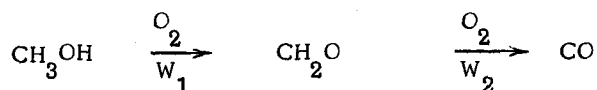
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Received November 15, 1975

Accepted February 9, 1976

Oxidation of methanol on a chromium-molybdenum oxide catalyst proceeds via the scheme:



The following kinetic equations have been obtained

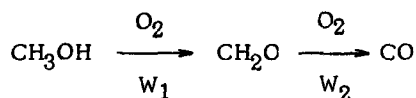
$$W_1 = \frac{K_1 C_{\text{CH}_3\text{OH}}}{1 + a_1 C_{\text{CH}_3\text{OH}} + a_2 C_{\text{H}_2\text{O}}}$$

for the oxidation of methanol, and

$$W_2 = K_2 C_{\text{CH}_2\text{O}}$$

for the oxidation of formaldehyde.

Окисление метанола на хромомолибденовом окисном катализаторе идет по схеме:



Кинетические уравнения имеют вид:
для окисления метанола

$$W_1 = \frac{K_1 C_{\text{CH}_3\text{OH}}}{1 + a_1 C_{\text{CH}_3\text{OH}} + a_2 C_{\text{H}_2\text{O}}}$$

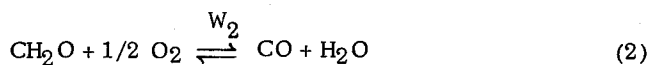
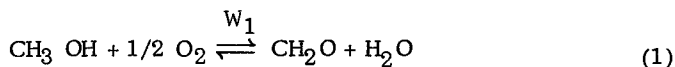
для окисления формальдегида

$$W_2 = K_2 C_{\text{CH}_2\text{O}}$$

It has been found earlier /1/ that iron- and chromium-molybdenum catalysts reveal similar catalytic properties in methanol oxidation. It was assumed that the reaction proceeds via similar mechanisms on both catalysts and, hence, has similar kinetic regularities. In the present study more detailed data are reported on the kinetics of methanol oxidation on chromium-molybdenum oxide catalysts.

The kinetic regularities were studied using a flow-circulation method /2/. The catalyst with an active mass of 10 % and an atomic ratio Cr/Mo \approx 3 was supported on spherical porous α -Al₂O₃ particles 0.5-1.0 mm in size. This size ensured that the reaction proceeded in the kinetic region. The kinetics was studied in an excess of oxygen, which allowed us to remain outside the lower ignition limit of methanol-air mixture and to maintain the steady state. The experiments were carried out at 300, 325 and 350°C. The concentrations of substances (mmol/l) were varied within the following ranges: 0.1-0.2; 0.7-3.1; 0.8-6.4 for methanol, formaldehyde and water, respectively.

According to the experimental data, the selectivity with respect to formaldehyde decreases with increasing overall degree of conversion, as stated earlier /1/. Thus, the oxidation of methanol proceeds via the scheme



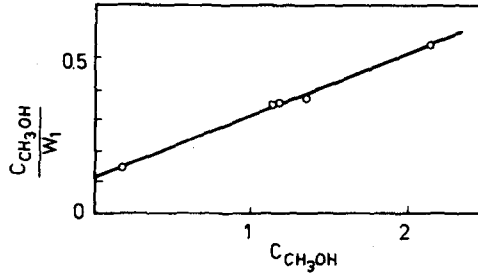


Fig. 1. Plot of C_{CH_3OH}/W_1 against C_{CH_3OH} at $C_{H_2O} = 1.9$ mmol/l (350°C)

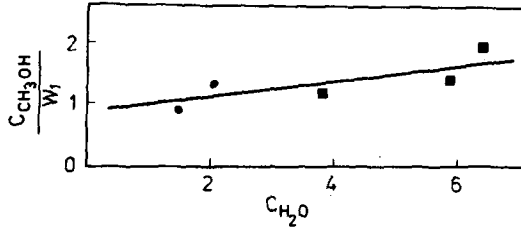


Fig. 2. Plot of C_{CH_3OH}/W_1 against C_{H_2O} at $C_{CH_3OH} 0.95$ mmol/l (300°C)

The experimental data have shown (Figs 1, 2) that the kinetic regularities for reaction (1) are similar to those observed earlier for iron-molybdenum oxide catalysts /3/. The rate of methanol oxidation can be described by

$$W_1 = \frac{K_1 C_{CH_3OH}}{1 + a_1 C_{CH_3OH} + a_2 C_{H_2O}} \quad (3)$$

where C_{CH_3OH} and C_{H_2O} are the concentrations of methanol and water (mmol/l), K_1 is the rate constant (ml/g sec), a_1 and a_2 are constants (1/mmol).

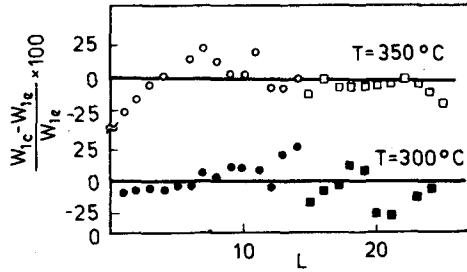


Fig. 3. Experimental and calculated rates in methanol oxidation

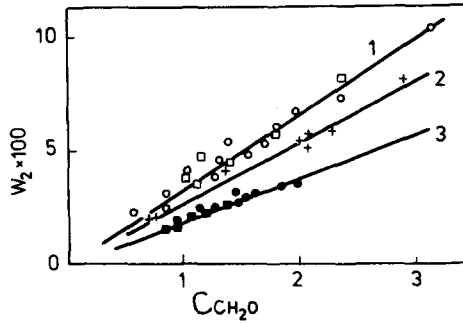


Fig. 4. Rate of formaldehyde oxidation against its concentration: 1 - 350°C; 2 - 325°C; 3 - 300°C

Approximate values of the coefficients in kinetic equation (3) have been found from the experimental data shown in Figs 1, 2.

The coefficients have been specified by minimizing

$$F = \sum_{i=1}^L (W_{1e} - W_{1c})^2$$

where W_{1e} , W_{1c} are the experimental and calculated values of the reaction rate; i and L are the current and total number of experiments. Minimization was

Table 1

Coefficients of the kinetic equations

| parameter | Temperature (°C) | |
|---|----------------------|----------------------|
| | 350 | 300 |
| K_1 (ml/g sec) | 13.22 | 3.77 |
| a_1 (l/mmol) | 1.84 | 1.47 |
| a_2 (l/mmol) | 0.544 | 0.862 |
| $\sum_{i=1}^L (W_{1e} - W_{1c})^2$ | 2.7 | 0.33 |
| $\sum_{i=1}^L (W_{1e} - W_{1c})$ | + 0.655 | + 0.34 |
| $\frac{100}{L} \sum_{i=1}^L \frac{W_{1e} - W_{1c}}{W_{1e}}$ | 9.5 | 13.1 |
| K_2 (ml/g sec) | 3.3×10^{-2} | 1.9×10^{-2} |

carried out by the method of conjugate gradients /4/ in combination with random search /5, 6/.

The coefficients for the kinetic equation of methanol oxidation are given in Table 1. Figure 3 shows the difference between the experimental and calculated data. From these results it is seen that the oxidation of methanol in an excess of oxygen is adequately described by eq. (3).

Oxidation of formaldehyde on a chromium-molybdenum oxide catalyst is insignificantly inhibited by water and methanol (in contrast to oxidation on iron-molybdenum catalysts). The experimental data show (Fig. 4) that in the presence

of methanol the rate of formaldehyde oxidation can be described by the following equation

$$W_2 = K_2 C_{\text{CH}_2\text{O}} \quad (4)$$

where $C_{\text{CH}_2\text{O}}$ is the concentration of formaldehyde (mmol/l), K_2 is the rate constant (ml/g sec).

It is noteworthy that in the absence of methanol the rate of formaldehyde oxidation is higher by a factor of about 1.5 than that calculated from eq. (4). This implies that the catalyst is affected by the reaction mixture /7/.

The dependence of K_1 and K_2 on temperature over the range 300-350°C is expressed by the equations

$$K_1 = 2.5 \times 10^7 \exp(-18000/RT) \quad (5)$$

$$K_2 = 20 \exp(-7900/RT) \quad (6)$$

Since the activation energy of the side reaction is lower than that of the main reaction, the selectivity with respect to formaldehyde increases with temperature. The optimum regime for the catalyst under steady-state conditions corresponds to the maximum permissible temperature at which the catalyst is stable and no reactions proceed in the gas phase.

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Acknowledgement. The authors wish to express their thanks to L. N. Shkuratova for preparation of the catalyst used in the experiments.

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