

NOTES

The Oxidation of Methane on Heteropolyoxometalates
II. Nature and Stability of the Supported Species

The results of studies of the partial oxidation of methane with a number of silica-supported heteropoly oxometalates have been reported (1). Within the range of experimental conditions used, it has been found that molybdenum-containing heteropoly acids are active and selective catalysts for the partial oxidation of methane, with activities greater than those of the molybdena/silica catalysts but less than those of vanadium pentoxide/silica. Selectivities are rather similar in all cases. In contrast, tungsten-based heteropoly acids showed little or no activity in the partial oxidation of methane. As a consequence of the importance in the partial oxidation of methane of supporting of the 12-molybdophosphoric acid (HPMo), the earlier work has been extended to examine various aspects of these supported catalysts, particularly the nature and stability of the supported species.

The supported catalysts (wt% HPMo) were prepared by impregnation of a silica gel (Grace Davison grade 400, $740 \pm 20 \text{ m}^2 \text{ g}^{-1}$) with an excess of solution of recrystallized HPMo (BDH Analar grade). The slurry was then evaporated to dryness at 353 K overnight and calcined in air at 623 K for 1 h.

For the determination of the weight percentage of the supported HPMo, the molybdenum was extracted from the supported catalysts by elution with concentrated ammonium hydroxide solution. After evaporation and addition of aqueous nitric acid solution to achieve a standard volume, the samples were analyzed for molybdenum with an appropriately calibrated Direct Coupled Plasma Spectroscan (Beckman

Model 5). The molybdenum loadings of the samples measured before and after use are reported in Table 1.

Catalytic experiments were performed as previously described (1).

To remove the soluble HPMo from the support for infrared analysis, approximately 0.3 g of the supported catalyst was washed with 10 ml of acetonitrile (Baker Analyzed). After filtration, the IR spectra (Perkin-Elmer Model 983) of the solution were recorded. No evidence of significant decomposition of the heteropoly acids nor of generation of these compounds from molybdate and phosphate was found in acetonitrile solutions after 24 h.

The effects of the temperature and duration of calcination on the activity, selectivity, and remaining molybdenum loading of the 23-HPMo catalyst in the $\text{CH}_4\text{-N}_2\text{O}$ reaction are shown in Fig. 1. The conversion and selectivity in the oxidation of methane with nitrous oxide on silica-supported HPMo remains relatively constant for calcination temperatures up to 773 K (Figs. 1A and 1B). For higher temperatures the conversion decreases sharply while the production of CO and CO_2 remains constant up to approximately 900 K. Above 900 K the production of H_2CO and CO decreases, while that of CO_2 increases, all three apparently approaching that found with the support alone. Above 700 K there is a concomitant small, but significant, decrease in the amount of supported molybdenum, whereas the conversion becomes negligibly small.

At a calcination temperature of 823 K (at which temperature thermal degradation is evidently occurring (Figs. 1A and 1B)), the

TABLE I
Loading of the Different Samples before and after Catalytic Test

Amount deposited wt% HPMo	Loading found before test			After test at 843K ^a wt% HPMo
	wt% HPMo	10 ⁻⁶ mol KU g ⁻¹ support	KU nm ⁻²	
1.45	1.16	5.16	0.0042	1.22
2.85	1.72	7.74	0.0063	1.51
4.22	3.08	14.0	0.0115	2.52
5.54	2.94	13.4	0.011	2.89
8.09	6.49	30.7	0.025	4.44
9.89	8.32	40.2	0.033	—
12.8	11.10	55.3	0.045	9.92
16.2	9.80	48.1	0.039	9.06
18.2	17.21	92.1	0.075	14.4
20.0	16.0	84.3	0.068	—
22.7	21.2	119	0.097	15.2
26.1	25.3	150	0.122	18.6
29.4 ^b	20.1	111	0.090	15.9
29.4 ^c	21.7	123	0.100	—
29.4 ^d	23.0	132	0.108	—
37.1	30.9	198	0.161	25.3
46.4	39.0	283	0.130	—

^a Same experimental conditions as Fig. 2.

^{b,c,d} Different preparations.

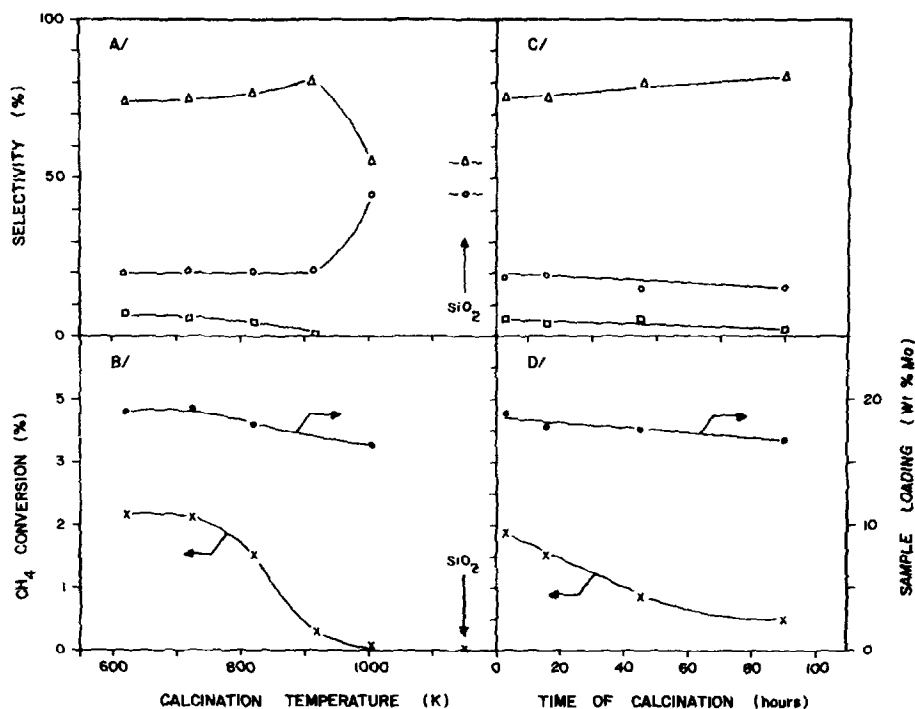


FIG. 1. Effect of the temperature of calcination during 16 h (left) and of the time of calcination at 823 K under air (right) on the CH₄ conversion, selectivity, and Mo loading of the 23-HPMo catalyst. Reaction conditions: CH₄ (67%), N₂O (33%), T_R = 843 K, W = 0.5 g, F = 30 ml min⁻¹. Symbols: (Δ) CO,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

conversion of methane decreases relatively slowly with the duration of calcination while a small loss of HPMo can be observed (Fig. 1D). Concurrently, the production of CO increases slightly while that of CO₂ and of H₂CO decreases slowly. Evidently the activity of the HPMo catalysts can be attributed to a thermally sensitive species whose degradation products have a considerably reduced activity in the oxidation of methane.

The rates of formation of the various products from the reaction of CH₄ and N₂O at 843 K are shown for various loadings of HPMo on silica (Fig. 2). With the exception of that of methanol, these rates increase approximately linearly with the amount of HPMo contained on the support and, at low loading values, extrapolate to those results found for the support itself. The rates of formation for the various products reach maxima at a loading of approximately 120 μmol of KU per gram of support. The positions of the maxima for methanol and formaldehyde are less clearly defined, but will be taken as that given above. With further increase in the loading the rates of formation decrease markedly to approximately constant values at loadings as high as 200 μmol KU per gram of support. It is of particular interest to note that while the rate of production of formaldehyde has become negligible at such relatively high loadings, the rate of formation of CO₂ has decreased relatively little as compared with that of CO, for example.

Similar features have been observed for a reaction performed at 793 K (reaction parameters: $W = 0.5$ g, $F = 15$ ml min⁻¹, CH₄ 67%, N₂O 33%) with, however, a maximum for formaldehyde occurring at a lower loading of approximately 50 μmol KU per gram of support, whereas all other products displayed a maximum at a loading of 120 μmol KU per gram of support, similar to that observed at the higher temperature.

As expected, the product distributions vary with the loading on the silica support (Fig. 3). At 843 K, for example, the per-

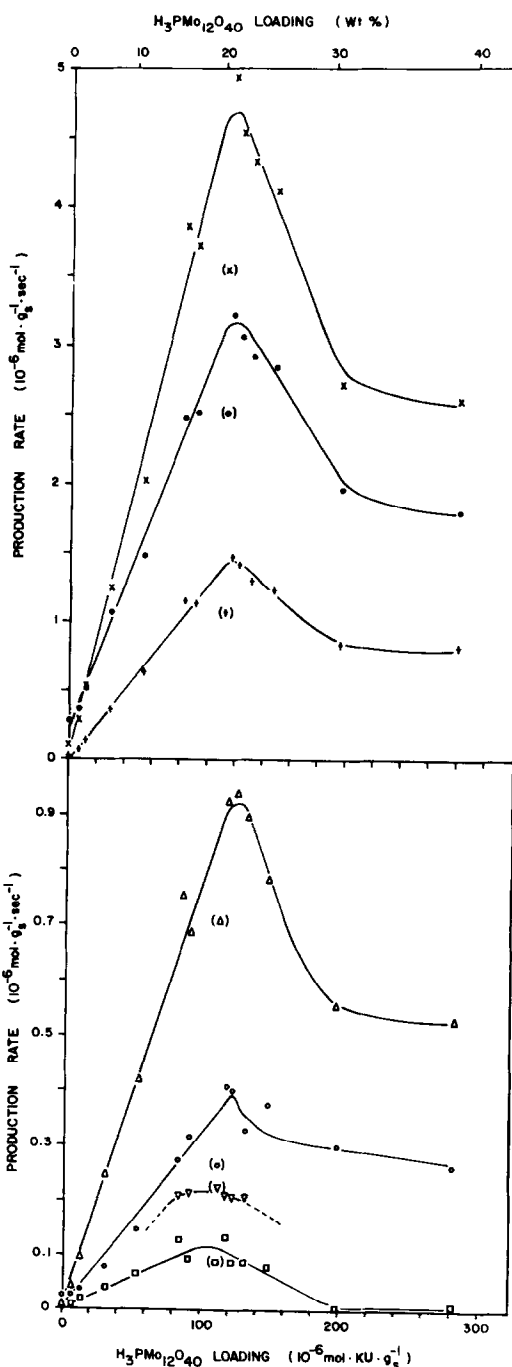


FIG. 2. Effect of the HPMo loading of the support on the production rate of the different products of the CH₄ + N₂O reaction at 843 K. Reaction conditions: CH₄ (67%), N₂O (33%), $W = 0.5$ g, $F = 30$ ml min⁻¹. Symbols: (x) N₂, (+) total carbon detected, (●) H₂O, (∇) CH₃OH, (Δ) CO, (○) CO₂, (□) CH₂O.

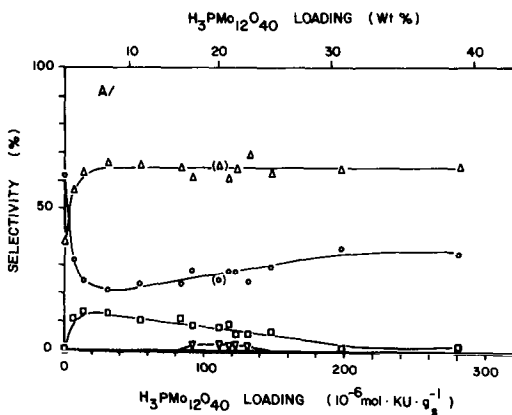


FIG. 3. Effect of the HPMo loading of the support on the selectivity of the $\text{CH}_4 + \text{N}_2\text{O}$ reaction at 843 K. Same experimental conditions as Fig. 2. Symbols: (Δ) CO, (\circ) CO_2 , (\square) CH_2O , (∇) CH_3OH .

centage of CO in the product from the $\text{N}_2\text{O} + \text{CH}_4$ reaction increases sharply with the loading and reaches a constant value at relatively small loadings of HPMo. In contrast, the CO_2 contained in the product decreases, passes through a minimum, and attains a constant level for loadings of approximately $200 \mu\text{mol KU}$ per gram of support. The quantities of formaldehyde appear to be reciprocally related to that of CO_2 in their dependences on the amount of supported HPMo, with the quantity of formaldehyde increasing to a maximum at a loading of $20 \mu\text{mol KU}$ per gram of support and with further increase in loading decreasing to a negligible level at that quantity of HPMo at which CO_2 achieves a constant value.

At least for one set of conditions it is evident that the loading of the support has a substantial effect on both the activity and selectivity. However, while under the present conditions the maximum in activity occurs for a relatively large loading of $120 \mu\text{mol KU}$ per gram of support, that for the selectivity to partial oxidation product is reached at a much lower loading of $20 \mu\text{mol KU}$ per gram of support. It is anticipated that reaction temperature and residence time will not alter the position of the maximum for activity but will undoubtedly ef-

fect that for selectivity. As has been shown earlier, better selectivity to partial oxidation products can be expected at higher total flow rates and lower reaction temperatures.

Infrared spectra of acetonitrile solutions obtained by washing the silica-supported HPMo confirm the existence of $\text{PMo}_{12}\text{O}_{40}^{3-}$ anions with the Keggin structure on a variety of samples (Fig. 4). IR spectra of the 12-molybdophosphoric acid in acetonitrile

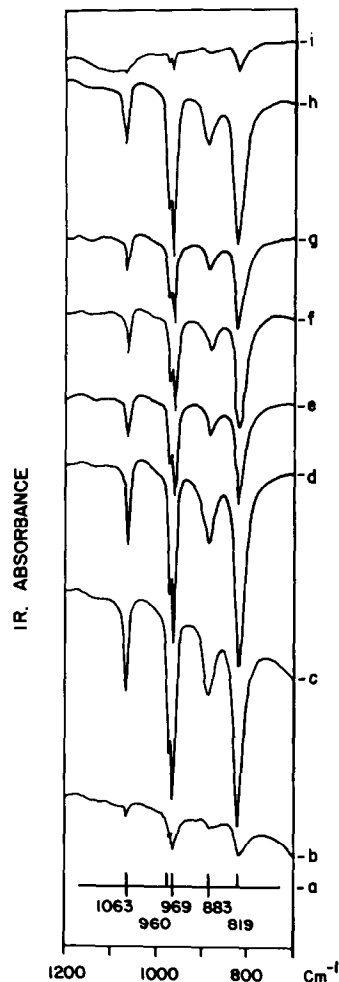


FIG. 4. Infrared spectra of acetonitrile solution after washing of the following supported HPMo samples calcined in different conditions. (a) Bulk $\text{H}_3\text{PMo}_{12}\text{O}_{40}$, (b) 1.16 HPMo, 350°C , 2 h, (c) 11.1 HPMo, 350°C , 2 h, then 20.1 HPMo sample, (d) 350°C , 16 h, (e) 450°C , 16 h, (f) 550°C , 16 h, (g) 640°C , 16 h, (h) 640°C , 16 h, followed by a test at 570°C , 10 h, (i) 730°C , 16 h.

shows the bands at 1080 and the doublet at 969–960 cm^{-1} characteristic of the Keggin structure and attributed to the triply degenerate asymmetric stretch of the central PO_4 tetrahedron and that of the outer Mo–O bond, respectively. As reported in Fig. 4, spectra of species extracted from samples covering a wide range of loadings show these characteristic bands. With the sample of smallest loading, 1.16 HPMo/ SiO_2 , the spectra obtained from the extraction of this catalyst show relatively weak but nevertheless characteristic Keggin structure IR bands. With those samples more heavily loaded (11.1 HPMo) the characteristic bands are considerably more intense, even after heating of the sample to 623 K for 2 h. With a 20.1-HPMo sample heated for 16 h under air some diminution of the intensities occurs as temperatures up to 923 K are reached, but there can be no doubt as to the existence of the Keggin structure even at such a high temperature treatment. After use of the 20.1-HPMo catalyst in an oxidation experiment at 843 K, the Keggin structure is still clearly evident, and even after the sample is heated to 1003 K, some vestiges of the Keggin structure still exist.

The beneficial effects of the participation of the heteropolyoxometalate $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ in the oxidation of methane can be clearly seen from the results presented in this work. The infrared spectra provide evidence that the deposited species at various loadings of the support are the 12-molybdophosphate anions with Keggin structure. Furthermore these results clearly demonstrate that portions of the original amounts of these species still exist after vigorous treatment such as calcination at 913 K for 16 h or exposure to methane and nitrous oxide under oxidation conditions.

That the Keggin unit is primarily responsible for the catalytic activity in the partial oxidation of methane is evident from the studies of the effects of loading, calcination temperature, and duration. The linear increase in the rate of formation of various products with increase in loading clearly

indicates that the active species are associated directly with the supported materials. In addition this active species is thermally sensitive since, at temperatures of approximately 923 K, the activity and selectivity of the supported catalyst abruptly change to those expected from the support itself. Clearly the oxides formed at high calcination temperatures are either inactive or poorly active for methane oxidation. It is therefore apparent that the active species are those anions possessing the Keggin structure.

The production rate increases linearly to a maximum at 120 μmol KU per gram of support. This optimum loading of HPMo on SiO_2 corresponds to a coverage of approximately 1000 $\text{\AA}^2/\text{KU}$, a substantially larger area than the 100 \AA^2 estimated for the cross-sectional area of a Keggin unit. Therefore each KU is likely to be isolated on the support surface. Although such an optimum loading may be referred to as a monolayer coverage, it may be advantageous to view such a loading in terms of the saturation of a number of fixation centers as has been proposed elsewhere for unrelated supported catalysts (2). This number is characteristic of the support, the species adsorbed, the pretreatment, and the conditions of preparation of the supported system. For the silica support used in the present work, the maximum number of fixation sites of the KU is therefore the saturation limit, that is, 120 μmol sites g^{-1} or approximately 0.1 sites nm^{-2} . In comparison, 0.3 sites nm^{-2} have been estimated for Al_2O_3 (2).

While emphasis here has been placed on the quantity of heteropoly species contained on the support surface, it should be noted that the method of preparation of the supported samples is not unimportant. For example, it may be observed (Fig. 2) that one particular sample, near the optimum value, produced results considerably lower than expected. It appears that the method of preparation may occasionally lead to poorly dispersed samples. However, the

linear dependence of production rate appears to confirm that the optimum dispersion has been, in general, achieved at least for loadings less than 120 μmol KU per gram of support.

For loadings greater than 200 μmol KU per gram of support (600 $\text{\AA}^2/\text{KU}$), the production rates of N_2 , total carbon, H_2O , CO , and CO_2 have decreased to apparently constant values considerably less than those found at the individual maxima, but greater than those for the support itself. At this same loading, the rate of production of formaldehyde has decreased to a negligible level, as was found after calcination at 900 K (Fig. 1). Evidently this corresponds to the attainment of a stationary surface concentration which is apparently less than optimum for the oxidation process. However, it is not clear at this time whether the disadvantage of heavier loadings of HPMo on SiO_2 is a consequence of the inability of the support to stabilize quantities of the heteropoly compound greater than that at saturation, or is due to the effect of the formation of particles of HPMo which may exert a blocking effect on those in direct contact with the support. It is important to note here that while polar molecules can readily penetrate into the bulk structure of heteropoly compounds, nonpolar species such as alkanes are unable to do so. Consequently the formation of particles of HPMo on the surface of the support will render any KU contained within the bulk of the particle inaccessible to methane and hence inactive in the oxidation of methane. However, the observed changes in selectivity at high loading may, at least in part, arise from secondary processes resulting from the penetration and reaction of the polar products, H_2CO and CH_3OH , within the bulk of HPMo particles to produce CO and/or CO_2 .

As has been noted, the infrared spectra

provide evidence that the supported species retain the Keggin structure. Clearly the supported species not only have this structure but retain it even after being heated to temperatures as high as 973 K and after reactions at 843 K. A very large stabilizing effect is therefore occurring as bulk HPMo is known to be decomposed at 350–340°C (4). The SiO_2 support is clearly acting, not only as a means of increasing the available surface area of the heteropoly compound, but also as a stabilizer for the Keggin structure of the anion.

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