

On the Mechanism of CH₃OH Oxidation to CH₂O over MoO₃-Fe₂(MoO₄)₃ Catalyst

N. PERNICONE, F. LAZZERIN, G. LIBERTI, AND G. LANZAVECCHIA

*From the "G. Donegani" Research Institute, Montecatini Edison S.p.A.,
Novara, Italy*

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The kinetics of methanol oxidation over MoO₃-Fe₂(MoO₄)₃ catalyst were studied by means of a differential flow reactor and a pulse reactor in the temperature range 180–280°C. The reaction rate does not depend on the partial pressures of the reactants, except for the lowest ones. Formaldehyde and, especially, water act as inhibitors of the reaction. A competitive adsorption was observed between methanol and water. The reaction rates measured in the pulse reactor were much higher than those measured in the steady-state flow reactor, while the reverse was found for the apparent activation energies. A mechanism is proposed which satisfactorily agrees with the experimental results. The rate-determining step seems to be the desorption of the products.

INTRODUCTION

The most widely used industrial catalysts for the oxidation of methanol to formaldehyde are mixtures of MoO₃ with Fe₂(MoO₄)₃ (1, 2). Adkins and Peterson (3) first prepared this type of catalysts in 1931, but only recently the interest of several researchers was attracted by these catalysts, though already seven years ago Dixon and Longfield (2) had pointed out that this catalytic system might "provide an excellent opportunity for a fundamental investigation of the mechanism of oxidation reactions over oxide type catalysts in general."

Kinetic studies on this catalytic reaction were first made by Jiru *et al.* (4) by means of integral reactors. Experimental results were explained by these authors on the basis of a redox mechanism, previously reported by Mars and van Krevelen (5) for the oxidation of aromatic hydrocarbons on V₂O₅. Jiru's results were substantially confirmed by the work of Dente *et al.* (6). In a following paper (7), from kinetic data obtained by means of recycle reactors, Jiru *et al.* stated that the Langmuir-Hinshel-

wood method cannot be applied to the kinetics of methanol oxidation on MoO₃-Fe₂(MoO₄)₃ mixed catalysts. In the same paper results are reported about the influence of the products on the reaction rate; it was found that formaldehyde acts as inhibitor, while water has no effect.

In order to get a further insight on the reaction mechanism, we decided to re-examine the kinetics of this reaction with the differential reactor method, which is known (8) to be more suitable for kinetic studies. In a previous note (9) we have reported a marked inhibiting effect of water on the reaction rate; the effect was explained in terms of competitive adsorption of water with methanol on the catalyst surface.

EXPERIMENTAL PROCEDURE

A. Catalyst

The method of catalyst preparation was very similar to that described by Kolovertnov *et al.* (10). The chemical analysis gave the following results: Fe 12.95%, Mo 54.3%. X-Ray measurements showed the

catalyst to be composed by MoO_3 and $\text{Fe}_2(\text{MoO}_4)_3$. Its surface acidity, measured according to Johnson (11) using phenylazonaphthylamine as indicator, was 0.030 meq/gr. Its surface area was $7.7 \text{ m}^2/\text{gr}$.

B. Flow Apparatus

When the reaction was carried out in a flow system, conversion was kept in each run at about 5% in order to be within differential conditions. Nitrogen was used as the carrier gas. A schematic representation of the system is given in Fig. 1.

Gas flow measurement. Gases were first passed through drying towers, containing CaCl_2 and dehydrated alumina. The flow rates of nitrogen and oxygen were measured by means of calibrated rotameters or capillary flowmeters. The precision of these measurements was estimated to be about 2%.

Saturators. The saturator we have used for methanol and water consists of a 250-cc flask, containing the boiling liquid,

equipped with a bulb condenser; in the outer jacket of the condenser water is circulated from a thermostat. The bulbs of the condenser were filled with small glass beads. We have checked that such device ensures the complete saturation of the gas with the vapor at the temperature of the highest bulb of the condenser; however, it is advisable to use gas flow rates below 20 liters/hr. The partial pressure of methanol and water was calculated from the saturation temperature.

The formaldehyde generator consists of a 500-cc flask containing a suspension of paraformaldehyde in vaseline oil, with a small amount of H_3PO_4 as a depolymerization catalyst. The flask was heated at temperatures ranging from 60 to 170°C . After the saturator a trap, cooled at -20°C , is placed, in which traces of water and vaseline oil condense, together with some formaldehyde.

Reactor. A sketch of the Pyrex reactor we have used is reported in Fig. 2. The

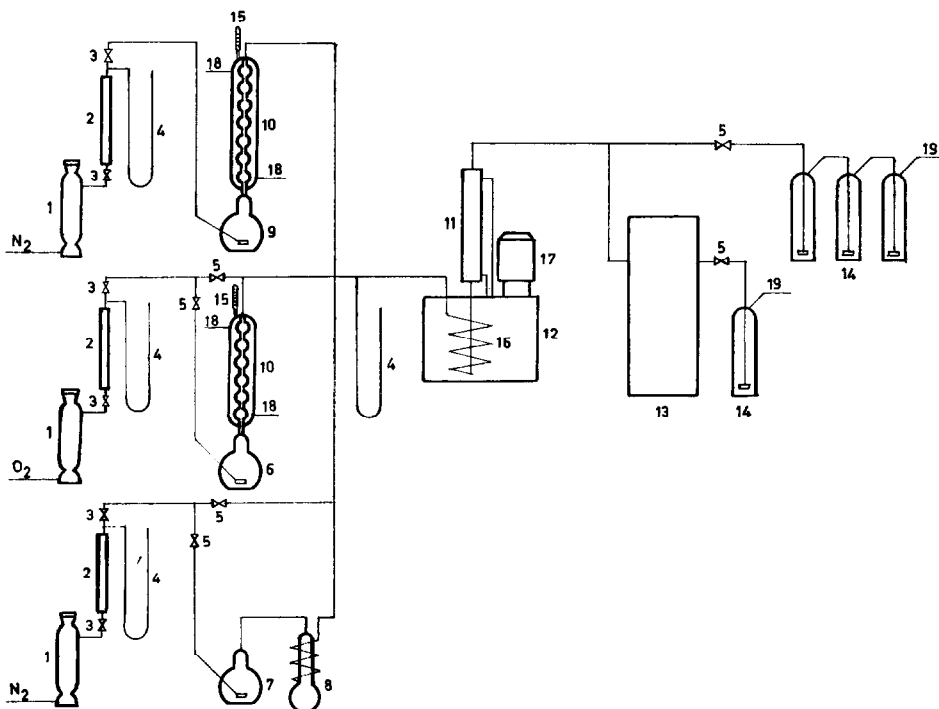


FIG. 1. Schematic view of the flow apparatus: 1, drying towers; 2, rotameters; 3, needle valves; 4, mercury manometers; 5, valves; 6, water saturator; 7, formaldehyde generator; 8, cooled trap; 9, methanol saturator; 10, bulb condensers; 11, reactor (see Fig. 2); 12, thermostat; 13, gas chromatograph; 14, drechsels; 15, thermometers; 16, preheater; 17, oil-circulation pump; 18, thermostating water inlet and exit; 19, to vent.

inner diameter of the reactor was 10 mm, while the outer diameter of the thermocouple well was 4 mm.

The reactor inlet is connected with a preheater placed in the thermostat. The lines from the saturators to the preheater and from the reactor to the chromatograph were electrically heated above 100°C to prevent vapor condensation. The catalyst granules (35–50 mesh) were diluted with glass granules of the same size. Blank runs confirmed that no parts of the equipment contributed to conversion.

The difference between the minimum and the maximum temperature in the catalytic bed during a run was always less than 2°C. The reaction temperature was defined as the mean of the temperatures measured in five equidistant places of the catalytic bed.

After leaving the reactor, the gaseous mixture passes through a Carlo Erba "Fractovap C" gas chromatograph and through some water-containing drechsels, before being vented. The sampling valve of the gas chromatograph and its connections to the katharometer were heated in an air thermostat at 120°C.

C. Pulse Apparatus

We have used an accessory of a Perkin-Elmer gas chromatograph, described by Ettre and Brenner (12). The furnace around the reactor was modified in order to have a constant temperature, within $\pm 1^\circ\text{C}$, over a length of 10 mm. Furthermore a thermocouple well was added to the reactor, to measure the temperature in the catalytic bed. The whole valve system was heated in an air thermostat at 120°C. The other parts of the apparatus were similar to those described for the flow system. The catalyst was used without dilution.

The following experimental conditions were used:

Total pressure	1 atm
Reactant mixture	N ₂ 80%; CH ₃ OH 20%
Pulsed reactant volume	1 cc
Total surface area of the catalyst	3.3 m ²
Flow rate of the carrier gas (He)	3.6 N liters/hr

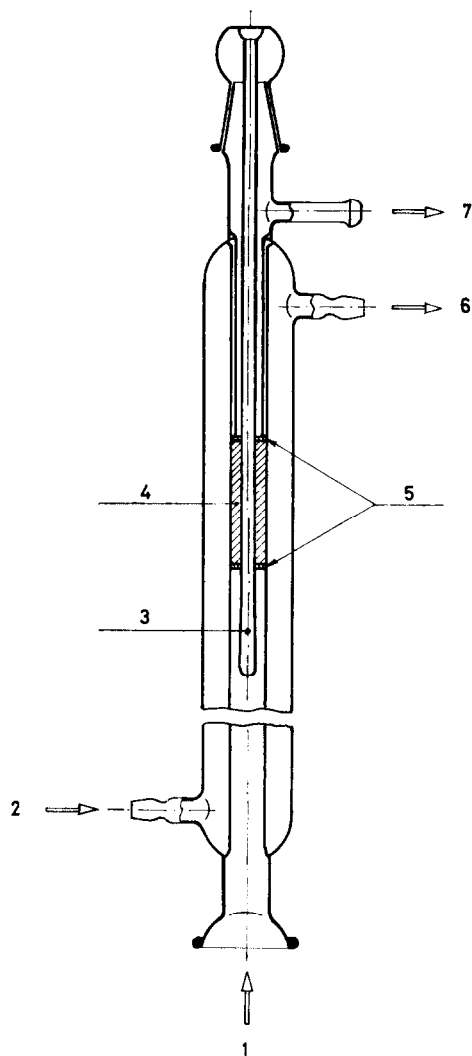


FIG. 2. Schematic view of the reactor: 1, gas inlet; 2, oil inlet; 3, thermocouple well; 4, catalyst; 5, glass wool plugs; 6, oil exit; 7, gas exit.

Oxygen was removed from the carrier gas by passing it over Cu turnings at 450°C.

D. Analysis

In the runs with no formaldehyde in the reactant mixture, the formaldehyde analysis was made using a standardized iodometric method. We have checked that methanol and methylal do not disturb the formaldehyde determination. The precision of the analysis was about 1%. The quantitative determination of all the components of the gaseous mixture leaving the reactor

was made through a gas chromatographic method, using a column of Teflon-supported Carbowax 1500. In the runs with formaldehyde, chromatographic analyses of the gaseous mixture at the reactor inlet were also performed. The precision of the chromatographic analysis was about 5%.

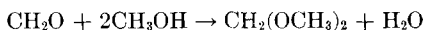
CALCULATION

Flow reactor. The reaction rate was calculated with the general equation

$$F_A dX_A = r_A dW, \quad (1)$$

in which F_A is the flow rate of reactant A; X_A , the conversion of reactant A; r_A , the reaction rate referred to reactant A; W the mass of catalyst.

A correction was made to account for the slight decrease of catalytic activity with time. The volume change of the gaseous mixture during the reaction was neglected, owing to the low conversion levels. It is noteworthy that over the catalyst the reaction also occurs



which is catalyzed by the acid centers on the catalyst surface. Therefore, in order to calculate the true conversion of methanol to formaldehyde from the analytical results, it is necessary to account for the effect of such reaction, especially at lower

temperatures and higher methanol partial pressures.

We have checked that the partial material balance

$$F_W = F_F + 2F_M \quad (2)$$

in which F_W , F_F , F_M are, respectively, the changes of the flow rates of water, formaldehyde, and methylal between the inlet and the exit of the reactor, is satisfactorily fulfilled within the experimental errors. When formaldehyde was added to the reactants, the flow rate of the formaldehyde formed by methanol oxidation was calculated, with a precision of about 10%, from both water and methylal analysis, using Eq. (2), provided water is not added to the reactants.

Pulse reactor. The reaction rate was calculated from Eq. (1), therefore considering the reactor as a differential one. Methanol conversion was obtained from methanol gas-chromatographic analysis both at the inlet and at the exit of the reactor. A correction was made to account for the volume change of the gaseous mixture during the reaction.

The available surface oxygen was in a great excess with respect to the pulsed methanol, as it was shown by calculation. Indeed subsequent pulses gave the same results, within the experimental errors.

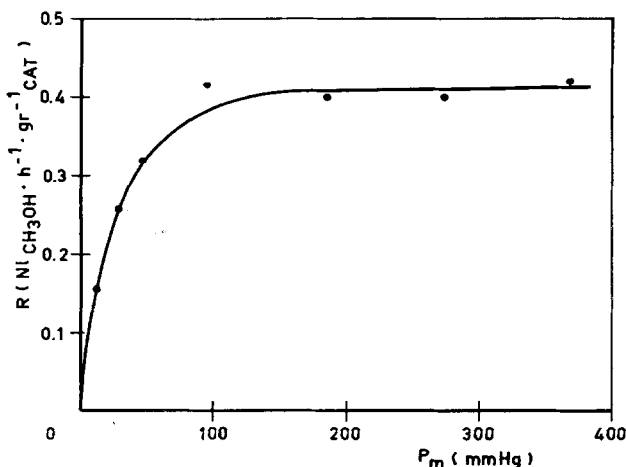


Fig. 3. Reaction rate vs. methanol partial pressure, oxygen partial pressure being constant ($P_O = 180$ mm Hg) and products partial pressures negligible.

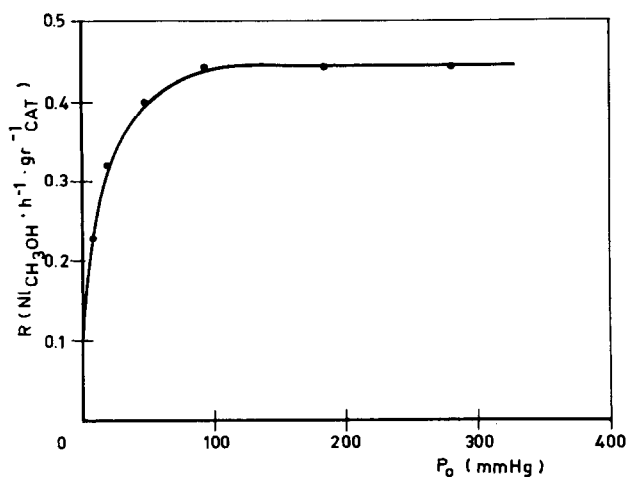


FIG. 4. Reaction rate vs. oxygen partial pressure, methanol partial pressure being constant ($P_M = 180$ mm Hg) and products partial pressures negligible.

RESULTS

The runs with the flow reactor were performed in experimental conditions such as to exclude the influence of the effects of internal and external diffusion. The absence of such effects was experimentally proved through the standard methods (13). The runs were performed within the temperature range 180°–280°C and especially at the temperatures of 180°C, 232°C, and 260°C. The results of the runs performed at 232°C are reported in the following figures; the plots obtained at the two other

temperatures show a quite analogous behavior.

In Fig. 3 the reaction rate R is plotted versus the partial pressure of methanol P_M , the partial pressure of oxygen P_O being constant and the partial pressures of the reaction products negligible. It may be seen that R increases rapidly with P_M till reaching practically a constant value.

In Fig. 4 R is plotted versus P_O , P_M being constant and the partial pressures of the reaction products negligible. It is observed that R increases rapidly with P_O

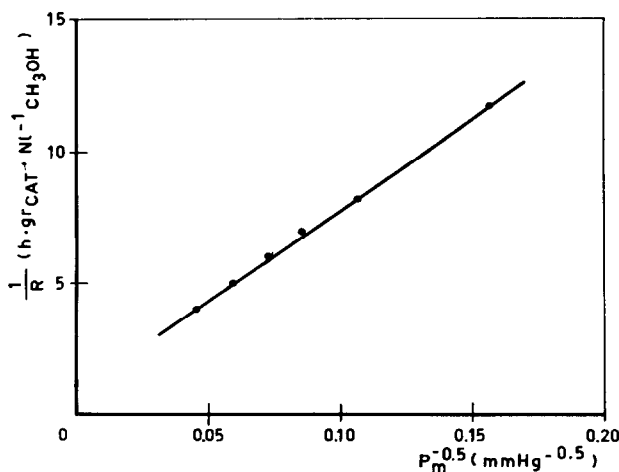


FIG. 5. Reciprocal reaction rate vs. $P_M^{-0.5}$ at high water partial pressure ($P_W = 90$ mm Hg), oxygen partial pressure being constant ($P_O = 180$ mm Hg) and formaldehyde partial pressure negligible.

till reaching practically a constant value.

The effect of water on the reaction rate, P_M and P_O being constant, was previously reported (9); a marked decrease of R is observed with the increasing of P_W .

Also, formaldehyde behaves as inhibitor; indeed a decrease of R was noted with the increase of P_F , but much less than one observes with the increase of P_W .

In Fig. 5 $1/R$ is plotted versus $P_M^{-0.5}$, P_O and P_W being constant and P_F negligible. The P_M values are in the range in which, if P_W is negligible, R is practically independent from P_M (see Fig. 3). It is observed that, in the presence of H_2O , R increases remarkably with increasing P_M , also in the range of the highest P_M values. This behavior is not observed in the case of P_O .

Measurements of reaction rate were also performed in the pulse reactor, feeding only nitrogen and methanol (20%); the values obtained at 232°C were about 5 times

higher than those obtained in similar conditions in the flow reactor in the presence of 20% oxygen. It was also revealed, that under the same conditions, pulses of composition N_2 80%, CH_3OH 20%, gave the same conversion as pulses of composition N_2 60%, CH_3OH 20%, O_2 20%. The whole results obtained with the pulse reactor will be reported later.

Finally, the apparent activation energies E_F (in flow reactor) and E_P (in pulse reactor) were determined for a reactant mixture of standard composition (N_2 70%, O_2 20%, CH_3OH 10% in flow reactor; N_2 80%, CH_3OH 20% in pulse reactor). The obtained values are as follows: $E_F = 22$ kcal/mole, $E_P = 10$ kcal/mole (Fig. 6). It is to be noted that in pulse reactor the values of reaction rate calculated from methanol analysis were always higher, especially at lower temperatures, than those

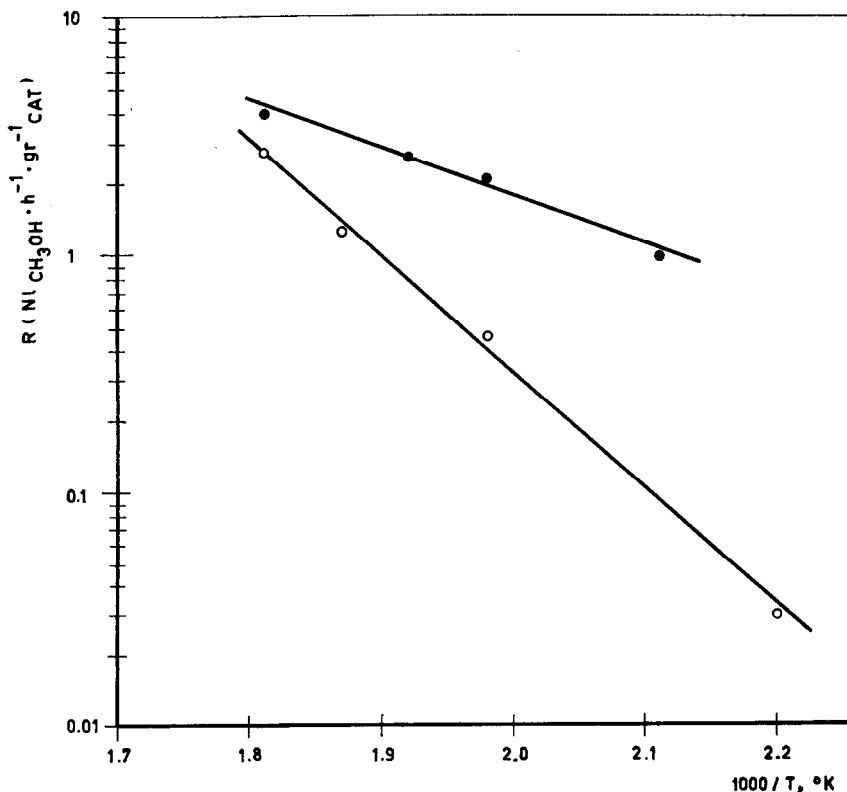


FIG. 6. Arrhenius plots for methanol oxidation in flow and pulse reactors (○, flow reactor; ●, pulse reactor).

calculated from product analysis; the former ones were reported in Fig. 6.

DISCUSSION

In the kinetic studies, carried out by previous authors (4, 6, 7) on MoO₃-Fe₂(MoO₄)₃ mixed catalysts, the experimental results have been explained on the ground of an equation proposed by Mars and van Krevelen (5) for oxidation reactions, in which the lattice oxygen of the catalyst participates. The same kinetic equation has also been used by Bhattacharyya *et al.* (14) to correlate the experimental data of the methanol oxidation on V₂O₅. The Mars-van Krevelen equation may be written as:

$$\frac{1}{R} = \frac{B}{K_2 P_O^m} + \frac{1}{K_1 P_M^n} \quad (3)$$

where B is a stoichiometric coefficient. From Eq. (3) it results that, plotting $1/R$ versus P_M^{-n} , at constant P_O , for various P_O values, and $1/R$ versus P_O^{-m} at constant P_M , for various P_M values, one should obtain two series of parallel straight lines. This is not verified in our experimental data, neither in the range of lower partial pressure of the reactants, as it is seen in Figs. 7 and 8 (straight lines were obtained for $m = n = 0.5$). On the basis of this, and since such equation does not consider the possible influence of the reaction products, we believe that the reaction mechanism, proposed by Jiru *et al.* (4) and by Dente

et al. (6), gives only an approximate description of a more complex phenomenon. However, the basic idea, that the lattice oxygen of the catalyst participates in methanol oxidation, remains valid, as it is supported by the following experimental data:

- (1). The same reaction products are obtained by passing methanol over the catalyst with and without oxygen; indeed, there is a close agreement between the quantity of lattice oxygen and the quantity of gaseous oxygen, used up during the reoxidation (4).
- (2). The reaction rate in the pulse reactor is the same in the presence as well as in the absence of oxygen.

However, in stationary conditions the re-oxidation of the reduced catalyst should be equivalent to an adsorption of oxygen on adsorption centers different from the methanol ones, and therefore the reaction mechanism may also be arranged in the classic manner; i.e.: (1) adsorption of the reactants; (2) surface reaction; (3) desorption of the products.

Therefore, surface lattice oxygen is, in practice, oxygen adsorbed and reduced to O⁻ ion. The possibility to arrange the reaction mechanism in the classic manner, however, does not permit the application of Hougen and Watson's theory (15) for a quantitative treatment of the kinetic data,

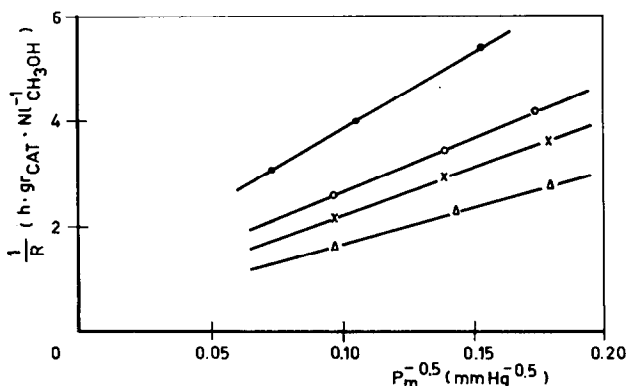


FIG. 7. Plot of the kinetic data, in the range of low methanol partial pressures, according to the Mars-Van Krevelen equation. (●, $P_O = 9$ mm Hg; ○, $P_O = 28$ mm Hg; ×, $P_O = 46$ mm Hg; △, $P_O = 92$ mm Hg; P_W and P_F are negligible).

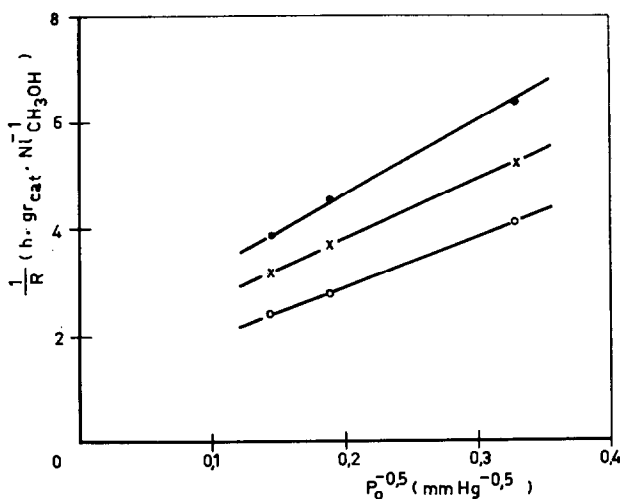


Fig. 8. Plot of the kinetic data, in the range of low oxygen partial pressures, according to the Mars-Van Krevelen equation (●, $P_M = 28$ mm Hg; ×, $P_M = 44$ mm Hg; ○, $P_M = 83$ mm Hg; P_W and P_F are negligible).

because methanol and oxygen are adsorbed on different adsorption centers.

It is, however, possible to discuss our results from a qualitative viewpoint, starting from the mechanism proposed by Batist, Lippens, and Schuit (16) for the oxidation of 1-butene to butadiene on bis-muth molybdate catalysts.

Adsorption of methanol should therefore be a dissociative adsorption on centers constituted by an anionic vacancy and by an $O^=$ ion (however, this does not imply the presence of associated defects).

The dissociative adsorption seems also supported by the fact that in Fig. 5 a straight line for an exponent 0.5 of methanol partial pressure has been obtained. Substantially it would be a matter of a reaction of the acid-base type; the anionic vacancy would have the function of a Lewis acid center, while the $O^=$ ion would behave as a Bronsted basic center. A correlation between surface acidity and catalyst activity has already been reported by us (17).

This statement agrees with the most recent views (18) on reaction mechanisms on acid catalysts, in which not only acid but also basic centers would participate. Therefore, the proposed mechanism corresponds to admitting that the $O^=$ ion is a

stronger Bronsted base than the CH_3O^- ion, which appears to be completely reasonable. In conclusion, a hydroxyl should be formed and an anionic vacancy should be occupied by a methoxyl. Thorough studies on methanol adsorption over MoO_3 and molybdate catalysts have not yet been performed; however, there are infrared data concerning Al_2O_3 (19, 20). It has been shown (19) that methanol is adsorbed on $\gamma-Al_2O_3$ in a dissociative way, for which hydroxyls are formed and methoxyls occupy anionic vacancies.

If we suppose, as is common practice, that there is one rate-determining step in our reaction, we can exclude that it may be methanol adsorption, as in this case (for practically irreversible reactions): (1) one should have a R from P_M dependence also for the highest P_M values (Fig. 3); (2) the reaction rate in pulse reactor should be equal to the one in flow reactor.

After the dissociative adsorption of methanol, the surface reaction should occur by transfer of an H^+ ion from the methoxyl to a near $O^=$ ion, with the formation of a second hydroxyl and electron transfer to the reducible cation (either Mo^{+6} or Fe^{+3}). This is equal to CH_2O formation on a reduced anionic vacancy. It seems that we can exclude that this reaction step is a

determining, because, in this case, the reaction rates, measured in flow and in pulse-reactor, should be equal, and also because one should observe a maximum of the reaction rate versus the partial pressure of the reactants. It may seem unusual that the abstraction of an H⁺ ion from a methoxyl is a fast reaction, but it should be made easier by the transfer of electronic density to the reducible cation. At this point, from the two neighboring hydroxyls, arisen in consequence of the methanol adsorption and of the surface reaction, water can be removed with the formation of a new methanol adsorption center, constituted, as we have already mentioned, by an anionic vacancy and by an O⁼ ion. The hypothesis, previously reported (9), as to the competitive adsorption of water and methanol, is thus justified, if the dehydration reaction is reversible. This reversibility has been proved by IR spectrometry (21). The presence of such a competitive adsorption is also confirmed by the plot reported in Fig. 5. Indeed, owing to the presence of water together with the reactants, the free catalyst surface is no longer saturated by methanol at P_M higher than about 100 mm Hg. Formaldehyde, in turn, is desorbed from the reduced anionic vacancy, which then acts as an oxygen adsorption center (reoxidation of the catalyst). Neither does this reoxidation seem to be the slowest step, as in this case R should depend from P_O also in the range of the highest P_O values (Fig. 4).

Therefore, the slowest step of the reaction should be sought for in the desorption of the products. This would be in agreement (22) with the fact that the reaction rate in pulse reactor is higher than the one in flow reactor and also with the fact that in pulse reactor the reaction rate calculated from methanol analysis is higher than that calculated from products analysis, especially at lower temperatures. However, we must distinguish between dehydration of the hydroxyl groups and formaldehyde desorption from reduced anionic vacancies. Indeed, water is not strongly adsorbed as such on the catalyst (21). We can observe that, if formaldehyde desorption is the

slowest step, in flow reactor in stationary conditions the greatest part of the catalytic surface is occupied by formaldehyde. Therefore, even a remarkable increase of the partial pressure of this product should cause only a slight decrease of R , as has been experimentally verified. Furthermore, if on the free adsorption centers a competitive adsorption occurs between another product (in our case, water) and a reactant (methanol), the negative influence of the partial pressure of this product on R should be rather marked (we must remember that the reduced anionic vacancies, from which formaldehyde would slowly desorb, arise from the anionic vacancies on which methanol is adsorbed). As also this condition is experimentally verified (9), we can conclude that on the ground of our results, if our reaction mechanism is valid, the most probable rate-determining step is formaldehyde desorption.

It must be stressed that the above-mentioned statements as to the slowest step are true only for high partial pressures of reactants and for temperatures not higher than a certain limit. Indeed the behavior of the Arrhenius plots (Fig. 6) suggests that above a certain temperature the slowest step should be the same in both reactors and therefore no longer formaldehyde desorption. Indeed, in no case it is right to foresee a higher reaction rate in flow reactor than in pulse reactor. It is known that desorption rates generally increase very rapidly with the increasing of temperature, and, therefore, a change in the slowest step at higher temperatures seems to be quite reasonable, when, at lower temperatures, it is product desorption. Likewise, at low partial pressures of reactants the reaction order is not zero (Figs. 3 and 4), so that some step other than product desorption becomes rate-controlling; there may be also more than one rate-controlling step.

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