The Oxidation of Methanol over Pure MoO_3 Catalyst

Since many years it is known that MoO_3 is a very selective catalyst for the oxidation of methanol to formaldehyde (*1*); nevertheless, no thorough kinetic study was performed on this catalytic system up to now. On the contrary, many investigations (*2–5*) were made concerning the mixed catalyst MoO_3–$Fe_2(MoO_4)_3$, which is used in the industrial plants. Thus, we thought it useful to perform a kinetic study on methanol oxidation over MoO_3, and to compare the results with those we have previously obtained (*5*) on the mixed catalyst.

MoO_3 was prepared by thermal decomposition of amorphous $MoO_3 \cdot nH_2O$ at 400°C, and was used in granules of 0.3–0.5 mm.

The apparatuses and the techniques for the measurements of catalytic activities were described in a previous paper (*5*).

In Table 1 the results of two series of runs are reported; in one, the partial pressure of methanol was changed and the partial pressure of oxygen was kept constant, in the other, *vice versa;* for comparison the corresponding values of the reaction rate on the mixed catalyst are reported in the same table. As it may be seen, at 232°C the mixed catalyst is about 4 times more active than MoO_3, but in both cases the reaction order is zero in the range of reactants' partial pressures we have investigated.

Likewise, as well as in the mixed catalyst (*6*), water has an inhibiting effect on methanol oxidation (Fig. 1).

The apparent activation energy (Fig. 2) is 23 kcal/mole, therefore practically equal to that determined on the mixed catalyst (*5*).

From runs performed with a pulse reactor at 232°C following the technique previously described (*5*), a reaction rate about 10 times higher than that measured in stationary conditions was obtained.

Due to the close similarity between the results reported here and those previously obtained on the mixed catalyst (*5*), we believe that the reaction mechanism, as well as the rate-determining step, should be the same on MoO_3 and on the mixed catalyst. Therefore, the rate-determining step should be (*5*) the desorption of the reaction products. A strictly similar behavior was also found between MoO_3 and the mixed catalyst in an infrared study on ammonia adsorption (*7*). However, the high activity of the mixed catalyst with respect to MoO_3 should be explained. Because the activation energy is the same on both catalysts, it seems right to exclude

TABLE 1
KINETIC DATA FOR MoO_3 AND MIXED CATALYST AT 232°C

Oxygen partial pressure (mm Hg)	Methanol partial pressure (mm Hg)	Reaction rate on MoO_3 ($Nl_{CH_3OH} \cdot h^{-1} \cdot m^{-2}$)	Reaction rate on mixed catalyst ($Nl_{CH_3OH} \cdot h^{-1} \cdot m^{-2}$)
180	90	0.015	0.054
180	180	0.015	0.054
180	270	0.018	0.052
180	360	0.016	0.055
90	180	0.012	0.056
180	180	0.015	0.054
270	180	0.013	0.056
450	180	0.014	

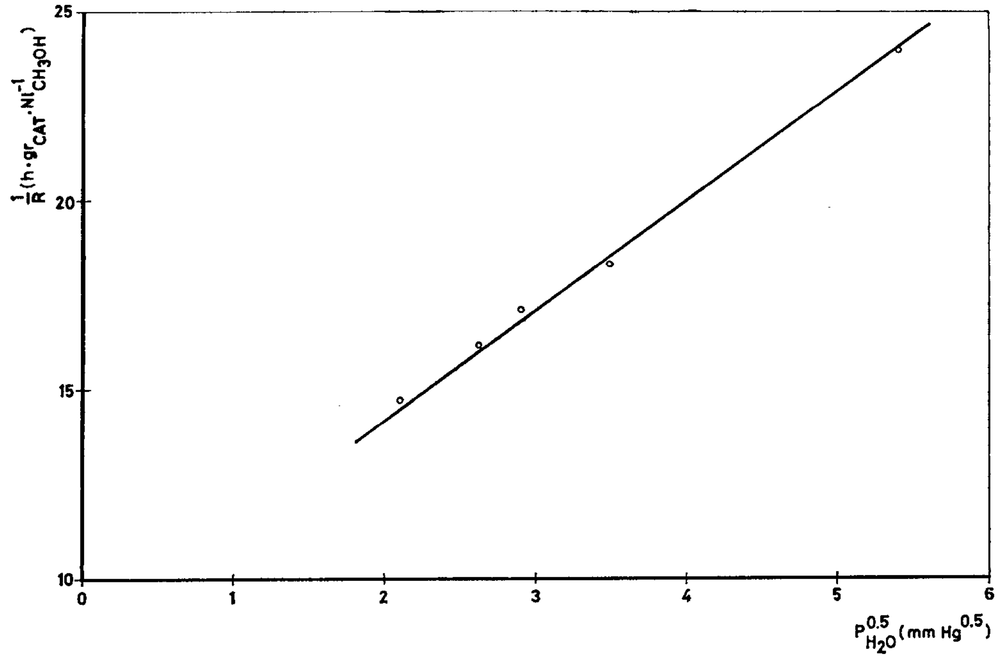

FIG. 1. Reciprocal reaction rate vs. square root of water partial pressure, methanol and oxygen partial pressures being constant (180 mm Hg); temperature, 232°C.

that Fe^{3+} ions have the effect of accelerating the rate-determining step. The presence of Fe^{3+} ions increase the Arrhenius pre-exponential factor, which, in the case of a reaction on solid surfaces, increases with the concentration of active centers (*8*). One possibility to explain this behavior is that the presence of Fe^{3+} ions increases the concentration of methanol adsorption centers existing in the

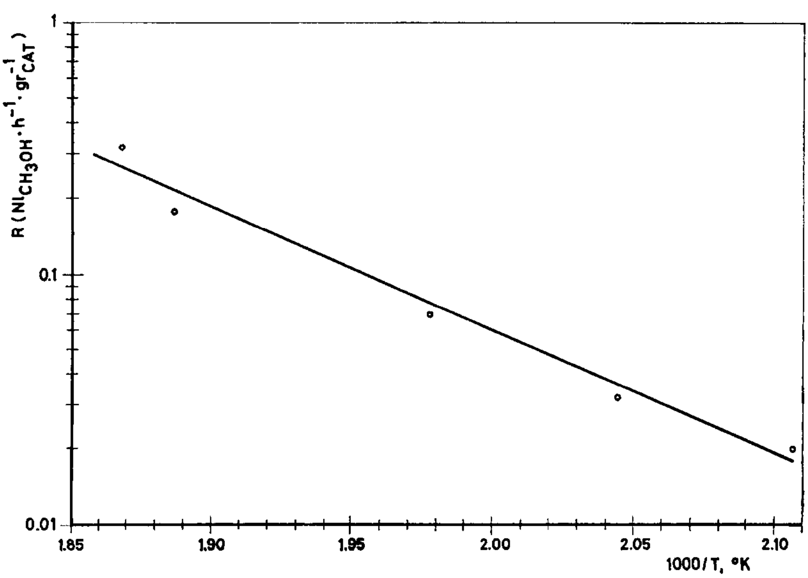

FIG. 2. Arrhenius plot for methanol oxidation on MoO_3 ($P_{CH_3OH} = P_{O_2} = 180$ mm Hg).

stationary conditions of the reaction. Each of these centers may be described as consisting of an anionic vacancy and an O^{2-} ion, and results from dehydroxylation of two neighboring hydroxyls (*5*). In other words, this dehydroxylation should be made easier by the presence of Fe^{3+} ions. A similar explanation was proposed by Batist, Lippens, and Schuit (*9*) for the promoting effect of Bi^{3+} ions in Bi molybdate catalysts.

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