

The Oxidation of Methane on Silica-Supported Heteropoly Oxometalates

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Abstract

The conversion of methane with nitrous oxide is shown to be catalyzed by silica-supported heteropoly oxometalates of Keggin structure, in particular 12-molybdophosphoric acid (HPMo). The activity of the HPMo catalysts is related to the presence of a thermally sensitive species whose degradation products are considerably less active in the oxidation of methane. The thermally sensitive species are identified as the heteropoly anions which are stabilized on the silica support.

Introduction

In many countries, supplies of natural gas are more plentiful than those of crude oil, often necessitating the importation of crude oil while, at least in some cases, natural gas is exported. While the heat released per carbon atom in oxidation is higher with methane than with any other hydrocarbon, methane suffers from the disadvantage of its gaseous state under ambient conditions. Further, although decreases in free energy are observed for the successive elimination of hydrogen atoms, the complete oxidation of methane is thermodynamically more spontaneous than any processes associated with the partial elimination of hydrogen. Consequently, while natural gas, whose predominant component is methane, has found considerable use as a fuel in stationary applications, it has seen relatively little use in motorized vehicles, nor as a feedstock in the production of chemicals.

Interest in the conversion of methane to more amenable substances has resulted in research efforts on the partial oxidation and oligomerization of the gas. A number of excellent recent reviews are available (1-4). The studies of partial oxidation by Lunsford and co-workers on Mo/SiO₂ (5) and Somorjai and co-workers on Mo/SiO₂ and V/SiO₂ (6) and that on oxidative coupling with transition metal oxides by Sofranko and coworkers (7-8) are particularly noteworthy. In this laboratory studies of the surface, structural and catalytic properties of heteropoly oxometalates have been in progress for a number of years. Heteropoly oxometalates are ionic solids with discrete anions of cage-like structure. The anions of Keggin structure have a central atom such as, for example, phosphorus or silicon, surrounded by four oxygen atoms arranged tetrahedrally. Twelve octahedra with, for example, tungsten or molybdenum at their centres envelope the central tetrahedron and share oxygen atoms with each other and with the former (Fig. 1).

Semiempirical extended Huckel calculations have predicted that the solid heteropoly acid containing tungsten as peripheral metal element has more acidic protons than that with molybdenum (9). In addition, the oxygen atoms in the latter anions should be more labile than those in the former anions. Indeed, methanol is converted to hydrocarbons on tungsten-containing heteropoly oxometalates but to CO and CO₂ on those containing molybdenum (10). Photoacoustic FTIR studies have shown that polar molecules such as ammonia (11), pyridine (12) and methanol (13) are able to enter the bulk structure of the heteropoly oxometalates but nonpolar species apparently cannot do so. The acidic proton has been shown to protonate the methanol molecule and at elevated temperatures the C-O bond undergoes a scission and the heteropoly anions are methylated apparently at the terminal oxygen atoms (14).

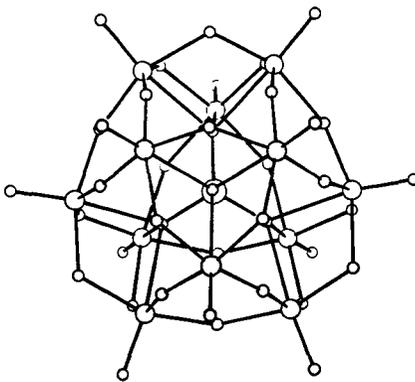


Fig.1 Heteropoly Oxometalate Anion of Keggin Structure

In the present work the oxidative conversion of methane with nitrous oxide is studied on various heteropoly oxometalates, but primarily 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$, abbreviated to HPMo).

Experimental

Since methane cannot enter the bulk structure of the heteropoly oxometalates and the parent heteropoly acids have low surface areas, it is necessary to support the acids on a high area solid, in the present case silica (Davison Grade 407). An incipient wetness technique is employed to load the solid. A fixed-bed continuous flow reactor with on-line gas chromatograph (HP 5890) was employed for the catalytic studies (15-17).

Results

Table 1 provides a comparison of the results for various supported heteropoly oxometalates as well as supported molybdenum and vanadium catalysts. It is evident that the molybdenum-containing heteropoly oxometalates produce higher conversions and better selectivities to partial oxidation products than those containing tungsten. For comparison samples of molybdenum and of vanadium on silica have been prepared by the method of Liu (5) and the results are included in Table 1.

Table 1
Conversion and Selectivity^a

Catalyst ^b	Conversion			Selectivity		
	CH ₄	N ₂ O	CO	CO ₂	CH ₂ O	CH ₃ OH
HPMo (20.0)	5.1	36.4	65.0	22.5	12.0	0.5
HPW (26.2)	0.4	3.2	56.0	44.0	τ	nd
HSiMo (19.9)	2.5	17.0	58.6	32.3	8.7	0.4
HSiW (26.2)	0.4	2.8	44.0	56.0	τ	nd
V (1.66)	8.9	59.1	81.8	14.5	3.5	0.2
Mo (3)	0.4	3.3	57.0	31.0	12.0	τ

a Reaction Conditions: $T_R = 843$ K, $W = 0.35$ g, $F = 30$ ml min^{-1} CH₄ (67%), N₂O (33%)

b Figures in brackets refer to loading of the silica support in wt%.

The remaining of the results reported here pertain to silica-supported HPMo. As expected the selectivity to partial oxidation products increases with decreasing contact time until a maximum is reached. A maximum is also observed for the selectivity to CO while the CO₂ selectivity shows a minimum. The production of CO₂ is found to increase with reaction temperature while that of CO and formaldehyde decreases. The selectivity to partial oxidation products and the conversion have been shown to be inversely related.

It is of interest to consider the evidence for the participation of the heteropoly oxometalate in the conversion process. The conversion and selectivity in the oxidation of methane with nitrous oxide on silica-supported HPMo remain relatively unchanged for pretreatment temperatures up to approximately 773 K (Figures 2A and 2B). However at higher temperatures the conversion decreases markedly while the production of CO and CO₂ remains constant up to approximately 900 K. For temperatures higher than 900 K the production of H₂CO and CO decreases while that of CO₂ increases with all three apparently approaching that found with the support above.

Experiments in which the pretreatment temperature was held at that for which thermal degradation is occurring (823 K) and the duration of pretreatment varied (Fig. 2C and 2D) show a relatively gradual decrease in the conversion of methane and a small loss of HPMo while CO increases slightly in quantity and the production of CO₂ and H₂O decreases slowly. It is evident that the activity of the HPMo catalysts is related to the presence of a thermally sensitive species whose degradation products are considerably less active in the oxidation of methane.

The rates of reaction are found to be strongly dependent on the loading of HPMo on silica (Fig. 3). The rates increase approximately linearly (except for that of methanol) and reach maxima at a loading of approximately 120 μ mol of heteropoly anions per gram of support. This corresponds to a coverage of approximately 1000 \AA^2 /anion, to be compared with an estimate of 100 \AA^2 for the cross-sectional area of the heteropoly anion. It seems reasonable to assume, at least tentatively, that each anion is isolated on the silica support surface.

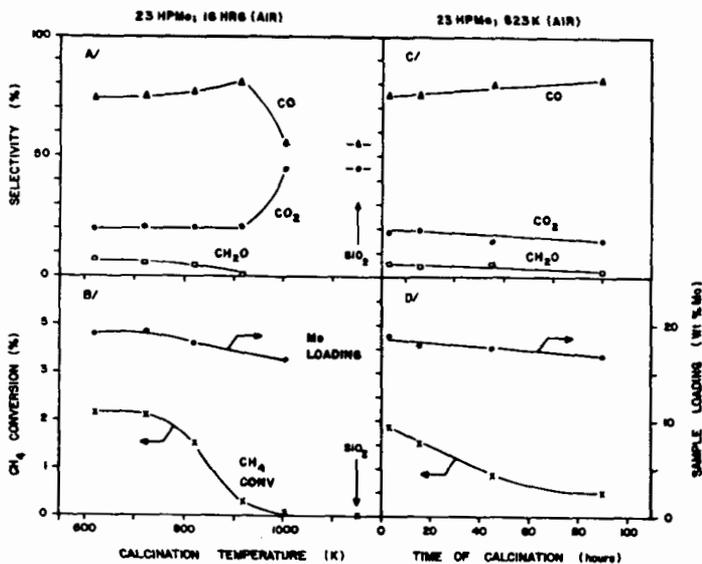


Fig.2 Effect of the temperature of pretreatment during 16 h (left) and of the time of calcination at 823 K under air (right) on the CH₄ conversion, selectivity, and Mo loading of the 23-HPMo catalyst. Reaction conditions: CH₄ (67%), N₂O (33%), T_R = 843 K, W = 0.5 g, F = 30 ml min⁻¹. Symbols: (Δ) CO, (○) CO₂, (□) CH₂O, (X) CH₄ conversion, (●) Mo loading.

Infrared spectra show that the supported HPMo retains the heteropoly anion structure up to temperatures as high as 973 K, suggesting that the silica is, in addition to providing a high area support for the HPMo, also acting to provide a thermal stabilization for the HPMo.

Acknowledgements

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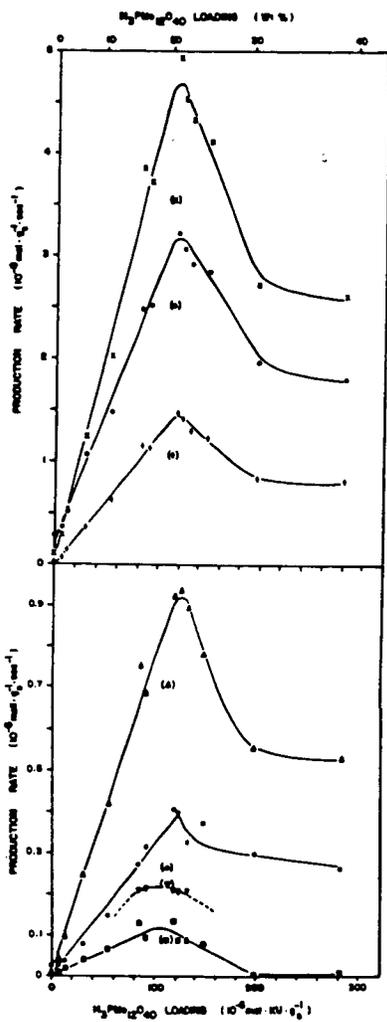


Fig. 3 Effect of the HPMo loading of the support on the production rate of the different products of the $\text{CH}_4 + \text{N}_2\text{O}$ reaction at 843 K. Reaction conditions: CH_4 (67%), N_2O (33%), W - 0.5 g, F = 30 ml min⁻¹. Symbols: (X) N_2 , (+) total carbon detected, (●) H_2O , (V) CH_3OH , (Δ) CO, (○) CO_2 , (□) CH_2O .

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