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The Oxidation of Methane on Heteropolyoxometalates

I. Catalytic Properties of Silica-Supported Heteropolyacids

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The catalytic properties in the partial oxidation of methane of a number of silica-supported heteropolyacids, 12-tungstophosphoric, 12-molybdophosphoric, 10-molybdo-2-vanadophosphoric, 12-tungstosilicic, and 12-molybdosilicic acids have been investigated. The effects of pretreatment environment, residence time, reaction temperature, reactant concentrations, and reactivity of the products have been studied with 12-molybdophosphoric acid on SiO_2 and N_2O as oxidant.

INTRODUCTION

Interest in the carbon–hydrogen bond activation and the possibility of producing liquid from gaseous fuels has encouraged considerable work on the use of heterogeneous catalysts in the partial oxidation of methane (*1–3*). Much of the recent work has concentrated on the use of nitrous oxide as oxidant following earlier gas-phase studies by Bohme and Fehsenfeld (*4*) which showed that the O^- ion is capable of stripping a hydrogen atom from an alkane:

$$O^- + RH \rightarrow OH^- + R \qquad (1)$$

More recently Lunsford and co-workers (*5, 6*) have shown that low molecular weight alkanes can be partially oxidized on MgO (*5, 6*) and on Mo/SiO_2 (*7–11*) with N_2O, apparently as a result of the abstraction of a hydrogen atom by O^-, followed by the reaction of alkyl radicals with surface O^{2-} ions. Most recently the same workers (*12*) have shown that conversion of methane to ethylene and ethane can be achieved with O_2 as the oxidant over a lithium-promoted magnesium oxide catalyst. Lipatkina *et al.* (*13*) have provided evidence for the formation of methyl radicals from the reaction of surface O^- with methane on Mo/SiO_2. Lunsford and co-workers (*14*) have also demonstrated that gas-phase radical formation during the reactions of methane and other hydrocarbons on oxides is dependent on three factors, the bond strength of the weakest C–H bond, the presence of particular radical-forming sites on the catalyst surface, and the ability of the radicals to desorb or take part in further surface reactions. The influence of experimental conditions on the formation of O^- ions from N_2O adsorption on reduced grafted Mo/SiO_2 and the role of these ions in surface charge-transfer reactions have also been analyzed (*15, 16*).

Somorjai and co-workers (*17, 18*) have recently reported on the kinetics of the partial oxidation of methane with N_2O over Mo/SiO_2 and V/SiO_2. At low temperatures methanol and formaldehyde are apparently formed from the same intermediate by parallel processes, while at higher temperatures formaldehyde is formed from methanol.

The present work is concerned with the use of heteropolyoxometalates with Keggin structure as heterogeneous catalysts in the

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partial oxidation of methane. These ionic solids possess high molecular weight, cage-like anions with an atom such as phosphorus, silicon, or arsenic at the center of the latter and four oxygen atoms arranged tetrahedrally around the central atom. Twelve octahedra, with an oxygen atom at each of the vertices and a metal atom such as molybdenum, tungsten, or vanadium at each of their centers, surround the central tetrahedron and share oxygen atoms with each other and the former.

The structural, surface, and heterogeneous catalytic properties of heteropolyoxometalates have recently been studied by a variety of techniques in this laboratory (*19–27, 30*). Temperature-programmed-desorption, -reduction, and -exchange experiments (*19–21*) have shown that water is desorbed at two temperatures, that at the higher temperature resulting from the abstraction of oxygen from the heteropolyanion by the acidic protons. Further, photoacoustic FTIR studies (*20, 22*) have shown that the dehydration of methanol on 12-tungstophosphoric acid involves the methylation of anionic (presumably terminal) oxygen atoms. Extended Hückel calculations (*23*) have shown that the acid strength of the protons in the heteropolyacids is inversely related to the charge on these terminal oxygen atoms, while the catalytic activity in oxidation processes appears to be proportional to the strength of the anionic peripheral metal–oxygen bond.

Earlier work from this laboratory has shown that 12-tungstophosphoric acid (*24, 25*) and its metal and ammonium salts (*25–27*) are capable of converting methanol to hydrocarbons ($>C_1$) apparently via a route in which the anionic terminal oxygen atoms are methylated. In contrast, with 12-molybdophosphoric acid, methanol is primarily converted to oxidation products, principally carbon monoxide. In the former case higher reaction temperatures, for example, those greater than 400°C produce a reaction product which is predominantly methane, rather than higher hydrocarbons. It thus appeared possible that the methylation of the terminal anionic oxygen atom may be achieved by the use of methane as reactant rather than methanol.

A number of other workers (see, for example, (*28*)) have shown that certain heteropolyoxometalates are effective in oxidation processes, although no work has yet been published relating to the oxidation of methane.

In the present work the first report of the partial oxidation of methane on the heteropolyoxometalates, 12-molybdophosphoric (HPMo), 12-molybdosilicic (HSiMo), 12-tungstophosphoric (HPW), 12-tungstosilicic (HSiW), and 10-molybdo-2-vanadophosphoric ($HPMo_{10}V_2$) acids is presented. Emphasis has been placed on the effect of reaction variables and on the comparison of N_2O and O_2 as oxidant on the catalytic properties of 12-molybdophosphoric acid supported on SiO_2.

EXPERIMENTAL SECTION

Catalyst preparation. A silica gel (Grace-Davison grade 400, 740 ± 20 $m^2\ g^{-1}$) with particle size of 8–20 mesh has been used as a support. The supported heteropolyoxometalates have been prepared by impregnation of the silica with aqueous solutions of HPMo (B. D. H. Analar grade), HSiMo (Pressure Chemical Co.), HPW (B. D. H. Analar grade), HSiW (J. T. Baker analyzed), and $HPMo_{10}V_2$ prepared following the procedure reported by Tsigdinos (*29*). The acids were purified by recrystallization in distilled water prior to use. Ten grams of support was impregnated with 20 ml of solution of the acid at its natural pH ($\simeq$2–3). The solutions were then evaporated to dryness at 80°C and the solids calcined at 350°C for 2 h. The samples were then sieved and the 8–15 mesh particle size kept for use.

Samples containing 3 wt% molybdenum and 1.66 wt% vanadium on silica have also been prepared following the method used by Liu *et al.* (*9*). A large excess of basic solution (pH $\simeq$ 11 by NH_4OH addition) of ammonium molybdate (J. T. Baker analyzed) or ammonium vanadate (Fisher purified) was added to the support, then evaporated at 80°C to dryness. The Mo/SiO_2 catalyst has been calcined at 600°C for 16 h and the V/SiO_2 catalyst at 350°C for 2 h.

The samples will be symbolized in the text by the wt% of the acids followed by the abbreviation HPMo, HSiMo, HPW, HSiW, HPV_2Mo_{10} for $H_3PMo_{12}O_{40}$, $H_4SiMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_5PV_2Mo_{10}O_{40}$ and the wt% of the metal followed by Mo or V for supported molybdenum and vanadium, respectively.

The loading of a set of different supported heteropolyoxometalates has been chosen in order to obtain a similar surface concentration of the heteropolyanionic unit, the Keggin Unit (KU), of 0.087 KU per nm^2 of support surface area. This corresponds to loadings of 20.0, 19.9, 26.2, 26.2, and 20.4 wt% of the HPMo, HSiMo, HPW, HSiW, and HPV_2Mo_{10} 30 H_2O hydrated acids, respectively. A 29.4 wt% HPMo on SiO_2 has also been prepared.

A sample of the silica support was impregnated with an acidic aqueous solution (HNO_3, pH = 2), then dried, and calcined at 350°C for 2 h in order to simulate the effect of the impregnation of the heteropolyacids. This sample has been used as the support reference catalyst.

Catalytic experiments. The catalytic tests have been performed in a fixed-bed continuous-flow reactor. The flow of reactant was regulated by needle valves and monitored by rotameters. All the gases, He (99.9%), CH_4 (99.0%), N_2O (99.0%), O_2 (99.0%), and CO (99.0%), were used without further purification. The H_2O, CH_3OH, or CH_2O vapor was generated by a saturator under helium when necessary. The impurities in CH_4 were predominantly C_2H_6 ($\approx$0.5%), N_2, O_2, and traces of alkanes (C_3H_8, C_4H_{10}). Experiments showed that ethane oxidation does not generate methanol and formaldehyde, but rather CO, CO_2, and C_2H_4. Consequently, since the conversion of ethane was small under the conditions and with the catalysts employed in the present work, the contribution of ethane and lesser impurities is negligible.

The Pyrex glass or quartz reactor measured 33 cm in length and 0.9 cm in diameter (o.d.). The catalyst bed was supported between pads of Pyrex glass wool of 5 cm thickness. The temperature was monitored by a thermocouple located in the catalyst bed. Temperature variations were found to be in the range ± 1°C along the central part of the reactor ($\approx$8 cm). The reaction manifold was constructed from stainless steel $\frac{1}{8}$ in. o.d. and heated at 150°C. A 6-port gas sampling valve (VALCO) with a 5-ml sample loop was connected to the reactor exit and to a reactor by-pass. This permitted the analysis of both the reactor inlet and outlet flow.

The samples were preheated in He, unless otherwise reported, for one hour at the reaction temperature. This produced extensively dehydrated samples as only traces of water were then detected by GC analysis.

All the products were analyzed with a Hewlett-Packard 5890 gas chromatograph equipped with a thermal conductivity detector and with a Porapak Q column of 5.5 m length and helium as a carrier gas (flow, 60 ml min^{-1}; column pressure, 60 psi). The temperature program of 4 min at 35°C, ramp of 25°C min^{-1} to 120°C, 10 min at 120°C, ramp of 10°C min^{-1} to 200°C gave satisfactory separation of all gases except N_2–O_2. The presence of these gases was checked with a 3A molecular sieve column when necessary. The calibrations have been made for each component in actual analysis condition. When N_2O is used as oxidant a mass balance of N better than 98% was usually found. Carbon and oxygen mass balances are generally better than 95% when the conversion is higher than 1% but is always better than 90%. The imprecision arises in part because of the coking of the samples and a lower precision in the detection of small amounts of CO, CO_2, CH_2O, and CH_3OH.

The steady state was reached after several hours of reaction. The conversion of CH_4 was calculated as 100× (amount of C product detected/amount of CH_4 in the inlet flow). The conversion of N_2O was calculated from the N_2 produced and conversion of O_2 from the oxygenated products formed.

The selectivity was calculated as the mole percent of the CO, CO_2, CH_2O, and CH_3OH product formed. Traces of C_2H_6, C_2H_4, and other hydrocarbons and dimethylether have been omitted from the calculation.

Blank runs have been performed with the reactor full of glass wool heated at 570°C with conditions similar to those employed when a catalyst was present. In helium, CH_4 and CO produced no decomposition or reaction products whereas N_2O yielded traces of N_2 and O_2, CH_3OH formed traces of dimethylether, and CH_2O gave traces of CO, H_2, CH_3OH, and H_2O. In the presence of N_2O or O_2, CH_3OH, CH_2O, and CO each produced traces of CO, CO_2, and H_2O whereas CH_4 gave no detectable products.

Activation energies have been calculated from 4 to 6 runs at different temperatures, recorded in random order when the system was in steady state.

RESULTS

The conversion and selectivity of the supported heteropolyoxometalates and comparison catalysts are reported in Table 1 together with the N_2 production turnover rate per Keggin Unit or atom of metal when nitrous oxide is used as the oxidant (Table 1A).

With nitrous oxide as oxidant the conversion of methane on the silica support is small and only complete oxidation products are produced. The conversion of methane on supported 12-tungstophosphoric and 12-tungstosilicic acid, although higher than that with the support above, is also small (<0.5%). However, when heteropolyoxometalates containing molybdenum in the anion are employed, conversions of at least a factor of 10 higher are obtained. In addi-

TABLE 1

Conversion and Selectivity of the Supported Heteropolyoxometalates and Reference Catalysts

Sample	Conversion (%)			Selectivity (%)				N_2 Production Turnover Rate	
	CH_4	N_2O	O_2	CO	CO_2	CH_2O	CH_3OH	10^{-2} molec. KU^{-1} sec^{-1}	10^{-2} molec. (at metal)$^{-1}$ sec^{-1}
(A) 1.66 V[a]	8.9	59.1	—	81.8	14.5	3.5	0.2	—	2.77
20.0 HPMo[a]	5.1	36.4	—	65.0	22.5	12.0	0.5	6.9	0.575
20.4 HPV_2Mo_{10}[a]	4.2	28.5	—	64.9	23.6	10.9	0.5	5.35	0.446
19.9 HSiMo[a]	2.51	17.0	—	58.6	32.3	8.7	0.4	2.48	0.207
3 Mo	0.41	3.3	—	57.0	31.0	12.0	t	—	0.15
26.2 HPW	0.40	3.2	—	56.0	44.0	t	n.d.	0.63	0.052
26.2 HSiW	0.35	2.8	—	44.0	56.0	t	n.d.	0.54	0.045
SiO_2	0.12	1.1	—	32.0	68.0	n.d.	n.d.	—	—
(B) HPMo[b]	0.8	—	4.5	74.0	26.0	t	n.d.		
SiO_2[b]	0.15	—	1.5	15.0	51.0	34.0	n.d.		

Note. Reaction conditions: $T_R = 843$ K, (a) $W = 0.35$ g, $F = 30$ ml min^{-1}, CH_4 (67%), N_2O (33%); (B) $W = 0.35$ g, $F = 60$ ml min^{-1}, CH_4 (67%), O_2 (33%). t, trace; n.d., not detected.

[a] Traces of dimethylether and H_2 were observed.

[b] No traces of H_2 were found.

tion the molybdenum- and tungsten-based heteropolyanions show distinct differences in selectivity, the former producing significant quantities of the partial oxidation products, formaldehyde and methanol, while the latter generate only traces of formaldehyde. While such results demonstrate the importance of the peripheral metal elements of the anion, the anion containing both vanadium and molybdenum atoms ($PV_2Mo_{10}O_{40}^{-5}$) produces little change compared to the HPMo catalysts, the conversion being slightly lower and the selectivity similar.

The effect of the nature of the central heteroatom P or Si can also be estimated from the results contained in Table 1. Both for Mo- or W-containing anions the change of the central heteroatom from phosphorus to silicon produces a decrease of the catalytic activity and a change of selectivity, the silicon central heteroatom favoring the production of CO_2 at the expense of CO with only a slight decrease of the selectivity of formaldehyde and methanol relative to the anion containing phosphorus as the central atom.

Although the loadings are slightly different, a comparison of the N_2 production turnover rate per metal atom of the different heteropolyoxometalates and the supported Mo and V catalysts can be made. The supported HPMo, HPV_2Mo_{10}, and HSiMO gave a turnover somewhat higher than the Mo catalyst whereas the V catalyst is clearly much more active. The selectivity of the Mo and HSiMo catalysts are surprisingly similar whereas the V catalyst has a very different selectivity with a higher CO production, less CO_2 and CH_2O but still with some CH_3OH produced. A net difference of the ratio of CH_2O/CH_3OH produced can also be found between the V and the other catalysts.

When oxygen is used as the oxidant (Table 1B), the silica support shows a surprisingly good selectivity toward the production of formaldehyde with a small conversion. The conversion of the HPMo catalyst remains small with now a very poor selectivity to partial oxidation products. On that catalyst, for rather similar experimental conditions, the use of oxygen gives a much smaller methane conversion than that obtained with nitrous oxide as oxidant.

In order to examine the effect of a number of variables, supported 12-molybdophosphoric acid has been chosen for a more detailed study.

While helium was generally used for pretreatment of catalyst samples in the present work, a number of different gases (N_2O, He, O_2, H_2, CH_4, CO) were tested for their effect on reactions subsequent to pretreatment of 29.4 $HPMo/SiO_2$ at 843 K for 1 h. For such reactions steady-state conditions were reached in all cases after 2–3 h at a reaction temperature of 843 K, but 4–5 h at a lower reaction temperature of 793 K. After pretreatment in oxygen, the conversion of methane initially increased, while that with the other gases decreased. In general, pretreatment in an oxidizing atmosphere (N_2O, O_2) resulted in lower steady-state conversions than that in reducing and inert gases (CH_4, H_2, CO, He).

With all pretreatment gases the partial oxidation selectivity of the $CH_4 + N_2O$ reaction is greater at steady state than found initially. While catalysts regenerated with O_2 or N_2O produced lower steady-state conversion in the $CH_4 + N_2O$ reaction than that found with the original catalysts the selectivity was similar to that observed with the latter catalysts.

In the $CH_4 + N_2O$ reaction on $HPMo/SiO_2$, the selectivity to partial oxidation products increases with decreasing contact time (*W*/*F*) (Fig. 1A and 1B) until a maximum is reached. A maximum is also found for the CO selectivity while the CO_2 selectivity shows a minimum. An increase in reaction temperature displaces these extrema toward lower apparent contact time. Evidently higher temperatures favor the subsequent oxidation of the partial oxidation products and CO. The CH_4 conversion in-

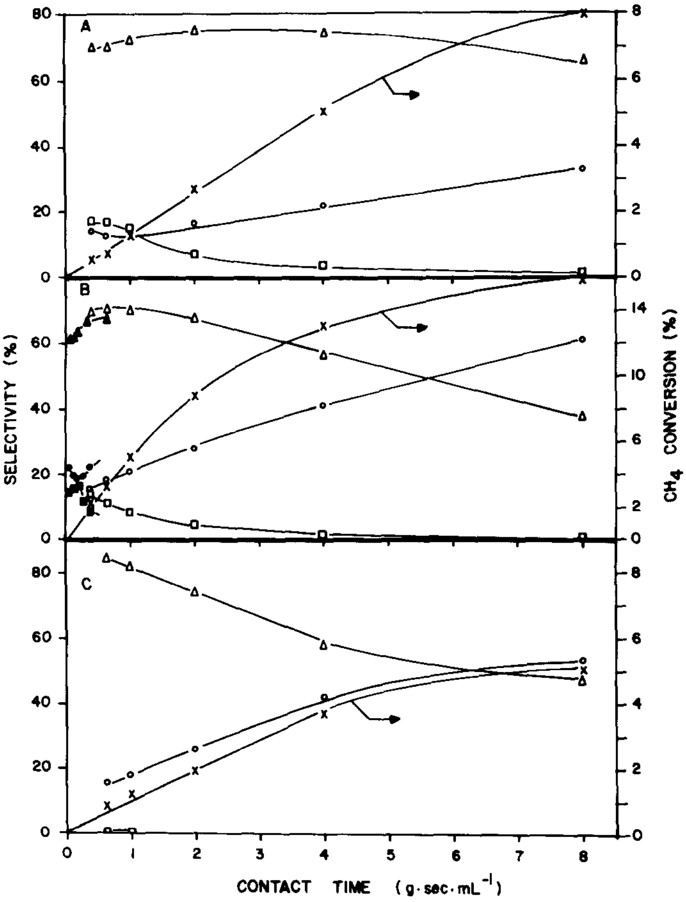

FIG. 1. Effect of the contact time on the conversion and selectivity of 29.4 HPMo/SiO_2 for the CH_4 + N_2O and CH_4 + O_2 reactions. Reaction conditions: (A) T_R = 793 K, W = 1.0 g, CH_4 (67%), N_2O (33%); (B) T_R = 843 K, open symbols W = 1.0 g, black symbols W = 0.17 g, CH_4 (67%), N_2O (33%); (C) T_R = 843 K, W = 1.0 g, CH_4 (67%), O_2 (33%). Symbols: (△) CO, (○) CO_2, (□) CH_2O, (×) CH_4 conversion.

creases linearly with increase in contact time up to approximately 5%.

With oxygen as an oxidant (Fig. 1C) the production of CO is favored by lower contact times while a trace of formaldehyde appears. Since the latter may be formed on the support, it cannot be concluded that HPMo is the only source of the catalytic activity in producing partial oxidation products in the CH_4 + O_2 reaction. Changes in the conversion with apparent contact time are similar to those found with N_2O.

The effect of reaction temperature on the selectivity is illustrated in Fig. 2. With the HPMo catalyst and N_2O as the oxidant (Fig. 2B), increase in the reaction temperature leads to an increase of the CO_2 production at the expense of CO and formaldehyde. This effect is, however, strongly attenuated when a high flow rate is used (Fig. 2B). On silica a similar effect of the reaction temperature is also evident (Fig. 2A).

When oxygen is employed as an oxidant and the reaction studied on silica alone, an increase in the reaction temperature produces a decrease and increase in the production of CO_2 and CO, respectively, while that of formaldehyde remains constant until a temperature higher than 850 K is reached

(Fig. 2A). With oxygen as the oxidant, the $HPMo/SiO_2$ catalyst shows a variation in selectivity similar to that observed with N_2O, but very different from that observed with the support alone (Fig. 2C).

Variation in the reactant composition has an important effect on the selectivity (Fig. 3). Low values of the molar ratio N_2O/CH_4 favor the production of partial oxidation products until a maximum is reached at approximately $N_2O/CH_4 = 0.1$ for the experimental conditions used (Fig. 3A). The CH_4 conversion increases linearly as the N_2O fraction increases from 0 to 17% whereas the CH_4 conversion decreases when the fraction of CH_4 increases (Fig. 3B). Evidently the selectivity in the present system is approximately inversely related to the conversion.

The effect of the presence of water on the partial oxidation of methane has been studied with other heterogeneous catalysts (*17*). In the present work with supported HPMo the introduction of H_2O into the reactant system results in a decrease in the conversion with either N_2O or O_2 as an oxidant (Fig. 4). Subsequent elimination of the water reestablished the initial conversion.

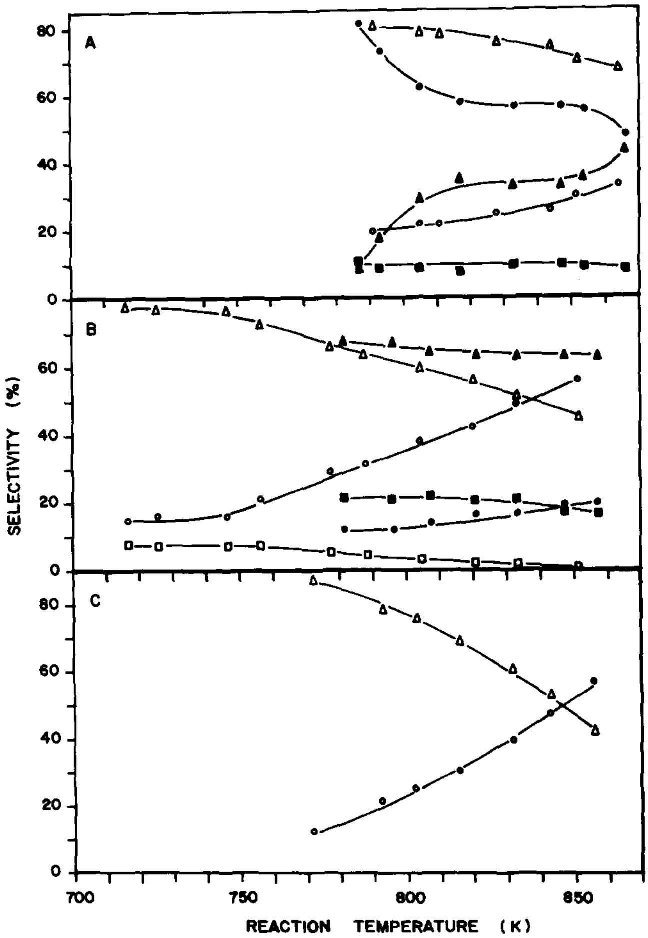

FIG. 2. Effect of the reaction temperature on the selectivity of the $CH_4 + N_2O$ or $CH_4 + O_2$ reactions on 29.4 $HPMo/SiO_2$ and the SiO_2 support. Reaction conditions: (A) SiO_2, $F = 15$ ml min^{-1}, $W = 2.0$ g, open symbols CH_4 (67%), N_2O (33%), black symbols CH_4 (67%), O_2 (33%); (B) HPMo open symbols $F = 7.5$ ml min^{-1}, black symbols $F = 90$ ml min^{-1}, $W = 1.0$ g, CH_4 (67%), N_2O (33%); (C) HPMo open symbols $F = 15$ ml min^{-1}, $W = 1.0$ g, CH_4 (67%), O_2 (33%). Symbols: (△) CO, (○) CO_2, (□) CH_2O.

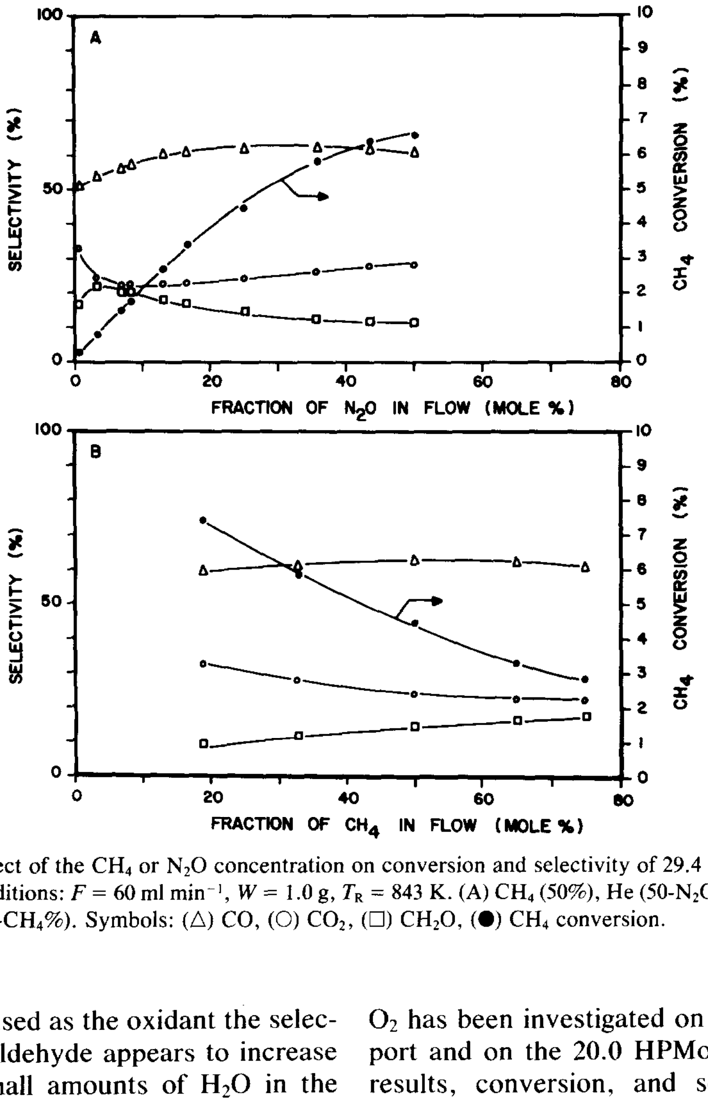

FIG. 3. Effect of the CH_4 or N_2O concentration on conversion and selectivity of 29.4 HPMo/SiO_2. Reaction conditions: $F = 60$ ml min^{-1}, $W = 1.0$ g, $T_R = 843$ K. (A) CH_4 (50%), He (50-N_2O%); (B) N_2O (25%), He(75-CH_4%). Symbols: (△) CO, (○) CO_2, (□) CH_2O, (●) CH_4 conversion.

When N_2O is used as the oxidant the selectivity to formaldehyde appears to increase slightly for small amounts of H_2O in the flow but then decrease when the water content increases. When oxygen is the oxidant, little change in selectivity is evident. In both cases, however, elimination of the H_2O reestablishes the original selectivity. It appears that with HPMo, water is acting as a poison rather than a promoter as has been reported for Mo/SiO_2 (*10*) and that no net improvement of the selectivity is induced by water at least for the set of experimental conditions used.

For one set of experimental conditions, the reaction of the products of the CH_4 oxidation, namely, CO, CH_2O, and CH_3OH, alone in helium or in the presence of N_2O or O_2 has been investigated on the silica support and on the 20.0 HPMo catalyst. The results, conversion, and selectivity, are summarized in Table 2.

With no oxidant added, formaldehyde and methanol in helium react readily on SiO_2, whereas the CO conversion is very small. Interestingly, methane and hydrogen are produced in small amounts from CH_2O and in large quantity from CH_3OH reacting on SiO_2. Moreover in both cases CO_2 is a minor product whereas CO is strongly favored. These results show that the support is not inert in the system studied and that both hydrogenation and oxidation processes are occurring with CH_2O and CH_3OH. These two processes are obviously detrimental to the production of partial oxidation products from the CH_4 oxidation.

The presence of HPMo on the support catalyzes the hydrogenation process, when CH_3OH and CH_2O react alone, as more CH_4 is produced than with SiO_2 as catalyst. Moreover, CO reacts on the HPMo species presumably by disproportionation, a reaction apparently catalyzed by the HPMo species and possibly by one of the sources of CO_2 and the carbonaceous deposits during methane oxidation.

The main effect of the addition of N_2O to either CH_3OH or CH_2O is to increase the conversion and displace the selectivity toward more oxidized products, i.e., more CO_2 and CO and less CH_4. However, the hydrogenation function is still effective as witnessed by the presence of CH_4 and a trace of H_2. Again the effect of the HPMo, relative to the SiO_2 catalyst, is to increase the conversion and, at least when CH_3OH is the reactant, to increase the CH_4 production. The latter observation is consistent with earlier work from this laboratory in which HPMo was studied in unsupported form (*24*, *25*).

When O_2 was employed as oxidant, the conversion became higher than that in the two previous cases with now a displacement of the selectivity to complete oxidation products. CH_4 production tended to disappear completely and no trace of H_2 was observed. Again the presence of the HPMo species increases the conversion of either CH_3OH or CH_2O. These results demonstrate that oxygen is a more powerful oxidant for formaldehyde and methanol than

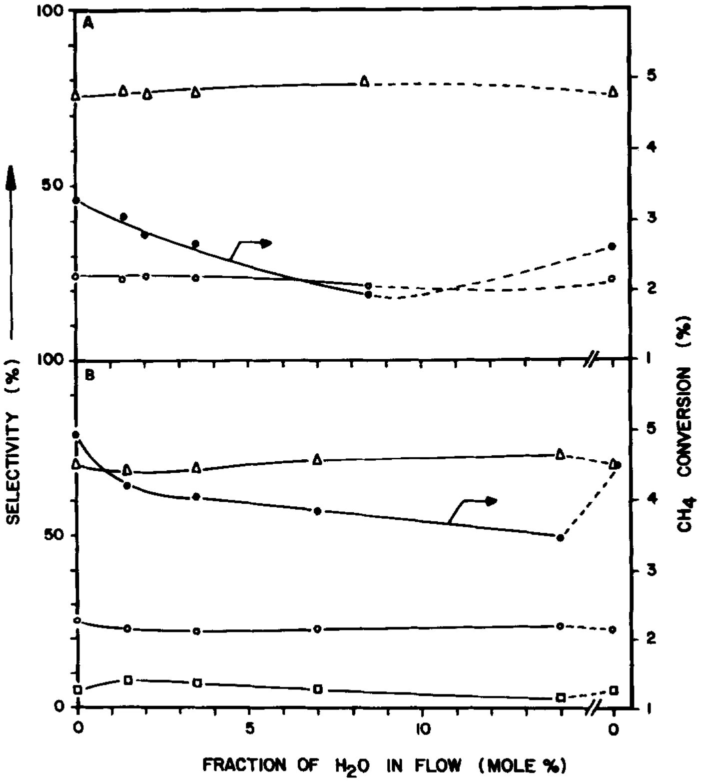

FIG. 4. Effect of the amount of water on the conversion and selectivity of the (A) $CH_4 + N_2O$ and (B) $CH_4 + O_2$ reactions on 29.4 $HPMo/SiO_2$. Reactions conditions: $T_R = 843$ K, $W = 1.0$ g. (A) $F = 30$ ml min^{-1}, CH_4 (40%), O_2 (21%), He (40-H_2O%); (B) $F = 60$ ml min^{-1}, CH_4 (51%), N_2O (26%), He(23-H_2O%). (△) CO, (○) CO_2, (□) CH_2O, (●) CH_4 conversion.

TABLE 2

Conversion and Selectivity of Different Reactants CO, CH_2O, CH_3OH, Involved in the Partial Oxidation of Methane

Catalyst	SiO_2 20.0 HPMo		SiO_2 20.0 HPMo		SiO_2 20.0 HPMo	
Flow	CO (50%)		CO (50%) N_2O (50%)		CO (50%) O_2 (50%)	
CO conversion	0.75	8	16	16	34	34
Selectivity CO_2	100	100	100	100	100	100
Flow	CH_2O (10%)		CH_2O (10%) N_2O (17%)		CH_2O (10%) O_2 (17%)	
CH_2O conversion	52	87	48	68	55	83
Selectivity CO	83	51	86	82	67	18
CH_4	5	13.5	2	0.5	n.d.	n.d.
CO_2	9	34	12	16.5	33	82
CH_3OH	3	0.5	1	0.5	0.5	n.d.
H_2	lt	lt	lt	t	n.d.	n.d.
Other	t	1	t	0.2	n.d.	n.d.
Flow	CH_3OH (10%)		CH_3OH (10%) N_2O (28%)		CH_3OH (10%) O_2 (28%)	
CH_3OH conversion	49	94	65	80	96	100
Selectivity CO	30	22	50	47	46	61
CH_4	32	58	18	24	1.5	n.d.
CO_2	2	7	11	11	39.5	30
CH_2O	16	7	16	17	9	9.3
H_2	lt	lt	lt	t	n.d.	n.d.
Other	t	6	5	1	n.d.	n.d.

Note. Reaction conditions: $T_R = 843$ K, $W = 0.35$ g, $F = 60$ ml min^{-1}. Complementary gas: helium. t, trace; lt, large trace; n.d., not detected.

[a] C deposits are not accounted for in the selectivity.

[b] C_2, C_3, C_4 hydrocarbons and dimethylether.

N_2O whereas the latter is more efficient in oxidizing CH_4 than O_2. It is apparent that the failure to observe partial oxidation products in the $CH_4 + O_2$ reaction may be the result of their complete oxidation in subsequent steps rather than their actual absence from the initial product composition.

DISCUSSION

The present work has illustrated the activity and selectivity of 12-molybdophosphoric acid supported on SiO_2 and its dependence on pretreatment environment, contact time, reaction temperature, reactant concentrations, deactivation of the catalyst, reactivity of the products, and the presence of water. Results presented here show, however, that not all heteropolyoxometalates with anions possessing the Keggin structure are equally effective as catalysts in this process, but their catalytic capabilities depend on the nature of the central and peripheral metal elements. For example, substitution of tungsten for molybdenum as the peripheral metal element produces a reduction in both the activity and selectivity. A less severe reduction is also observed where silicon is the central atom in the anion of the heteropolyoxometalate. Such observations appear to be consistent with the results of earlier calculations from this laboratory (*21*, *23*) which showed that the strength of the bond between the peripheral metal atoms and the outer or terminal oxygen atoms of the heteropolyanion was much higher in the case of tungsten than in that of molybdenum, while the magnitude of the charge on the outer oxygen atoms in the latter case was considerably higher than that in the former, implying a reduced proton mobility when molybdenum serves as the peripheral metal element. Apparently the terminal oxygen atoms in the molybdenum-containing anions are sufficiently labile to permit their participation in the oxidation process while those in the tungsten-containing species are relatively more tightly bound and hence cannot easily participate in such a reaction. In contrast the V/SiO_2 catalyst evidently has such highly active oxygen atoms that a high conversion but low selectivity to partial oxidation products results.

The effects of pretreatment provide valuable insight into the source of the catalytic properties of the heteropolyoxometalates in the oxidation reaction. Pretreatment of $HPMo/SiO_2$ in a reducing atmosphere has been found to increase the activity of the catalyst but little or no influence on the selectivity is observed. Interestingly, the increase in conversion, rather than being temporary, appears to remain relatively unchanged for long periods of time. Although the effect of pretreatment in a reducing atmosphere may speculatively be attributed to the reduction of the oxidation state of a critical element of the heteropolyanion, for example, molybdenum, it appears difficult to rationalize such a process with the duration of the effect. Previous temperature-programmed desorption (TPD) studies in this laboratory (*19–21*) have shown that, at sufficiently high temperatures, protons contained within the unsupported heteropolyacid will extract oxygen atoms from the heteropolyanion and be desorbed as water. With HPW this process occurs at approximately 773 K while with HPMo the maximum of the corresponding desorption peak is observed at approximately 673 K. This difference was attributed to the greater lability of oxygen in HPMo as contrasted with HPW. Parenthetically it should be noted that photoacoustic FTIR studies of these two acids showed that the heteropolyanion remained intact at these temperatures in spite of the loss of up to two oxygen atoms per anion (*30*). Temperature-programmed reduction experiments (*20*) with hydrogen produced peaks of similar overall shape and positions to those found in the analogous TPD experiments (*19*), the latter having employed helium as a carrier gas. However, whereas in the TPD experiments 1.5 water molecules per KU were desorbed with HPMo, 8.0 water molecules were measured with the high-temperature TPR peak. Evidently the added hydrogen in the TPR experiments is capable of augmenting the protons in stripping oxygen atoms from the heteropolyanion. Temperature-programmed exchange experiments with deuterium were also performed with the heteropolyacids (*20*). The temperature at which exchange began to be detected for the tungsten acids was approximately 623 K, which corresponds to the temperature at which the high-temperature peak began to appear in TPR experiments. However, no exchange was observed with HPMo but consumption of deuterium and reduction of the acid were observed. Thus in the present work it appears that pretreatment in a reducing atmosphere may remove a number of terminal oxygen atoms from each heteropolyanion, thereby establishing sites for the reversible replacement and consumption of oxygen.

The detrimental effect of high contact times on the generation of partial oxidation products appears to be primarily the result of further oxidation of these products although hydrogenation is evidently also occurring to a lesser extent. The observation that for short contact times both the selectivity to partial oxidation products and the conversion increase appears to be consistent with the hypothesis that such species are precursors to the products of more complete oxidation.

The oxidant in the present work appears to be of particular importance. Although oxidation occurs in the presence of oxygen, a small conversion and no partial oxidation products are observed. In contrast a mixture of methane and nitrous oxide produces formaldehyde, the amounts of which decrease with increasing temperature and with decreasing residence time. Since CH_4 and N_2O or O_2 undergo no reaction in the absence of the catalyst, the N_2O or O_2 are evidently playing the role of a source of regenerative oxygen for the catalyst. However, the difference between both oxidants may be that different oxygen species or different amounts of the same active oxygen species are created by the reaction of N_2O or O_2 with the HPMo. Significantly, after pretreatment by O_2, the increase in conversion in the $CH_4 + N_2O$ reaction may be the result of a slow replacement of the active oxygen species generated by O_2 by that generated by N_2O. The relative quantities of CH_4 and N_2O are also important. It appears that while nitrous oxide is required for the regeneration of the active oxygen atoms of the catalyst and for continuation of the oxidation cycle, an excess of this oxidant increases the conversion while decreasing the selectivity. The source of labile oxygen atoms may then be dependent on the ability of N_2O to replace these species as they are consumed. A concentration of such species greater than that expected at steady state may encourage complete, rather than partial, oxidation.

Although evidence presented here shows that the heteropolycompound, HPMo, is participating catalytically in the oxidation process, it is evident that the SiO_2 support is playing a more active role than simply that of a high-area inert solid. In particular, the support has a detrimental effect on the selectivity to partial oxidation products as carbon monoxide reacts only barely while formaldehyde and methanol are easily converted into CO and CO_2.

Kinetic orders with respect to CH_4 and N_2O have been calculated at two reaction temperatures (793 and 843 K) from log–log plots of the production turnover rates versus the fraction of CH_4 or N_2O in the feed stream. No major effect of the reaction temperature on the kinetic order was found. Therefore for the reaction temperature range 773–863 K, at atmospheric pressure and for a wide range of N_2O/CH_4 molar ratios the rate equation may be described by

$$\frac{-d[CH_4]}{dt} = k[CH_4]^{1/2}[N_2O]^{1/2}.$$

The activation energy for H_2CO formation on HPMo/SiO_2, 20 ± 2 kcal/mole, is similar to that observed by Somorjai *et al.* (*18*) for CH_4 and N_2O on the V_2O_5/SiO_2 catalyst, but considerably less than the values of 40 ± 2 and 82 ± 4 kcal/mole found with the molybdena/SiO_2 catalyst at temperatures above and below 540°C, respectively (*17*). The kinetic orders found for H_2CO in the present work were 0.3 and 1.0, from log–log plots of N_2O and CH_4, respectively. Somorjai and co-workers obtained values of 0.2 and 0.3, respectively, with the molybdena/SiO_2 catalyst and 0.33 and 0.5 for the V_2O_5/SiO_2 catalyst. Although the evidence is not conclusive, nevertheless, it appears that the mechanisms of the two molybdenum-based catalysts may be similar. However, further work is obviously necessary to provide information not only on the mechanism of the process on the HPMo/SiO_2 catalyst but also to supply information on the nature of the participation of the catalyst in the oxidation process.

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