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The Kinetics of Methanol Oxidation on a Supported Silver Catalyst

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The oxidation of methanol to formaldehyde on silver catalysts was studied at about 420°C and atmospheric pressure in a fixed-bed differential reactor. The reaction was zero order to oxygen except at very low pressures, slightly less than first order to methanol, and inhibited by the reaction products. The data can be fitted by the following equation, which is based on competitive adsorption of methanol and products on sites formed by reversible chemisorption of oxygen on the silver and reaction of adsorbed methanol with underlying oxygen atoms:

$$r = \left(\frac{kK_mP_m}{1 + K_mP_m + K_pP_p}\right)\left(\frac{K_oP_o^{1/2}}{1 + K_oP_o^{1/2}}\right).$$

NOMENCLATURE

k	Rate constant
K	Equilibrium constant atm^{-1}
P	Partial pressure (atm)
R_T	Total relative rate of methanol conversion
X_T	Total conversion of methanol to CO_2 and CH_2O
Selectivity	Methanol converted to CH_2O/total methanol converted
θ	Time variable in Eq. (4)

Subscripts

av	Average
c	Carbon dioxide
f	Formaldehyde
m	Methanol
o	Oxygen
p	Products
w	Water

INTRODUCTION

The commercial process for the air oxidation of methanol to formaldehyde using silver catalysts generally operates at 500–600°C, with a thin layer of catalyst pellets supported between layers of silver screen. Excess methanol is used, and the oxygen is almost completely converted, giving methanol conversions of 30 to 80% and selectivities of 95 to 80%. The major byproduct is carbon dioxide, but carbon monoxide, hydrogen, formic acid, and methylal are also formed.

Laboratory studies of methanol oxidation have been made by several Russian workers (*1–3*), but mass transfer limitations, temperature gradients, and high conversions made it difficult to determine the kinetics. Integral reactor data indicated a transition from the kinetic region to the diffusion-controlled region at about 350°C.

Recently Bhattacharyya, Nag and Ganguly (*4*) carried out a differential reactor study of methanol oxidation at relatively low temperatures (264–290°C), where mass transfer effects were negligible. They found fractional reaction orders for both methanol and oxygen, and they proposed a steady-state adsorption model with the rate of oxygen adsorption equal to the rate of oxygen removal by reaction with methanol from the gas phase. Water added to the feed inhibited the reaction, but the data do not fit simple competitive adsorption models. Only 65% of the methanol reacting was converted to formaldehyde, a lower selectivity than for the commercial process.

In this work, the oxidation of methanol was studied at an intermediate temperature of 420°C using silver supported on a porous alumina. The size of the support, the silver content of the catalyst, and the reactor dimensions were made small enough to eliminate mass and heat transfer effects and permit a study of the intrinsic kinetics.

Apparatus and Procedure

The reactor was a glass U-tube 9.0 mm i.d. containing a glass thermowell 6.0 mm o.d. with a movable thermocouple. Catalyst particles diluted 20:1 with extra particles of alumina were packed in the 1.5 mm annulus between plugs of glass wool. The bed height was 1.2–4 cm. The reactor was immersed in a stirred molten-salt bath, and the empty arm of the U-tube served as a preheater. Tests with pure helium indicated that the gas temperature in the bed was essentially the same as the bath temperature. Oxygen and helium were fed to the reactor after passing through capillary flowmeters. A separate helium stream was passed through a saturator in a temperature bath to carry methanol vapor to the reactor. The exit gases flowed to a Hewlett-Packard Model 700 chromatograph for analysis of carbon dioxide, formaldehyde, and methanol following the method of Onuska and co-workers (*5*).

The catalyst was prepared by impregnating 20–28 mesh particles of Alcoa T-71 alumina with an aqueous solution of silver-ammonia complex followed by reduction to metallic silver with formaldehyde. The catalyst had 1.25 wt% silver, and electron micrographs showed an average crystallite size of about 55 Å. Some of this catalyst was crushed to 65–100 mesh, and most of the data were obtained with the fine particles. A few tests were also made with a catalyst containing 27% silver on silica. The alumina itself had a negligible catalytic effect on the reaction.

Because of changes in catalyst activity with time, nearly every other run was made at standard conditions, and the measured rate for a kinetic run was divided by the average rate for the standard runs which bracketed it. The result is a relative rate which can be compared to relative rates for other runs to test kinetic models. The correction procedure is similar to that used in previous studies of silver catalysts (*6*, *7*), although no attempt was made to correct the standard rates to the same conversion, since product inhibition effects were relatively small in this study. Conditions for the standard runs were: partial pressure of methanol in feed, 0.011 atm; partial pressure of oxygen in feed, 0.016 atm; total reactor pressure, 1.12 atm; reactor temp, 422°C; feed gas flow rate, 500 cc/min @ 1.72 atm, 25°C; wt of active catalyst, 0.050 g.

Results

Activity Changes

The activity of the fine catalyst decreased severalfold during the test period, which comprised about 50 hr of exposure to reacting gases and 400 hr total exposure to reaction temperature in a helium atmosphere. The conversion for standard runs ranged from 30 to 6%. However the gradual decline in activity was interrupted by short-term fluctuations which depended on the feed conditions. When the methanol to oxygen ratio was high for kinetic runs, the next standard run showed an increase in activity over the previous value, whereas high oxygen concentrations led to a larger than average decrease in standard activity. The activity for the majority of successive standard runs varied by less than 15%. Similar behavior has been reported by Wu (*8*) and Czanderna (*9*). The selectivity also varied with catalyst age, increasing from 75 to 80% at the start to nearly 100%.

The overall change in activity with age was at least partly due to sintering. At the end of the kinetic tests, the fine catalyst had silver crystallites about 120 Å in diameter, twice the initial size. The larger silver particles might also have had a lower activity per unit area, as was found by Wu (*8*) for ethylene oxidation. The catalyst particles removed from the reactor were discolored, which suggests poisoning by impurities in the feed or by carbonaceous by-products.

The short-term changes in activity with gas composition have been attributed to roughening or smoothing of the surface (*9*). The mobility of silver atoms may be enhanced by the presence of oxygen, which in view of the data suggests that the level of activity decreases with increased silver atom mobility.

Kinetic Tests

The effect of oxygen partial pressure on the relative total rate of methanol oxidation is shown in Fig. 1. The rate was essentially constant over a 10-fold range of oxygen pressures. About the same results were obtained in a few tests with the coarse catalyst. The rate must eventually fall with decreasing oxygen concentration if only because of diffusion limitations. The departure from zero-order behavior seems to occur at an oxygen partial pressure of about 0.01 atm.

The relative oxidation rates, taken from Fig. 1, are plotted against average methanol pressure in Fig. 2. The shape of the curve shows a less than first-order dependence of R_T on P_m, and over the range of pressures studied, the reaction is about 0.8 order with respect to methanol. Although the conversions for a few runs were 20–30%, higher than desirable for a differential reactor, little error is introduced in using average pressures if the reactant order is 1.0 or less and product inhibition is slight. The effect of conversion on average rate was studied by varying the flow rate, and Fig. 3A shows little effect in the range 5–25% conversion. Similar tests for the coarse catalyst were carried to higher conversions, and Fig. 4A shows that the average rate drops more rapidly with conversion than for a first-order reaction. Since the initial rate data showed that the reaction is fractional order to methanol and zero order to oxygen, the more rapid decrease must be due to inhibition by the reaction products.

Selectivity

The tests at different flow rates gave nearly constant selectivity at low conver-

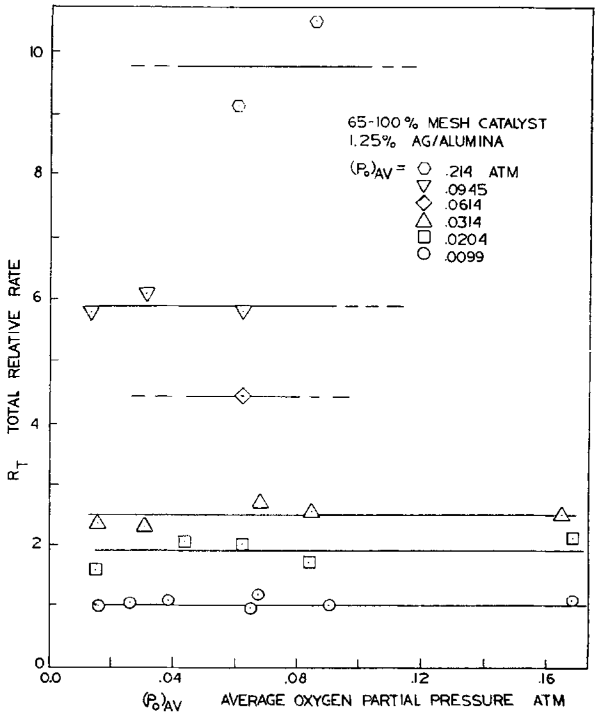

FIG. 1. Effect of average oxygen partial pressure on relative rate.

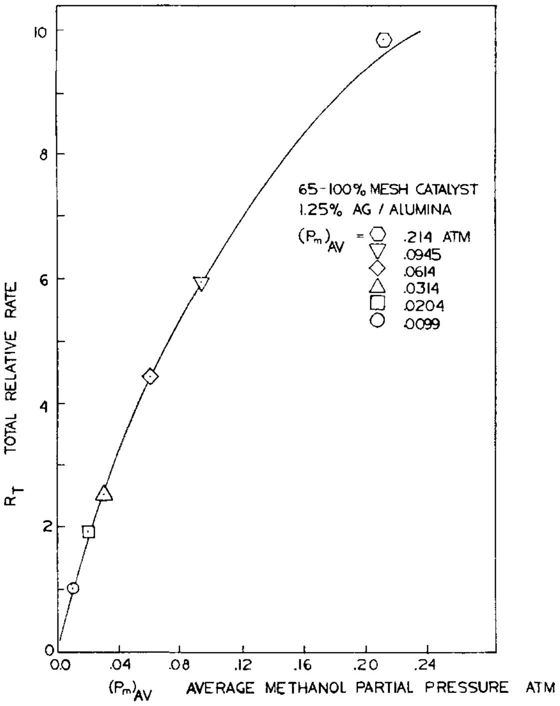

FIG. 2. Effect of average methanol partial pressure on relative rate.

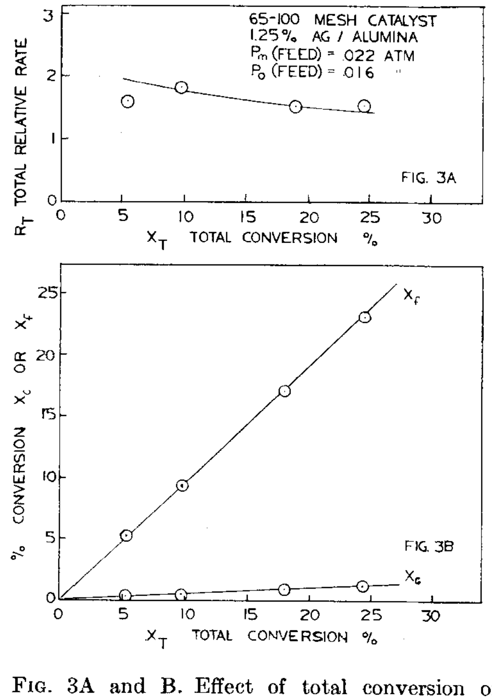

FIG. 3A and B. Effect of total conversion of relative rate and selectivity.

sions, as shown by the straight lines for conversion to formaldehyde or to carbon dioxide in Fig. 3B. This indicates formation of carbon dioxide directly from methanol by a reaction parallel to the main reaction. With the coarse catalyst, the data were extended to higher conversions, and the selectivity decreased significantly in the range 30–70% conversion, indicating oxidation of the formaldehyde. Relative rate constants for the parallel and consecutive reactions can be obtained by assuming all the reactions to be first order and fitting the data in Fig. 4B:

$$M \xrightarrow{a} F \xrightarrow{c} CO_2$$

$$M \xrightarrow{b} CO_2,$$

$$k_a = 7.6,$$

$$k_b = 1.0,$$

$$k_c = 3.5,$$

The data in Fig. 3B indicate a higher ratio of k_a/k_b for the fine catalyst, but this is probably an age effect rather than a particle

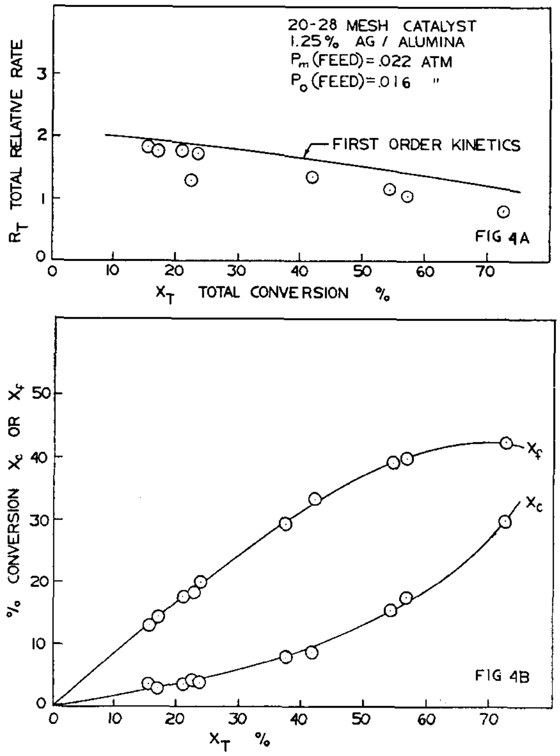

FIG. 4A and B. Effect of total conversion of relative rate and selectivity.

size or diffusion effect. The selectivity for both coarse and fine catalysts increased with age, and the data in Fig. 3 were taken after several days at reaction temperature, whereas Fig. 4 is for nearly fresh catalyst. Further evidence that sintering affects selectivity came from tests of the 27% silver catalyst, which was presintered at 620°C to produce silver particles 500 Å in size. This catalyst gave a selectivity of 90% after 1 day under reaction conditions, compared to values of 75–80% for the other catalysts.

Mass Transfer

The effectiveness factor could not be determined by a direct comparison of the rates with coarse and fine catalyst because of the change in catalyst activity. The constant rate over a range of oxygen pressures for both catalyst sizes is evidence against a diffusion limitation, since a zero-order reaction becomes 1/2 order when pore diffusion becomes important. Also, pore diffusion calculations based on a tortuosity of 2.0 and diffusion of methanol indicated minimum effectiveness factors of 1.0 and 0.96 for the fine and coarse catalysts, respectively. The external mass transfer resistance was negligible for all runs.

A few runs were made at temperatures between 378 and 457°C without any intervening check runs. The apparent activation energy was 27 kcal/mole, about 20% higher than the values reported by previous workers for the kinetic region (*1*, *3*).

KINETIC MODELS

Several kinetic models can be postulated based on the chemisorption behavior of silver and silver oxide. It is generally assumed that oxygen is strongly adsorbed on silver, while methanol and the products are not significantly adsorbed on silver, although they may be adsorbed on top of a layer of adsorbed oxygen. Methanol may react directly from the gas phase with an adsorbed oxygen species or it may actually adsorb on the oxygen layer and then react. Assuming that the various oxidation processes involved all have nearly the same functional dependence on P_m, P_o, P_p, the expression for the total relative rate takes the form:

$$R_T = k\phi(P_m, P_o, P_p). \qquad (1)$$

Based on the data of this study the kinetic model must allow for almost zero-order dependence on oxygen, less than first-order dependence on methanol, and inhibition by the products. The first requirement is satisfied by assuming dissociative reversible adsorption of oxygen on the surface with a large adsorption constant. Except at very low pressures, the fraction of the available sites covered by oxygen will approach unity. The second requirement is met by assuming that methanol adsorbs on the oxygen layer and reacts with the underlying oxygen. Models based on competitive adsorption of both reactants on the same sites are ruled out, since negative reaction orders were not observed. A simple model that meets the above requirements is based on equilibrium formation of an adsorbed oxygen layer (O·S) and partial coverage of these (O·S) sites by methanol and products. The presence of methanol and products on top of the oxygen layer is assumed to have no effect on desorption of oxygen. The steps of the sequence are:

$$O_2 + 2S \underset{-1}{\overset{1}{\rightleftharpoons}} 2(O{\cdot}S),$$

$$M + (O{\cdot}S) \underset{-2}{\overset{2}{\rightleftharpoons}} M{\cdot}(O{\cdot}S),$$

$$M{\cdot}(O{\cdot}S) \overset{3}{\rightarrow} P + S,$$

$$P + (O{\cdot}S) \underset{-4}{\rightleftharpoons} P{\cdot}(O{\cdot}S).$$

Assuming the rate controlling step is the surface reaction the rate expression is

$$R_T = \left(\frac{k_3K_mP_m}{1 + K_mP_m + K_pP_p}\right)\left(\frac{K_oP_o^{1/2}}{1 + K_oP_o^{1/2}}\right), \qquad (2)$$

where $K_o = k_1/k_{-1}$,
$K_m = k_2/k_{-2}$,
$K_p = k_4/k_{-4}$.

If the oxygen adsorption constant is large, then the rate expression simplifies to

$$R_T = \frac{k_3K_mP_m}{1 + K_mP_m + K_pP_p}. \qquad (3)$$

This rate expression allows for a variable fractional order with respect to methanol and takes into account the effect of product inhibition. Water is assumed to be the inhibiting product. In order to obtain the constants in the rate expression the integrated form of Eq. (3) is fitted to the data in Fig. 4.

$$k_3K_m\theta = (K_pP_{m_1} + 1)\ln 1/(1 - X_T) + (K_m - K_p)P_{m_1}X_T. \qquad (4)$$

The constants are $K_m = 4.4$ atm^{-1}, $K_p = 53.5$ atm^{-1}, and $k_3K_m = 107.5$ atm^{-1}. These constants also fit the initial rate data for different methanol pressures as shown by the predicted curves in Fig. 5. It should be emphasized that possible sintering, fouling, or absolute conversion level have no effect on the rate expressions since relative rates are used.

The apparent reaction orders and the model presented above differ from those given by Bhattacharyya, Nag, and Ganguly (*4*). In their study at 264–290°C, the overall reaction was about 0.4 order to oxygen and nearly zero order to methanol above $P_m = 0.04$ atm. They assumed reaction between adsorbed oxygen and gas phase methanol and developed the following rate expression.

$$r = \frac{2k_ok_mP_mP_o^{1/2}}{k_mP_m + 2k_oP_o^{1/2}}. \qquad (5)$$

Equation (5) indicates that the reaction would be first order to methanol if it was zero order to oxygen, which does not agree with the present results at 420°C. The data of this study are best correlated assuming reaction of adsorbed methanol, and the adsorption coefficient $K_m = 4.4$ atm^{-1} at 420°C corresponds to 50% coverage of the oxide sites at $P_m = 0.23$ atm. The value of K_m would be much greater at 264°C, and the zero-order behavior at $P_m > 0.04$ atm is consistent with the model and data of this study. Although both models can fit

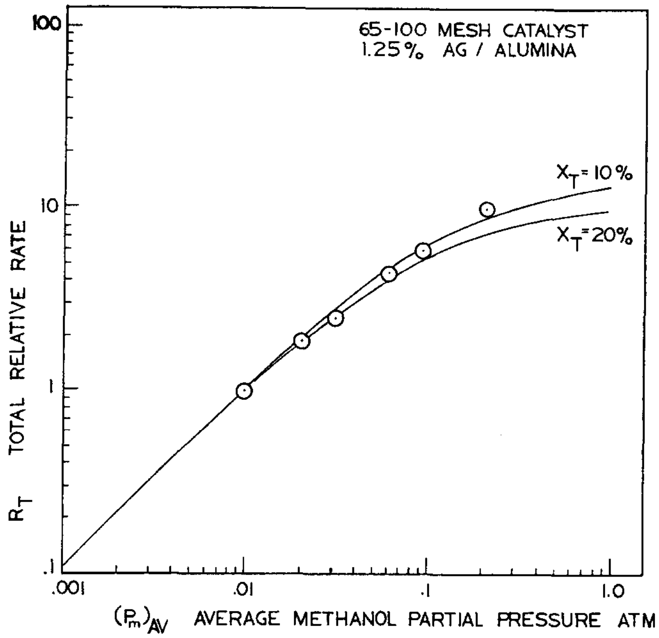

FIG. 5. Predicted curves of model II for the effect of average methanol partial pressure on relative rate.

zero-order data, it is interesting that the Eley–Rideal model, Eq. (5), predicts that the surface is almost bare when the rate is independent of methanol pressure, and the rate of oxygen adsorption is then controlling. The Langmuir–Hinshelwood model, Eq. (2), predicts that all the oxide sites are covered with methanol in the zero-order region, and the number of such sites depends on oxygen pressure. Perhaps transient adsorption tests or tests with isotopes could be used to measure the amount of adsorbed species and discriminate more clearly between the models.

Although Eq. (2) can be fitted to the data of both studies, the effect of oxygen pressure at 264°C is greater than predicted for equilibrium adsorption. Chemisorption studies have shown that silver adsorbs about half a monolayer of oxygen extremely rapidly at low pressures, and further activated adsorption leads to equilibrium coverage of about a monolayer at 2 Torr and 200°C (*10*, *11*) and about 20% less at 275°C. About 30% more oxygen is adsorbed as the pressure is increased from 2 to 20 Torr and another 20% on going to 150 Torr. The 2-fold increase in methanol oxidation rate for a 6-fold increase in oxygen pressure (*4*) therefore indicates less than equilibrium oxygen coverage. However, this does not prove that oxygen adsorption controls, since the equilibrium amount adsorbed decreases for temperatures above 180°C, and desorption at 264–290°C is fairly rapid. A model consistent with both the moderate and the high temperature data could be developed by setting the rate of oxygen adsorption equal to the sum of the rates of desorption and removal by reaction with adsorbed methanol. At higher temperatures the amount of oxygen adsorbed under reaction conditions is closer to the equilibrium value, and the effect of oxygen is smaller.

The reaction to produce formaldehyde is believed to involve strongly bound atomic oxygen, since the reaction at 420°C is independent of oxygen pressure in a range where the total equilibrium adsorption is increasing. This increase comes mainly from activated adsorption of molecular and perhaps additional atomic oxygen, which are less strongly held than the first half monolayer. The reaction to produce carbon dioxide from methanol may involve adsorbed molecular oxygen. The data of this study showed an increase in selectivity as the oxygen pressure was decreased, or the methanol pressure increased. This suggests competitive adsorption of oxygen and methanol on the oxide sites. The fact that the selectivity was higher at 420°C than at 260°C is also consistent with this hypothesis, since the amount of molecular oxygen adsorbed should decrease more rapidly with increasing temperature than the total amount adsorbed.

REFERENCES

1. Gavrilin, V. N., and Popov, B. I., *Kinet. Catal.* (*USSR*) **6**, 799 (1965).
2. Vitvitskii, A. I., and Mukhlenov, I. P., *J. Appl. Chem. USSR* **39**, 1056 (1966).
3. Obraztsov, A. E., Popov, B. I., Shashalevich, M. P., Taraban, L. P., Pronina, E. A., and Shevchenko, A. G., *Kinet. Catal.* (*USSR*) **12**, 970 (1971).
4. Bhattacharyya, S. K., Nag, N. K., and Ganguly, N. D., *J. Catal.* **23**, 158 (1971).
5. Onuska, F., Janak, J., Duras, S., and Kremarova, M., *J. Chromatogr.* **40**, 209 (1969).
6. Klugherz, P. D., and Harriott, P., *AIChE J.* **17**, 856 (1971).
7. Metcalf, P. L., and Harriott, P., *Ind. Eng. Chem. Process Des. Develop.* **11**, 478 (1972).
8. Wu, J., PhD thesis, Cornell Univ., Ithaca, NY, 1973.
9. Czanderna, A. W., *J. Phys. Chem.* **70**, 2120 (1966).
10. Czanderna, A. W., *in* "Ultra Micro Weight Determination in Controlled Environments" (S. P. Wolsky, Ed.), p. 389. Wiley, New York, 1969.
11. Kilty, P. A., Rol, N. C., and Sachtler, W. M. H., *Int. Congr. Catal., 5th* (Miami, FL) No. 67 (1972)