JOURNAL OF CATALYSIS **118**, 281–298 (1989)

The Conversion of Methane on 12-Tungstophosphoric Acid in the Presence of Dichloro- or Tetrachloromethane

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Received September 21, 1988; revised January 24, 1989

The introduction of small quantities of dichloro- or tetrachloromethane to the feed stream in the conversion of methane on silica-supported 12-tungstophosphoric acid produces substantial changes in the conversion, selectivity, and rates of consumption of reactants and formation of products. With 0.4% tetrachloromethane in the feed stream the selectivity to CH_3Cl and conversion of methane at 450°C were approximately 80 and 1 mol%, respectively, over a 5 wt% loaded catalyst. Elimination of the oxidant N_2O from the feed stream produced a marked decrease in the yield of CH_3Cl suggesting a pivotal role of the oxidant in the chlorination process. The conversions, selectivities, and rates are also shown to depend on the loading of the catalyst, the reaction temperature, and the ratio of CH_4 to N_2O. Evidence is presented to show that the process apparently operates through the incorporation of chlorine in the catalyst, although the form of the latter is at this time unknown. Although the conversions are low the high selectivity to methyl chloride provides considerable attraction for this new route for the conversion of methane.

INTRODUCTION

The availability of supplies of natural gas in many countries has led to increased interest in techniques for the conversion of methane to liquid products (*1–3*). A number of workers have investigated catalysts and processes for partial oxidation or oligomerization of methane (see, for example, Refs. (*4–8*)). Recent work in this laboratory has examined the applicability of heteropoly oxometalates and fluorinated mordenite as heterogeneous catalysts for such purposes (*9–15*).

In view of the well-known advantageous effect of the addition of halogens to acidic catalysts (*16*) it appeared both interesting and worthwhile to investigate such possibilities with heteropoly oxometalates as catalysts for the conversion of methane. The use of chlorine as an additive in the production of ethylene oxide is well documented (*17*) although the mechanism through which it operates is not fully understood. There have been relatively few reports of the use of haloadditives in the oxidation of methane (*18–27*). Earlier studies on supported metals (*19, 20*) have shown that the addition of various additives, including halomethanes, inhibits the deep oxidation of methane on palladium and platinum catalysts. The conversion of methane by chlorine-catalyzed oxidative pyrolysis has recently been reviewed (*21*) and the addition of hydrogen chloride to a methane–oxygen conversion mixture passed over an oxyhydrochlorination catalyst has been studied (*22*). The addition of alkali halides to metal oxides has been reported to suppress deep oxidation of methane while enhancing the direct synthesis of ethylene (*23*). There have also been reports of the conversion of methane by chlorination and oxychlorination (*24–26*) and a dual-function catalyst has been suggested for such purposes (*27*).

In the present work the conversion of methane has been studied over 12-tungstophosphoric acid (HPW) supported on silica with dichloro- or tetrachloromethane as additives.

0021-9517/89 $3.00

12-Tungsto- and 12-molybdophosphoric acid (HPMo) heteropoly oxometalates are complex ionic solids having large cage-like anions. The anion consists of a tetrahedral PO_4 at its center, and 12 octahedra with tungsten (or molybdenum) at their centers and oxygen at their vertices enveloping the central tetrahedron and sharing oxygen atoms with the latter and with each other. Three types of oxygen atoms may be distinguished in the anion. One of these bridges the central phosphorus and peripheral metal tungsten (or molybdenum) atoms while a second bridges two of the latter. Twelve terminal oxygen atoms are bonded only to the tungsten (or molybdenum atoms) and protrude from the anion. Extended Hückel calculations (*28*) have shown that the net atomic charge on the terminal oxygen atoms is higher with HPMo than with HPW. Consequently protons in the former solid are expected to be less mobile and hence less acidic than those in the latter. Calculations have demonstrated further that the bond energy between the terminal oxygen atoms and the peripheral metal atoms is lower with HPMo than with HPW, so that terminal oxygen atoms of HPMo are expected to be more labile than those of HPW.

Earlier work from this laboratory has suggested that the proton is necessary, but not sufficient, in the oxidative conversion of methane on heteropoly oxometalates (*15*). Studies of the effect of exchange of the proton by cesium provided strong evidence that the proton plays an active but indirect role in the oxidation through the extraction of oxygen atoms from the anions (*15*) and the production of vacancies, as had been earlier suggested from temperature-programmed desorption studies (*32*),

$$2\text{KUOH} \rightarrow \text{KUO} + \text{KU}\square + H_2O.$$

In addition it was suggested that the nitrous oxide interacts with the anion to restore the extracted oxygen atoms and eliminate the vacancies.

Temperature-programmed desorption, reduction, and exchange experiments also showed that the oxygen extraction process occurs at lower temperatures in HPMo than in HPW, reflecting the higher lability of the oxygen atoms in the former species compared with the latter (*29, 30*). The extraction process in HPW apparently commences at approximately 400°C and the evolution of water resulting from the process passes through a maximum in the neighborhood of 500°C.

Although earlier work in this laboratory has shown that HPW is a less effective catalyst than 12-molybdophosphoric acid in the oxidative conversion of methane (*9*), HPW has been found to be active and selective in the conversion of methanol to hydrocarbons (*31, 22*). Consequently it appeared of considerable interest to examine the effect of the addition of chloromethanes to an acidic catalyst employed in the methane conversion process. The present report provides the results from examination of a number of variables including temperature, residence time, feed composition, time on stream, and pretreatment conditions.

EXPERIMENTAL

12-Tungstophosphoric acid (GFS, reagent-grade, recrystallized before use) was supported on silica (Grace-Davison, grade 407, 8–20 mesh) with an incipient wetness technique in which the silica was placed in contact with an aqueous solution of HPW, followed by evaporation to dryness with stirring at approximately 80°C. The samples were further dried at 80–90°C in air and then in a vacuum oven for several hours. Immediately before each run, the catalyst was calcined for 2 hr *in situ* in a flow of helium (30 ml min^{-1}) at the reaction temperature.

Methane (Linde, 99%), nitrous oxide (Matheson, 99.0%), and helium (Linde, 99.9%) were used as received. Analytical-grade dichloromethane (DCM) and tetrachloromethane (TCM) were obtained from BDH.

The catalytic conversion of methane was performed in an isothermal fixed-bed continuous-flow reactor operating at a total pressure of about 1 atm. The flow of reactants was regulated by metering valves and monitored by rotometers. The additive, dichloro- or tetrachloromethane, was introduced to the system by flowing helium through a gas dispersion tube in a glass saturator containing the liquid at ice-water temperature. The flow of helium was so adjusted that after dilution following introduction into the main flow of reactants (CH_4 + N_2O) the desired concentration of the additive in the feed was obtained. The reactor was made of Pyrex tube (12 mm (in some cases, 15 mm) o.d., 30 mm long) sealed to 6-mm-o.d. Pyrex tubes at the two sides (total length of the reactor was ~200 mm) and was heated electrically. The catalyst was held at the center of the reactor by glass wool plugs. The temperature was controlled and monitored by a thermocouple placed at one end of the catalyst bed. The reaction manifold was constructed from a stainless-steel tube and was heated to prevent liquid condensation. Inlet and exit gas compositions were determined periodically using on-line gas chromatographic analysis (H.P. 5890 equipped with a thermal conductivity detector). The column packing was Porapak Q (5 m × $\frac{1}{4}$ in. o.d., programmed 28–200°C at two levels).

The main products of the reaction were monochloromethane, carbon monoxide, carbon dioxide, formaldehyde, and ethylene. Polychloromethanes and methanol were, at most, produced in trace quantities and have been neglected. The conversion of methane was calculated on a carbon-account-for basis. The selectivities were calculated on the basis of the conversion of methane (expressed as mole percentage) to each product. For example, the selectivity to ethylene was calculated as 100 × [2× moles of ethylene produced]/(moles of methane converted). The rate of formation of a particular product was obtained by multiplying its mole fraction in the effluent as determined by GC analysis by the total gaseous flow through the reactor system measured at STP.

The possibility of gas-phase reactions was tested by the passage of a DCM (or TCM) + CH_4 + N_2O mixture through the empty reactor packed with glass wool and was found insignificant.

In the absence of CH_4, experiments performed with feed mixtures of He + N_2O + DCM (or TCM) indicated that, in the presence of the catalyst, under the conditions of flow rate and concentrations employed, the additive itself undergoes oxidation, DCM producing mainly CO and H_2CO, and TCM producing almost exclusively CO_2. When higher concentrations of the additive were used, this reaction rate became appreciable with respect to the rate of formation of C_1-oxygenated products when methane was present in the feed. Monochloromethane, however, was present in the effluent only when CH_4 was included in the reactant stream. No CH_3Cl was detected in the exit stream when the feed consisted of He + N_2O + DCM (or TCM), i.e., during reaction in the absence of CH_4. Because of this significant contribution of additive (DCM or TCM) oxidation to the measured rates of formation of C_1 products when CH_4 was present in the feed, the experimental approach was as follows: An experiment was first performed with the feed consisting of He + N_2O + DCM (or TCM), the flow of He (note that this flow was separate from that used as carrier for DCM or TCM) was adjusted to obtain the desired residence time (W/F), and the rates of formation of different C_1-oxygenated products were measured. Subsequently, a reactant stream consisting of CH_4 + N_2O + DCM (or TCM) was admitted to the reactor the CH_4 flow used being the same as that of the He flow in the experiment where no CH_4 was present in order to maintain the same W/F), and the effluent was analyzed periodically. In some experiments, before the introduction of the reaction mixture (CH_4 + N_2O + additive), the system was purged with helium. The rate of formation of different products from methane conversion was then obtained by subtracting the reaction rate measured in the absence of CH_4 from the total rate. Since DCM produced CO, CO_2, and H_2CO, and TCM produced only CO_2, with the former additive, rates of all three oxygenated products from CH_4 conversion required correction, but with the latter additive, only the CO_2 rates were subject to correction. Since the experimental procedure followed means in effect, the investigation of conversion of methane with nitrous oxide in the presence of a halomethane on a *halomethane-pretreated* 12-tungstophosphoric acid, the duration of the reaction performed in the absence of CH_4 was kept constant in a particular series of experiments.

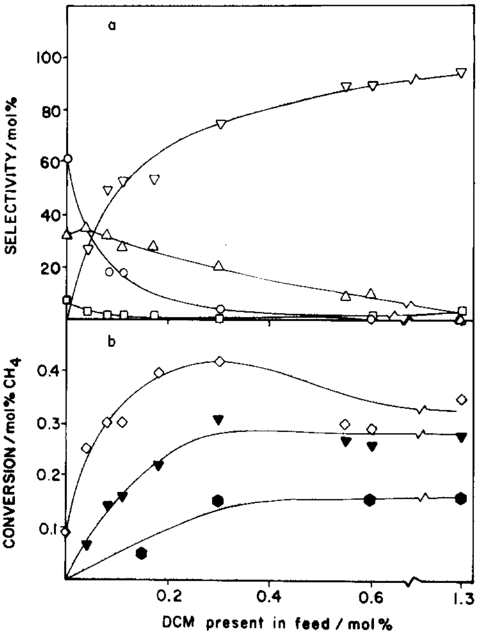

FIG. 1. Selectivity and conversion as functions of DCM added to the feed. (a) △, CO; □, CO_2; ○, CH_2O; ▽, CH_3Cl. (b) ◇, Conversion; ▼, yield of CH_3Cl (DCM present); ●, yield of CH_3Cl (no DCM present during pretreatment). $W = 2.0$ g, $F = 60$ ml min^{-1}, $T =$ 450°C, $CH_4/N_2O = 4$, time on stream = 15 min.

RESULTS

Effects of Concentration of the Additive

The effect of the amount of DCM in the feed on the conversion of methane and the selectivity to different products is shown in Fig. 1. The catalyst was subjected to 1½ hr of reaction (He + N_2O + DCM) in the absence of CH_4 followed by purging with helium before introduction of the CH_4 + N_2O + DCM stream. The addition of DCM clearly led to a large increase in the conversion of methane, compared to that in its absence, and the effect was most pronounced with low concentrations of DCM in the feed (Fig. 1b). Increasing concentrations of DCM caused increases in the selectivity to monochloromethane and decreases in the selectivities to CO and H_2CO. After an initial decrease the selectivity to CO_2 increased slightly with further additions of DCM in the feed. The yield of monochloromethane, shown in Fig. 1b, increased with increasing additions of DCM up to a concentration of 0.3%, beyond which the yield remained practically constant. Figure 1b also includes yields of monochloromethane observed in a separate series of experiments in which a feed mixture of CH_4 + N_2O + DCM was passed over the catalyst without first pretreating the catalyst with He + N_2O + DCM, which, as mentioned earlier, was the usual procedure followed. The yield of monochloromethane in this second series was approximately half of that observed in the first series. This suggests that during the pretreatment period, some "chlorine" accumulated on the catalyst bed, so that the effective concentration of the catalyst chlorine encountered by methane (when the CH_4 + N_2O + DCM mixture was introduced) was higher in this case than when no pretreatment was done, thus producing an increase in the yield of monochloromethane in the former series.

Figure 2 shows the effect of the presence of oxidant N_2O on conversion and selectivity on 20% HPW/SiO_2 and on the silica carrier itself, with CCl_4 as the additive. In each case, the catalyst was pretreated in a stream of He + N_2O + CCl_4, followed by

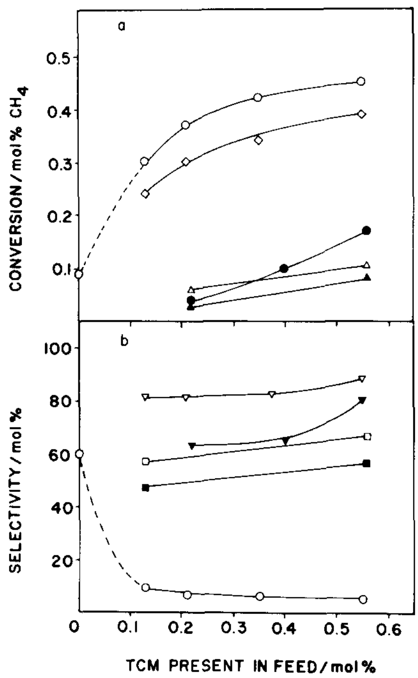

FIG. 2. Conversion and selectivity as functions of TCM added to the feed. (a) ○, ●, Conversion of 20% HPW/SiO_2; ◇, yield of CH_3Cl; △, ▲, conversion on SiO_2. (b) ▽, ▼, ○, selectivity to CH_3Cl and H_2CO on 20% HPW/SiO_2; □, ■, selectivity to CH_3Cl on SiO_2. Open and solid symbols: N_2O present and absent, respectively. In all cases balance in selectivity is CO (not shown for clarity). $W = 2.0$ g, $F = 60$ ml min^{-1}, $T = 450°C$, $CH_4/N_2O \approx 4$, time on stream = 15 min.

purging with helium. As in the case of DCM, in the presence of N_2O, the addition of CCl_4 strikingly increased the conversion of CH_4 to selective formation of monochloromethane on HPW/SiO_2. However, when the feed stream consisted of CH_4 + He + CCl_4 (N_2O replaced by an equal flow of He), the conversion of CH_4 and the yield of CH_3Cl fell dramatically, indicating that N_2O plays a vital role in chlorinating methane. It may be noted that in the absence of N_2O, not only the conversion of CH_4 (Fig. 2a) but also the selectivity to CH_3Cl (Fig. 2b) were lower. Experiments were also done on the bara silica support to test its activity with respect to that when it is loaded with HPW. In the presence of N_2O, the activity of the HPW/SiO_2 was much higher than that of the bare support (Fig. 2a), as was also the selectivity to monochloromethane (Fig. 2b). However, in the absence of the oxidant N_2O, these effects were less pronounced. It should be mentioned that with CCl_4 as the additive, the amount of CO_2 found in the exit stream when CH_4 was present in the feed was very similar to that present in the reaction from which methane was absent and this species was ignored in the calculation of product distribution.

Effects of Pretreatment with the Additive on CH_4 + N_2O Reaction

It was mentioned earlier that observations indicated that chlorine is retained by the catalyst during the pretreatment stage with the chloroadditive. That this was indeed the case was clearly evident from a set of experiments which involved the exposure of the catalyst to a flow of CH_4 + N_2O (no CCl_4) following its usual pretreatment with a He + N_2O + CCl_4 mixture. This is illustrated in Fig. 3 for two different loadings of the catalyst, viz. 20 and 10% HPW on silica, where the rates of formation of CH_3Cl as a function of time on stream are compared between the following two cases (in each case, the catalyst was subjected to pretreatment with CCl_4 + N_2O + He):

(i) When the feed was a mixture of CH_4 and N_2O (no CCl_4) following pretreatment stage.

(ii) When the feed was a mixture of CH_4, N_2O, and CCl_4 following pretreatment stage.

(In the case of (i), the reactor was purged with helium after pretreatment to eliminate CCl_4 in the gas phase.)

It is apparent from Fig. 3 that in the early periods of reaction, the rates of production of CH_3Cl in two cases (i.e., with or without CCl_4 in the feed) are very similar. This suggests that during the early hours of reaction, at least, the chlorine appearing in the product CH_3Cl is obtained almost entirely from that retained by the catalyst during the

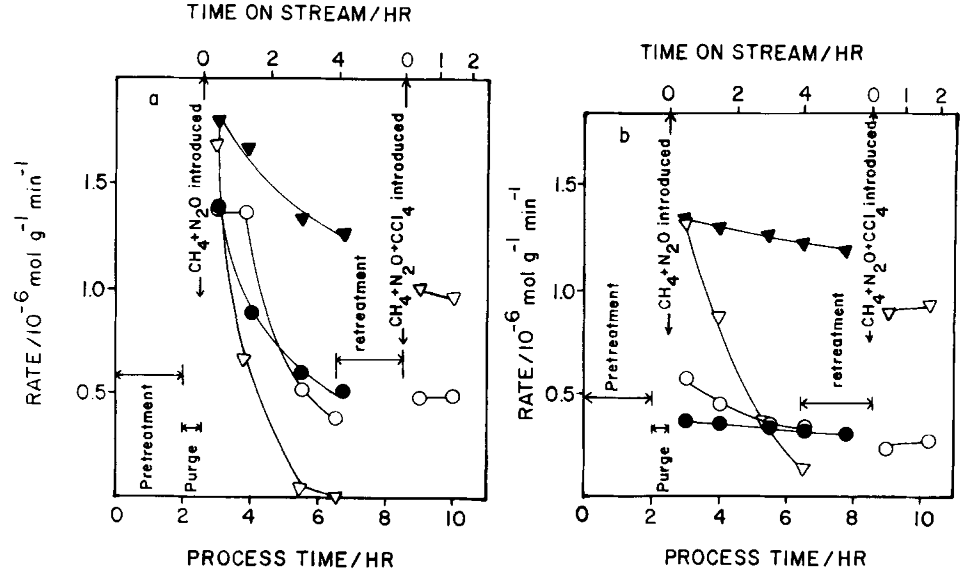

FIG. 3. Rates of production of CH_3Cl and CO with time on stream (a), (b) 20 and 10% HPW/SiO_2, respectively. ∇, ▼, CH_3Cl; ○, ●, CO. Open symbols: pretreatment, CCl_4; reactants, CH_4, N_2O. Solid symbols: pretreatment, CCl_4; reactants, CH_4, N_2O, CCl_4. $W = 2.0$ g, $F = 11$ ml min^{-1}, $[CCl_4] = 0.38$ mol%, $CH_4/N_2O \approx 1$, $T = 450°C$ (pretreatment conditions as above except read He for CH_4).

pretreatment stage with CCl_4. When CCl_4 was not subsequently present in the feed, the rates of production of CH_3Cl decreased rapidly with time on stream, approaching a negligible value in a few hours. This was apparently due to the rapid depletion of chlorine taken up by the catalyst during the pretreatment stage. On the other hand, when CCl_4 was present in the feed, a high rate of production of CH_3Cl was maintained throughout, indicating a continuous process of consumption (by CH_4) and buildup (by CCl_4) of chlorine on the catalyst. It is also seen in the figure that when the catalyst was retreated with the additive (that is, with a flow of He + N_2O + CCl_4) subsequent to reaction with CH_4 + N_2O for a few hours and CH_4 + N_2O + CCl_4 was readmitted, a high rate of formation of CH_3Cl was reestablished (although not as high as that observed after the initial pretreatment). Figure 3 also demonstrates that the rates of production of CO were of comparable magnitude over the entire period of time on stream monitored (whether or not CCl_4 was present in the feed). The formaldehyde rates, which were much smaller than those of CH_3Cl and CO, were also comparable in two cases (not shown in Fig. 3 for clarity). This suggests that the oxidation products, CO and H_2CO, are produced mainly by direct oxidation of CH_4 from an unperturbed (by CCl_4) HPW/SiO_4 catalyst; that is, the pretreatment of the catalyst with CCl_4 or its subsequent presence in the feed had little influence on the production of H_2CO and CO (i.e., on the formation of oxygenated species from methane conversion).

It may be mentioned that in the presence of additives DCM and TCM, in addition to C_1-oxygenated products and monochloromethane, appreciable quantities of HCl were also present in the effluent when methane was both present in and absent from the feed. The approximate chlorine balance for reactions described in Fig. 3 is given in Table 1.

Effects of Loading of the Catalyst

Figure 4a illustrates the conversion and product distribution for CH_4 + N_2O reaction in the presence of CCl_4 at different

TABLE 1

Approximate Chlorine Balance for Reactions[a]

Reaction feed	Reaction duration (hr)	Maximum chlorine accumulation on catalyst			Chlorine produced during reaction[d] (10^{-4} mol)
		Pretreatment stage[b] (He + N_2O + CCl_4) (10^{-4} mol)	Reaction stage[c] (CH_4 + N_2O + CCl_4) (10^{-4} mol)	Total (10^{-4} mol)	
CH_4 + N_2O[e]	4	7.1	—	7.1	6.0
CH_4 + N_2O + CCl_4[e]	4	6.6	16.0	22.6	21.0
CH_4 + N_2O[f]	5	7.0	—	7.0	5.5
CH_4 + N_2O + CCl_4[f]	5	6.2	20.0	26.2	18.5

[a] Refer to Fig. 3.

[b] 4(CCl_4 reacted). HCl produced; in all cases pretreatment period was 2 hr.

[c] 4(CCl_4 reacted).

[d] (CH_3Cl + HCl) produced.

[e] Refer to Fig. 3a.

[f] Refer to Fig. 3b.

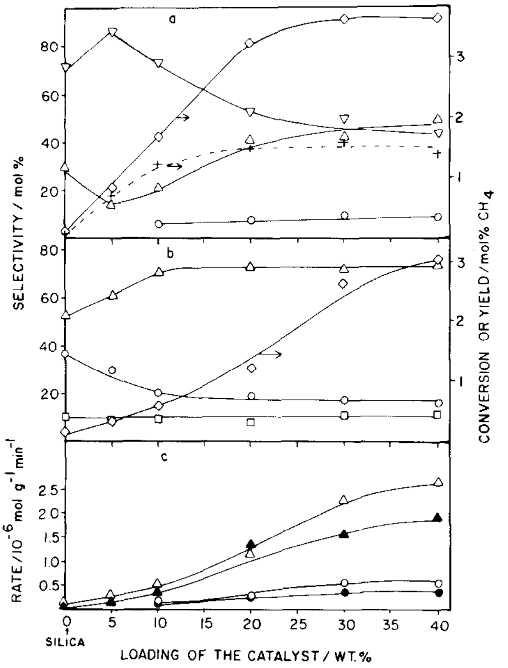

FIG. 4. Dependence of conversion, selectivity, and rate on the catalyst loading. (a) △, CO; ○, H_2CO; ▽, CH_3Cl; ◇, conversion, +, yield CH_3Cl. Feed stream [CCl_4] = 0.38 mol%. (b) △, CO; ○, H_2CO; □ CO_2, ◇ conversion (no CCl_4 present). (c) △, ▲, CO; ○, ●, H_2CO. Open, filled symbols: CCl_4 absent and present, respectively. W = 2.0 g, F = 11 ml min^{-1}, T = 450°C, $CH_4/N_2O \approx 1$, time on stream = 30 min.

loadings of the catalyst and on bare silica support. It is clearly evident that with increased loading the conversion of methane increases almost linearly up to a loading of about 20% (by wt.) and beyond this remains relatively constant. The selectivity to CH_3Cl also decreases with increased loading up to a loading of about 20% and then remains approximately constant. The selectivity to H_2CO, which is relatively small (<10%), is affected very little by the loading. The selectivity to CO shows a trend opposite to that of CH_3Cl. The yields of monochloromethane after a rapid increase also tend to level off at a loading of approximately 20%. It is also evident that, for a selectivity comparable to that of CH_3Cl, the conversion on an HPW-loaded catalyst is much higher than that of the bare support (cf. silica vs 10% HPW/SiO_2, similar selectivity) (Fig. 4a).

From the results presented so far, it is clearly evident that the presence of CCl_4 leads to the production of a substantial amount of monochloromethane and that, as far as the specific selectivities to chloromethanes are concerned, the selectivity to monochloromethane is almost 100% (since with CCl_4 as the additive, CH_2Cl_2 and $CHCl_3$ were produced in trace amounts, and with CH_2Cl_2 as the additive, $CHCl_3$ and CCl_4 were produced in trace amounts). However, it is not clear, whether the presence of CCl_4 has any influence on the formation of CO, CO_2, and H_2CO, the products of reaction in the oxidation of methane by nitrous oxide on HPW/SiO_2 in the absence of CCl_4. In order to explore this, a series of experiments was performed with CH_4 and N_2O in the feed (no CCl_4) at different loadings of the catalyst (Fig. 4b). The rates of production of the oxidized products in the presence and absence of CCl_4 are compared in Fig. 4c.

In the absence of CCl_4, it appears that with increases in the loading of the catalyst, the selectivity to H_2CO after an initial decrease, and to CO after an initial increase, remains practically constant (the selectivity to CO_2 is constant throughout), although a several-fold increase in the conversion of methane has occurred. Furthermore, it may be noted that the selectivity of HPW/SiO_2 to formaldehyde even at very low conversions is very small. This may be contrasted with that of the $HPMo/SiO_2$ catalyst, which at low conversion is usually very high (*11*, *27*).

Figure 4c shows that the rates of production of CO and H_2CO in the presence and absence of CCl_4 are, on an absolute scale, approximately identical. This implies that the relative increase in the conversion of CH_4 in the presence of CCl_4 is almost entirely due to the production of CH_3Cl and that, in addition, the presence of CCl_4 has no significant effect on the formation of oxidized products. However, a closer examination of rates (Fig. 4c) reveals that, on a relative basis, the rates of formation of CO and H_2CO, particularly that of CO, are noticeably lower in the presence of CCl_4. The effect is not large, yet sufficient to draw attention. It will appear from the experiments described in the next section that with the pretreatment of the catalyst with DCM or TCM for a prolonged period, this effect becomes significantly enhanced.

Effects of Duration of Pretreatment with DCM or TCM

In order to examine the effect of the pretreatment of the catalyst with the additive on the conversion and product composition, the catalyst was subjected to different periods of pretreatment with a flow of He + N_2O + additive, prior to the introduction of the reactant stream consisting of CH_4 + N_2O + additive. The results are shown in Table 2.

With DCM, 2 hr of pretreatment had an insignificant effect on the rates of formation of oxidized products (Table 2) and it is obvious that the additional conversion of methane in the presence of DCM is almost exclusively due to the production of CH_3Cl. However, when the duration of pretreatment is extended, it is clearly seen that the rates of production of CO and H_2CO have dropped significantly (with 16 hr of pretreatment, each of these rates was reduced to about 50%) and the rate of production of CH_3Cl has increased, but the conversion of CH_4 has remained more or less the same. An increase in the pretreatment period from 2 to 16 hr reduced the selectivity to CO from 33 to 19% and to H_2CO from 19 to 6% while that to CH_3Cl increased from 45 to 72%.

With CCl_4 as the additive, the decrease in the rates of production of CO and H_2CO with increased duration of pretreatment became even more pronounced (Table 2). Following 17 hr of pretreatment, the rates of formation of CO and H_2CO dropped to about one-third and one-fifth, respectively, compared to those when the reaction was carried out in the absence of CCl_4, and the selectivity to CH_3Cl reached 87% at 1.1% conversion of methane. However, longer periods of pretreatment have detrimental effects on the conversion producing large decreases in the conversion of CH_4 although a high selectivity to CH_3Cl (>90%)

TABLE 2

Effect of Duration of Pretreatment with Additive on Rates and Conversion[a]

Pretreatment		Reaction						CH_4 conv.[c] (mol %)
Duration (hr)	Additive	Rate of production[b] (10^{-6} mol g^{-1} min^{-1})		Rate of production[c] (10^{-6} mol g^{-1} min^{-1})				
		CO	H_2CO	CO	CO_2	H_2CO	CH_3Cl	
0	—	—	—	0.85	0.08	0.04	—	0.57
2	DCM	0.25	0.06	0.92	0.05	0.50	1.2	1.05
4	DCM	0.25	0.06	0.75	0.03	0.30	1.4	0.97
16	DCM	0.25	0.06	0.50	0.03	0.15	1.9	1.05
			CO_2					
0	—		—	0.85	.08	0.40	—	0.57
2	TCM		0.90	0.65	—	0.17	2.1	1.2
(2)[d]			(0.65)	(0.38)	—	~0	(0.45)	(0.35)
17	TCM		0.70	0.27	—	0.08	2.2	1.1
30	TCM		0.33	0.065	—	~0	1.0	0.45
45	TCM		0.083	0.075	—	~0	1.0	0.45

[a] Conversion and rates measured at ~½ hr on stream time.

[b] Feed, N_2O + additive + He; $T = 450°C$, $W = 2.0$ g, $F = 15$ mol min^{-1}, $He/N_2O \sim 3.5$, 20% HPW/SiO_2.

[c] Feed, N_2O + additive + CH_4; $T = 450°C$, $W = 2.0$ g, $F = 15$ ml min^{-1}, $CH_4/N_2O \sim 3.5$, 20% HPW/SiO_2.

[d] Values in parentheses indicate silica support (2.0 g).

is still maintained. The observed rate of formation of CO_2 from the oxidation of CCl_4 after pretreatment is shown in Table 2. It will be shown later that in the case of CCl_4 (and also CH_2Cl_2) oxidation, oxygen consumed is provided directly by the catalyst without subsequent replenishment by N_2O. As a consequence, there is a continuous depletion of oxygen from the catalyst bed. The extent of CCl_4 conversion (or the rate of production of CO_2 therefrom) may be considered a rough guide of the oxygen content of the catalyst after a given duration of pretreatment. It is seen from Table 2 that after very long periods of pretreatment (for example 30 and 43 hr), the conversion of CCl_4 has dropped by substantial amounts, indicating a substantial loss of oxygen from the catalyst (hence probable partial destruction of the catalyst structure). This may be partly responsible for the decrease in the conversion after an optimum pretreatment period. In Table 2 results on a bare silica support following 2 hr of pretreatment with CCl_4 are also included, and show that silica itself is also very active in oxidizing CCl_4 to CO_2, the source of oxygen being, again, the silica itself (N_2O playing practically no role). In view of this high activity of silica in the conversion of CCl_4, it is not possible to estimate the oxygen content of the catalyst (total oxygen minus oxygen used in the oxidation of CCl_4) as a function of pretreatment time.

The Effects of Residence Time

In the absence of CCl_4 from the feed, the conversion increased proportionally with residence time, indicating the absence of any mass transfer and/or thermodynamic equilibrium limitation effects (Fig. 5b) while the selectivities to different products, ex-

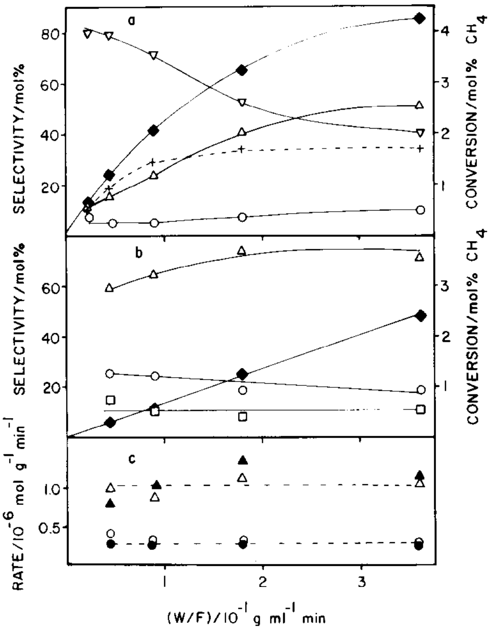

FIG. 5. Dependence of conversion, selectivity, and rate on contact time. (a) △, CO; ○, H_2CO; ▽, CH_3Cl; ◆, conversion, +, yield CH_3Cl. Feed stream [CCl_4] = 0.38 mol%. (b) △, CO; ○, H_2CO; □, CO_2; ◆, conversion (no CCl_4 present). (c) △, ▲, CO; ○, ●, H_2CO. Open, filled symbols: CCl_4 absent and present, respectively. $W = 0.25$–4.0 g, $F = 11$ ml min^{-1}, $T = 450$°C, $CH_4/N_2O \approx 1$, 20% HPW/SiO_2 catalyst, time on stream = 30 min.

cept at very short residence times (or at very low conversions), were practically insensitive to the residence time (Fig. 5b). This may be contrasted with the observations on $HPMo/SiO_2$ where the selectivities to CO and H_2CO showed strong but reciprocal dependence on conversion (*11*).

In the presence of CCl_4, the conversion of methane, unlike that in its absence, does not increase linearly with *W*/*F*. The yield of CH_3Cl increases with increasing *W*/*F* and becomes approximately constant. However, the yields of CO and H_2CO increase linearly with *W*/*F* (not shown, but, evident from the constancy of rate shown in Fig. 5c). Evidently, the nonlinearity in the conversion of methane with *W*/*F* in the presence of CCl_4 stems from the constant yield of CH_3Cl beyond a certain residence time. Since *W*/*F* in these experiments was varied by changing the mass of the catalyst (at a constant flow) and the concentration of CCl_4 was kept constant, the total mass of CCl_4 flowing through the system was independent of *W*/*F*. This may account for the absence of any dependence on *W*/*F* of the yield of CH_3Cl at high values of residence time.

The rates of formation of the oxidized products, CO and H_2CO, are also essentially independent of residence time in the presence or absence of CCl_4 (Fig. 5c). This provides further evidence that under the present set of conditions the increase in the conversion of methane in the presence of CCl_4 is almost entirely due to the formation of CH_3Cl.

Effects of Time on Stream

On a 20%-loaded catalyst, at 450°C, the activity of the catalyst, represented in terms of the conversion of methane, decreases slowly with time on stream (Fig. 6a). However, when the reaction temperature is reduced, the decrease in the activity becomes less noticeable. At 400°C (Fig. 6b), after an initial increase, the conversion remains more or less constant. Indeed, at a lower temperature (375°C), the conversion continues to increase slowly even after 8 hr of reaction. With a reduced catalyst loading also at the higher temperature (450°C) the conversion gradually increases with time on stream. Catalysts with 30 and 40% loading show, at 450°C, behavior similar to that found with the 20% catalyst, while the results with a 10% catalyst are intermediate to those for the 5 and 20% catalysts (not shown). The selectivities, on the other hand, in all cases, after a small initial change, remain more or less constant with time on stream.

It is of interest to note that the selectivities to CH_3Cl reach as high as 90% although the conversions are only approximately 1% under such conditions.

Effects of CH_4/N_2O Ratio

The effects of feed composition (CH_4/

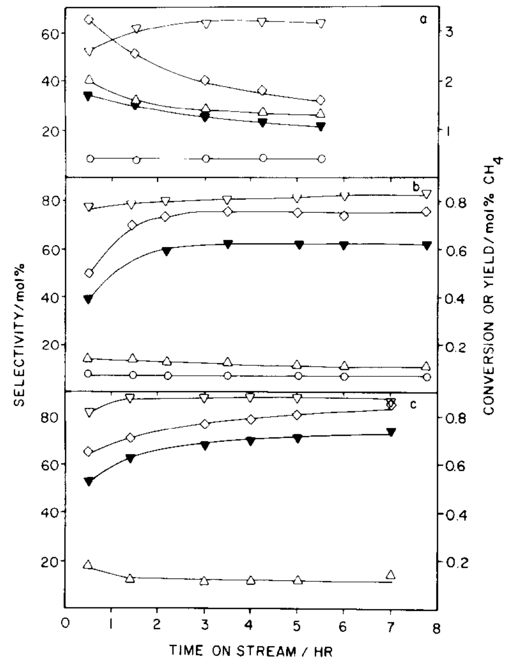

FIG. 6. Typical plots of effects of time on stream on conversion, selectivity, and yield of CH_3Cl. $W = 2.0$ g, $F = 11$ ml/min^{-1}, $[CCl_4] \sim 0.38\%$ (by mol); $CH_4N_2O \sim 1$. (a) 20% HPW/SiO_2, $T = 450°C$. (b) 20% HPW/SiO_2, $T = 400°C$. (c) 5% HPW/SiO_2, $T = 450°C$. △, CO; ○, H_2CO; ▽, CH_3Cl; ◇, conversion; ▼, yield CH_3Cl. (Note differences in scales of conversion and yield.)

N_2O ratio) on the rates of formation of individual products and on the total rate of reaction in the presence of CCl_4 are given in Fig. 7a. Evidently, each rate appears to reach a maximum at ratios of CH_4/N_2O of approximately 1/2–2/1. Orders in the range 0.8–0.9 w.r.t. CH_4 have been calculated for the total rate and for rates of formation of CH_3Cl and CO. However, w.r.t. N_2O orders of approximately 0.7, 0.5, and 1.2 have been obtained for the total rate, the rate of production of CH_3Cl, and the rate of production of CO, respectively.

The effects of reactant composition on the conversion and selectivities are shown in Fig. 7b. As usual, selectivity to H_2CO is very low (<10%) and remains relatively constant regardless of feed composition. The selectivities to CO and CH_3Cl show reciprocal trends and each undergoes maximum change at values of the CH_4/N_2O ratio between 1/4 and 4/1.

Effects of Temperature

With increasing temperature, the conversion increases; the selectivity to CO increases and to CH_3Cl decreases, while that to H_2CO remains approximately constant (Fig. 8a). These trends in selectivities indicate that the activation energy for the production of CO is higher than that for CH_3Cl. It was suggested earlier that at 450°C (and, probably also below 450°C) the oxygenated products are produced almost entirely by the direct oxidation of CH_4 by N_2O on unperturbed HPW/SiO_4 (CCl_4 playing no part in this process) and that the main function of CCl_4 is to provide surface (catalyst) chlorine for conversion of methane to monochloromethane. Since CO accounts for the major portion (>70%) of CH_4 oxidized, one may suggest that the activation energy for

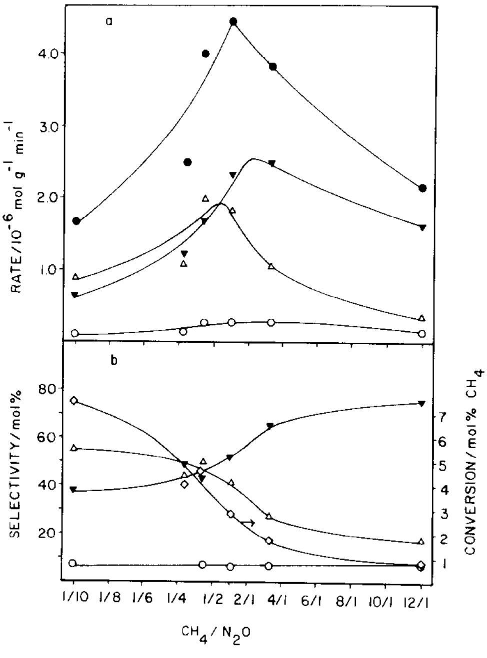

FIG. 7. Effects of CH_4/N_2O ratio on rates, conversion, and selectivity on 20% HPW/SiO_2 catalyst. $W = 2.0$ g, $F = 15$ ml min^{-1}, $[CCl_4] \sim 0.30\%$ (by mol), $T = 450°C$, time on stream = 30 min. (a) ●, Total rate (CO + H_2CO + CH_3Cl); ○, CO; ▼, CH_3Cl; ○, H_2CO. (b) △, CO; ▼, CH_3Cl; ○, H_2CO; ◇, conversion.

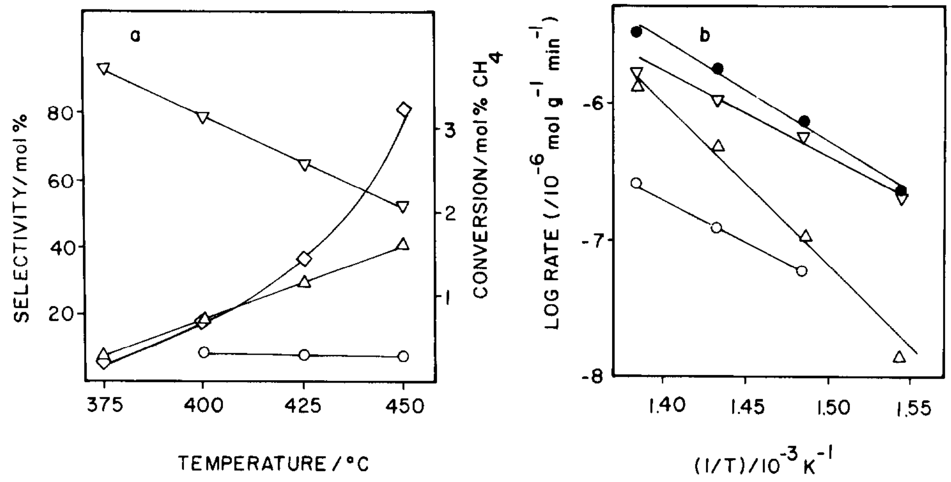

FIG. 8. Effects of temperature on conversion, selectivity, and rates for 20% HPW/SiO_2 with TCM as additive. $W = 2.0$ g, $F = 11$ ml min^{-1}, $CH_4/N_2O \sim 1$, $[CCl_4] \sim 0.38\%$ (by mol), time on stream = 30 min. (a) △, CO; ○, H_2CO; ▽, CH_3Cl; ◇, conversion. (b) ●, Total rate; △, CO; ○, H_2CO; ▽, CH_3Cl.

the oxidation of CH_4 is higher than that for chlorination of CH_4 on HPW/SiO_2. From Arrhenius plots of the rates (Fig. 8b), activation energies of about 142, 121, 121, and 226 kJ mol^{-1} were obtained for total methane conversion, CH_3Cl, H_2CO, and CO formation, respectively.

With CH_2Cl_2 as the additive, the effect of temperature was investigated over a wide range of temperatures and under a different set of contact times and concentrations of the additive. The selectivities and conversion are shown in Fig. 9a and the rates in the form of Arrhenius plots are shown in

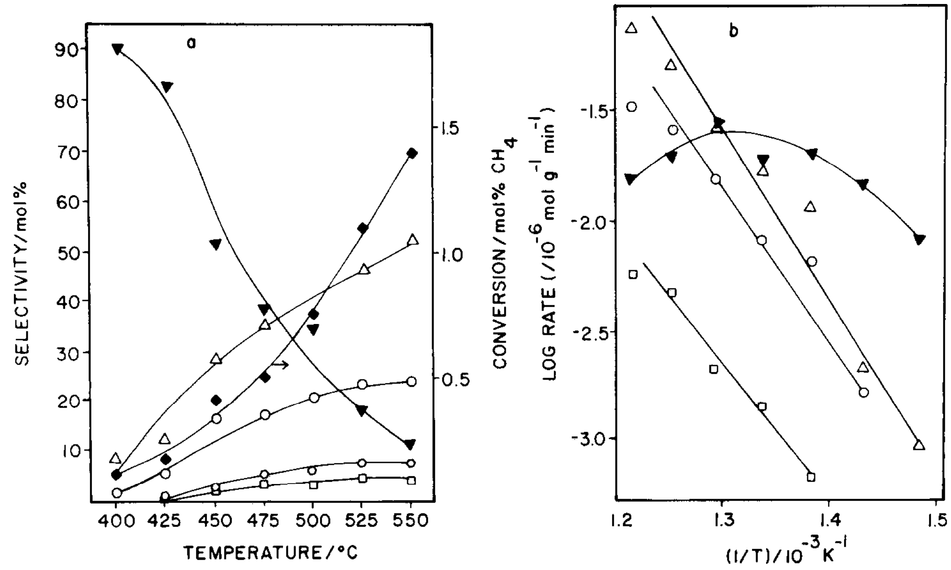

FIG. 9. Effects of temperature on conversion, selectivity, and rates for 20% HPW/SiO_2 with DCM as additive. $W = 2.0$ g, $F = 60$ ml min^{-1}, $CH_4/N_2O \sim 4$, $[CH_2Cl_2] \sim 0.18\%$ (by mol), time on stream = 15 min. (a) △, CO; □, CO_2; ○, H_2CO; ▼, CH_3Cl; ⬡, C_2H_4; ◆, conversion. (b) △, CO; □, CO_2; ○, H_2CO; ▼, CH_3Cl.

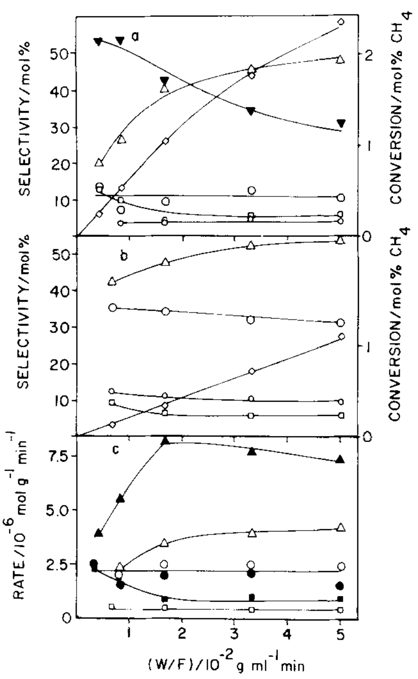

FIG. 10. Conversion, selectivity, and rates as functions of contact time in the presence and absence of CCl$_4$ in the feed on 20% HPW/SiO$_2$ at 525°C. W = 0.25–3.0 g, F = 60 ml min^{-1}, CH$_4$/N$_2$O ≈ 4, [CCl$_4$] ~ 0.17% (by mol), time on stream = 15 min. (a) △, CO; □, CO$_2$; ○, H$_2$CO; ◯, C$_2$H$_4$; ▼, CH$_3$Cl. (b) △, CO; □, CO$_2$; ○, H$_2$CO; ◯, C$_2$H$_4$. (c) Filled symbols: CCl$_4$ present; open symbols: CCl$_4$ absent. ▲, △, CO; ■, □, CO$_2$; ●, ○, H$_2$CO.

Fig. 9b. Interestingly, the rate of production of CH$_3$Cl passes through a maximum with temperature, suggesting that at higher temperatures of reaction the role of the additive may be more than simply chlorinating methane to monochloromethane. This was further substantiated by an examination of conversion of CH$_4$ in the presence and absence of the additive at a higher temperature. The results, as a function of contact time, are shown in Fig. 10. The trends in the conversion and selectivities shown in Figs. 10a and 10b are qualitatively similar to those observed at lower temperature. Again, in the absence of the additive, the selectivity to H$_2$CO, the partial oxidation product, was very little affected by the contact time, although the conversion did increase by several-fold. The figure shows that small quantities of C$_2$H$_4$ were also formed in both the presence and the absence of the additive, accounting for about 5 and 10% of the products, respectively.

The rate of formation of H$_2$CO at 525°C is essentially independent of residence time with or without the additive and is little changed when the latter is added. In contrast the rate of production of CO is increased by a factor of approximately 2 on addition of the additive. The rate of formation of CO$_2$ is increased slightly by the additive. Since the total rates of formation of oxygenated products are considerably higher in the presence of the additive than in its absence, it appears that the additive, in addition to converting methane to monochloromethane, also promotes the oxidation of methane, at least at higher temperatures. However, this enhanced oxidation of CH$_4$ simply increases the yield of deep oxidation products and has little or no effect on the production of H$_2$CO and ethylene.

The effect of the reactant ratio (CH$_4$/N$_2$O) on the reaction characteristics was also examined at a higher temperature (525°C), using CH$_2$Cl$_2$ as the additive (Fig. 11). The selectivities to CO and CH$_3$Cl changed significantly at a CH$_4$/N$_2$O ratio in the range 1/4–8/1, and to H$_2$CO in the range 1/8–1/1. On either side of these ranges, selectivities were relatively insensitive to the feed composition. The total rate of CH$_4$ conversion and rates of formation of CO and H$_2$CO each showed a maximum at a feed ratio of about 1/4–1/1. From the data of Fig. 11b, orders of approximately 0.4 and 0.6 w.r.t. CH$_4$ and N$_2$O for the total conversion of methane were obtained, reflecting appreciable change in the order w.r.t. CH$_4$ from that at lower temperatures.

Oxygen Balance in CCl$_4$ Oxidation and Methane Conversion

In Table 3, the rates of production of CO$_2$ from CCl$_4$ oxidation and the corresponding rate of N$_2$ formation from N$_2$O reduction

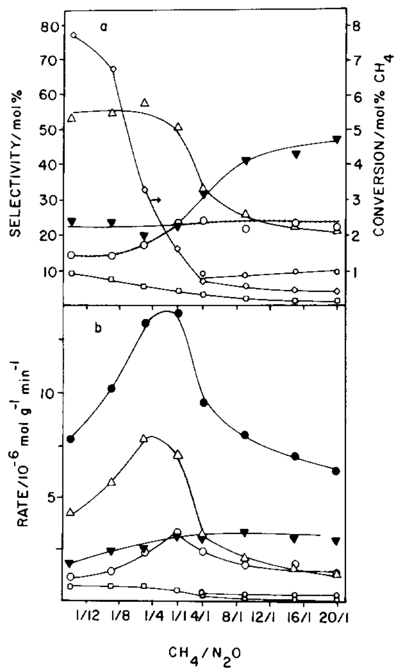

FIG. 11. Effects of feed composition on the reaction at 525°C. $W = 1.5$ g, $F = 60$ ml min^{-1}, $[CH_2Cl_2] \sim 0.17\%$ (by mol), time on stream = 15 min. (a) △, CO; □, CO_2; ○, H_2CO; ▼, CH_3Cl; ⬡, C_2H_4; ◇, conversion. (b) ●, Total rate; ○, CO; □, CO_2; ○, H_2CO; ▼, CH_3Cl; ⬡, C_2H_4.

are given. It should be mentioned that under most conditions used in the present study, CCl_4 underwent 80–100% oxidation and the product was exclusively CO_2 (CO, at most, was produced in traces). If N_2O was providing all the oxygen needed for the observed formation of CO_2 from CCl_4 oxidation, the expected rate of production of N_2 would be double that of CO_2. Clearly, as shown in Table 3, the observed rate of N_2 production is in most cases negligible compared to that of the expected rate, indicating that the catalyst bed is the main source of oxygen appearing in the product CO_2 from CCl_4 oxidation. This was further verified by excluding N_2O from the reactant stream (He was added instead) when the rate of formation of CO_2 was found to be very similar to that when N_2O was present. However, it was observed that the silica support itself (Table 5) was also very active in oxidizing CCl_4 to CO_2 (sole product), so that the oxygen source for CCl_4 oxidation was not only HPW but also the support itself. In Table 3 the observed rates of N_2 production for CH_4 oxidation and the corresponding expected rates of N_2 production based on the following assumed overall

TABLE 3

Rates[a] of Production of CO_2 and N_2 in the Oxidation of CCl_4 and CH_4

Reaction conditions	Rates of production[b]			Rates of production[c]	
	CO_2	N_2		N_2	
	Obs.	Obs.	Exp.	Obs.	Exp.
Temp (°C)[d]					
450	1.0	0.25	2.0	7.0	6.5
425	1.95	0.10	1.9	3.3	2.7
400	0.90	0.08	1.8	0.85	1.0
375	0.85	0.08	1.7	0.35	0.25
CCl_4 (mol%)[e]					
0.13	1.5	0.13	3.0	3.8	3.7
0.21	2.2	0.15	4.4	4.8	4.8
0.35	3.3	0.25	6.6	5.0	5.3
0.55	5.5	0.25	11.0	5.0	5.3
W(g)[f]					
4.0	0.42	0.25	0.84	4.7	4.8
2.0	1.1	0.25	2.2	7.0	6.5
1.0	2.2	0.17	4.4	6.7	6.7
0.50	4.2	0.60	8.4	5.7	7.0
0.25	5.8	1.3	11.6	8.3	6.7
CH_4/N_2O[g]					
12	0.75	0.03	1.5	1.8	1.8
3.3	0.85	0.05	1.7	3.9	3.8
1.1	0.85	0.15	1.7	5.3	5.0
1/2.5	0.75	0.20	1.5	4.8	5.0
1/3.5	0.65	0.15	1.3	3.1	2.9
1/10	0.85	0.20	1.7	2.0	2.2

[a] 10^{-6} mol g^{-1} min^{-1}.

[b] He + N_2O + CCl_4; pretreatment conditions same as reaction conditions except read He/N_2O for CH_4/N_2O, 20% HPW/SiO_2.

[c] $CH_4 + N_2O + CCl_4$, 20% HPW/SiO_2.

[d] 0.38 mol% CCl_4; $W = 2.0$ g, $CH_4/N_2O = 1.0$, $F = 11$ ml/min.

[e] $T = 450$°C, $W = 2.0$ g, $CH_4/N_2O = 4.0$, $F = 60$ ml/min.

[f] $T = 450$°C, 0.38 mol% CCl_4, $CH_4/N_2O = 1.0$, $F = 11$ ml/min.

[g] $T = 450$°C, 0.30 mol% CCl_4, $W = 2.0$ g, $F = 15$ ml/min.; for He + N_2O + CCl_4 feed, this represents He/N_2O ratio.

stoichiometry for the production of different products of reaction are also included:

$$CH_4 + 3N_2O \rightarrow CO + 2H_2O + 3N_2$$

$$CH_4 + 2N_2O \rightarrow H_2CO + H_2O + 2N_2$$

$$CH_4 + N_2O + Cl \rightarrow CH_3Cl + N_2 + \cdots$$

A close correspondence between observed and expected rates is clear from the table. In many cases included in Table 3 the selectivity to CH_3Cl was more than 70%. This suggests that the assumption that the formation of 1 mol CH_3Cl requires 1 mol N_2O is reasonable (otherwise, a large discrepancy would be expected). It should also be stressed that N_2O is vital in the formation of CH_3Cl because, as shown earlier, exclusion of N_2O from the feed results in a large decrease in the rate of formation of CH_3Cl.

DISCUSSION

The present study opens up a potentially new area for the application of heteropoly oxometalates with Keggin structure as solid catalysts, namely, the selective oxychlorination of methane to monochloromethane. Previous studies in this laboratory have demonstrated that heteropoly compounds are active catalysts for the conversion of methanol to higher hydrocarbons and, among them, those with tungsten as peripheral metal atom are much more active than those with molybdenum as the peripheral atom (*31*). More recent studies have shown that these heteropoly oxometalates when supported on silica are also active catalysts for the partial oxidation of methane and, in this case, those with molybdenum as the peripheral metal atom are much superior to those with tungsten, in terms of both overall conversion of methane and selectivity to partial oxidation products. Furthermore, it has been observed that the addition of a small quantity of a halomethane (e.g., DCM or TCM) substantially augments the activity of 12-molybdophosphoric acid supported on silica in the oxidation of methane (*33*). However, in the presence of a halomethane, methane undergoes in addition to oxidation, oxychlorination producing monochloromethane although the overall selectivity to monochloromethane is very low (<5–10%) on 12-molybdophosphoric acid. On the other hand, the present study clearly reflects that below 450°C the presence of DCM or TCM in the feed has little effect on the oxidation of CH_4 by N_2O on HPW/SiO_2, but CH_4 is selectively converted to CH_3Cl with reasonable yield. Indeed, selectivity of 60% at a conversion of methane of ~3% is obtained. As far as specific selectivity to a chloromethane is concerned, selectivity to monochloromethane is nearly 100%. Not only is the selectivity to CH_3Cl much higher on HPW/SiO_2 than on $HPMo/SiO_2$, but actual rates of formation of CH_3Cl are also four to five times higher on the former catalyst than on the latter under comparable conditions. Thus it is clearly evident that the nature of the peripheral metal atom (Mo/W) of the 12-heteropoly oxometalate has a dramatic influence on the distribution of products for methane conversion by nitrous oxide in the presence of DCM or TCM.

As noted in the Introduction, calculations have predicted that the terminal anionic oxygen atoms of HPW have a lability smaller than that found in HPMo. Consequently, it is plausible that, on HPW, at lower temperatures the oxidation of methane and the subsequent replenishment of these terminal oxygen atoms by nitrous oxide are more difficult processes than the adsorption or incorporation of chlorine in the catalysts and its subsequent reaction with methane. On the other hand, as a consequence of the labile nature of terminal oxygen atoms in HPMo, the oxidation process would be expected to dominate over the oxychlorination process.

It may be noted that on HPW/SiO_2, in the absence of chloro additive, selectivities to oxygenated products are practically independent of W/F or of conversion at both 450 and 525°C (Figs. 5b and 10b). This situation may be contrasted with that observed on $HPMo/SiO_2$, where CO and H_2CO showed strong, but reciprocal, dependence on conversion of methane (*11*). This suggests that while on $HPMo/SiO_2$, CO is primarily produced by the subsequent degradation of H_2CO, on HPW/SiO_2 they are produced mainly by independent and parallel processes. CO_2, however, showed little or no dependence on conversion on both these catalysts, suggesting that it is produced by a process independent of and distinct from those producing CO and H_2CO on each of these heteropoly oxometalate catalysts.

The method developed in this study for the oxychlorination of methane is quite distinct from the usual catalytic method suggested in patent and scientific literature involving, for example, supported copper chloride catalysts and feed streams consisting of CH_4, O_2, and HCl or Cl_2. In this process, HCl or Cl_2 is used in large concentrations. In contrast, in the present study with HPW/SiO_2, only small quantitites of a chloromethane are required in the feed. Results with the present catalyst are distinguishable from those with copper chloride-based catalysts in another important respect. While with the latter catalysts, methylene chloride and chloroform are produced in addition to methyl chloride, with the present catalyst only methyl chloride is produced and the yield is comparable to that obtained with copper-based catalysts.

It should be emphasized that the role in the oxychlorination process played by O_2 in other studies and by N_2O in the present study is unclear. Yet, its presence is found to be necessary in order to obtain reasonable conversion of methane. In the case of the oxychlorination process using cupric chloride catalyst, it is suggested that the function of oxygen is to reoxidize ($CuCl \rightarrow CuCl_2$) the catalyst after reduction in the chlorination process (*26*). Although conclusive evidence is not yet available with the present catalysts, a similar rationalization may be possible here.

The experiments involving pretreatment of the catalyst with DCM or TCM followed by introduction of $CH_4 + N_2O$ feed mixture (Fig. 3) revealed that chlorine is accumulated on the catalyst during the pretreatment stage. This is subsequently converted to CH_3Cl and HCl when allowed to interact with CH_4 in the presence of N_2O. However, it remains unclear whether this chlorine is simply in the chemisorbed state on the catalyst or is actually incorporated into the catalyst structure (for example, by replacing some of the terminal oxygen). Although infrared analysis of spent catalysts (where the supported catalyst was washed with acetonitrile to remove the soluble HPW from the carrier and the IR spectrum of the solution was recorded) clearly indicates that the Keggin structure is maintained intact (as evident from characteristic bands) after reaction with $CH_4 + N_2O +$ DCM (or TCM) feed mixture, no band characteristic of W–Cl was seen; nor was this evident when unsupported HPW was treated with DCM or TCM and infrared spectra were taken (after pressing KBr disk). However, the relatively small quantities of chlorine taken up undoubtedly render detection difficult.

The effects of reaction temperature on the rates of formation of products of oxidation as well as of oxychlorination are also worth noting. While at lower temperatures the formation of oxygenated products is little influenced (Figs. 4 and 5) and in some cases even inhibited (Table 2) by the presence of chloro additives in the feed, at higher temperatures (for example, at 525°) their formation is substantially accelerated by the presence of additives. The situation at higher temperatures is comparable to that observed with $HPMo/SiO_2$ (*33*). On the other hand, the rate of formation of CH_3Cl seems to pass through a maximum as the reaction temperature increases (Fig. 9). These results suggest that CH_3Cl could well be an intermediate in the formation of oxygenated products at higher temperatures (e.g., 525°C). However, experiments conducted with $CH_3Cl + N_2O +$ He and no CH_4 in the feed indicated that CH_3Cl undergoes substantial oxidation (the product being overwhelmingly CO) in the presence of catalyst under the conditions of *W/F* used in actual reactions at both higher (525°C) and lower temperatures (450°C), suggesting that CH_3Cl may have been an intermediate product at both temperatures. However, Fig. 5a shows that at 450°C, although the yield of CH_3Cl levels off at higher *W/F*, a concomitant increase in the rates of formation of CO, H_2CO (Fig. 5c), and CO_2 (not shown) is not observed, a result which would be expected with CH_3Cl as an intermediate product. This suggests that CH_3Cl is not undergoing appreciable oxidation under actual reaction conditions. This could, at least, be partly due to the presence of TCM (or DCM) which may have inhibited oxidation of CH_3Cl. Thus if the oxidation and oxychlorination of CH_4 are occurring independently of each another at lower temperatures, it is evident (Fig. 8) that the activation barrier for the oxidation (230 kJ mol^{-1}), calculated from the temperature coefficient of the rate of formation of CO which is the major product (>70%) of oxidation, is substantially higher than that for oxychlorination (145 kJ mol^{-1}). Although at this time there is no direct evidence to link the present results with earlier observations of the high-temperature lability of the anionic oxygen atoms in HPW, nevertheless some rationalization for the dominance of the oxidation process at higher temperatures may be available.

It may be noted that while the orders w.r.t. N_2O (0.6–0.7) for the overall conversions of methane are similar at 450 and 525°C, the corresponding orders w.r.t. CH_4 change significantly with temperature, being 0.8–0.9 and 0.4 at 450 and 525°C, respectively.

Perhaps the most difficult aspect of the present results is related to the explanation of the chlorine transfer process. Although there is no evidence in the literature for the existence of chlorinated anions of Keggin structures this is the most appealing hypothesis. However, since earlier work has demonstrated that the heteropoly anions may be methylated in the preliminary stages of the methanol-to-gasoline process it is tempting to argue that the "sorbed" methyl groups may interact with the anion-incorporated chlorine atoms.

It is of course obvious that such comments on mechanism require additional studies for verification. However the present results, regardless of the mechanism provide an interesting and potentially useful new route for the conversion of methane. Indeed, the production of methyl chloride rather than methanol or formaldehyde is particularly attractive because of the relatively high thermal stability of the chloride and the ease with which it may be further processed to useful precursors.

SUMMARY

The silica-supported 12-tungstophosphoric acid is shown to be an active and selective catalyst for the oxychlorination of methane to CH_3Cl in the presence of N_2O and small quantities of dichloro- or tetrachloromethane. The presence of N_2O, though its precise role is unclear, is found essential for the chlorination of methane. Experiments involving the pretreatment of catalysts with the chloro additive reveal that chlorine in some form is taken up by the catalyst in the pretreatment stage and is subsequently transferred to CH_4 when the catalyst is exposed to the feed stream of CH_4 + N_2O. Increasing the loading of the catalyst up to about 20 wt% increases the conversion of methane and decreases the selectivity of CH_3Cl while beyond this loading both conversion and selectivity remain virtually constant. The chloro additive is shown to influence only chlorination of methane at lower temperatures while both chlorination and oxidation of methane are affected at higher temperatures. This is partly accountable by the higher activation energy required for the oxidation process compared to that required for the oxychlorination process. From the contact

time effects, it is concluded that H_2CO and CO are produced by independent and parallel routes on HPW/SiO_2 in contrast to the observations with $HPMo/SiO_2$ (*11*). It is observed that while in the case of CH_4, gas-phase N_2O is used up in the oxidation process, in the case of oxidation of CCl_4 only lattice oxygens of the catalysts are consumed. The reasons for the differences in the behavior of HPMo and HPW in the oxidation of methane in the presence of a small quantity of chloro additive are discussed.

ACKNOWLEDGMENTS

The financial support of the Natural Sciences and Engineering Research Council of Canada and of Imperial Oil Canada is gratefully acknowledged.

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