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NOTES

The Effect of Water on the Catalytic Oxidation of Methanol to Formaldehyde

The most common industrial catalysts for the oxidation of CH_3OH to CH_2O are mixtures of MoO_3 with $Fe_2(MoO_4)_3$ (*1, 2*). Kinetic studies on this catalytic reaction were made by Jiru *et al.* (*3, 4*) and by Dente *et al.* (*5*). Experimental results were explained by these authors by means of a simple redox mechanism, firstly reported by Mars and Van Krevelen (*6*) for the oxidation of aromatic compounds on V_2O_5 catalysts. This mechanism accounts only for the influence of the reactants on the reaction rate.

Jiru *et al.* (*4*) also investigated the influence of the products on the reaction rate, and found that CH_2O acts as inhibitor of the oxidation reaction, while H_2O has no effect.

We have carefully studied the kinetics and the mechanism of this oxidation reaction; while total results and details of the experimental methods will be pub-

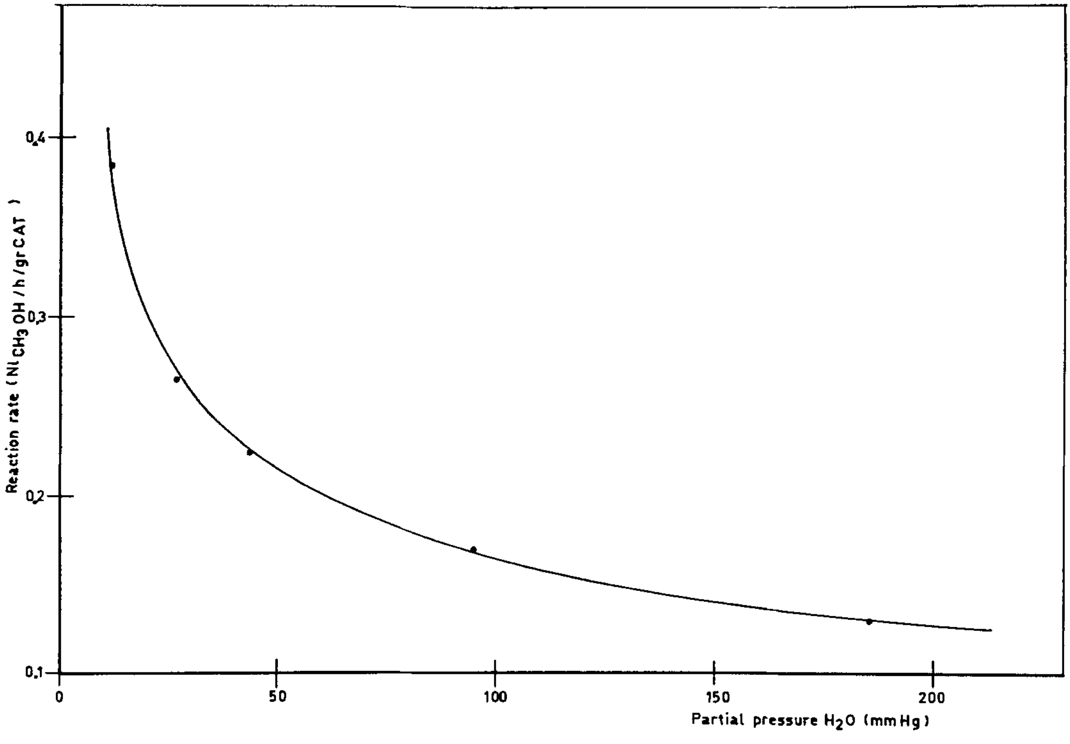

FIG. 1. Dependence of reaction rate on the partial pressure of H_2O for the following values of the reaction parameters: temperature, 232°C; total pressure, 920 mm Hg; $P_{CH_3OH} = 180$ mm Hg; $P_{O_2} =$ 180 mm Hg.

lished later, we report now some new interesting data on this catalytic system. Kinetic data were obtained by the differential reactor technique.

During this research we have found a marked inhibiting effect of H_2O on the reaction rate, especially at lower H_2O partial pressures. In Fig. 1 the reaction rate is plotted versus the partial pressure of H_2O for fixed values of the reactants partial pressure and catalyst temperature. The partial pressure values are the mean ones between the inlet and the exit of the differential reactor. The catalyst temperature in the bed was constant within ±0.5°C. We have obtained also similar behavior for other values of these parameters.

These experimental results may be explained in terms of competitive adsorption of H_2O with CH_3OH on free active catalyst surface. Surface acidity seems to be necessary for the reaction to go on (*7*); therefore we may explain competitive adsorption in terms of higher basicity of H_2O than CH_3OH.

Indeed the retention time of CH_3OH in a chromatographic catalyst column is lowered by the presence of H_2O (*8*).

It is possible to explain why the influence of H_2O on the reaction rate was not found by previous workers. Jiru *et al.* obtained their data by means of recycle reactors, therefore at rather high H_2O concentrations. As may be seen from Fig. 1, at high partial pressures the relative effect of water is rather small and probably of the order of magnitude of experimental errors.

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Application of the Power Rate Law to the Compensation Effect Observed in Propylene Oxidation over Metal Oxides

The compensation between the activation energy E and the pre-exponential factor A for a given reaction over a series of related catalysts, has been reported with many systems (*1*). It is usually of the form

$$\log A = mE + C \qquad (1)$$

and is referred to as the compensation effect. Some interpretations for this effect have been offered (*2*), whereas none of them can be a sole interpretation. We wish to report here briefly an instance in which the Power Rate Law (*3*) is successfully applied to the compensation effect observed in the oxidation of propylene over a series of metal oxides.

In a previous study of the catalytic oxidation of propylene (*4*), the authors