JOURNAL OF CATALYSIS 27, 52–55 (1972)

Pulse Microreactor Study of Methanol Oxidation Over MoO_3–$Fe_2(MoO_4)_3$ Catalyst

G. LIBERTI, N. PERNICONE, AND S. SOATTINI

G. Donegani Research Institute, Montecatini Edison S.p.A., Novara, Italy

Received November 1, 1971

The oxidation of methanol to formaldehyde by the solid phase oxygen of a MoO_3–$Fe_2(MoO_4)_3$ catalyst was studied with a pulse microreactor. Temperature, pulse flow rate and methanol concentration were chosen as independent variables. A defective mass balance always occurred. The kinetic results were explained on the basis of catalyst surface heterogeneity and/or of poisoning by products.

INTRODUCTION

The kinetics of oxidation of methanol to formaldehyde over MoO_3–$Fe_2(MoO_4)_3$ mixed catalyst has already been studied by means of an integral flow reactor (*1, 2*), a differential flow reactor (*3*) and a recycle reactor (*4*). The reaction appeared to be practically of zero order with respect to methanol and oxygen (*3*) and poisoned by products, mainly by water (*5*). We have now carried out a kinetic study of this reaction by means of a pulse microreactor as it was reported that, for zero order reactions, this technique gives information complementary to that obtainable from a continuous flow reactor (*6*). The investigation was restricted to the interaction of methanol with solid phase oxygen, as it was already found (*3*) that the conversion in the pulse reactor is the same both in the presence and in the absence of gaseous oxygen.

EXPERIMENTAL METHODS

The experimental apparatus, by which the pulse flow rate in the reactor could be varied, while keeping constant the carrier gas flow rate in the chromatographic column (1 ml/sec), is described elsewhere (*7*). The catalyst was the same as previously used (*3*). Particle diameter was about 0.4 mm; the amount of catalyst was 0.214 g. (total surface area, 1.6 m^2); the length of the catalytic bed was 3 mm, its cross section, 0.67 cm^2. Chromatographic analysis was carried out by means of a 2-m Carbowax on Teflon column, at 120°C.

Methanol concentration in the input pulse was changed by varying the temperature of a saturator, using nitrogen as diluent gas. The result of each run is the average of 4–5 subsequent pulses: catalyst deactivation was never observed. However, after each run the catalyst was reoxidized in an oxygen stream at 250°C for 2 hr. A correction was made for the volume change of the pulse during the reaction.

The estimated error for the conversion is about ±10% for methanol and water and ±15% for formaldehyde (90% probability level). Reaction rates were calculated assuming differential conditions (*3*), which is justified by the low conversion, usually not greater than 0.3, and by the nearly rectangular shape of the pulse (*8*).

RESULTS AND DISCUSSION

In Fig. 1 the amounts of reacted methanol (calculated as difference between input and output methanol) and of produced formaldehyde are reported versus the pulse flow rate, the methanol concentration in the input pulse and the temperature being constant. The water curve is quite similar to

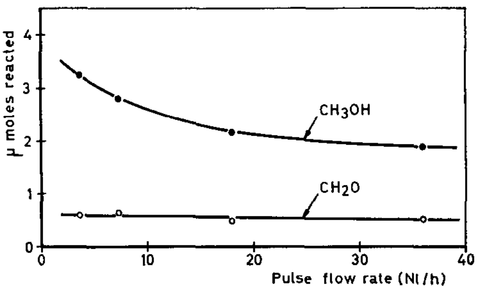

FIG. 1. Amounts of methanol reacted and of formaldehyde produced versus pulse flow rate, at 230°C and 23.5% methanol in the input pulse.

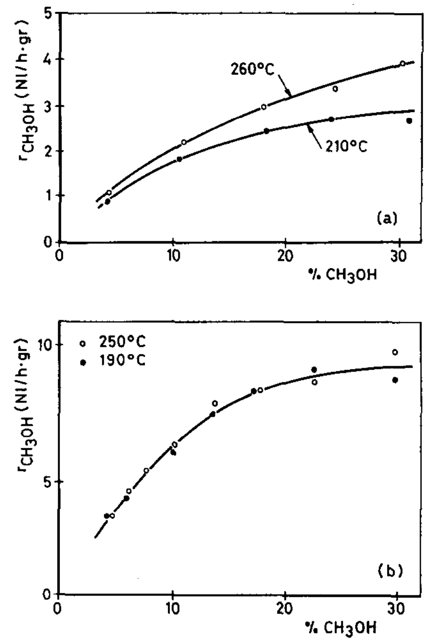

FIG. 2. Reaction rate, relative to methanol disappearance, versus methanol concentration in the input pulse. (a) Pulse flow rate 7.2 nl/hr; (b) pulse flow rate 36 nl/hr.

that of formaldehyde. It may be seen that a strongly defective mass balance occurs (that is, a marked amount of substance remains in the adsorbed phase). The significance of this phenomenon, already found for other reactions also (*6*, *9*, *10*), was previously discussed (*8*). As a result of the mass balance defect, the reaction rate is different if measured as methanol disappearance or as products formation. It is important to point out, from Fig. 1, that by increasing the flow rate, the amounts of reacted methanol and of the products seem to reach a nearly asymptotic value. A similar behavior has been reported for another zero order reaction (*6*). This means that a fixed amount of reactant has time enough for adsorption, surface reaction and desorption to take place even when the contact time is very short (about 20 msec at the highest flow rate). The presence of strong surface heterogeneity and/or poisoning by products could provide an explanation for this behavior, as discussed below.

In Figs. 2, 3 and 4 the reaction rates referred to methanol disappearance and to products formation are reported versus methanol concentration for various temperatures and pulse flow rates. It may be seen that the two products, water and formaldehyde, show a different behavior, especially at higher pulse flow rates; this suggests, in accordance with the continuous flow experiments (*3*), that product desorption is slow. Indeed, a slow surface reaction should give rise to an equal yield of the two reaction products. From the same figures, a marked difference results concerning the variation of the reaction rates with temperature: the corresponding apparent activation energies, at various flow rates, are reported in Table 1. The values pertaining to formaldehyde appearance are the

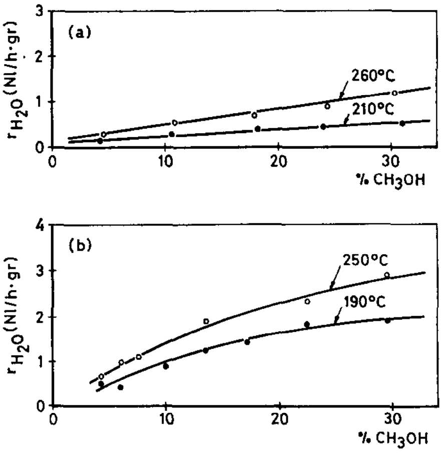

FIG. 3. Reaction rate, relative to water formation, versus methanol concentration in the input pulse. (a) Pulse flow rate 7.2 nl/hr. (b) pulse flow rate 36 nl/hr.

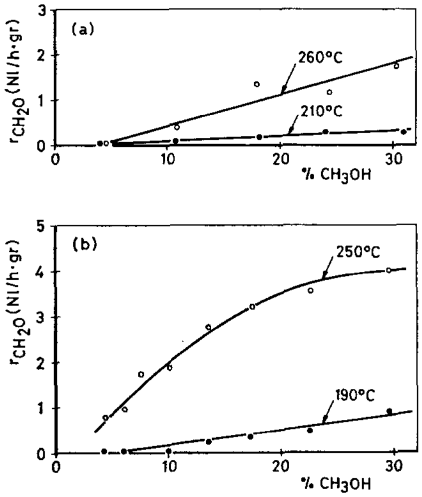

FIG. 4. Reaction rate, relative to formaldehyde formation, versus methanol concentration in the input pulse. (a) Pulse flow rate 7.2 nl/hr; (b) pulse flow rate 36 nl/hr.

highest; therefore the desorption of formaldehyde seems to be favored as the rate—determining step, in accordance with the continuous-flow reactor results (*3*). Although the activation energies for products do not appreciably depend on the pulse flow rate, in the case of methanol a strong dependence exists; at high flow rates methanol adsorption is practically nonactivated. This behavior excludes the presence of diffusion phenomena (in which case it should be the reverse) and can be explained assuming the clean surface of the catalyst to be inhomogeneous with respect to adsorption and/or to poisoning by products. In this respect, it is interesting to report the results obtained with pure iron molybdate (prepared by heating the mixed catalyst at 700°C for more than 1 week up to complete MoO_3 sublimation): it is as active as the mixed catalyst in pulse conditions but practically inactive in the continuous-flow reactor, these latter tests being made as previously described (*3*) for the mixed catalyst.

TABLE 1

APPARENT ACTIVATION ENERGIES (kcal/mole)

Nl/hr	CH_3OH	H_2O	CH_2O
3.6	10	10	15
7.2	5	10	16.5
36.0	0	7	19.5

This fact can be explained by supposing that in these catalysts there are fast reacting centers which are not operating in continuous flow conditions either because they are difficult to reoxidize or owing to poisoning by products or by surface intermediate species. This assumption would also explain the flow rate independent behavior of formaldehyde yield (Fig. 1). On the mixed catalyst less active centers would also be present by which the reaction is carried on in continuous flow conditions. They could be connected with the iron-defective structure typical of the mixed catalyst (*11*).

The existence of oxidation centers of different activity could be connected with the presence of two reducible cations (Fe^{3+}; Mo^{6+}) (*12*). However, in stationary conditions, the prevailing role of Mo^{6+} ions in methanol oxidation now seems to be definitively established (*13*, *14*).

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