JOURNAL OF CATALYSIS 55, 1-9 (1978)

Kinetics of Vapor Phase Oxidation of Methyl Alcohol over Supported V_2O_5–K_2SO_4 Catalyst

D. C. AGARWAL, P. C. NIGAM,[1] AND R. D. SRIVASTAVA[2]

Department of Chemical Engineering, Indian Institute of Technology, Kanpur, Kanpur-208016, India

Received October 19, 1977; revised March 28, 1978

The kinetics of oxidation of methanol to formaldehyde over vanadium pentoxide–potassium sulfate catalyst supported on silica gel was investigated between 330 and 410°C at atmospheric pressure. The catalyst, 10% V_2O_5, 20% K_2SO_4, and 70% silica gel, was found to be optimum in terms of conversion and selectivity to formaldehyde. The following rate expression, deduced assuming a steady state involving simultaneous reduction of catalyst by methanol and oxidation of the catalyst to the original state by gaseous oxygen, represents the experimental data satisfactorily: $r = k_1 p_M/[1 + (k_1 p_M/2k_2 p_{O_2}{}^{0.5})]$. The activation energies of the two steps were 14.7 and 17.5 kcal/mole, respectively.

NOTATION

F	Molar feed rate (moles/hr)
k	Total number of data points
k_1	Rate constant of oxidation of methanol by oxygen from catalyst S_{0x}, grams of catalyst, moles, seconds, and atmospheres
k_2	Rate constant of oxidation of catalyst S_{red} by oxygen, grams of catalyst, moles, seconds, and atmospheres
p_M	Partial pressure of methanol (atm)
p_{O_2}	Partial pressure of oxygen (atm)
m	Reaction order with respect to methanol
n	Reaction order with respect to oxygen
r	Experimental reaction rate (g moles)/(hr)(g catalyst)
$\bar{r}$	Calculated reaction rate (g moles)/(hr)(g catalyst)
r_0	Initial reaction rate (g moles)/(hr)(g catalyst)
S_{0x}	Catalyst in oxidized form
S_{red}	Catalyst in reduced form
T	Temperature
W	Weight of catalyst (g)
o	A subscript placed before a symbol means in the feed
α	Number of oxygen molecules required for converting one methanol molecule to formaldehyde = 0.5

DEFINITIONS

$$\text{Average absolute percent error} = \frac{1}{k}\sum_{i=1}^{k}\frac{\bar{r}(i) - r(i)}{r(i)} \times (100).$$

$$\text{L.R., likelihood ratio} = \left(\frac{\text{RSS of the model in consideration}}{\text{RSS of the other models}}\right)^{n/2}$$

$$\text{R.S.S.} = \sum_{i=1}^{k}[\bar{r}(i) - r(i)]^2.$$

0021-9517/78/0551-0001$02.00/0

INTRODUCTION

The kinetics of oxidation of methanol to formaldehyde over a supported V_2O_5–K_2SO_4 system has not hitherto been reported.

Most of the earlier work (*1–6*) was concerned with the study of suitable composition of oxide catalysts on the basis of Fe_2O_3 and MoO_3 with the verification of their catalytic activity in the oxidation of methyl alcohol. Recently, the kinetics of methanol oxidation on MoO_3 mixed with other metal oxides has received wide attention (7–16). Bliznakov *et al.* (*17*) studied tungstates of metals of the IVth period with regard to their catalytic properties of methanol oxidation. The highest reactivity was for ferric tungstates; however, they all showed medium activity.

The activities of the mixed vanadium pentoxide catalysts (V_2O_5–Fe_2O_3, V_2O_5–Co_3O_4, and V_2O_5–NiO) in the reaction of selective oxidation of methanol to formaldehyde have recently been reported by Malinski *et al.* (*18*), and Mann and Dosi (*19*) studied the kinetics over oxides of V_2O_5 and MoO_3. Bhattacharya *et al.* (*20*) investigated the kinetics of methanol oxidation using pure V_2O_5 catalyst.

The structure of the catalysts of the V_2O_5–K_2SO_4 system was studied by Tarama *et al.* (*21*) by ir and magnetic susceptibility measurements. These authors reported that K_2SO_4 had promotional action on vanadium pentoxide for oxidation reaction. There appears to be, however, no prior kinetic study, where the oxidation of methanol was performed over this catalyst.

In this investigation, kinetic studies of the oxidation of methanol catalyzed by V_2O_5–K_2SO_4 were made by using an isothermal fixed bed reactor in the temperature range of 330 to 410°C at atmospheric pressure. To provide a sufficiently large surface area, the catalyst was supported on silica gel. The effects of several process variables on the conversion, yield, and selectivity were determined.

The purpose of this study was to obtain some understanding of the catalytic activity of the V_2O_5–K_2SO_4 system and to examine the possibilities of interpreting the mechanism. The experimental results are analyzed on the basis of two-stage redox kinetics with statistical data interpretation.

EXPERIMENTAL METHODS

Preparation of the catalyst. A thick paste of ammonium metavandate was prepared in distilled water. A saturated solution of oxalic acid in water at 70°C or below was added slowly, with constant stirring, to the ammonium metavanadate paste. The temperature control was necessary to prevent decomposition of vanadium oxalate. A weighed amount of potassium sulfate was added to this vanadium oxalate solution. The resulting solution was then added to silica gel ($-30 + 40$ mesh size) with constant stirring. The impregnated catalyst solution was vacuum dried at 70°C. This quick drying was required to avoid the hydrolysis of the support as well as to prevent the decomposition of vanadium oxalate. The catalyst was calcined at 500°C for 6 hr and activated at 600°C for 8 hr. For example, the catalyst with a composition of 10% V_2O_5–20% K_2SO_4 required the following amounts of reagents: 12.88 g of ammonium metavandate, 20 g of K_2SO_4, and 70 g of dried silica gel. The surface area of this catalyst, as determined by the BET method, was 308 m^2/g. The mean radius of the pores of the catalyst, determined by a high pressure mercury porosimeter (*23*), was 33 Å. The pore volume amounted to 0.52 ml/g.

Apparatus. A general schematic diagram of the experimental equipment is shown in Fig. 1. Compressed air was passed through the drier and purifying towers containing fused calcium chloride, po-

---

[1] Department of Chemistry, Indian Institute of Technology, Kanpur-208016, India.

[2] Author to whom correspondence should be sent.

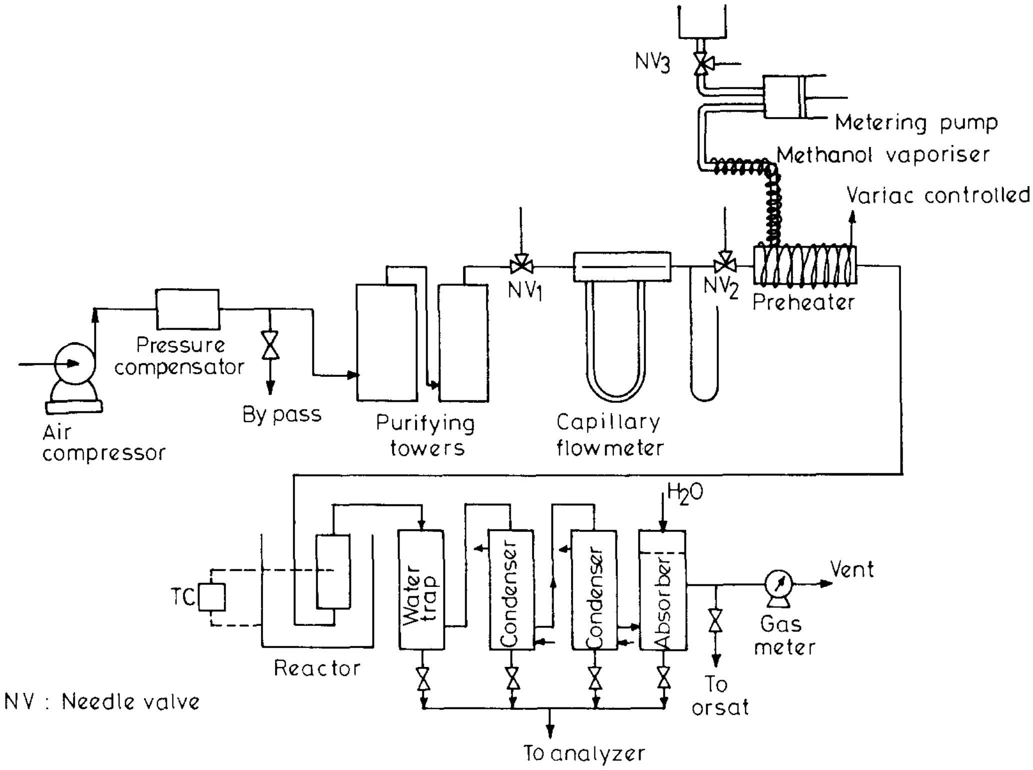

FIG. 1. Experimental set-up.

tassium hydroxide pellets, and active charcoal and metered through a flow meter to the preheater. Methanol was vaporized in $\frac{1}{4}$-in. o.d. tube wrapped with insulating heating tape. The methanol vapors were carried by an incoming airstream 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 to air ratios were obtained by adjusting the air flow rate.

The reactor was stainless steel tubing (1-in. diameter and 6 in. long) placed into a salt bath. A wire mesh (−60 + 80 size) was welded at the bottom of the reactor for the catalyst support. Temperatures at various points in the reactor, including the catalyst bed and preheater, were measured with the help of iron constantan thermocouples. The thermocouples were calibrated against a 25 Ω Leeds and Northrup platinum resistance thermometer and Mueller bridge assembly. The catalyst bed temperature was maintained within ±2°C of the desired temperature.

All the experimental runs were taken under steady state conditions. For this purpose a stream of reactants was passed on the catalyst at the required temperature for 1 hr. The products were finally collected for another 30 min. The reaction products passed through a water trap where the heavier products, formaldehyde, water, and unused methanol, condensed. The lighter gaseous products, carbon dioxide and carbon monoxide, passed through an orsat apparatus. The gaseous products were analyzed intermittently.

The heavier liquid components collected in the liquid trap were analyzed for formaldehyde and methanol. The analytical procedure was similar to one described in Ref. (*20*). The accuracy of these analytical techniques was checked by taking known mixtures of methanol and formaldehyde. The precision of the analysis was about 1%. The reaction products were also analyzed by chromographic methods (*18*). The analytical techniques were found to be as reliable as those of the chromatographic method. The conversion, yield, and the selectivity are defined as follows:

$$\text{Conversion} = \frac{\text{moles of methanol reacted per hour}}{\text{moles of methanol fed per hour}},$$

$$\text{Yield (\%)} = \frac{\text{moles of formaldehyde formed per hour}}{\text{moles of methanol fed per hour}} \times 100,$$

$$\text{Selectivity (\%)} = \frac{\text{moles of formaldehyde formed per hour}}{\text{moles of formaldehyde} + \text{moles of carbon oxides formed per hour}} \times 100,$$

$$\text{Reaction rate} = \frac{\text{moles of methanol reacted}}{\text{(hours) (grams of catalyst)}}.$$

The rate of formation is referred to as the moles of various products formed per hour per gram of catalyst.

RESULTS AND DISCUSSION

The rate of catalytic oxidation of methyl alcohol to formaldehyde was measured in an isothermal fixed bed reactor at atmospheric pressure. The effects of various variables, namely, the methanol:air ratio in feed mixture, $\bar{R}$, reaction temperature, T, and the ratio of the catalyst weight to the methanol feed rate, W/F, on the conversion, selectivity, and the yield, were investigated. The reciprocal space velocity (W/F) was changed by changing the weight of the catalyst charged into the reactor.

Reference to the various samples will be made giving their composition as weight percent V–K: Hence, V-10–K-5 means a sample of V_2O_5–K_2SO_4 supported on silica gel having 10% of the active element as V_2O_5, 5% of the promoter as K_2SO_4, and the balance as silica gel.

By preliminary experiments and calculations it was found that the rate of oxidation of methyl alcohol on the catalyst is influenced by neither internal nor external diffusion (*22*). The fair constancy of the conversion obtained by changing the feed rate while keeping W/F constant suggested that the diffusion of the gases was not controlling the rate. The internal diffusional resistance in the catalyst particles was practically negligible, as observed by insignificant change in the reaction rate on varying the catalyst size between 1.40 and 0.37 mm.

Effect of Catalyst Composition

Figure 2 shows the effect of catalyst composition on conversion, yield, and selectivity at 410°C with 10% methanol in the feed and $W/F = 42.0$ g-hr/g-mole. The conversion increased as the ratio of V_2O_5/K_2SO_4 increased; however, the selectivity remained low after the ratio of 0.5. A 10% V_2O_5–20% K_2SO_4 ratio ($V_2O_5/K_2SO_4 = 0.5$) was chosen to be an optimum composition of the catalyst in terms of conversion and selectivity and was used for further detailed kinetic study of the reaction.

Prior to each data point, the activity of the catalyst was established by running a standard and comparing it with the initial standard. There was essentially no deactivation of the catalyst within 10 runs.

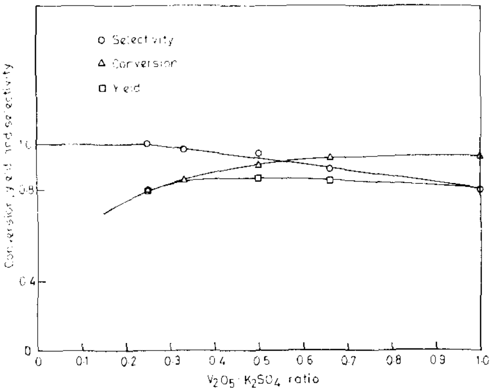

FIG. 2. Effect of catalyst composition on conversion, yield, and selectivity: $W/F = 42.0$; temperature = 410°C; 10% methanol in air.

Effect of Temperature

Figure 3 shows the effect of temperature on conversion and selectivity of the catalyst (V-10-K-20) in the temperature range of 330 to 410°C and W/F of 41.0 g-hr/mole for a 10% methanol in air. The conversion of methanol increased up to 95% as the temperature increased. The selectivity of the catalyst was 100% at the lower temperature but decreased as the reaction temperature increased.

Effect of W/F Ratio and Methanol Concentration

The experimentally determined relationship between the conversion and the value W/F in the integral reactor with varying concentration of methanol between 4 and 10% at the temperatures of 330, 360, 380, and 400°C is presented in Figs. 4 through 7. For all methanol concentrations, an increase in W/F increased the conversion of methanol.

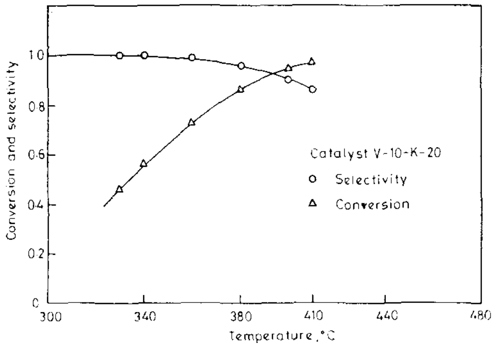

FIG. 3. Effect of temperature on conversion and selectivity for $W/F = 41.0$ g-hr/mole and 10% methanol in air.

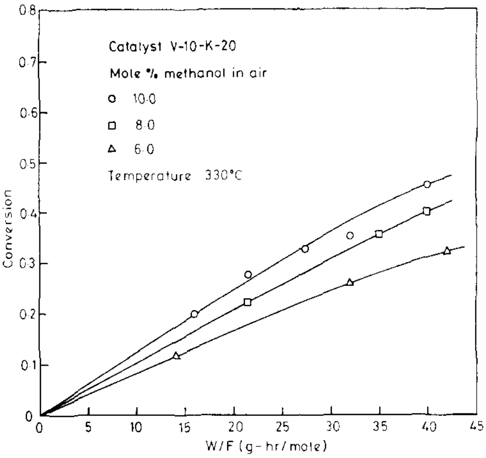

FIG. 4. Effect of W/F on conversion of methanol for various methanol concentrations in the feed mixture at 330°C.

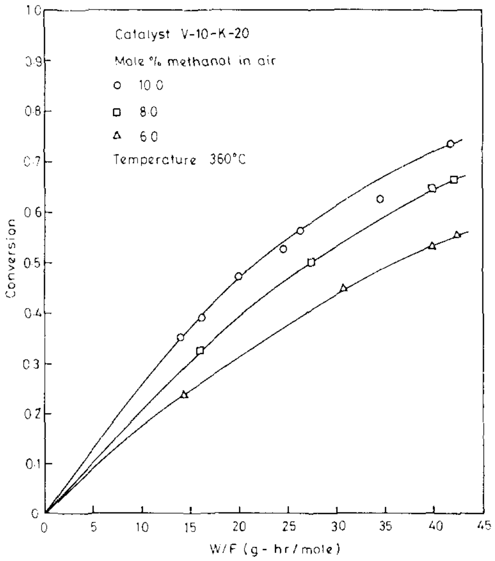

FIG. 5. Effect of W/F on conversion of methanol for various methanol concentrations in the feed mixture at 360°C.

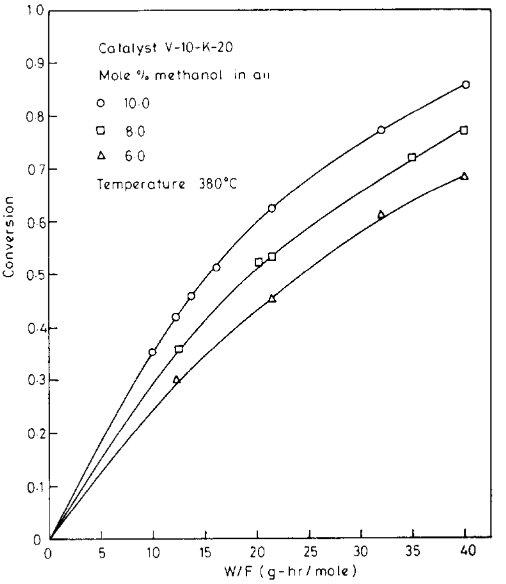

FIG. 6. Effect of W/F on conversion of methanol for various methanol concentrations in the feed mixture at 380°C.

Mann and Dosi (*19*) studied the methanol oxidation over unsupported V_2O_5–MoO_3 catalyst. The maximum conversion was achieved at 466°C. To compare the activity of supported V_2O_5–K_2SO_4 catalyst, their result is also plotted in Fig. 7. From the plot it is evident that the supported V_2O_5–K_2SO_4 catalyst is comparable to that of V_2O_5–MoO_3, bearing in mind that the same conversion and selectivity are achieved at a much lower temperature.

Kinetic Analysis

The heterogeneous catalytic reactions are traditionally described as diffusion of reactants and products, adsorption and desorption of reactants and products, and surface reaction. The mass transfer effects were found to be negligible. A plot of initial rate versus partial pressure of methanol (Fig. 8) indicated that the desorption of product was not a rate-controlling step. These initial rates were derived from Figs. 4 to 7 by taking tangents at the origin.

During the course of investigation, it was observed that the color of the catalyst became black (characteristics of lower oxides of vanadium) when only methanol

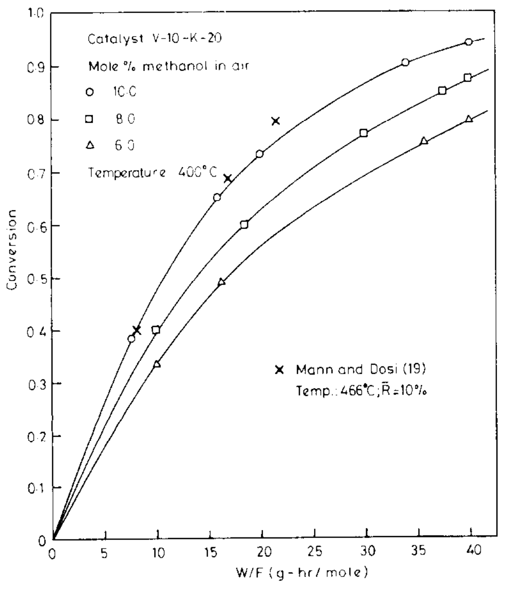

FIG. 7. Effect of W/F on conversion of methanol for various methanol concentrations in the feed mixture at 400°C.

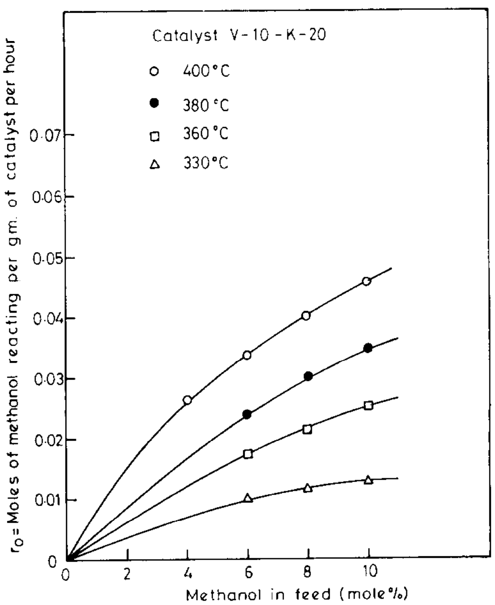

FIG. 8. Initial ratio (r_0) vs mole percentage methanol in air.

TABLE 1

Two-Stage Redox Models

Model no.	Reaction order		Integrated rate equation
	m CH_3OH	n O_2	
1	1	0.5	$\frac{W}{F}\frac{{}_0p_M}{\ln(1-x)} = -\frac{1}{k_1} + \frac{4\alpha[{}_0p_{O_2}{}^{\frac{1}{2}} - ({}_0p_{O_2} - 1/2^x{}_0p_m)^{\frac{1}{2}}]}{k_2 \ln(1-x)}$
2	1	0	$\frac{W}{F}\frac{1}{x} = -\frac{1}{k_1}\frac{\ln(1-x)}{{}_0p_M x} + \frac{\alpha}{k_2}$
3	0.5	0	$\frac{W}{F}\frac{1}{x} = \frac{2}{k_1}\frac{[1-(1-x)^{\frac{1}{2}}]}{{}_0p_M{}^{\frac{1}{2}}x} + \frac{\alpha}{k_2}$
4	1	1	$\frac{W}{F}\frac{{}_0p_M}{\ln(1-x)} = -\frac{1}{k_1} + \frac{2\alpha}{k_2}\frac{\ln[{}_0p_{O_2}/{}_0p_{O_2} - \frac{1}{2}{}_0p_M x]}{\ln(1-x)}$
5	0.5	0.5	$\frac{W}{F}\frac{{}_0p_M{}^{\frac{1}{2}}}{[1-(1-x)^{\frac{1}{2}}]} = \frac{2}{k_1} + \frac{4\alpha}{k_2}\frac{{}_0p_{O_2}{}^{\frac{1}{2}} - ({}_0p_{O_2} - \frac{1}{2}{}_0p_M x)^{\frac{1}{2}}}{{}_0p_M{}^{\frac{1}{2}}[1-(1-x)^{\frac{1}{2}}]}$

was allowed to pass over it for a short time. The change in color of the catalyst, the possibility of the active component existing in a state of lower valency, and similar kinetic studies of methanol oxidation carried out by previous authors (*1, 19, 20*) suggested the interpretation of the results of kinetic measurements (Figs. 4–7) to be based on a two-stage oxidation–reduction mechanism similar to one proposed by Mars and Van Krevelen (*24*):

$$m\,CH_3OH(g) + S_{Ox} \xrightarrow{k_1} HCHO(g) + H_2O(g) + S_{red} \quad (1)$$

$$n\,O_2(g) + S_{red} \xrightarrow{k_2} S_{Ox}. \quad (2)$$

When the rates of the both Process (1) and (2) are equal, it is possible to derive an expression for the oxidation of methyl alcohol:

$$r = \frac{k_1 p_M{}^m}{1 + (\alpha k_1 p_M{}^m / k_2 p_{O_2}{}^n)}, \quad (3)$$

where m and n are the reaction order with respect to methanol and oxygen, respectively, and α is the number of oxygen molecules required to oxidize one molecule of methanol to formaldehyde.

Equation (3) can be integrated for the integral reactor. Table 1 presents the kinetic equations in integral form for the exponents m and n between 0 and 1.

To determine the effectiveness of the mathematical correlation and predicti-

TABLE 2

Isothermal Regression

Model	Temperature (°C)	$k_1 \times 10^4$	$k_2 \times 10^4$	Average absolute percent error
1	330	0.4633	0.3467	0.1286
1	360	0.9513	0.8130	0.1570
1	380	1.3697	1.2650	0.2000
1	400	1.9800	1.9025	0.3073
2	330	0.3802	0.0121	79.1815
2	360	1.0640	0.0351	43.4005
2	380	2.2275	0.0476	27.5590
2	400	4.3994	0.0472	17.2411
3	330	0.0830	0.0122	83.1892
3	360	0.2155	0.0358	54.3431
3	380	0.4069	0.0513	36.9006
3	400	0.9827	0.0440	18.2967
4	330	0.4660	0.7347	0.1297
4	360	0.9508	2.0671	0.2728
4	380	1.3685	3.1297	0.2466
4	400	1.9688	5.2022	0.8950
5	330	0.1018	0.0130	144.3952
5	360	0.2127	0.1231	38.1963
5	380	0.3417	0.1128	53.6735
5	400	0.3585	1.0499	9.1426

bilities within the experimental range, a statistical analysis was made. The program prepared used a centralization and correlation matrix for minimizing rounding off errors. Regressions of the models were made at each temperature. The converged values for the constants of these models are presented in Table 2.

The least value of the average absolute percentage error was found in the case of the rate constants for combination of order $m = 1$ and $n = 0.5$ (model 1). Although model 4 also had a relatively least value of the average absolute percentage error, the likelihood ratio, L.R., was so large as to be meaningless (>100). In our further considerations we shall therefore discuss model 1, the rate equation

$$r = \frac{k_1 p_M}{1 + (k_1 p_M / 2k_2 p_{O_2}{}^{0.5})}, \quad (4)$$

which is of the first order for methyl alcohol and 0.5 order for oxygen. The ratios of k_1 and k_2 of this model was found to be similar to those obtained by Jiru *et al.* (*1*) and Mann and Dosi (*19*).

The effect of temperature on the rate expression was induced by substituting the Arrhenius temperature dependency relation. Regressions were performed on all the data using model 1. The following expressions were obtained for the rate constants:

$$\ln k_1 = 2.5937 - \frac{0.7405 \times 10^4}{T} \quad (5)$$

$$\ln k_2 = 4.7513 - \frac{0.8827 \times 10^4}{T} \quad (6)$$

The activation energies for the steps (1) and (2) were 14.7 and 17.5 kcal/mol, respectively. The value of the activation energy in each step is positive, indicating a satisfactory temperature relationship.

The proposed rate equation can represent a modified Hinshelwood mechanism for a surface sparsely covered by one or both reactants. In that case, one or both constants then represent the product of a rate constant and an adsorption constant. The rate equation does not exclude the possibility that the reoxidation of partially reduced catalyst is realized by adsorbed oxygen. It is unlikely, however, that the required amount of oxygen available for methanol oxidation could be adsorbed oxygen on the *n*-type semiconducting catalyst employed (*1*).

The strength of the V=O bond has been known to be a controlling factor for the catalytic activity. The promotive action of K_2SO_4 on V_2O_5 in the selective oxidation of methanol to formaldehyde may be due to weakening of this bond by doping. Tarama *et al.* (*21*) have established by ir absorption that doping of V_2O_5 with K_2SO_4 caused a shift in sharp absorption from the 1025 to 1000 cm^{-1} band which showed the promotive action for oxidation of carbon monoxide or hydrocarbons. This characteristic feature of the V=O bond was attributed to $VOSO_4$ or a similar compound formed by K_2SO_4.

REFERENCES

1. Jiru, P., Wichkerlova, B., and Tichy, J., "Proceedings of the Third Congress on Catalysis (Amsterdam)," p. 199. North-Holland, Amsterdam, 1965.
2. Dente, M., Poppi, R., and Pasquon, L., *Chim. Ind.* **46**, 1326 (1964).
3. Adkins, H., and Peterson, W. H., *J. Amer. Chem. Soc.* **53**, 1513 (1931).
4. Boreskov, G. K., Kolovertnov, G. D., Kefeli, L. M., Karachiev, L. G., and Popov, B. I., *Kinet. Catal. (USSR)* **7**, 144 (1966).
5. Pernicone, N., Lazzerin, F., Liberti, G., and Lanzavecchia, G., *J. Catal.* **14**, 293 (1969).
6. Pernicone, N., *J. Less-Common Metals* **36**, 289 (1974).
7. Klissourski, D., and Bliznakov, G. C. R., *Acad. Bulgare Sci.* **18**, 549 (1965).
8. Bliznakov, G., Jiru, P., and Klissourski, D., *Coll. Czech. Chem. Commun.* **31**, 2995 (1966).
9. Mann, R. S., and Hahn, K. W., *J. Catal.* **15**, 329 (1969).
10. Miki, N., Makoto, M., and Yuichi, M., *Chem. Lett. Japan* **1295** (1975).

11. Bliznakov, G., Popov, T., and Klissourski, D., *Nauch Tr. Plovdivaki Univ. Mat. Fiz. Khim. Biol.* **11**, 115 (1973).
12. Fedvich, E. V., and Zhiznevski, V. M., *Khim. Tekhnol. Resp. Mezhved Nauch-Tekh.* **15**, 70 (1969).
13. Arnold, H. R., U.S. Patent No. 2320253 (1943).
14. Popov, T., *Natura Plovdiv* **3**, 91 (1970).
15. Liminov, V. E., Gooshko, O. N., and Semikina, L. E., *Katal. Katal.* **9**, 41 (1972).
16. Mann, R. S., Jain, S. K., and Dosi, M. K., *J. Appl. Chem. Biotechnol.* **27**, 198 (1977).
17. Bliznakov, G., Popov, T., and Klissourski, D., *Izv. Inst. Obshta Neorg. Khim. Bulg. Akad. Nauk.* **4**, 83 (1966).
18. Malinski, R., Akimoto, M., and Echigoya, E., *J. Catal.* **44**, 101 (1976).
19. Mann, R. S., and Dosi, M. K., *J. Catal.* **28**, 282 (1973).
20. Bhattacharya, S. K., Jankiram, K., and Ganguli, N. D., *J. Catal.* **8**, 128 (1967).
21. Tarama, K., Tarnishi, S., Yoshida, S., and Tamura, N., "Proceedings of the Third Congress on Catalysis (Amsterdam)," p. 282. North-Holland, Amsterdam, 1965.
22. Corrigan, T. E., *Chem. Eng.* **62**, 199 (1955).
23. Agarwal, A. K., and Srivastava, R. D., *J. Catal.* **45**, 86 (1976).
24. Mars, P., and Van Krevelen, D. W., *Chem. Eng. Sci. Special Suppl.* **3**, 41 (1954).