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Kinetics of Vapor-Phase Oxidation of Methyl Alcohol on Vanadium Pentoxide–Molybdenum Trioxide Catalyst

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The vapor phase catalytic air oxidation of methanol to formaldehyde over vanadium pentoxide-molybdenum trioxide was investigated between 250 and 530°C at atmospheric pressure. By using gas chromatographic technique, accurate analysis of the products were obtained, and the effects of several process variables on the conversion of methanol and the selectivity of the catalyst for formaldehyde formation were determined. The maximum yield of formaldehyde (100% selectivity) and more than 99% conversion were achieved at 466°C for a W/F ratio of 31.7 g h/mole, containing 8% methanol in the feed.

The rate expression,

$$r = [k_1 p_M / 1 + (k_1 p_M / 2k_2 p_{O_2}{}^{0.5})],$$

deduced assuming a steady state involving a two-stage irreversible oxidation–reduction process represented the data very satisfactorily.

INTRODUCTION

Formaldehyde is commercially manufactured by the partial oxidation of methanol using either a silver catalyst or a mixture of oxides. While the silver catalysts employ a rich mixture of methanol–air at low conversion, oxide catalysts employ a lean methanol–air mixture and have the advantage of higher rates and higher selectivities.

Most of the patent literature, since 1955, has been devoted chiefly to the improvements in the method of preparation of the iron–molybdenum-oxide-based catalysts. Recently the kinetics of methanol oxidation over oxides of iron and molybdenum, have been reported by Boreskov (*1*), Jiru *et al.* (*2*, *3*), and Dente (*4*). Bliznakov *et al.* (*5*) and Mann and Hahn (*6*, *7*) studied the oxidation of methanol over oxides of molybdenum and manganese. Bhattacharya *et al.* (*7*) investigated the kinetics of methanol oxidation at low conversions using V_2O_5 catalyst between 246 and 281°C and deduced a rate equation based on a two-stage redox mechanism.

Tarama *et al.* (*8*) studied the structure of the catalysts of V_2O_5–MoO_3 and V_2O_5–K_2SO_4 systems, by X-ray, infrared, ESR, and magnetic susceptibility measurements, and found that both MoO_3 and K_2SO_4 had promotional action on V_2O_5 for oxidation reaction. In 1968, Kurina *et al.* (*9*) patented the preparation of V_2O_5–MoO_3 catalysts. However, no information is available as yet regarding the kinetics of the reaction.

Recently we studied the oxidation of methanol over a vanadium pentoxide–molybdenum trioxide catalyst under fairly wide range of operating conditions. This paper reports the affect of a number of variables on the conversion of methanol to formaldehyde in the presence of the catalyst and a rate expression which might be used effectively for industrial reactor design.

EXPERIMENTAL

Apparatus

The air oxidation of methanol to formaldehyde was investigated in a flow system. The equipment was constructed of 316 stainless steel and was similar to that used by Mann and Hahn (*6*) with modification in the feed system.

The experimental apparatus is shown schematically in Fig. 1. The methanol feed system consisted of an infusion syringe pump and a Hamilton hot inlet. Methanol was introduced at a constant flow rate into the hot inlet by the syringe driven by motorized infusion pump. Methanol vapors from the Hamilton hot inlet were then carried away by an incoming hot air stream and the air–methanol mixture was led to the reactor through a preheating section. The flow rate of methanol was kept constant and various methanol:air ratios were obtained by adjusting the air flow rate.

All the experimental runs were taken under steady-state conditions. For this purpose, a stream of reactants was passed over the catalyst at the required temperature for 1 hr. The reaction products passed through a liquid trap where the heavier products, formaldehyde, water, and unused methanol, condensed. The lighter gaseous products, carbon dioxide, carbon monoxide, unreacted oxygen, and nitrogen passed through a sampling valve, connected to Model 25 Fisher gas partitioner and vented. The gaseous products were analyzed intermittently.

Preparation and Physical Characteristics of the Catalyst

A paste obtained by wet mixing of ammonium molybdate and ammonium meta vanadate in water, in the required proportions, was subjected to 12 hr drying at 40°C and 6 hr at 150°C. The temperature of the dried paste was increased stepwise and maintained successively for 2 hr at 200, 300, and 400°C. The catalyst was calcined at 500°C for 6 hr and activated at 600°C. MoO_3 and V_2O_5 were prepared by the thermal decomposition of ammonium molybdate and ammonium meta vanadate, respectively, and activated in a manner similar to that of the oxides.

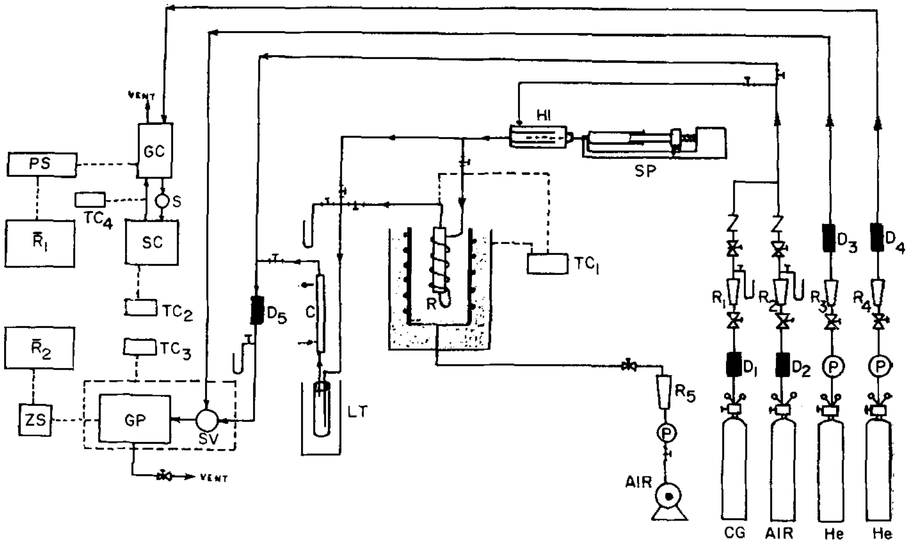

FIG. 1. Schematic diagram of apparatus. c = Water condenser; CG = calibrating gas; D_1, D_2, D_3, D_4, D_5 = drying tubes; GC = Gow Mac cell; GP = gas partitioner; HI = hot inlet; LT = liquid trap; P = pressure regulator; PS = power supply unit; R = reactor; R_1, R_2, R_3, R_4, R_5 = rotameters; $\bar{R}_1$, $\bar{R}_2$ = chart recorders; S = sample injection block; SC = separating column; SP = syringe pump; SV = sample valve; TC_1, TC_2, TC_3, TC_4 = temperature controllers; ZS = zero suppressor.

A 40–60 mesh size of the catalyst (20% V_2O_5, 80% MoO_3) was used. The surface area of the catalyst as determined by BET method using N_2 was 3.87 m^2/g. The catalyst was activated by passing air over it for 8 hr before any experimental run was made.

Analytical Procedure

The analytical procedure was similar to the one described by Mann and Hahn (*6*) except for minor modifications. A 6 ft long HMPA (hexamethylphosphoramide) column followed by a 1 ft long column containing 30% DEHS [di(2-ethylhexyl)sebacate] coated on Celite diatomaceous silica and a 7 ft long 5A molecular sieve column followed by a 5 ft long uncoated Celite diatomaceous silica column connected in series were used.

RESULTS AND DISCUSSION

Experimental data was obtained by means of a quasiisothermal fixed-bed reactor. The steady state was not only realized from the operating conditions but also from the product analysis. The effect of various variables, namely, methanol:air ratio in the feed mixture, $\bar{R}$, reaction temperature, T, and the ratio of the catalyst weight to the methanol feed rate, W/F, on the conversion, X, selectivity, S, of the catalyst for formaldehyde formation and the yield of the formaldehyde, Y, were investigated.

While the conversion, X, is referred to as the ratio of moles of methanol reacted per hour, to the moles of methanol feed per hour, the rate of formation is referred as the moles of various products formed per gram of catalyst. The ratio of the moles of formaldehyde to the sum of the moles of formaldehyde and carbon oxides formed has been defined as selectivity. The yield is based upon the moles of formaldehyde formed per mole of methanol fed.

The activity of the catalyst remained fairly constant during the course of the investigation. No reaction between methanol and air was observed to take place in the absence of the catalyst, even after 3 hr at 460°C.

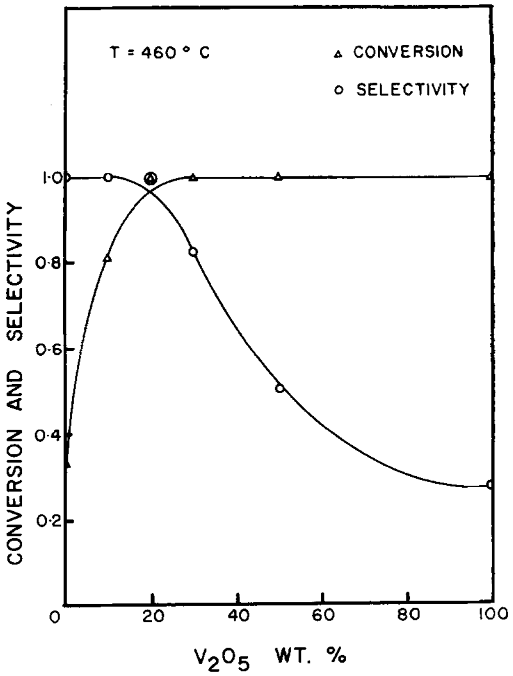

FIG. 2. Effect of catalyst composition on conversion and selectivity at 460°C.

Effect of Catalyst Composition

Figures 2 and 3 show the effects of catalyst composition on the conversion and selectivity at 460°C, and on the yield of

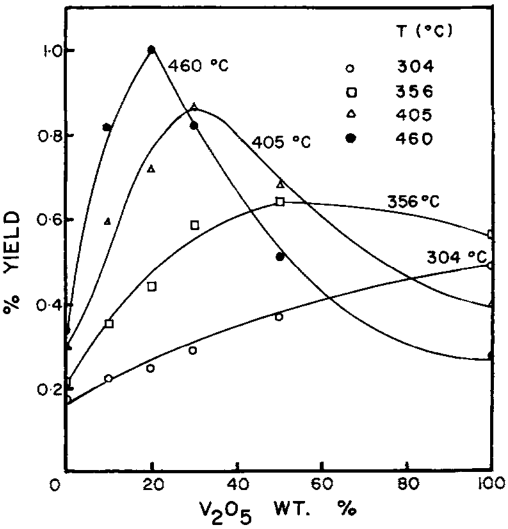

FIG. 3. Effect of catalyst composition on yield of formaldehyde.

formaldehyde between 304 and 460°C. The W/F ratio and percentage of methanol in air were kept at 27.5 g hr/mole and 8.0, respectively. The catalyst containing 20% V_2O_5 and 80% MoO_3 was found to give best results, and hence used for detailed kinetic study of the reaction and evaluation of a rate expression.

Effect of Temperature

Figure 4 shows the effect of temperature on conversion and selectivity of the catalyst (20% V_2O_5–80% MoO_3) in the temperature range 375–531°C, and a W/F ratio of 31.7 for a 8% methanol in air. While the conversion of methanol increased with increasing temperature up to 466°C, the selectivity of the catalyst remained fairly constant at 100%. At temperatures higher than 466°C, the conversion of methanol remained at 100%, but the yield of formaldehyde decreased due to its further oxidation.

Effect of Methanol to Air Ratio

Figure 5 shows the effect of methanol to air ratio on conversion and selectivity at a temperature of 466°C and a W/F ratio of 31.7 g hr/mole. The conversion of methanol increased with increased percentage of methanol in air in the feed at all temperatures. However, the selectivity of the catalyst for formaldehyde formation decreased below 100% for methanol/air ratios greater than 8.

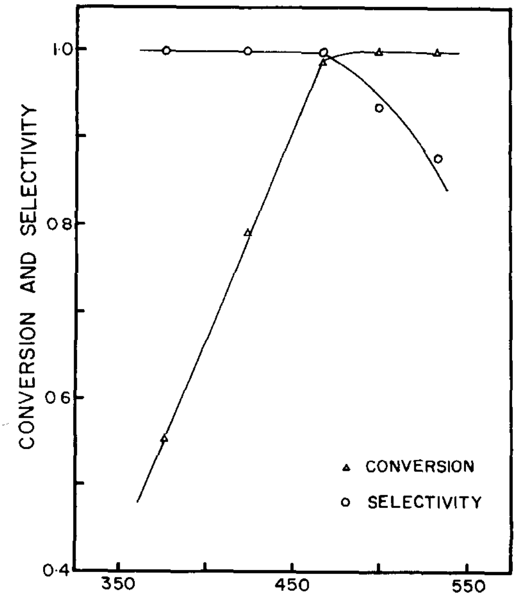

Fig. 4. Effect of temperature on conversion and selectivity for $W/F = 31.7$ g-hr/mole and 8% methanol in air.

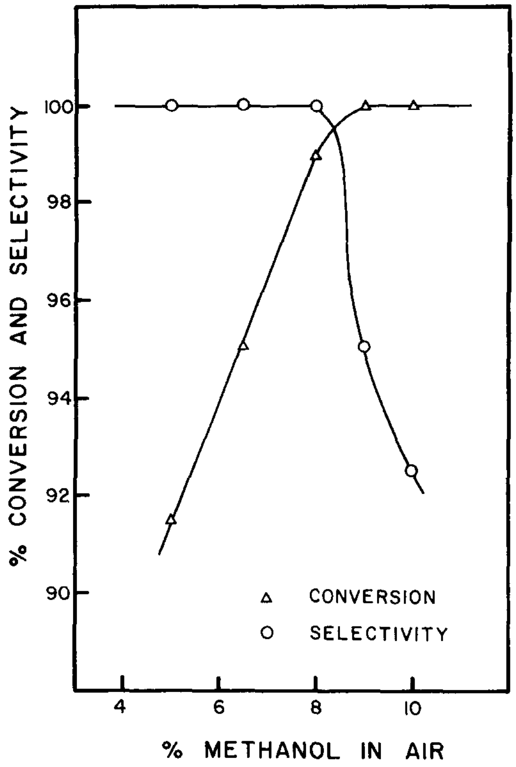

Fig. 5. Effect of methanol concentration on conversion and selectivity for $W/F = 31.7$ g-hr/mole at 466°C.

Effect of W/F Ratio

Figure 6 shows the effect of different W/F ratios on the conversion of methanol for various methanol–air mixtures (5–10% methanol) at a temperature of 466°C. While the selectivity remained constant at 100%, the conversion increased with increasing values of W/F.

The catalyst containing oxides of vanadium and molybdenum in a ratio of 20:80 proved to be most active and selective for the formation of formaldehyde and gave

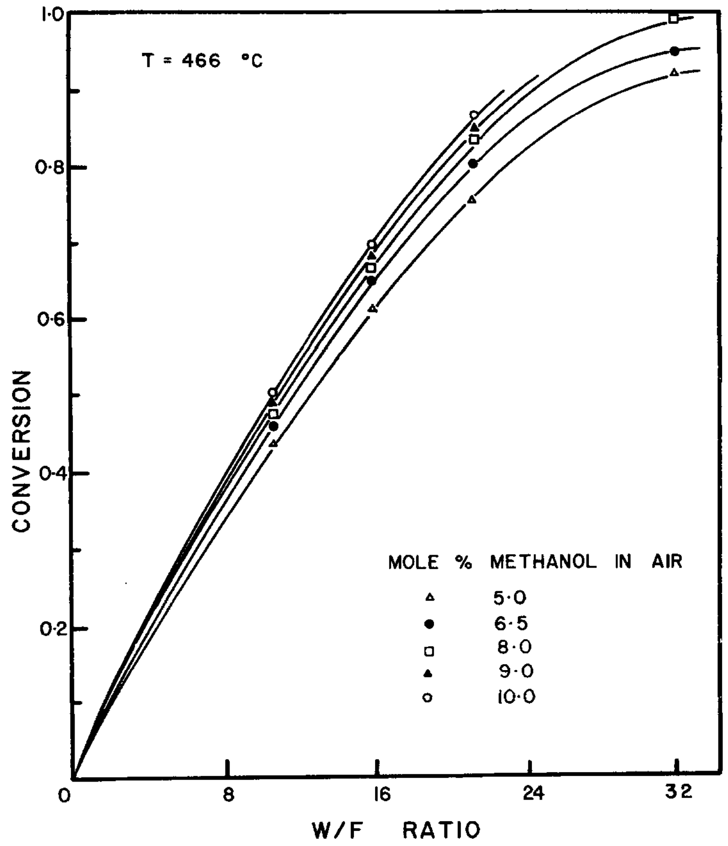

FIG. 6. Effect of W/F (g-hr/mole) on conversion of methanol to formaldehyde at 466°C.

nearly 99% conversion of methanol to formaldehyde (100% selectivity) for a W/F ratio 31.70, g-mole/hr and 8% methanol in air at 466°C.

In making a kinetic analysis of the experimental data, an approach suggested by Hougen and Watson (*10*) is used whereby various mechanisms which might control the rate of reaction are postulated and the rate of expressions consistent with these hypotheses are derived. The rate-controlling mechanism of the solid-catalyzed gas reaction may be the mass transfer of the reactants or products or adsorption of the reactants or desorption of products or chemical action of adsorbed molecules at the catalyst surface. The rate expressions thus derived are then fitted to the experimental data and the one which gives the best fit is retained, and the others are discarded.

The temperature and partial pressure gradient between the bulk fluid and the surface of the catalyst were evaluated by the method of Yoshida *et al.* (*11*). The temperature difference across the film was less than 1°C, and the partial pressure gradient was found to be of the order of 0.001 atm. Thus, heat and mass transfer effects were insignificant and, hence, could be neglected.

The effects of diffusion were kept to a minimum by using high velocity of the gas, and the possibility of diffusion in the pores controlling the reaction rate was eliminated by using small particle size (40–60 mesh) of the catalyst. The method of Yang and Hougen (*12*) was applied to the experimental data to further eliminate some of the controlling steps. A plot of initial rates (Fig. 7) against partial pressure of methanol indicated that the desorption of the

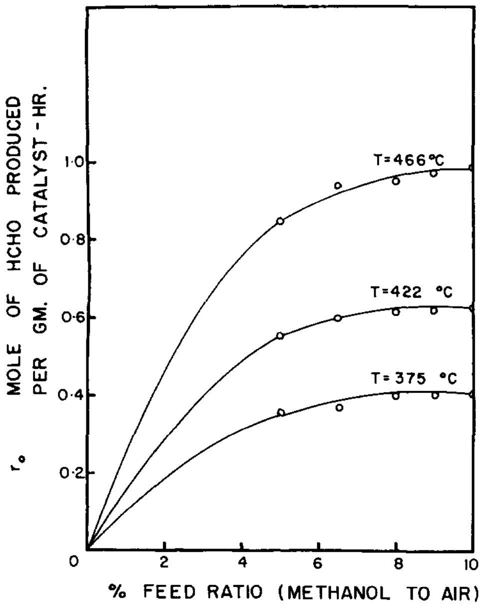

FIG. 7. Initial rates (r_o) vs mole percentage methanol in air.

products was definitely not rate controlling. Thus, the adsorption of the reactants and the surface reaction between the adsorbed reactants were possibly the rate-controlling steps.

The change in the color of the catalyst from greenish yellow to grey and the possibility of V_2O_5–MoO_3 existing in a state of lower valency and similar kinetic studies of methanol oxidation carried out by others suggested the interpretation of the results of the kinetic measurements to be based on a "two-stage oxidation-reduction" mechanism, similar to the one postulated by Mars and Van Krevelen (*13*). Accordingly, the reaction can be expressed to be taking place as follows:

$$m\mathrm{CH_3OH(g)} + \mathrm{S_{ox}} \xrightarrow{k1} \mathrm{HCHO(g)} + \mathrm{H_2O}. \quad (1)$$

$$n\mathrm{O_2(g)} + \mathrm{S_{red}} \xrightarrow{k2} \mathrm{S_{ox}}. \quad (2)$$

Based on the above mechanisms, different rate expressions were derived for various values of m and n (Table 1). The rate coefficients were evaluated by the method of least squares. The theoretical values of W/F, calculated by substituting the values of k_1 and k_2 into the respective rate equations, were compared with the experimental values. The following rate expression with $m = 1.0$, and $n = 0.5$ was found to give best possible fit to the experimental data:

$$r = \frac{k_1 p_\mathrm{M}}{1 + (k_1 p_\mathrm{M}/2k_2 p_{\mathrm{O_2}}{}^{0.5})}. \quad (3)$$

Figure 6 shows the comparison between the experimental and calculated data. While the solid curve refers to the data obtained from the above rate expression, the circles represent actual experimental data. The deviations between the calculated values of W/F from the experimental were less than 4%.

TABLE 1
TWO-STAGE REDOX MECHANISMS

No.	Reaction order m CH$_3$OH	 n O$_2$	Integrated rate equation
1	1	0.5	$\frac{W}{F}\frac{o^pM}{\ln(1-x)} = -\frac{1}{k_1} + \frac{4\alpha}{k_2}\frac{[o^{p1/2}O_2 - (o^pO_2 - \frac{1}{2}x_o o_\mathrm{M})^{1/2}]}{\ln(1-x)}$
2	1	0	$\frac{W}{F}\frac{1}{x} = -\frac{1}{k_1}\frac{\ln(1-x)}{\sigma^p\mathrm{M}^x} + \frac{a}{k_2}$
3	0.5	0	$\frac{W}{F}\frac{1}{x} = \frac{2}{k_1}\frac{[1-(1-x)^{1/2}]}{o^{p1/2}\mathrm{M}^x} + \frac{a}{k_2}$
4	1	1	$\frac{W}{F}\frac{o^p\mathrm{M}}{\ln(1-x)} = -\frac{1}{k_1} + \frac{2a}{k_2}\frac{\ln[o^p\mathrm{O_2}/(o^p\mathrm{O_2} - \frac{1}{2}o^p\mathrm{M}^x)]}{\ln(1-x)}$
5	0.5	0.5	$\frac{W}{F}\frac{o^{p1/2}\mathrm{M}}{[1-(1-x)^{1/2}]} = \frac{2}{k_1} + \frac{4a}{k_2}\frac{o^{p1/2}\mathrm{O_2} - (o^p\mathrm{O_2} - \frac{1}{2}o^p\mathrm{M}^x)^{1/2}}{o^{p1/2}\mathrm{M}[1-(1-x)^{1/2}]}$

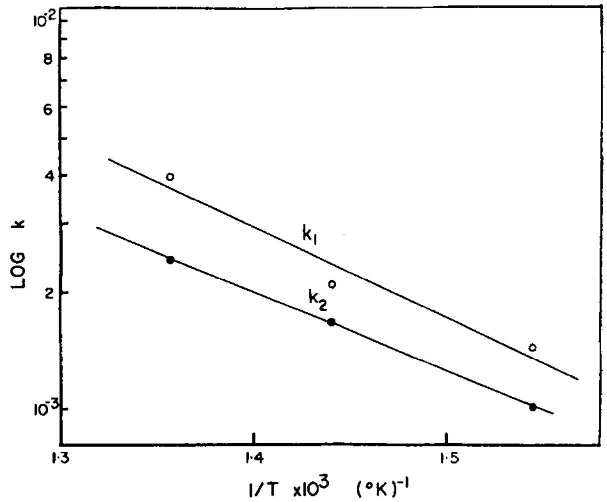

FIG. 8. Temperature effect on rate constants.

Temperature Effect on Rate Constants

The temperature dependence of the rate constants k_1 and k_2 was determined for temperatures between 375 and 466°C (Fig. 8). The reaction followed the Arrhenius law in the temperature range studied. The following expressions were obtained for rate constants.

$$\log k_1 = 0.773 - [(2.358 \times 10^3)/T], \quad (4)$$

$$\log k_2 = 0.157 - [(2.04 \times 10^3)/T]. \quad (5)$$

The activation energies of the two steps (Eqs. (1 and 2)) evaluated from Eqs. (4 and 5) are 10.8 and 9.3 kcal/mole respectively. These values are of the same order as reported by Bhattacharya (*7*) and Friedlander (*14*).

The general kinetics and mechanism of the reaction over oxides of vanadium and molybdenum investigated in the present study have been found to be similar to those obtained by Jiru *et al.* (*2*, *3*), Bhattacharya *et al.* (*7*), and Mann and Hahn (*6*).

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