

# INVESTIGATION OF IRON MOLYBDATE CATALYSTS. I. OXIDATION OF METHANOL

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The oxidation of methanol on iron molybdate, molybdenum trioxide, and on their binary mixtures yields formaldehyde under the reaction conditions studied; on catalysts containing iron(III) oxide also carbon monoxide, on pure  $\text{Fe}_2\text{O}_3$  besides that carbon dioxide is produced. The catalytic reaction on iron molybdate is of the first order with respect to oxygen ( $k = 1.2 \cdot 10^{-7}$  mol  $\cdot$  g $^{-1}$  s $^{-1}$  Torr $^{-1}$  at 435°C), and its activation energy is 10.8 kcal/mol.

Among the catalysts used in the industrial production of formaldehyde by oxidation of methanol those of the type  $\text{Fe}_2\text{O}_3\text{-MoO}_3$  (Fe-Mo-O catalysts) are of great importance, especially because of their high selectivity. The kinetics and the mechanism of methanol oxidation on these catalysts<sup>1-3</sup> as well as the influence of their composition (the Fe : Mo ratio) on their catalytic activity<sup>4,5</sup> have been investigated. All the previous work in this field, however, was performed with catalysts prepared by coprecipitation of iron and molybdenum salts in solution. The aim of the present work was to investigate the catalytic oxidation of methanol on catalysts containing iron molybdate prepared by a solid state reaction<sup>6</sup>.

## EXPERIMENTAL

*Apparatus and substances.* The reaction rates were determined using a catalytic flow apparatus with gas circulation and differential reactor. The description of this apparatus and the description of the methods used in measurements was given previously<sup>7</sup>.

*Methanol* (R.G.) was purified by dehydration and distillation; the partial pressure of its vapours was 98 Torr at 20°C, the water content  $2.5 \cdot 10^{-3}$  w.%. Oxygen and nitrogen from steel cylinders were used; the gases were dried by passing through carbon dioxide cooled traps.

*The catalysts* studied were iron(III) oxide, molybdenum(VI) oxide, iron(III) molybdate, and mixtures of the latter with either  $\text{Fe}_2\text{O}_3$  or  $\text{MoO}_3$ . The preparation and properties of these catalysts will be described in the second paper of this series<sup>6</sup>.

## RESULTS

The standard conditions of the catalytic reaction were: a) catalyst: iron molybdate; b) amount of catalyst: 0.4 g; c) feed: 6 liters of the reaction mixture per hour (N.T.P.); d) composition of the reaction mixture: nitrogen with 5.5 vol.%  $\text{CH}_3\text{OH}$  and 20 vol.%  $\text{O}_2$ ; e) reaction temperature: 435°C. Whereas the conditions under b) and c) were kept constant in all experiments, in each series of measurements one of the other conditions was varied and the resulting effect was measured.

*Partial pressure of methanol and oxygen.* In this series of experiments the influence of the composition of the feed was investigated by varying the content of  $\text{CH}_3\text{OH}$  in the range of 1.4 to 7.6 vol.% and that of  $\text{O}_2$  between 2.5 and 20 vol.% (i.e. under the lower explosion limit). From the conversion data the formation rate of formaldehyde  $r_{\text{HCHO}}$  and the actual partial pressures of methanol and oxygen ( $p_{\text{CH}_3\text{OH}}$ ,  $p_{\text{O}_2}$ , respectively) were calculated. In Fig. 1  $r_{\text{HCHO}}$  is plotted against  $p_{\text{CH}_3\text{OH}}$ . The numbers at individual points give the corresponding values of  $p_{\text{O}_2}$ .

*Reaction temperature.* In this series of experiments the temperature of the catalyst bed was varied, while the other conditions were kept constant. The results are given in Table I.

*Composition of the catalyst.* In Fig. 2 the following reaction rates as function of the composition of the catalyst (given in w.% of  $\text{Fe}_2(\text{MoO}_4)_3$  in both binary mix-

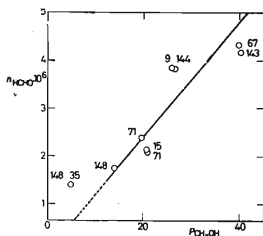


FIG. 1

Formation Rate of Formaldehyde  $r_{\text{HCHO}}$  as Function of the Partial Pressure of Methanol

$p_{\text{CH}_3\text{OH}}$

The numbers give the corresponding  $p_{\text{O}_2}$  (in Torr).

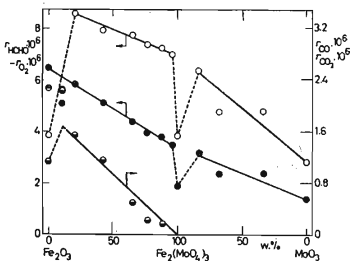


FIG. 2

Reaction Rates as Function of Catalyst Composition

○  $r_{\text{HCHO}}$ , ●  $-r_{\text{O}_2}$ , ⊙  $r_{\text{CO}}$ , ⊖  $r_{\text{CO}_2}$ .

tures with either  $\text{Fe}_2\text{O}_3$  or  $\text{MoO}_3$ ) are given:  $r_{\text{HCHO}}$  rate of formaldehyde formation,  $r_{\text{CO}}$  rate of carbon monoxide formation,  $r_{\text{CO}_2}$  rate of carbon dioxide formation, and  $-r_{\text{O}_2}$  rate of oxygen consumption (all in  $\text{mol g}^{-1} \text{s}^{-1}$ ).

## DISCUSSION

Considering the effect of the partial pressures  $p_{\text{CH}_3\text{OH}}$  and  $p_{\text{O}_2}$  on the reaction rate  $r_{\text{HCHO}}$  of the formation of formaldehyde on iron molybdate under the above mentioned standard conditions, we can see that  $r_{\text{HCHO}}$  was nearly proportional to  $p_{\text{CH}_3\text{OH}}$ , whereas changes of  $p_{\text{O}_2}$  had practically no effect over the pressure range studied. From the data obtained (with exception of those at lowest  $p_{\text{CH}_3\text{OH}}$  which exhibit the largest analytical error) the following equation for the reaction rate (corresponding to a first order reaction with respect to  $\text{CH}_3\text{OH}$  and of zero order with respect to  $\text{O}_2$ ) was deduced:

$$r_{\text{HCHO}} = k p_{\text{CH}_3\text{OH}}, \quad (1)$$

where the rate constant is  $k = 1.2 \cdot 10^{-7} \text{ mol g}^{-1} \text{ s}^{-1} \text{ Torr}^{-1}$ . The values of  $r_{\text{HCHO}}$  obtained by measurement in the  $p_{\text{CH}_3\text{OH}}$  range of 14–40 Torr (corresponding to 2.8 to 7.6 vol.%  $\text{CH}_3\text{OH}$  in the feed) were within  $\pm 20\%$  of the calculated ones; the line corresponding to equation (1) is plotted in Fig. 1.

From the data in Table I the rate constants  $k$  for the various temperatures were calculated and the corresponding Arrhenius plot was constructed. The calculated value of the activation energy of the reaction is 10.8 kcal/mol.

Another interesting effect is the influence of the composition of the Fe–Mo–O catalysts on their catalytic activity and selectivity. The results in Fig. 2 show that both iron molybdate and molybdenum trioxide acted under the experimental condi-

TABLE I  
Reaction Rates  $r_{\text{HCHO}}$  and  $r_{\text{CO}}$  and Actual Partial Pressure of Methanol  $p_{\text{CH}_3\text{OH}}$  as Function of Temperature of the Reaction

$^{\circ}\text{C}$	$p_{\text{CH}_3\text{OH}}$ Torr	$r_{\text{HCHO}} \cdot 10^6$ $\text{mol g}^{-1} \text{s}^{-1}$	$^{\circ}\text{C}$	$p_{\text{CH}_3\text{OH}}$ Torr	$r_{\text{HCHO}} \cdot 10^6$ $\text{mol g}^{-1} \text{s}^{-1}$
270	5.1	0.66	435	3.5	3.82
295	5.0	0.96	460	2.8 <sub>5</sub>	4.92
325	4.3	2.25	485	2.5	5.31 <sup>a</sup>
380	3.8 <sub>5</sub>	3.04			

<sup>a</sup>  $r_{\text{CO}} \cdot 10^6 = 0.19 \text{ mol g}^{-1} \text{ s}^{-1}$ .

tions studied as selective catalysts for the oxidation of methanol to formaldehyde. The catalytic activity of  $\text{Fe}_2(\text{MoO}_4)_3$  was higher than that of  $\text{MoO}_3$ , and the catalytic activity of the mixtures of both these compounds increased with the rising content of iron molybdate. In the case of the catalyst, consisting solely of  $\text{Fe}_2(\text{MoO}_4)_3$  a lower activity was observed than that which would be expected from the course of the curves in Fig. 2. This effect was probably due to a certain decrease of the active surface of the catalyst caused by the stronger sintering of pure iron molybdate when compared with the mixtures<sup>6</sup>.

On the contrary, iron(III) oxide appears to be, under the reaction conditions studied, a highly active catalyst for the oxidation of methanol. Its selectivity, however was very low, as considerable amounts of higher oxidation products of oxidation ( $\text{CO}$  and  $\text{CO}_2$ ) were formed. When  $\text{Fe}_2(\text{MoO}_4)_3$  was added to  $\text{Fe}_2\text{O}_3$ , the activity of the mixed catalyst decreased but its selectivity increased: no formation of  $\text{CO}_2$  and a decrease in the formation of  $\text{CO}$  was observed. The latter was nearly proportional to the content of  $\text{Fe}_2(\text{MoO}_4)_3$ .

The dependence of  $r_{\text{HCHO}}$  and  $r_{\text{CO}}$  on the catalyst composition was practically linear, at least in the studied concentration ranges of 21–96 w.%  $\text{Fe}_2(\text{MoO}_4)_3$  in mixtures with  $\text{Fe}_2\text{O}_3$  and (although not so distinctly) of 0–84 w.%  $\text{Fe}_2(\text{MoO}_4)_3$  in those with  $\text{MoO}_3$ . This suggests that in the mixed Fe–Mo–O catalysts of this kind both compounds present, *i.e.* iron molybdate and the respective oxide, acted independently. Thus the resulting activity of such a catalyst is a sum of their partial activities. That would mean that the rate  $r_{\text{AB}}$  of a reaction on a catalyst consisting of a mixture of the compounds A and B in proportions  $\alpha : \beta$  (where  $\alpha + \beta = 1$ ) should obey the equation

$$r_{\text{AB}} = \alpha r_{\text{A}} + \beta r_{\text{B}}, \quad (2)$$

where  $r_{\text{A}}$  and  $r_{\text{B}}$  are the rates of reactions on the pure compounds A or B, respectively used as catalysts. This equation would lead to correct results, if the reaction rates were related to a surface unit (*e.g.*  $\text{m}^2$  of the catalyst) and if both  $\alpha$  and  $\beta$  expressed the proportion of the surface occupied by the respective compound.

As the total surface area (which is of the order of some  $\text{m}^2/\text{g}$ )<sup>6</sup> of the catalysts in question could be determined with a considerable error only, and the proportion of A and B in the surface was considered to be nearing that one in the bulk<sup>6</sup>, the results obtained for the various reaction rates as the function of the catalyst composition were compared with equation (2) into which reaction rates related to a mass unit and for  $\alpha$  and  $\beta$  the mass proportions of the respective compounds were introduced.

The above mentioned effect of sintering on the catalytic activity of pure iron molybdate indicates that rather than the reaction rates actually measured on this catalyst (with the exception of  $r_{\text{CO}} = 0$ ), the values obtained by extrapolation of the reaction rates found on its mixtures must be used in equation (2).

An analogous extrapolation must be performed in the case of pure  $\text{Fe}_2\text{O}_3$  too, because of the great variety of products formed on this catalyst. For this reason the catalytic activity of all catalysts was normalised to a single parameter, *i.e.* the rate of oxygen consumption  $-r_{\text{O}_2}$  which is related to the rates of formation of the various products by the stoichiometric relation

$$-r_{\text{O}_2} = 0.5r_{\text{HCHO}} + r_{\text{CO}} + 1.5r_{\text{CO}_2} \quad (3)$$

For this rate of oxygen consumption no extrapolation to pure  $\text{Fe}_2\text{O}_3$  was needed and the activities of all the catalysts could be easily compared.

The linear parts (drawn in full line) of the curves in Fig. 2 correspond to the range of the composition of the catalysts in which equation (2) (with proper quantities introduced) is in a good agreement with the experimental data. The resulting (partly extrapolated) reaction rates are (all given in  $\text{mol g}^{-1} \text{s}^{-1}$ ):  $r_{\text{HCHO}} = 9.0 \cdot 10^{-6}$ ,  $r_{\text{CO}} = 1.9 \cdot 10^{-6}$  and  $-r_{\text{O}_2} = 6.4 \cdot 10^{-6}$  on  $\text{Fe}_2\text{O}_3$ ,  $r_{\text{HCHO}} = 6.8 \cdot 10^{-6}$ ,  $r_{\text{CO}} = 0$  and  $-r_{\text{O}_2} = 3.4 \cdot 10^{-6}$  on  $\text{Fe}_2(\text{MoO}_4)_3$ ,  $r_{\text{HCHO}} = 2.8 \cdot 10^{-6}$  and  $-r_{\text{O}_2} = 1.4 \cdot 10^{-6}$  on  $\text{MoO}_3$ . The rates of oxygen consumption determined by measurement on the mixtures of  $\text{Fe}_2(\text{MoO}_4)_3$  with  $\text{MoO}_3$  were within about  $\pm 15\%$  of the values derived from the corresponding line for  $-r_{\text{O}_2}$  in Fig. 2. For the mixture of  $\text{Fe}_2(\text{MoO}_4)_3$  with  $\text{Fe}_2\text{O}_3$  a still better agreement was obtained: the values of  $-r_{\text{O}_2}$  measured were within  $\pm 3\%$  of the values found from the corresponding line in Fig. 2. A larger difference was observed only with the catalyst containing 10.5 w.% of iron molybdate; even here however the measured value of  $-r_{\text{O}_2}$  was still within a  $\pm 20\%$  error limit.

From all these results a conclusion may be drawn that the catalysts consisting of iron molybdate, molybdenum trioxide or mixtures of these two compounds have essentially the same qualitative properties as far as the oxidation of methanol to formaldehyde is concerned, regardless of whether they were prepared by solid state reaction (as described in this paper) or by a precipitation method. All these catalysts exhibit a high degree of selectivity in the oxidation of methanol to formaldehyde. This behaviour of both  $\text{MoO}_3$  and Fe-Mo-O catalysts was also confirmed by a study of their reaction with methanol, both with and without oxygen in the gas phase: formaldehyde was the main product, and only small quantities of higher oxidation products ( $\text{CO}$  and  $\text{CO}_2$ ) were observed<sup>8,9</sup>.

Our results on the oxidation of methanol on  $\text{Fe}_2\text{O}_3$  have been confirmed by the tendency of this compound to oxidize methanol in the presence of oxygen to  $\text{CO}$  and  $\text{CO}_2$  (ref.<sup>9</sup>)

In the catalytic behaviour of catalysts consisting of mixtures of  $\text{Fe}_2\text{O}_3$  with  $\text{Fe}_2(\text{MoO}_4)_3$  a difference between the catalytic properties of the catalysts studied in this work and of those prepared by precipitation from solutions was observed: whereas Fe-Mo-O catalysts with an atomic ratio Fe:Mo even slightly greater than 2:3 (*i.e.* corresponding to mixtures of  $\text{Fe}_2(\text{MoO}_4)_3$  with  $\text{Fe}_2\text{O}_3$ ) prepared

by precipitation have a much lower activity for the oxidation of methanol to formaldehyde than catalysts consisting solely of iron molybdate<sup>4,5</sup>, the same catalysts prepared by a solid state reaction showed an increase of activity with a rising content of  $\text{Fe}_2\text{O}_3$  up to a certain level. As the unfavourable effect of  $\text{Fe}_2\text{O}_3$  on the selectivity of the catalysts may be eliminated by suitable conditions of the preparation of the catalysts and of the catalytic reaction<sup>10,11</sup> the catalysts of the type studied in this work might even be of practical interest for the industrial production of formaldehyde.

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