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Kinetics of the Vapor-Phase Oxidation of Methyl Alcohol on Manganese Dioxide–Molybdenum Trioxide Catalyst

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The kinetics of methanol oxidation was studied over manganese dioxide–molybdenum trioxide catalyst in an integral flow reactor between 250 and 460°C, at space velocities of 9.6×10^3 to 8.4×10^4 hr^{-1}. The highest conversion of methanol and yield of formaldehyde under these conditions were 84% with a selectivity of almost 100% at 365°C. The rate equation: $r = [k_1 P_M/(1 + k_1 P_M/2k_2 P_{O_2}{}^{1/2})]$ deduced, assuming a steady state involving a two-stage irreversible oxidation–reduction process, represented the data satisfactorily.

INTRODUCTION

Formaldehyde, a very important industrial chemical, is now prepared mostly by the partial air oxidation of methanol under controlled conditions, rather than by the alternative dehydrogenation process. Two types of catalysts, silver metal and metallic oxides and their mixtures have been generally used in the manufacture of formaldehyde by methanol oxidation. While the classic procedure uses a silver catalyst and employs a rich mixture of methanol with air, the other method makes use of an oxide catalyst, and employs a lean methanol–air mixture. The oxide type catalysts operate at very high conversions and yields of formaldehyde. Much work has been reported on the mechanism and kinetics of catalytic oxidation of methanol to formaldehyde, using silver as a catalyst.

Several patents (*1–5*) have been issued in the past, envisaging the use of oxides of vanadium, iron, molybdenum, and tungsten, either alone or mixed with each other, for catalytic oxidation of methanol to formaldehyde. Most of the patent literature (*6–11*) since 1955 has been devoted to improvements in the methods of preparation and recovery of these catalysts, especially of iron–molybdenum oxide mixtures.

Recently the kinetics of methanol oxidation over oxides of iron and molybdenum have been reported by Boreskov (*12*), Jiru *et al.* (*13, 14*) and Dente (*15*). The effect of water on the oxidation has been studied by Pernicone *et al.* (*16*). Bhattacharyya *et al.* (*17*) investigated the kinetics of the vapor phase oxidation of methanol on vanadium pentoxide catalyst between 246 and 281°C and postulated a rate mechanism. Bliznakov *et al.* (*18*) studied the oxidation of methanol over oxides of molybdenum and manganese at 370°C. However, they did neither define the rate mechanism, study the effect of process variables on the conversion, nor provide any details of the reacting system.

While Boreskov (*12*) found the rate to be independent of oxygen and first order in methanol, Jiru *et al.* (*13, 14*) deduced a rate expression based on the redox mechanism, originally suggested by Mars and Van Krevelen (*19*) for the vapor-phase oxidation of aromatic hydrocarbons on vanadium pentoxide. A rate equation exactly similar to the one developed by Jiru *et al.* (*13*) can also be deduced from the modified Hinshelwood mechanism (*20*).

Recently we studied the oxidation of methanol over a manganese dioxide–molybdenum trioxide catalyst under a fairly wide range of operating conditions, in order to derive a simple, but accurate, rate equation, which might be used effectively for industrial reactor design and to obtain some insight into the actual mechanism of reaction.

NOMENCLATURE

F = feed rate (moles of feed/hr)
ΔG = free energy change
k_1,k_2 = reaction rate constants
p = partial pressure (atm)
r = reaction rate
K_p = equilibrium constant
$\bar{R}$ = oxygen/methanol ratio in feed
S_{ox} = active site of lattice or adsorbed oxygen
S_{red} = reduced site of lattice oxygen or the empty site
S = selectivity [(moles of formaldehyde formed/hr)/(moles of methanol reacted/hr)]
X = conversion [(moles of methanol reacted/hr)/(moles of methanol fed/hr)]
Subscript M and O = methanol and oxygen
Overscript m and n = integral or half number in rate equation
W = weight of catalyst (g)
$_0$, placed before a symbol, represents in the feed.

EXPERIMENTAL METHODS

Apparatus. Reactions were studied in an integral fixed bed flow reactor, heated by fluidized sand bath. The flow diagram of the apparatus used is shown in Fig. 1. Standard Copper Tubing (¼ in. o.d.) was used throughout the apparatus, except for those portions of the lines in contact with the reactants and products, which were of ⅛ in. 316 stainless steel tubing. All fittings were Swagelok standard stainless steel, and the valves, unless specified, were bellow valves.

Compressed gases, helium (1), nitrogen (2), and air (3) from the cylinders were passed through a series of pressure regulating devices and drying tubes (4) and metered through Brook's glass rotameters (5). Spectroscopic grade methanol was placed in containers (6) through funnels (7), partially compressed with nigrogen, and a needle valve (8) was used to adjust the flow rate. The rate of flow of methanol was measured by counting the number of droplets per unit time passing through a precalibrated sight glass (9), into the evaporating chamber (10).

The reactor (11) was made of 304 stainless steel (0.5 in. diam, and 6 in. long) and was heated with a fluidized sand bath (12), the temperature of which was controlled to within ±0.1°C. Two thermocouples (13) were inserted from the top through the Swagelok connector, and measured the temperature of the catalyst bed.

The reaction products were passed through an air cooled trap (14), water condenser (15) and a drying tube (4). While

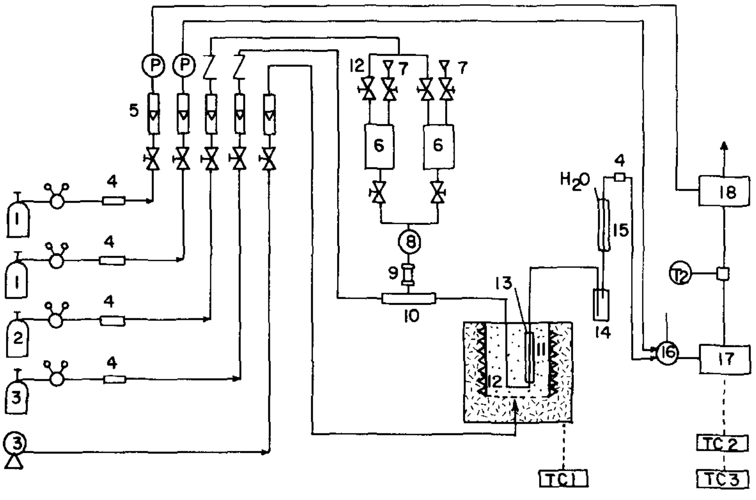

FIG. 1. Flow diagram for the oxidation of methanol to formaldehyde.

heavier products, formaldehyde, methanol, and water were thus condensed, the noncondensed gases were passed through a sampling valve (16) leading to a model 25, Fisher gas partitioner (17) and vented. The heavier products were analyzed in the gas chromatograph (18). Polymerization of formaldehyde in the gas stream was prevented by maintaining the lines from the methanol sight glass to the liquid trap including the last 2 ft of the air line immediately preceeding the evaporating chamber itself at a temperature of 100°C, by means of heating tapes, insulated with asbestos tape. Polymer formation in the liquid trap was avoided by the presence of 1% methanol.

All 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 about an hour. The products were then collected. Gas samples were analyzed intermittently.

Preparation and physical characteristics of the catalyst. The catalyst, containing 20 wt % manganese dioxide and 80 wt % molybdenum trioxide, was prepared in a manner similar to the one used by Klissourski and Bliznakov (*21*). Manganese dioxide and molybdenum trioxide was obtained by the thermal decomposition of Analar grade manganese nitrate, $Mn(NO_3)_2$ and ammonium molybdate, $(NH_4)_6Mo_7O_{24}$, $4H_2O$. A paste obtained from the mixture of these oxides in the required amounts was subjected to 6 hr drying at room temperature, 12 hr at 40°C, and 6 hr at 150°C. The catalyst was subsequently activated by successive 1 hr heatings at 200, 250, 300, and 350°C, and a 6-hr calcination at 420°C. The surface area of the fresh catalyst determined by the BET method was found to be 7.8 m^2/g. The average diameter of the catalyst particle size was 0.525 mm and had a bulk density of 4.6 g/ml.

Analytical Procedure

Acids. The total acid content was obtained by the titration of the condensate from the traps with 0.1 *N* KOH.

Gases. The inlet feed gases and the product gases were analyzed for carbon dioxide, carbon monoxide, nitrogen, and oxygen by periodic injection of a 0.5-ml sample into the Fisher gas partitioner which contained a 6-ft column of hexamethyl phosphoramide and a 13-ft 13X molecular sieve column connected in series.

Liquid products. Liquid samples were analyzed by injection into a gas chromatograph. The gas chromatograph, assembled in the department, consisted of a Gow-Mac model TR III A, 4W2, temperature regulated thermal conductivity cell, and model 405C:1 power supply control unit. A 5-m, 15 wt % sucrose octa acetate on Columnpak T, column was used in separating the liquid products, CH_3OH, HCHO, H_2O, HCOOH, and C_4H_7OH. This proved to be the most efficient column for such separations (*22*).

Thermodynamic considerations. The free energy change (ΔG) and the equilibrium constant (K_p) of the reaction

$$CH_3OH(g) + \tfrac{1}{2}O_2(g) = HCHO(g) + H_2O(g), \quad (1)$$

were calculated as functions of temperature, the necessary data being collected from the literature or calculated by the group contribution method (*23*, *24*).

The value of ΔG and K_p recorded in Table 1 indicate that the reaction is highly irreversible.

TABLE 1
THE VALUES OF ΔG AND K_p OF THE REACTION [EQ. (1)] AT 1 ATMOSPHERE AND DIFFERENT TEMPERATURES

Temp. (°C)	$-(\Delta G)$ (kcal/g mole)	K_p
25	26.266	1.785×10^{19}
127	25.713	1.115×10^{14}
227	25.068	9.040×10^{10}
327	24.347	7.371×10^{8}
427	22.749	1.637×10^{6}

RESULTS AND DISCUSSION

Experiments were conducted at atmospheric pressure, in the temperature range 250–460°C, for catalyst to feed ratios (W/F) of 2.5–22.0 g hr/mole, oxygen to methanol ratios ($\bar{R}$) of 2.42–5.04 and space velocities of 9.6×10^3 to 8.4×10^4 hr^{-1}. No

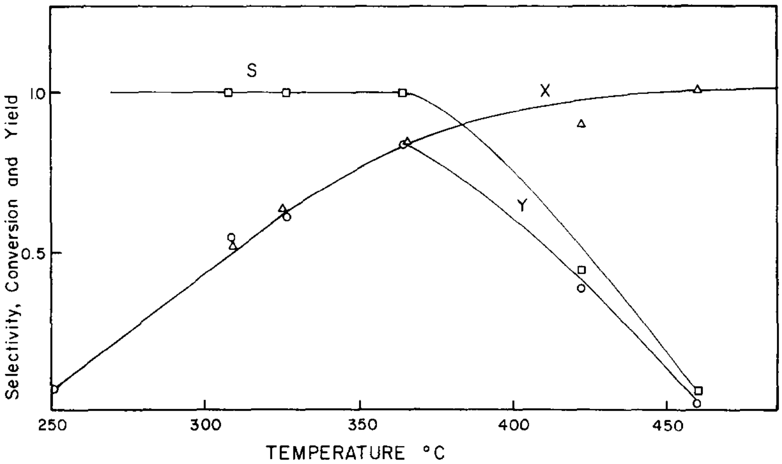

FIG. 2. Effect of temperature on the conversion and selectivity.

reaction between air and methanol was observed to take place even after several hours at 460°C, in the absence of the catalyst.

Feed rates were calculated on the basis of the rotameter readings, and the flow rate of methanol. The effluent rates were computed on the basis of the total flow rate and composition of the product stream. Air was used for the oxidation because the presence of nitrogen in it reduced the local heating effect on the catalyst, and its cheapness as compared to oxygen.

The activity of the catalyst remained fairly constant during the course of the study. The experiments were performed at random in order to nullify any effects due to change in catalytic activity.

While conversion (X) is referred to as the moles of methanol consumed (reacted per hour) to the moles of methanol fed per hour, the rate of formation is referred as the moles of various products formed per hour per gram of the catalyst. The ratio of moles of formaldehyde produced per hour to the moles of methanol reacted has been defined as selectivity (S).

Effect of temperature. The effect of temperature on the conversion and yield of formaldehyde was investigated in the temperature range 250–460°C. Figure 2 shows the effect of the temperature on conversion and yield at a catalyst to feed ratio (W/F) of 16.3 and oxygen to methanol ratio ($\bar{R}$) of 2.42. With increasing temperature, both conversion and yield increased up to 365°C, after which conversion continued to increase reaching almost 100% at 460°C, while the yield decreased. The selectivity was nearly 100% up to 365°C, and then decreased at higher temperatures.

Effect of oxygen/methanol ratio. The effect of oxygen to methanol ratio in the feed on the conversion of methanol and the yield of formaldehyde for a W/F ratio of 13.3 at 365°C is shown in Fig. 3. While with increasing reactant ratios, the conver-

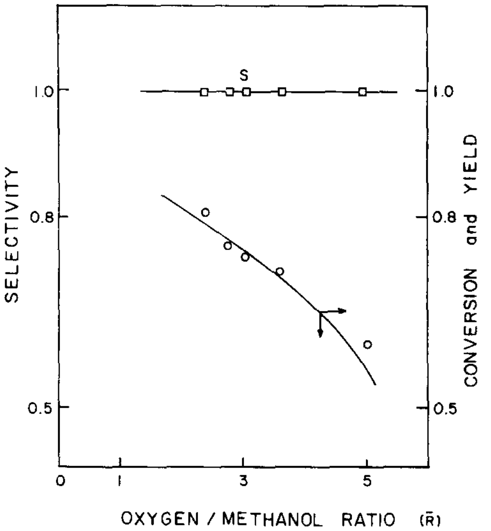

FIG. 3. Effect of oxygen/methanol ratio ($\bar{R}$) on conversion and selectivity.

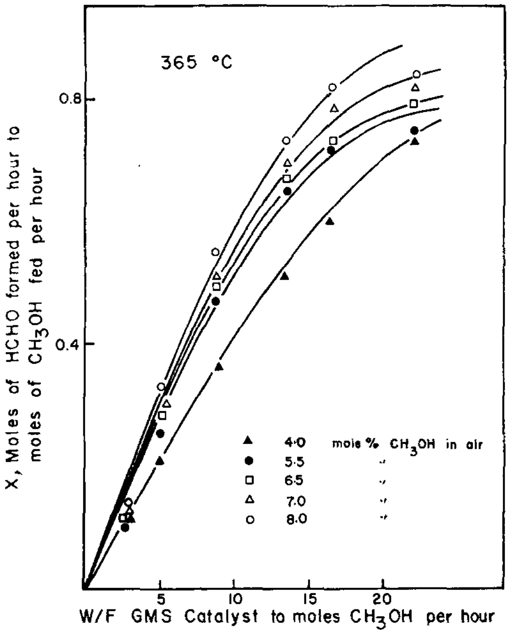

FIG. 4. Effect of *W/F* ratio on conversion, theoretical, and experimental values.

sion of methanol and the yield of formaldehyde decreased rapidly, selectivity remained constant at nearly 100%.

Effect of W/F ratio. Figure 4 shows the effect of various *W/F* ratios on the conversion of methanol at 365°C for several methanol–air mixtures (4–8% methanol in air). While the solid lines in Fig. 4 refer to the curves predicted by substituting the calculated values of k_1 and k_2 obtained from Eqs. (5) and (6) into the rate equation, the circles represent the experimental data. The conversion increased with the increased ratios of *W/F* and the yield with increased methanol in the methanol–air mixture.

The present kinetic data (Table 2) were critically examined following the approach suggested by Hougen and Watson (*25*), whereby various mechanisms, which might control the rate of reaction are postulated and the rate expressions consistent with these hypothesis are derived. The rate-controlling mechanism of the solid catalyzed gas reaction may be the mass transfer of the reactants or desorption of products or surface reaction between adsorbed gases or between an adsorbed gas and gaseous reactant at the catalyst surface. The rate expressions are then fitted into experimental data, and the expression giving the best fit is retained, while others are discarded.

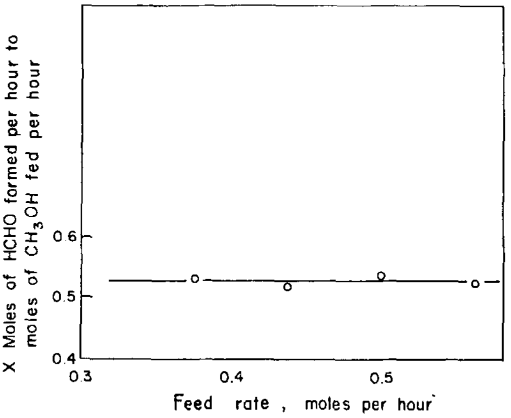

FIG. 5. Effect of feed rate on conversion and selectivity.

Heat and mass transfer effects. The temperature and partial pressure gradients between the flowing fluid and the exterior surface of the catalyst were evaluated by

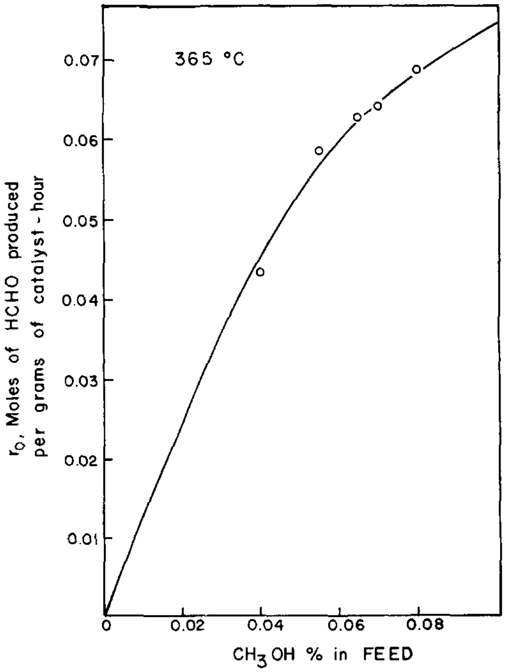

FIG. 6. Effect of partial pressure of methanol on the initial rate.

TABLE 2

Effect of Variables on Conversion, Rate of Formation and Selectivity for Formaldehyde Production in Methanol Oxidation

				Feed, moles/hr.			Analysis of Products, moles/hr.									
Run No.	Temp. °C.	W/F	R	CH_3OH	O_2	N_2	HCHO	CH_3OH	H_2O	CO	CO_2	O_2	N_2	Conversion (X)	Yield (Y)	Selectivity (S)
214	326	13.3	2.42	0.030	0.0788	0.2963	0.0159	0.0141	0.0159	0	0	0.0709	0.2963	0.530	0.530	1.00
215	326	13.3	2.42	0.035	0.0919	0.3456	0.0185	0.0165	0.0185	0	0	0.0827	0.3456	0.528	0.528	1.00
216	326	13.3	2.42	0.040	0.1050	0.3450	0.0213	0.0187	0.0213	0	0	0.0944	0.3450	0.532	0.532	1.00
217	326	13.3	2.42	0.045	0.1181	0.4444	0.0238	0.0331	0.0238	0	0	0.1062	0.4440	0.529	0.529	1.00
300	422	16.3	2.42	0.030	0.0788	0.2960	0.0114	0.0035	0.0416	0.00302	0.01208	0.0537	0.2730	0.88	0.38	0.42
301	460	16.3	2.42	0.030	0.0788	0.2960	0.0015	0	0.0585	0.00142	0.02708	0.0453	0.2730	1.00	0.05	0.05
302	365	2.5	5.04	0.030	0.1580	0.5930	0.0032	0.0269	0.0032	0	0	0.1560	0.5930	0.105	0.105	1.00
303	365	5.0	5.04	0.030	0.1580	0.5930	0.0063	0.0237	0.0063	0	0	0.1540	0.5930	0.210	0.210	1.00
304	365	8.8	5.04	0.030	0.1580	0.5930	0.0108	0.0192	0.0108	0	0	0.1520	0.5930	0.360	0.360	1.00
305	365	13.3	5.04	0.030	0.1580	0.5930	0.0154	0.0146	0.0154	0	0	0.1500	0.5930	0.513	0.513	1.00
306	365	16.3	5.04	0.030	0.1580	0.5930	0.0180	0.0120	0.0180	0	0	0.1490	0.5930	0.600	0.600	1.00
307	365	22.0	5.04	0.030	0.1580	0.5930	0.0219	0.0081	0.0219	0	0	0.1470	0.5930	0.730	0.730	1.00
308	365	2.5	3.61	0.030	0.1150	0.4310	0.0033	0.0267	0.0033	0	0	0.1060	0.4070	0.110	0.110	1.00
309	365	5.0	3.61	0.030	0.1150	0.4310	0.0084	0.0216	0.0084	0	0	0.1040	0.4070	0.280	0.280	1.00
310	365	8.8	3.61	0.030	0.1150	0.4310	0.0142	0.0158	0.0142	0	0	0.1010	0.4070	0.473	0.473	1.00
311	365	13.3	3.61	0.030	0.1150	0.4310	0.0195	0.0105	0.0195	0	0	0.0980	0.4070	0.650	0.650	1.00
312	365	16.3	3.61	0.030	0.1150	0.4310	0.0215	0.0085	0.0215	0	0	0.0973	0.4070	0.717	0.717	1.00
313	365	22.0	3.61	0.030	0.1150	0.4310	0.0225	0.0075	0.0225	0	0	0.0968	0.4070	0.749	0.749	1.00
314	365	2.5	3.02	0.030	0.0970	0.3650	0.00375	0.0263	0.0037	0	0	0.0891	0.3410	0.125	0.125	1.00
315	365	5.0	3.02	0.030	0.0970	0.3650	0.00900	0.0210	0.0090	0	0	0.0865	0.3410	0.300	0.300	1.00
316	365	8.8	3.02	0.030	0.0970	0.3650	0.01500	0.0150	0.0150	0	0	0.0835	0.3410	0.500	0.500	1.00
317	365	13.3	3.02	0.030	0.0970	0.3650	0.02030	0.0097	0.0203	0	0	0.0809	0.3410	0.677	0.677	1.00
318	365	16.3	3.02	0.030	0.0970	0.3650	0.02220	0.0078	0.0222	0	0	0.0799	0.3410	0.740	0.740	1.00
319	365	22.0	3.02	0.030	0.0970	0.3650	0.02370	0.0063	0.0237	0	0	0.0792	0.3410	0.790	0.790	1.00
320	365	2.5	2.79	0.030	0.0900	0.3390	0.00408	0.0259	0.0040	0	0	0.0817	0.3150	0.136	0.136	1.00
321	365	5.0	2.79	0.030	0.0900	0.3390	0.00870	0.0212	0.0087	0	0	0.0793	0.3150	0.290	0.290	1.00
322	365	8.8	2.79	0.030	0.0900	0.3390	0.01550	0.0146	0.0155	0	0	0.0760	0.3150	0.517	0.517	1.00
323	365	13.3	2.79	0.030	0.0900	0.3390	0.02090	0.0092	0.0209	0	0	0.0733	0.3150	0.697	0.697	1.00
324	365	16.3	2.79	0.030	0.0900	0.3390	0.02360	0.0064	0.0236	0	0	0.0719	0.3150	0.787	0.787	1.00
325	365	22.0	2.79	0.030	0.0900	0.3390	0.02450	0.0055	0.0245	0	0	0.0715	0.3150	0.817	0.817	1.00
326	365	2.5	2.42	0.030	0.0788	0.2960	0.0042	0.0258	0.0042	0	0	0.0767	0.2730	0.140	0.140	1.00
327	365	5.0	2.42	0.030	0.0788	0.2960	0.0099	0.0201	0.0099	0	0	0.0738	0.2730	0.330	0.330	1.00

TABLE 2 (Cont.)

Run No.	Temp °C.	W/F	R	Feed, moles/hr.			Analysis of Products, moles/hr.							Conversion (X)	Yield (Y)	Selectivity (S)
				CH_3OH	O_2	N_2	HCHO	CH_3OH	H_2O	CO	CO_2	O_2	N_2			
328	365	8.8	2.42	0.030	0.0788	0.2960	0.0165	0.0135	0.0165	0	0	0.0705	0.2730	0.500	0.500	1.00
329	365	13.3	2.42	0.030	0.0788	0.2960	0.0219	0.0081	0.0219	0	0	0.0678	0.2730	0.730	0.730	1.00
330	365	16.3	2.42	0.030	0.0788	0.2960	0.0246	0.0054	0.0246	0	0	0.0665	0.2730	0.820	0.820	1.00
331	365	22.0	2.42	0.030	0.0788	0.2960	0.0251	0.0049	0.0251	0	0	0.0662	0.2730	0.837	0.837	1.00
332	326	2.5	5.04	0.030	0.1580	0.5930	0.0030	0.0270	0.0030	0	0	0.1560	0.5930	0.100	0.100	1.00
333	326	5.0	5.04	0.030	0.1580	0.5930	0.0060	0.0240	0.0060	0	0	0.1550	0.5930	0.199	0.199	1.00
334	326	8.8	5.04	0.030	0.1580	0.5930	0.0100	0.0200	0.0100	0	0	0.1530	0.5930	0.333	0.333	1.00
335	326	13.3	5.04	0.030	0.1580	0.5930	0.0143	0.0157	0.0143	0	0	0.1500	0.5930	0.477	0.477	1.00
336	326	16.3	5.04	0.030	0.1580	0.5930	0.0167	0.0133	0.0167	0	0	0.1490	0.5930	0.557	0.557	1.00
337	326	22.0	5.04	0.030	0.1580	0.5930	0.0198	0.0102	0.0198	0	0	0.1480	0.5930	0.660	0.660	1.00
338	326	2.5	3.61	0.030	0.1150	0.4310	0.0033	0.0267	0.0033	0	0	0.1130	0.4070	0.110	0.110	1.00
339	326	5.0	3.61	0.030	0.1150	0.4310	0.0063	0.0237	0.0063	0	0	0.1110	0.4070	0.210	0.210	1.00
340	326	8.8	3.61	0.030	0.1150	0.4310	0.0102	0.0198	0.0102	0	0	0.1100	0.4070	0.340	0.340	1.00
341	326	13.3	3.61	0.030	0.1150	0.4310	0.0142	0.0158	0.0142	0	0	0.1080	0.4070	0.473	0.473	1.00
342	326	16.3	3.61	0.030	0.1150	0.4310	0.0167	0.0134	0.0167	0	0	0.1060	0.4070	0.557	0.557	1.00
343	326	22.0	3.61	0.030	0.1150	0.4310	0.0202	0.0098	0.0202	0	0	0.1050	0.4070	0.673	0.673	1.00
344	326	2.5	3.02	0.030	0.0970	0.3650	0.0033	0.0267	0.0033	0	0	0.0953	0.3410	0.110	0.110	1.00
345	326	5.0	3.02	0.030	0.0970	0.3650	0.0065	0.0235	0.0065	0	0	0.0937	0.3410	0.217	0.217	1.00
346	326	8.8	3.02	0.030	0.0970	0.3650	0.0107	0.0194	0.0107	0	0	0.0916	0.3410	0.357	0.357	1.00
347	326	13.3	3.02	0.030	0.0970	0.3650	0.0146	0.0154	0.0146	0	0	0.0896	0.3410	0.487	0.487	1.00
348	326	16.3	3.02	0.030	0.0970	0.3650	0.0170	0.0131	0.0170	0	0	0.0885	0.3410	0.567	0.567	1.00
349	326	22.0	3.02	0.030	0.0970	0.3650	0.0204	0.0096	0.0204	0	0	0.0867	0.3410	0.680	0.680	1.00
350	326	2.5	2.79	0.030	0.0900	0.3390	0.0035	0.0266	0.0035	0	0	0.0880	0.3150	0.115	0.115	1.00
351	326	5.0	2.79	0.030	0.0900	0.3390	0.0066	0.0234	0.0066	0	0	0.0867	0.3150	0.220	0.220	1.00
352	326	8.8	2.79	0.030	0.0900	0.3390	0.0110	0.0191	0.0110	0	0	0.0845	0.3150	0.367	0.367	1.00
353	326	13.3	2.79	0.030	0.0900	0.3390	0.0150	0.0150	0.0150	0	0	0.0825	0.3150	0.500	0.500	1.00
354	326	16.3	2.79	0.030	0.0900	0.3390	0.0173	0.0127	0.0173	0	0	0.0813	0.3150	0.577	0.577	1.00
355	326	22.0	2.79	0.030	0.0900	0.3390	0.0207	0.0093	0.0207	0	0	0.0797	0.3150	0.690	0.690	1.00
356	326	2.5	2.42	0.030	0.0788	0.2960	0.0036	0.0264	0.0036	0	0	0.0770	0.2730	0.120	0.120	1.00
357	326	5.0	2.42	0.030	0.0788	0.2960	0.0069	0.0231	0.0069	0	0	0.0753	0.2730	0.230	0.230	1.00
358	326	8.8	2.42	0.030	0.0788	0.2960	0.0114	0.0186	0.0114	0	0	0.0731	0.2730	0.380	0.380	1.00
359	326	13.3	2.42	0.030	0.0788	0.2960	0.0159	0.0141	0.0159	0	0	0.0708	0.2730	0.530	0.530	1.00

TABLE 2 (Cont.)

Run No.	Temp. °C.	W/F	R	Feed, moles/hr.			Analysis of Products, moles/hr.							Conversion (X)	Yield (Y)	Selectivity (S)
				CH_3OH	O_2	N_2	HCHO	CH_3OH	H_2O	CO	CO_2	O_2	N_2			
360	326	16.3	2.42	0.030	0.0788	0.2960	0.0182	0.0118	0.0182	0	0	0.0697	0.2730	0.607	0.607	1.00
361	326	22.0	2.42	0.030	0.0788	0.2960	0.0210	0.0090	0.0210	0	0	0.0683	0.2730	0.700	0.700	1.00
362	319	2.5	5.04	0.030	0.1580	0.5930	0.0029	0.0272	0.0029	0	0	0.1560	0.5930	0.095	0.095	1.00
363	319	5.0	5.04	0.030	0.1580	0.5930	0.0056	0.0245	0.0056	0	0	0.1550	0.5930	0.187	0.187	1.00
364	319	8.8	5.04	0.030	0.1580	0.5930	0.0094	0.0206	0.0094	0	0	0.1530	0.5930	0.314	0.314	1.00
365	319	13.3	5.04	0.030	0.1580	0.5930	0.0134	0.0167	0.0134	0	0	0.1510	0.5930	0.447	0.447	1.00
366	319	16.3	5.04	0.030	0.1580	0.5930	0.0155	0.0146	0.0155	0	0	0.1500	0.5930	0.517	0.517	1.00
367	319	22.0	5.04	0.030	0.1580	0.5930	0.0177	0.0123	0.0177	0	0	0.1490	0.5930	0.590	0.590	1.00
368	319	2.5	3.61	0.030	0.1150	0.4310	0.0029	0.0271	0.0029	0	0	0.1130	0.4070	0.098	0.098	1.00
369	319	5.0	3.61	0.030	0.1150	0.4310	0.0057	0.0243	0.0057	0	0	0.1121	0.4070	0.190	0.190	1.00
370	319	8.8	3.61	0.030	0.1150	0.4310	0.0096	0.0204	0.0096	0	0	0.1101	0.4070	0.320	0.320	1.00
371	319	13.3	3.61	0.030	0.1150	0.4310	0.0136	0.0164	0.0136	0	0	0.1080	0.4070	0.453	0.453	1.00
372	319	16.3	3.61	0.030	0.1150	0.4310	0.0158	0.0143	0.0158	0	0	0.1071	0.4070	0.527	0.527	1.00
373	319	22.0	3.61	0.030	0.1150	0.4310	0.0180	0.0120	0.0180	0	0	0.1062	0.4070	0.600	0.600	1.00
374	319	2.5	3.02	0.030	0.0970	0.3650	0.0031	0.0269	0.0031	0	0	0.0954	0.3410	0.103	0.103	1.00
375	319	5.0	3.02	0.030	0.0970	0.3650	0.0060	0.0240	0.0060	0	0	0.0939	0.3410	0.200	0.200	1.00
376	319	8.8	3.02	0.030	0.0970	0.3650	0.0100	0.0200	0.0100	0	0	0.0919	0.3410	0.333	0.333	1.00
377	319	13.3	3.02	0.030	0.0970	0.3650	0.0141	0.0159	0.0141	0	0	0.0899	0.3410	0.470	0.470	1.00
378	319	16.3	3.02	0.030	0.0970	0.3650	0.0162	0.0138	0.0162	0	0	0.0888	0.3410	0.540	0.540	1.00
379	319	22.0	3.02	0.030	0.0970	0.3650	0.0186	0.0114	0.0186	0	0	0.0876	0.3410	0.620	0.620	1.00
380	319	2.5	2.79	0.030	0.0900	0.3390	0.0030	0.0270	0.0030	0	0	0.0885	0.3150	0.100	0.100	1.00
381	319	5.0	2.79	0.030	0.0900	0.3390	0.0060	0.0240	0.0060	0	0	0.0870	0.3150	0.200	0.200	1.00
382	319	8.8	2.70	0.030	0.0900	0.3390	0.0100	0.0200	0.0100	0	0	0.0850	0.3150	0.333	0.333	1.00
383	319	13.3	2.79	0.030	0.0900	0.3390	0.0141	0.0159	0.0141	0	0	0.0830	0.3150	0.470	0.470	1.00
384	319	16.3	2.79	0.030	0.0900	0.3390	0.0164	0.0137	0.0164	0	0	0.0818	0.3150	0.547	0.547	1.00
385	319	22.0	2.79	0.030	0.0900	0.3390	0.0188	0.0113	0.0188	0	0	0.0806	0.3150	0.627	0.627	1.00
386	319	2.5	2.42	0.030	0.0788	0.2960	0.0032	0.0269	0.0032	0	0	0.0772	0.2730	0.105	0.105	1.00
387	319	5.0	2.42	0.030	0.0788	0.2960	0.0060	0.0240	0.0060	0	0	0.0758	0.2730	0.200	0.200	1.00
388	319	8.8	2.42	0.030	0.0788	0.2960	0.0102	0.0198	0.0102	0	0	0.0737	0.2730	0.340	0.340	1.00
389	319	13.3	2.42	0.030	0.0788	0.2960	0.0143	0.0158	0.0143	0	0	0.0716	0.2730	0.475	0.475	1.00
390	319	16.3	2.42	0.030	0.0788	0.2960	0.0165	0.0135	0.0165	0	0	0.0705	0.2730	0.550	0.550	1.00

TABLE 2 (Cont.)

Run No.	Temp. °C.	W/F	R	Feed, moles/hr.			Analysis of Products, moles/hr.							Conversion (X)	Yield (Y)	Selectivity (S)
				CH_3OH	O_2	N_2	HCHO	CH_3OH	H_2O	CO	CO_2	O_2	N_2			
391	319	22.0	2.42	0.030	0.0788	0.2960	0.0192	0.0108	0.0192	0	0	0.0692	0.2730	0.640	0.640	1.00
392	250	2.5	2.42	0.030	0.0788	0.2960	0.0003	0.0297	0.0003	0	0	0.0786	0.2730	0.0105	0.0105	1.00
393	250	5.0	2.42	0.030	0.0788	0.2960	0.0006	0.0294	0.0006	0	0	0.0784	0.2730	0.0210	0.0210	1.00
394	250	8.8	2.42	0.030	0.0788	0.2960	0.0011	0.0289	0.0011	0	0	0.0782	0.2730	0.0380	0.0380	1.00
395	250	13.3	2.42	0.030	0.0788	0.2960	0.0017	0.0283	0.0017	0	0	0.0779	0.2730	0.0565	0.0565	1.00
396	250	16.3	2.42	0.030	0.0788	0.2960	0.0021	0.0279	0.0021	0	0	0.0777	0.2730	0.0690	0.0690	1.00
397	250	22.0	2.42	0.030	0.0788	0.2960	0.0027	0.0273	0.0027	0	0	0.0774	0.2730	0.0900	0.0900	1.00

TABLE 3
Two-Stage Redox Mechanisms

No.	Reaction order m CH_3OH	 n O_2	Reaction
1	1	0.5	$\frac{W}{F}\frac{{}_0p_M}{\ln(1-x)} = -\frac{1}{k_1} + \frac{4\alpha}{k_2}\frac{[{}_0p_{O_2}{}^{1/2} - ({}_0p_{O_2} - 1/2x{}_0p_M)^{1/2}]}{\ln(1-x)}$
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	$\frac{W}{F}\frac{1}{x} = \frac{2}{k_1}\frac{[1-(1-x)^{1/2}]}{{}_0p_M{}^{1/2}x} + \frac{\alpha}{k_2}$
4	1	1	$\frac{W}{F}\frac{{}_0p_M}{\ln(1-x)} = -\frac{1}{k_1} + \frac{2\alpha}{k_2}\frac{\ln[{}_0p_{O_2}/({}_0p_{O_2} - 1/2{}_0p_M x)]}{\ln(1-x)}$
5	0.5	0.5	$\frac{W}{F}\frac{{}_0p_M{}^{1/2}}{[1-(1-x)^{1/2}]} = \frac{2}{k_1} + \frac{4\alpha}{k_2}\frac{{}_0p_{O_2}{}^{1/2} - ({}_0p_{O_2} - 1/2{}_0p_M x)^{1/2}}{{}_0p_M{}^{1/2}[1-(1-x)^{1/2}]}$

the method of Yoshida *et al.* (*26*). The highest temperature difference across the film, thus calculated, was of the order of 1°C. The highest partial pressure gradient, thus calculated, was of the order of 0.005 atm, which showed that the pressure drop across the gas film was insignificant and that the effect of mass transfer was negligible.

The effects of diffusion were kept at a minimum by using a high velocity of the gas through the catalyst. The fair constancy of conversion obtained by changing the feed rate, while keeping W/F constant as shown in Fig. 5, suggested that the diffusion of the gases was not rate controlling. The internal diffusional resistance in the catalyst particles was negligible since a change in particle size (0.20–1.65 mm) did not vary the reaction rate to any measurable degree.

Since the diffusion steps, which are physical processes, were found not to be rate controlling, the remaining steps, viz., the adsorption of the reactants, reaction between the adsorbed gases, and the desorption of gases were examined in detail. The method of initial rates as described by Yang and Hougen (*27*) was applied to the experimental data to eliminate some of the controlling steps. A plot of initial rates against partial pressure of methanol indicated that the desorption of the products was definitely not rate controlling (Fig. 6).

Since mass transfer from the gas stream to the catalyst surface and diffusion through the catalyst pores and desorption of the products were not rate controlling, the possibility of the adsorption of reactants and surface reaction as rate controlling was left.

The kinetic expressions derived by Mars and Van Krevelen (*19*) for the vapor phase oxidation of aromatic hydrocarbons on vanadium pentoxide on the basis of the oxidation–reduction mechanisms were tested. Fifteen different rate equations based on 2-stage and 3-stage mechanisms (Tables 3 and 4) were derived. Based on these equations, the rate coefficients were evaluated, and the mechanism giving a negative coefficient in the rate equation (as found by the method of least square error) was rejected.

The following two-stage mechanism with m equal to 1, and n equal to 0.5 was found to give the best fit:

$$CH_3OH(g) + S_{ox} \xrightarrow{k_1} HCHO(g) + H_2O, \quad (2)$$

$$O_2(g) + S_{red} \xrightarrow{k_2} S_{ox}, \quad (3)$$

S_{ox} being an active site of lattice or adsorbed oxygen and S_{red}, the reduced site of lattice oxygen or the empty site. The rate expression which most satisfactorily represented the data was:

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

where k_1 and k_2 were temperature dependent constants.

TABLE 4
THREE-STAGE REDOX MECHANISMS

No.	Reaction order m CH_3OH	 n O_2	Reaction mechanism	Rate equation
1	1, 2	0.5	$m\mathrm{CH_3OH(g)} + S_{\mathrm{ox}} \xrightarrow{k_1} (\mathrm{CH_3OH})_m\text{—}S_{\mathrm{ox}}$ $(\mathrm{CH_3OH})_m\text{—}S_{\mathrm{ox}} \xrightarrow{k_2} m\mathrm{HCHO(g)} + m\mathrm{H_2O(g)} + S_{\mathrm{red}}$ $S_{\mathrm{red}} + n\mathrm{O_2(g)} \xrightarrow{k_3} S_{\mathrm{ox}}$	$r = \dfrac{k_1 p_{\mathrm{M}}{}^m}{1 + (k_1/k_2)p_{\mathrm{M}}{}^m + 0.5k_1 p_{\mathrm{M}}{}^m/k_3 p_{\mathrm{O_2}}{}^n}$
2	1, 2	0.5	$m\mathrm{CH_3OH(g)} + S_{\mathrm{ox}} \xrightarrow{k_1} (\mathrm{HCHO})_m\text{—}S_{\mathrm{red}} + m\mathrm{H_2O(g)}$ $(\mathrm{HCHO})_m\text{—}S_{\mathrm{red}} \xrightarrow{k_2} m\mathrm{HCHO(g)} + S_{\mathrm{red}}$ $S_{\mathrm{red}} + n\mathrm{O_2(g)} \xrightarrow{k_3} S_{\mathrm{ox}}$	$r = \dfrac{k_1 p_{\mathrm{M}}{}^m}{1 + (k_1/k_2)p_{\mathrm{M}}{}^m + 0.5k_1 p_{\mathrm{M}}{}^m/k_3 p_{\mathrm{O_2}}{}^n}$
3	1, 2	0.5	$m\mathrm{CH_3OH(g)} + S_{\mathrm{ox}} \xrightarrow{k_1} m\mathrm{HCHO(g)} + (\mathrm{H_2O})_m\text{—}S_{\mathrm{red}}$ $(\mathrm{H_2O})_m\text{—}S_{\mathrm{red}} \xrightarrow{k_2} m\mathrm{H_2O(g)} + S_{\mathrm{red}}$ $S_{\mathrm{red}} + n\mathrm{O_2(g)} \xrightarrow{k_3} S_{\mathrm{ox}}$	$r = \dfrac{k_1 p_{\mathrm{M}}{}^m}{1 + (k_1/k_2)p_{\mathrm{M}}{}^m + 0.5k_1 p_{\mathrm{M}}{}^m/k_3 p_{\mathrm{O_2}}{}^n}$
4	1, 2	0.5	$m\mathrm{CH_3OH(g)} + S_{\mathrm{ox}} \xrightarrow{k_1} m\mathrm{HCHO(g)} + m\mathrm{H_2O(g)} + S_{\mathrm{red}}$ $S_{\mathrm{red}} + n\mathrm{O_2(g)} \xrightarrow{k_2} (\mathrm{O_2})_n\text{—}S_{\mathrm{red}}$ $(\mathrm{O_2})_n\text{—}S_{\mathrm{red}} \xrightarrow{k_3} S_{\mathrm{ox}}$	$r = \dfrac{k_1 p_{\mathrm{M}}{}^m}{1 + 0.5(k_1/k_3)p_{\mathrm{M}}{}^m + 0.5(k_1 p_{\mathrm{M}}{}^m/k_2 p_{\mathrm{O_2}}{}^n}$
5			$m\mathrm{CH_3OH(g)} + S_{\mathrm{ox}} \xrightarrow{k_1} m\mathrm{H_2O(g)} + (\mathrm{HCHO})_m\text{—}S_{\mathrm{red}}$ $(\mathrm{HCHO})_m\text{—}S_{\mathrm{red}} \overset{K_2}{\rightleftharpoons} m\mathrm{HCHO(g)} + S_{\mathrm{red}}$ $S_{\mathrm{red}} + n\mathrm{O_2(g)} \xrightarrow{k_3} S_{\mathrm{ox}}$	$r = \dfrac{k_1 p_{\mathrm{M}}{}^m}{1 + 0.5(k_1 p_{\mathrm{M}}{}^m/k_3 p_{\mathrm{O_2}}{}^n) + 0.5(k_1 p_{\mathrm{M}}{}^m p_f{}^m/K_2 k_3 p_{\mathrm{O_2}}{}^n)}$

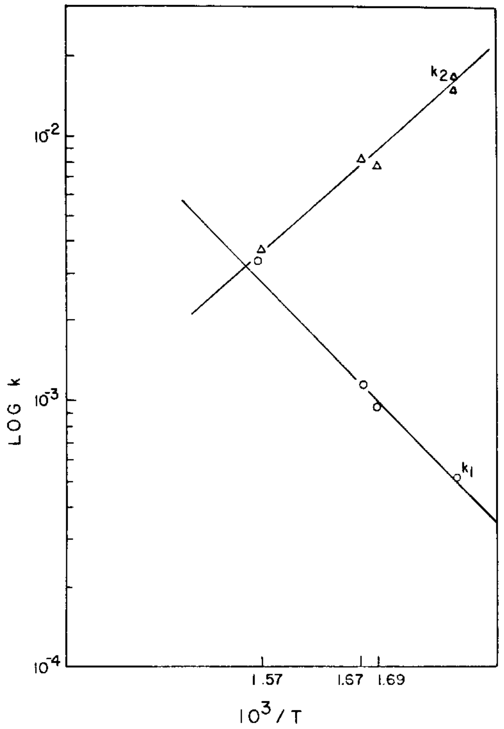

FIG. 7. Effect of temperature on the rate constants k_1 and k_2.

Equation (4) seems to indicate a pseudo-first-order rate equation. Since the percentage methanol in air (oxygen) is small, the term $k_1p_M/2k_2p_{O_2}{}^{1/2}$ in the denominator is always much less than one, and hence can be neglected.

The activation energies of the individual steps were evaluated from the Arrhenius plots, as shown in Fig. 7 and equations relating k_1 and k_2 with temperature were obtained.

$$\log k_1 = 3.432 - \frac{3.81 \times 10^3}{T} \quad (5)$$

$$\log k_2 = -7.508 + \frac{3.23 \times 10^3}{T} \quad (6)$$

The values of k_1 and k_2, obtained from Eqs. (5) and (6) were used to obtain theoretical rates from which the values of W/F were calculated at different conversions. The values of W/F thus calculated for different conversions were plotted (solid lines in Fig. 4). The percentage deviation between the experimental and calculated values was less than 5%, except for the last condition in which the experimental value of W/F exceeded 22 g hr/mole. The value of k_2 decreases with increasing temperature. This is possibly due to k_2 representing apparently an over all value, rather than a single step rate constant. Such a postulate is quite reasonable in view of the highly exothermic oxidation reaction.

The present kinetic results agree with those reported by earlier workers using iron–molybdenum oxide (*13–15*), vanadium pentoxide (*17*), and manganese–molybdenum oxide (*18*) catalysts in the vapor-phase oxidation of methanol. Also, the methanol oxidation in its thermodynamic aspects with those reactions reported in the literature (*28*) and in patents.

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