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A Kinetic Study of Partial Oxidation of Methane with Nitrous Oxide on a Molybdena–Silica Catalyst

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Silica-supported molybdena has been found to catalyze the partial oxidation of methane to methanol and formaldehyde. Nitrous oxide as the oxidizing agent and the presence of water vapor in the reactant gas stream were necessary to carry out this reaction at the temperature range of 480–590°C and a total pressure of 1 atm. Highest turnover rates of methanol and formaldehyde were, respectively, 2.24×10^{-4} and 6.25×10^{-4} molec · s^{-1} · site^{-1} at 590°C. The rate of methanol formation was first order with respect to methane and water, and zero order with respect to nitrous oxide; whereas the rate of formaldehyde formation was zero order with respect to all reactants. From activation energy measurements it was possible to identify a low- and a high-temperature mechanism of formaldehyde formation. Predominant at temperatures below 540°C were the processes leading to parallel formations of methanol (E_a = 41 kcal/mole) and formaldehyde (E_a = 82 kcal/mole) from the same intermediate, while at higher temperatures only the consecutive oxidation processes leading to formaldehyde via methanol with an overall E_a of 40 kcal/mole was the major route. © 1985 Academic Press, Inc.

INTRODUCTION

With a C–H (first) bond energy of 104 kcal/mole and a weak interaction with most surfaces that is dominated by dispersion forces, methane seems to be the most difficult molecule among all organic substances to activate. Nevertheless, when it is reacted with water (steam reforming) over nickel catalysts it dehydrogenates completely to produce CO and H_2 by an endothermic process (*1*). Its oxidation to the thermodynamically most stable products, CO_2 and H_2O, is also facile. It would be of considerable importance if the partial oxidation of methane to methanol with the insertion of an oxygen atom could be carried out. This appears to be a difficult reaction while the further partial oxidation of methanol to formaldehyde is a facile step and a well-researched industrial process (*2, 3*). The methane-to-methanol conversion is a thermodynamically favorable process and in light of the successes obtained with the partial oxidation of other small molecules, ethylene and propylene, the production of methanol from methane deserves serious experimental scrutiny.

The purpose of this work is to investigate the possibility of partial oxidation of methane under atmospheric pressure conditions. The observation by Liu *et al.* (*4, 5*) indicated that partial oxidation could be achieved under 1 atm pressure by the use of nitrous oxide as the oxidant and water vapor in the gas stream over a MoO_3–SiO_2 catalyst. We have carried out the study reported here to verify their observation, which claimed a 1.9% methane conversion at 560°C to formaldehyde and methanol at a four-to-one ratio without forming any carbon oxides. By using a set of experimental conditions identical to theirs we were able to reproduce their observations regarding conversion and selectivity at various temperatures.

We have considerably expanded the kinetic studies and observed several features that were different from those reported by Liu *et al.* (*5*). We measured the pressure

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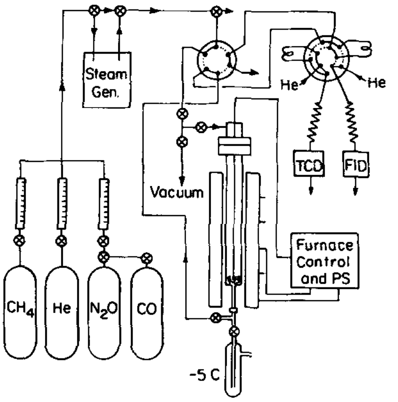

FIG. 1. Continuous-flow apparatus for partial oxidation of methane.

and temperature dependences of the individual rates of formation of methanol and formaldehyde. We observed a first-order dependence of the rate of methanol formation on the partial pressures of methane and water vapor and zero-order dependence on nitrous oxide. The rate of formaldehyde formation was found to be zero order with respect to all reactants. In our temperature-dependence measurements, we were able to observe two linear domains in the Arrhenius plots for formaldehyde formation; they corresponded to activation energies of 82 ± 4 kcal/mole below 540°C and 40 ± 2 kcal/mole above. For methanol only one linear regime giving an activation energy of 38 ± 4 kcal/mole could be observed. The activation energy value >540°C temperature domain for formaldehyde was close to a value of 42 ± 2 kcal/mole observed by Liu *et al.* (5) for the total conversion of methane over the temperature range of 550–594°C.

EXPERIMENTAL

Materials. The catalyst, 1.7% MoO_3–SiO_2, was prepared by impregnation from a basic solution of ammonium heptamolybdate at a pH of 11.0 and a subsequent drying followed by calcination in air at 590°C. The support, Cab-O-Sil grade HS-5 fumed silica, had a reported surface area of 350 ± 25 m^2g^{-1}. The finished catalyst was pressed and sieved to particle size 30–60 mesh. The final surface area, as determined by BET measurement, was found to be 220 ± 5 m^2g^{-1}. No attempt was made to determine the active molybdenum surface area by chemisorption measurements. The reactant gases, methane (99.9%) and nitrous oxide (99.0%); the reducing gas, carbon monoxide (99.0%); and the carrier gas, helium (99.9%) were used as received.

Apparatus and methods. The fixed-bed reactor and the continuous flow manifold used in this study are schematically represented in Fig. 1. The flow of reactant and carrier gases were regulated by needle valves and monitored by rotameters. The requisite amount of steam was introduced into the gas stream by passing it through a heated-water reservoir. The mixed gas stream, typically of the molar composition 0.1 CH_4 + 0.35 N_2O + 0.35 H_2O + 0.2 He, was led through a Valco six-port switch valve before and after passing through the reactor to allow for pre- and postreaction GC analyses. The entire reaction manifold was kept at 120°C to prevent condensation of the water vapor.

The fused-silica reactor measured 35 cm in length and 2.2 cm in diameter. The catalyst bed, supported between pads of silica wool, was usually 2-cm thick. The temperature was monitored by a quartz-shielded thermocouple probe embedded into the catalyst bed. The exit was made narrow enough (2 mm i.d.) to effect rapid quenching of methanol and formaldehyde. A valve assembly was placed at the exit in order to direct the exit-gas stream either through a cold trap or through the six-port valve. The catalyst bed was centered in a 6-in. heating zone of a tube furnace, the temperature of which could be maintained within 1°C over the entire reaction period. The radial temperature gradient was usually less than 2°C. The catalyst was outgassed at 500°C under a vacuum of <100 μm for 1 h. This was followed by a reduction in a 100-Torr pressure of CO at the same temperature for 1 h, at the end of which the reactor was evacuated and adjusted to the desired reaction temperature. The reaction was initiated by introducing an 80 SCCM flow of the reaction mixture taking care not to introduce any air during the process. One to two hours of time was allowed for the system to reach a steady-state condition and be ready for sample analysis.

Analytical procedure. A Hewlett–Packard Model 5793A dual-column gas chromatograph, equipped with a thermal conductivity and a flame ionization detector, was used for all analytical purposes. A 10-port Valco injection valve was installed in line to the reactant gas flow for sample analysis utilizing both the thermal conductivity and the flame ionization detectors. Separation and detection of N_2, CO, CO_2, and H_2O were accomplished with a Carbosieve S-II (Supelco) column and a thermal conductivity detector. For CH_3OH, HCHO, and hydrocarbons a Porapak-QS column and a flame ionization detector at a sensitivity of 5×10^{-12} AFS were used. For quantitative analysis the measured peak areas were corrected for the molar response factors of the various components as determined by Dietz (*6*). The concentrations of CH_3OH and HCHO were determined by injecting quantitatively 1.00 to 2.00 μl of the solution into the GC and matching the FID signal with calibration curves prepared from a series of aqueous standards. The methanol standards exhibited excellent linear response within the limits of 5×10^{-10} to 1×10^{-7} mole. The formaldehyde standards, prepared by dissolving paraformaldehyde and standardized by Romjin's iodometric titration method (*7*), showed linearity with respect to FID response within the range of 1×10^{-8} to 4×10^{-7} mole. The methanol to formaldehyde molar ratio determined by analysis of the gas phase agreed within 5% with that of the solution phase.

The rates of production of CH_3OH and HCHO were found by determining the total number of moles trapped in the liquid phase over a timed interval. The rate was calculated as the number of molecules formed per second per molybdenum atom. The reported rate data are based on the assumption of 100% dispersion of Mo, and hence set the lowest limit. The usual conversion versus contact time approach to kinetic studies was found not suitable for this reaction since selectivity was a function of contact time. This will be discussed later.

RESULTS

Conversion and selectivity. Data obtained over the temperature range of 480°C to 590°C are shown in Table 1. The observed methane conversion varied from as low as 0.06% at 480°C to as high as 2.7% at 590°C. At temperatures below 500°C CH_3OH was formed almost exclusively. Selectivity values were calculated as percentage molar ratios of the individual products to the molar sum of all the products. Above 500°C, HCHO selectivity continued to increase and reached the level of CH_3OH at 550°C. At higher temperatures the carbon monoxide formation became considerable. Over the entire temperature range of 480–590°C, there was a gradual tendency for CH_3OH selectivity to decline and HCHO and CO selectivities to increase with increasing temperature. It was interesting to note that even at the highest temperature studied (590°C), HCHO remained the major product. Small amounts of other hydrocarbons, such as ethylene, ethane, propane, and butane were also formed at all temperatures. They were found to form, however, when flowing the same reactant gas mixture over hot silica, and thus believed to be due to the interaction of the reactants with the silica support, and not the molybdenum oxide catalyst.

The threshold temperature for CO formation is apparently 570°C. However, it is possible that at the low overall conversions small amounts of CO that formed at lower temperatures escaped detection by the relatively less sensitive thermal conductivity detector. The 540°C temperature appears to be a more realistic upper temperature limit

TABLE 1

Turnover Rate, Conversion, and Product Distribution at Various Temperatures

T (°C)	Turnover number × 10^4 (molec · s^{-1} · $site^{-1}$)		Conversion (%)	Product distribution (mole%)				
	CH_3OH	HCHO		CH_3OH	HCHO	CO	CO_2	HC[a]
480	0.31	0	0.06	96	0	0	0	4
490	0.50	0	0.10	96	0	0	0	4
500	0.70	0.11	0.17	85	11	0	0	4
510	0.89	0.27	0.22	72	23	0	0	4
520	0.98	0.43	0.26	66	29	0	0	4
530	1.49	0.88	0.31	59	34	0	0	4
540	1.85	1.47	0.47	54	42	0	0	4
550	1.97	1.47	0.71	46	50	0	0	4
570	2.34	3.69	1.2	18	44	34	0	4
570[b]	—	—	2.9	13.8	64.3	19.1	2.8	—
590	2.74	6.25	2.6	16	40	39	0	5

Note. Molar Composition: 0.10 CH_4 + 0.35 N_2O + 0.35 H_2O + 0.20 He.

[a] Hydrocarbons include ethylene, ethane, propane, and butane.

[b] Ref. (*5*).

for the sole formations of the desired products, i.e., CH_3OH and HCHO. In the subsequent kinetic order determinations all reactions were therefore carried out at 540°C.

Dependence of the product selectivity on contact time was investigated. As shown in Table 2, we found that a longer contact time favored the formation of CO and CO_2 at the expense of CH_3OH and HCHO. Based on these findings, all kinetic measurements were carried out by keeping the contact time unchanged at a value of 2.3 s. and measuring the rates of formation of CH_3OH and HCHO directly as described earlier. The relationship between contact time and conversion cannot be given any kinetic interpretation, especially since there are only two observations available.

TABLE 2

Effect of Contact Time on Conversion and Product Distribution at 570°C

Contact time (sec)	Conversion (%)	Product distribution (mole%)				
		CH_3OH	HCHO	CO	CO_2	HC
2.3	1.2	18	44	34	0	4
4.6	4.2	10	42	39	4	4

Reaction rates and turnover numbers. In order to investigate the change in the catalyst activity over time an experiment was carried out at 590°C, slightly below the temperature at which considerable loss of MoO_3 due to sublimation was likely to occur. The initial turnover rates were 5.8 × 10^{-4} and 2.1 × 10^{-4} molec · s^{-1} · $site^{-1}$ for formations of HCHO and CH_3OH, respectively. As shown in Fig. 2, the activity for HCHO production dropped by about 40% within the first 40 h and then continued to drop at a much slower rate to about half of the initial activity over the next 5–6 days. The activity for methanol production declined by the same extent over the same period of time. Whether these declines in activities were due to poisoning or loss of MoO_3 through volatilization is not clear at present. The fact that the selectivity is changing with time may be indicative of a deactivation process more through selective poisoning of surface sites rather than the loss of molybdenum. No variation in rate could be observed when the reaction

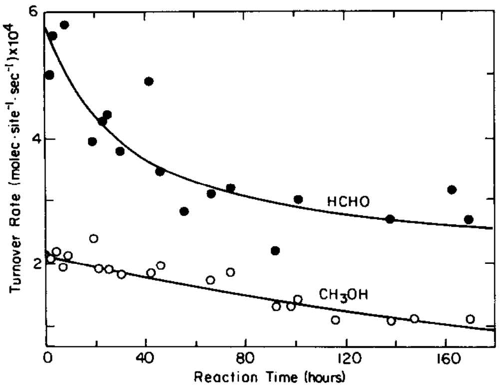

FIG. 2. Variation of catalyst activity with time.

was carried out over 8 h, a characteristic time period used in most of the kinetic measurements. The reaction was thus believed to be in a steady state. However, the turnover numbers, found to be 205 and 91 for HCHO and CH_3OH, respectively, for the period observed, indicate clearly that both of these partial oxidation products were formed catalytically.

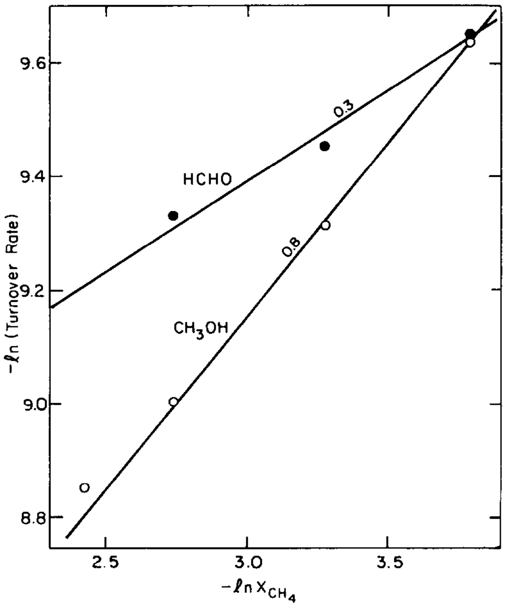

FIG. 3. Concentration dependences on methane of methanol and formaldehyde production rates plotted in logarithmic forms. Temperature: 540°C; mole fractions: $N_2O = 0.33$; $H_2O = 0.35$. Indicated slopes represent kinetic orders.

Kinetic orders. Kinetic orders with respect to CH_4, N_2O, and H_2O were determined at 540°C by following the rates of formation of CH_3OH and HCHO. The rate of CH_3OH formation was found to be roughly first order with respect to CH_4 and H_2O, and zero order with respect to N_2O. In the case of HCHO, the kinetic orders were zero with respect to all reactants. For these measurements, the mole fraction of one of the reactants was varied while others were held constant. The resulting mole fraction vs turnover rate data were plotted in the differential form and are presented in Figs. 3 through 5, where the slopes represent the kinetic orders.

For the determination of order with respect to CH_4, the mole fractions of N_2O and H_2O were held within 0.30 ± 0.03 and 0.33 ± 0.02, respectively, while that of CH_4 was varied between 0.023 and 0.210. It was interesting to note that at CH_4 mole fractions >0.09 the kinetic order approached zero. For studies of the kinetic order with respect to N_2O, its mole fraction ranged from 0.20 to 0.40, since lower concentrations tended to cause extremely low conversions and excessive buildup of carbonaceous deposits. The mole fractions of CH_4 and H_2O were held at 0.06 ± 0.01 and 0.33 ± 0.03, respectively. The kinetic order with respect to

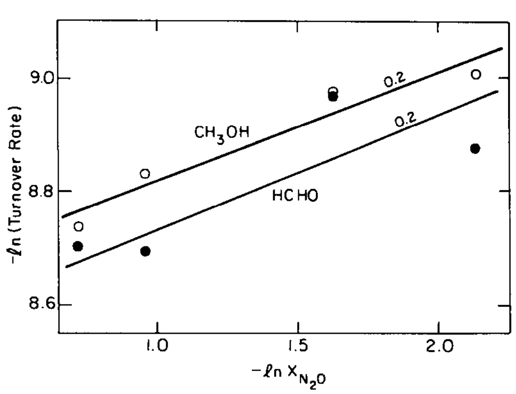

FIG. 4. Concentration dependence on nitrous oxide of methanol and formaldehyde production rates plotted in logarithmic forms. Temperature: 540°C; mole fractions: $CH_4 = 0.06$; $H_2O = 0.33$. Indicated slopes represent kinetic orders.

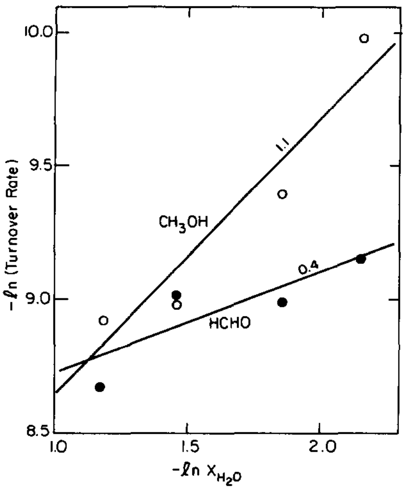

FIG. 5. Concentration dependence on water vapor of methanol and formaldehyde production rates plotted in logarithmic forms. Temperature: 540°C; mole fractions: $CH_4 = 0.10$; $N_2O = 0.44$. Indicated slopes represent kinetic orders.

H_2O was studied by varying its mole fraction within the range of 0.12 to 0.31. Those of CH_4 and of N_2O were held, respectively, at 0.10 ± 0.01 and 0.44 ± 0.02. Because of the considerable uncertainty in the data, the fractional magnitudes of the order have been approximated as the nearest integer.

Temperature dependence of the reaction rates. Rates of formations of CH_3OH and HCHO were measured over the temperature range of 480 to 590°C. The methanol turnover rate had a maximum value of 2.74×10^{-4} at 590°C. The formaldehyde turnover rate, measuring 0.11×10^{-4} at 500°C, increased monotonically to 6.25×10^{-4} at 590°C. As shown in Fig. 6, the Arrhenius plot for HCHO indicates two distinct linear regimes with activation energies of 40 ± 2 and 82 ± 4 kcal/mole at temperatures above and below 540°C, respectively. For CH_3OH, however, the plot is linear up to 520°C, above which further oxidation caused the net rate to drop somewhat. The estimated activation energy for methanol formation is 41 ± 4 kcal/mole.

Possible competing processes. In view of the enhancement of CH_3OH selectivity by H_2O, the possibilities of steam reforming of CH_4 to CO and H_2, water-gas shift reaction of CO and H_2O to produce H_2 and the hydrogenation of CO were all investigated through probe reactions. No detectable amount of H_2 could be observed by flowing steam/CH_4 mixture in the temperature range of 550–600°C over the catalyst; neither was there any detectable water-gas shift as tested under the same conditions by flowing a CO/H_2O mixture over the molybdenum oxide catalyst. The CO/H_2 reaction under these conditions resulted in the pro-

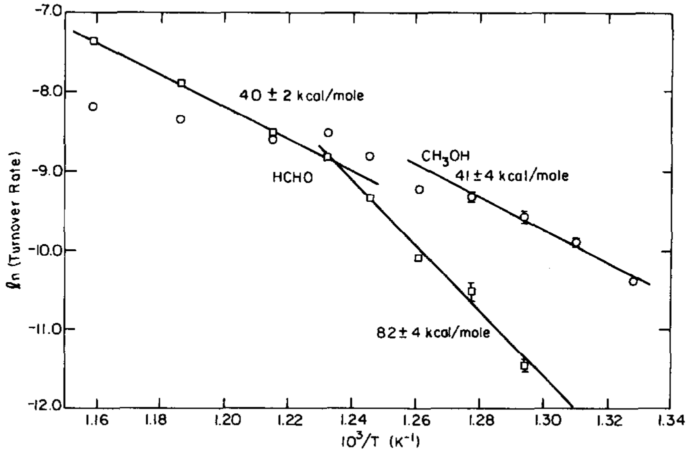

FIG. 6. Arrhenius plots of methanol and formaldehyde production rates over the temperature range of 480–590°C with the respective activation energies indicated.

duction of only C_1–C_2 hydrocarbons, but no trace of CH_3OH. In order to determine the role of steam, methane oxidation in the absence of steam was tried but was unsuccessful because of coking of the catalyst. It was therefore concluded that among other things, steam prevented the formation of carbonaceous deposits on the catalyst surface.

DISCUSSION

Conversion, selectivity, and turnover rates. The present study was carried out under conditions very similar to that reported by Liu *et al.* (*4, 5*). The comparison of our results with theirs, shown in Table 1, clearly indicates close agreement in conversion and selectivity at 570°C. It can be seen from the turnover rate data in Table 1 that methanol formation is a faster process as compared to that of formaldehyde. The reversed trend of rate data at temperatures higher than 550°C is due to the high rate of methanol oxidation to formaldehyde, a process for which MoO_3 is a good catalyst.

Kinetics and mechanism. The rate of formation of CH_3OH was first order in CH_4 and H_2O at lower concentration ranges and zero order with respect to these reactants at higher concentrations. That of HCHO, however, did not show any dependence on any of the reactant concentrations. From activation energy measurements we were able to identify a low- and a high-temperature mechanism for the production of HCHO. Besides, the high-temperature mechanism was characterized by the same activation energy, i.e., ca. 40 kcal/mole, as that of the CH_3OH formation. This data suggests a consecutive oxidation pathway leading to HCHO through the formation of CH_3OH at temperatures above 540°C. The production of HCHO at lower temperature with an activation energy of 82 kcal/mole can be considered independent of CH_3OH, i.e., it is a parallel process. The logical route from CH_4 to either CH_3OH or HCHO is not obvious from this study, since no attempt was made to identify any possible intermediate/s, even though activation energy data alone suggests the existence of one and the same intermediate involved.

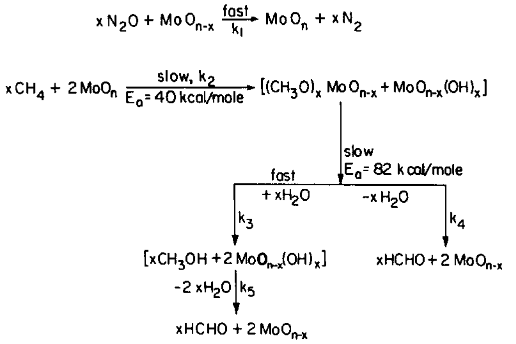

FIG. 7. The reaction scheme of oxidation of methane to methanol and formaldehyde with nitrous oxide on a molybdenum oxide surface.

The most plausible reaction scheme, as far as can be inferred from the above data, is summarized in Fig. 7. This scheme consists of five steps. In this scheme, MoO_{n-x} and MoO_n denote, respectively, an oxygen-deficient and an oxygen-rich site. Each of the five steps shown in the scheme is indexed by a subscript on the rate constant k. The zero kinetic order found for N_2O indicates that it acts indirectly as an oxidizing agent for the partial oxidation of methane in a manner not unlike oxygen does in the redox mechanism of other partial oxidation reactions (*8, 9*). In step one, it provides its oxygen to the molybdenum oxide catalyst to produce an active site where a hydrogen atom could be extracted from an adsorbed CH_4 molecule within its short residence time to produce CH_3O– and –OH groups as shown in step two. The activation energy of 40 kcal/mole can be associated with step two involving the formation of the methoxy intermediate which governs the chain of consecutive processes leading to HCHO via CH_3OH at steps three and five. Step four, which is the direct formation of HCHO from this intermediate and also a slow process having an activation energy of 82 kcal/mole, accounts for the low-temperature route for HCHO formation. The only reason this high activation energy process can successfully compete with the lower activation energy formation of HCHO from CH_3OH is the smaller concentration of the latter at the low-temperature range. This plausible reaction scheme is in general agreement with a more detailed description of the mechanism for this process reported by Liu *et al.* (*5*). In that study, infrared spectroscopic data provided evidence for the existence of the surface methoxy species that was shown to react rapidly with water at step three to form CH_3OH before any considerable degradation into HCHO and carbon oxides could occur. The direct formation of HCHO at step four with an activation energy of 82 kcal/mole may occur through a rearrangement of the surface methoxy intermediate by the breaking of a second C–H bond. Oxidation of CH_3OH to HCHO on MoO_3 is in fact known to involve such a rearrangement process (*2*). It could also be argued that the activation energy of 82 kcal/mole is for the desorption of HCHO from the catalyst surface as the rate limiting step, as has been suggested by Pernicone *et al.* (*3*) in the case of methanol oxidation to formaldehyde. Which one of these two is actually rate limiting in the present case remains to be determined, but either way it would account for the zero-order dependence of HCHO production rate on any of the reactants.

The data qualitatively fits the above reaction scheme that is presented in Fig. 7 if we assume that among the five elementary processes specified, steps two and four have lower rate constants, i.e., $k_2,k_4 \ll k_3,k_5$. Step one, being a fast process, has been excluded, for simplicity, from the discussion that follows. Assuming a steady-state condition for the surface methoxy intermediate, one can write

$$\frac{d[CH_3OH]}{dt} = \frac{k_2k_3}{k_3 + k_4}[CH_4][H_2O] - k_5[CH_3OH]. \quad (1)$$

At low conversions the second term on the right can be neglected, so that CH_3OH formation becomes a first-order process with CH_4. A first-order dependence of CH_3OH formation on H_2O at lower steam concentration is also apparent from Eq. (1). At low steam concentration, step three may be a slow enough process to govern the overall rate of formation of CH_3OH, but above a water mole fraction of 0.3 (not shown in Fig. 5), the rate of CH_3OH formation becomes essentially independent of H_2O. Likewise, for HCHO at and above 540°C where there is an appreciable buildup of CH_3OH and its conversion to HCHO, one could formulate

$$\frac{d[HCHO]}{dt} = \frac{k_2k_4}{k_3 + k_4}[CH_4] + k_5[CH_3OH]. \quad (2)$$

Since $k_2,k_4 \ll k_3,k_5$, the first term on the right in the above equation becomes much smaller as compared to the second term, which predicts a zero-order dependence of HCHO formation with respect to CH_4. This is consistent with our suggestion made in the previous paragraph that a slow step four (low k_4) would mean a zero-order kinetics of HCHO formation.

No evidence is available from our study regarding the oxidation state of molybdenum. Liu *et al.* (*4, 5*) however, showed evidence from ESR studies that the oxidation state of the active molybdenum species was Mo(V). Further information regarding the molybdenum oxidation state could be obtained by XPS measurements and the existence of CH_3O and OH species attached to molybdenum oxide surface could be investigated by HREELS and UPS techniques. These studies are currently in progress in our laboratory.

The difference between the present study and the findings of Liu *et al.* (*5*) consists in the measurement of the kinetic orders. According to their finding, the overall CH_4 conversion rate was first order with N_2O and zero order with CH_4, while our results suggest first-order dependence with respect to CH_4 for the rate of CH_3OH formation and zero-order dependence with respect to both N_2O and CH_4 for HCHO formation. While the discrepancy of the kinetic order with respect to N_2O cannot be readily resolved, an explanation does exist for the case of the kinetic order with respect to CH_4. The CH_4 mole fraction range of 0.02 to 0.09 over which we observed the first-order dependence was lower than was used in their study, which ranged above 0.07. According to their data, however, a slight dependence of the CH_3OH production on CH_4 at the lower CH_4 concentration range was discernible. Another possible reason for these discrepancies may be the temperatures used in the determination of kinetic orders. The temperature chosen for the present study was 540°C, at which there is no detectable of CO or CO_2 production. Our concern was the kinetics of formation of CH_3OH and HCHO only. Liu *et al.* (*5*), on the other hand, studied the kinetic orders at 580°C, under the condition of formation of all oxidation products with the overall kinetic order in mind.

CONCLUSIONS

It has been shown that methane can be partially oxidized with nitrous oxide to methanol and formaldehyde at maximum turnover rates of 2.74×10^{-4} and 6.25×10^{-4} molec $\cdot$ s^{-1} $\cdot$ $site^{-1}$, respectively, at a temperature of 590°C on silica-supported molybdenum oxide catalyst surfaces. The rate of methanol formation was first order with respect to methane and water, and zero order with respect to nitrous oxide. The rate of formaldehyde formation was zero order with respect to all reactants. The activation energy of 40 kcal/mole for methanol formation was found to be the same as for formaldehyde at temperatures above 540°C. This is suggested to be due to a common rate-limiting step involving a surface intermediate that forms upon adsorption of methane, possibly a surface methoxy species, which governs the chain of consecutive reactions from methane to formaldehyde via methanol. There was evidence for the existence of a direct route from the intermediate to formaldehyde with an activation energy of 82 kcal/mole. The latter process could be observed only at temperatures below 540°C. Further studies are needed to determine the composition and the oxidation state of the active molybdenum species on the catalyst surface and to identify the adsorbates and possible reaction intermediates that are thought to be surface methoxy and hydroxyl species.

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