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The Oxidation of Methane on Heteropolyoxometalates

IV. Properties of the Silica-Supported Salts of 12-Molybdophosphoric Acid

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Salts of 12-molybdophosphoric acid supported on silica were prepared by exchange of the supported parent acid with cesium, lithium, barium, magnesium, bismuth, aluminum, iron, silver, cobalt, chromium, copper, cadmium, mercury, nickel, lead, or vanadyl cations. Each of the supported salts was compared with supported free 12-molybdophosphoric acid and with the silica-supported cation as catalysts in the oxidation of methane by N_2O. Three effects on the properties of the supported 12-molybdophosphoric acid catalyst due to the addition of cations have been discerned. One is attributable to the removal of protons by substitution, leading to the blocking of the oxygen extraction step which generates vacancies in the Keggin structure. This blocking effect does not depend on the nature or charge of the cation. The second effect appears to have an electronic basis and is strongly dependent on the nature of the cation. The relationship of this electronic effect to the electronegativity is discussed. A third effect of the added cation is the generation of new sites related to the intrinsic activity of the cations themselves. © 1989 Academic Press, Inc.

INTRODUCTION

Silica-supported 12-molybdophosphoric acid has recently been shown to be an active catalyst for the partial oxidation of methane by N_2O (*1*, *2*). In addition, subsequent work has suggested that the Keggin unit (KU) structure of this heteropolyoxometalate is stable and responsible for the activity and selectivity in the reaction temperature range 793 to 843 K, demonstrating a remarkable stabilization effect due to the silica support (*3*, *4*).

The protons of 12-molybdophosphoric acid ($H_3PMo_{12}O_{40}$), the latter hereafter abbreviated to HPMo, can be easily, at least partly, exchanged by a large variety of inorganic or organic cations (*5*–*8*). This property allows the preparation of salts of the HPMo containing different amounts of cations and the study of the effect of these additives on the catalytic properties of these compounds. Such comparative studies of bulk heteropolymolybdate and tungstate salts for acid-catalyzed or oxidation reactions have been reported by Misono *et al.* (*9*) and Ai (*10*, *11*), for example. It was therefore of interest to use the exchange properties of this heteropolyoxometalate in order to investigate the properties of various supported salts of the HPMo in the partial oxidation of methane.

Indeed, a preliminary study of the effect of cesium on the HPMo catalyst produced interesting structural and catalytic information (*12*). In particular, it has been found that cesium has two effects. First it poisoned the oxidation reaction completely for loadings higher than 3.5 Cs per Keggin unit apparently as a result of the total substitution of the protons ($3H^+$/Ku). This poisoning was suggested to be due to a blocking of the dehydration reaction which generates

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vacancies suitable for the adsorption of N_2O and/or CH_4. Second, a strong electronic effect has been demonstrated to exist on partially saturated Keggin units. Such an effect resulted in a net increase in the turnover number of the nonblocked sites. Both phenomena were also found on the supported Mo, V, and Fe catalyst, an observation which emphasizes the similarity between these systems.

Although the intent of this study was centered on the improvement of both the activity and the selectivity of the supported heteropolyoxometalates for methane oxidation, the possibility of fine tuning the HPMo catalyst by doping techniques added an additional incentive for the investigation of the role of such additives. In particular it was predicted that the nature of the cation should not influence the blocking effect but should influence the electronic effect. The results reported in this work clearly support that prediction and the previous conclusions reached for the cesium salts.

EXPERIMENTAL

The reaction system and conditions as well as the activation energy measurements have already been reported in detail (*1–3*). The set of reaction conditions used in the present work were as follows: reaction temperature $T_R = 843$ K; catalyst weight $W = 0.5$ g; flow rate $F = 30$ ml min^{-1}; flow composition, CH_4 (67% mol), N_2O (33% mol); pretreatment, 1 hr in helium at the reaction temperature.

The supported salts of 12-molybdophosphoric acid were prepared similarly to the cesium salt (*12*). The impregnation of either a 16 wt% HPMo or 23.9 wt% HPMo on silica catalysts employed solutions of the following salts: cesium carbonate (Alpha products), potassium carbonate (J.T. Baker analyzed), sodium carbonate (J.T. Baker analyzed), lithium carbonate (J.T. Baker analyzed), magnesium acetate (BDH), calcium carbonate (BDH analar), strontium acetate (BDH), barium acetate (J.T. Baker analyzed), silver nitrate (Fisher certified), iron sulfate (B & A) or iron oxalate (BDH), bismuth nitrate (J.T. Baker analyzed), copper sulfate (Fisher certified), cadmium nitrate (J.T. Baker analyzed), manganese acetate (Fisher certified), cerium nitrate (Fisher certified), mercuric nitrate (Fisher certified), nickel nitrate (J.T. Baker analyzed), lead nitrate (BDH assured), zinc nitrate (J.T. Baker analyzed), and vanadyl sulfate (Fisher certified). These salts were chosen for their solubility. In some cases the salt solution was acidified by HNO_3 (1 *M*) in order to keep a slightly acid medium and facilitate the solubilization of the salt. No major problems of precipitation were encountered except with the bismuth impregnation.

The preparation of catalysts containing only the cation supported on silica has also been carried out in a similar way. A loading of 0.27 cation/nm^2 of support surface has been systematically chosen in order to correspond to the loading of 4 cations/KU on the 16 wt% $HPMo/SiO_2$ catalyst.

The samples will be symbolized by "*x* cation PMo" with *x* the number of cations per HPMo Keggin unit. For the reaction conditions previously reported, the activity of the HPMo catalysts has been used as a reference with a turnover TON = 0.022 mol. $sec^{-1}KU^{-1}$. All the activity results on HPMo catalysts have been reported relative to that value.

Supported vanadyl salts of 12-tungstophosphoric ($H_3PW_{12}O_{40}$) and 12-tungstosilicic ($H_4SiW_{12}O_{40}$) acids with loadings of 23.4 wt% HPW/SiO_2 and 23.4 wt% $HSiW/SiO_2$ were also prepared for comparison with the HPMo catalyst (*1–3*).

RESULTS

The activity and selectivity of the HPMo catalyst containing increasing amounts of different cations in the reaction of methane with nitrous oxide are reported in Figs. 1–7.

In Fig. 1 the results for the monovalent alkaline element cesium and lithium are reported. The results on cesium, reported

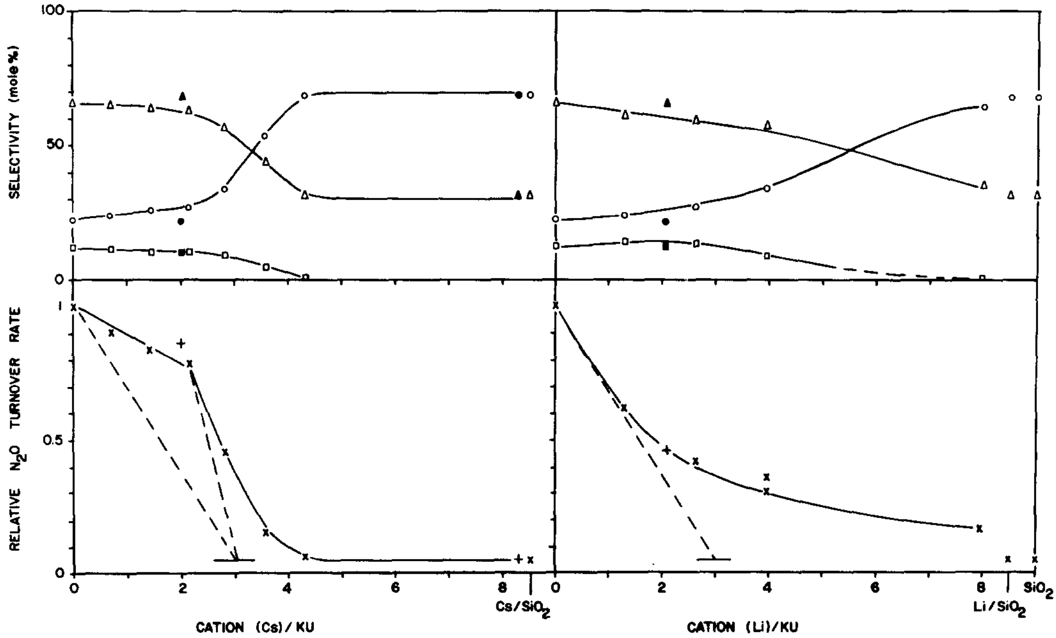

FIG. 1. Relative N_2O turnover rate and selectivity of the $CH_4 + N_2O$ reaction versus the amount of cesium carbonate (left) or lithium carbonate (right) added on the HPMo catalyst. Open symbol and × on 16 wt% HPMo. Solid symbol and + on 23.9 wt% HPMo. TON = 0.022 mol. sec^{-1} KU^{-1}. Reaction conditions $T_R = 843$ K, $W = 0.5$ g, $F = 30$ ml min^{-1}. CH_4 (67 mole%); N_2O (33 mole%). Symbols: (△) CO, (○) CO_2, (□) CH_2O, (▽) CH_3OH.

here for comparison, have already been extensively discussed in a previous part of this series (*12*). In that work it was concluded that on both supported heteropolymolybdate and supported oxides like Mo, V, or Fe on SiO_2, the cesium ions were replacing the exchangeable protons, a phenomenon which resulted in a complete or partial poisoning of the supported HPMo or oxides, respectively. The experimental saturation value of 3.5–4 Cs/KU found with HPMo was somewhat larger than the 3 H^+ possessed by each KU of HPMo, presumably due to a difficulty in saturating all the protons of the KU and/or to the presence of some oxide from HPMo decomposition.

The selectivity variation clearly indicated that saturation of the KU was reached since the selectivities of the 4 CsPMo, 8 CsPMo, Cs/SiO_2 and SiO_2 catalysts were similar. This shows that Cs itself has no catalytic effect for the reaction and therefore the silica selectivity was reached as a result of complete poisoning. This later observation led us to conclude that the proton has an important role in the reaction mechanism of the CH_4 oxidation on the supported 12-molybdophosphoric acid. This role has been proposed as allowing the generation of vacancies by a dehydration reaction such as

$$2\ \mathrm{KUOH} \rightleftharpoons \mathrm{KUO} + \mathrm{KU}\square + \mathrm{H_2O} \quad (1)$$

It is apparent that the absence of protons prevents such a reaction from occurring and consequently reduces the activity where no alternative reaction path is available.

The activity curve shown in Fig. 1 (left) is, however, not a straight line from 0 to 3 Cs/KU as would be expected from a simple blocking effect. This was interpreted as resulting from the existence of an additional effect, believed to be electronic in origin and associated with the cesium, on the ac-

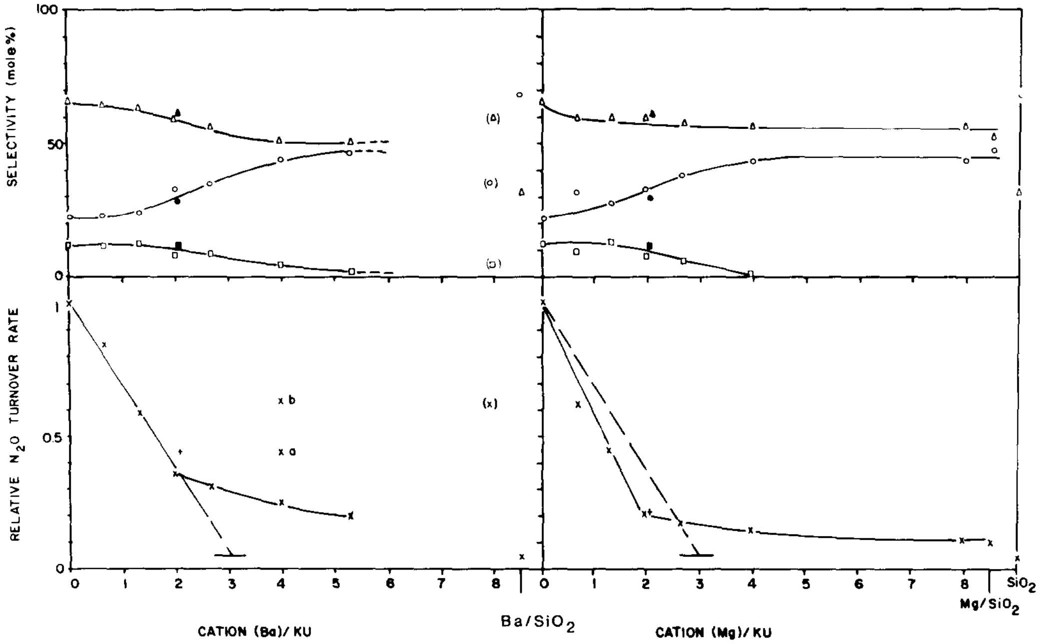

FIG. 2. Relative N_2O turnover rate and selectivity of the $CH_4 + N_2O$ reaction versus the amount of barium acetate (left) or magnesium acetate (right) on the 16 wt% HPMo catalyst. Same reaction conditions and symbols as those for Fig. 1. (a) Sample obtained by two successive impregnations of 1.5 Ba/KU; (b) sample obtained by impregnation of $Ba(OH)_2$.

tivity of the sites which can still be created on partially substituted Keggin units. Since a higher activity than that obtained from a purely blocking effect (Fig. 1, left, dotted line) was observed, this electronic effect is apparently strongly positive, that is promoting.

With lithium, complete saturation could not be attained with either a large amount of this cation or two consecutive impregnations (Fig. 1, right). However, the portion of the curve between 0 and 2 Li/KU is approximately coincident with the line expected for poisoning due to a purely blocking effect (dotted line, Fig. 1, right) thus indicating that the electronic effect of lithium is much weaker than that of cesium. The results found for samples with 2 Na and 2 K/KU showed an effect intermediate to 2 Cs and 2 Li, the relative activity for 2 cations/KU decreasing in the order Cs > K > Na > Li, corresponding to the increase of electronegativity.

In Fig. 2 the results for the alkaline earth elements barium and magnesium have been reported. Barium on silica shows no activity whereas magnesium develops a small activity confirmed by a selectivity very different from that of the support. The curve obtained with the *x* MgPMo samples shows little or no evidence of failure to reach saturation since the activity and selectivity shift to the value of the Mg/SiO_2 sample for 3.5–4 Mg/KU. Interestingly, with magnesium the effect on the activity of an HPMo site which is attributed to an electronic factor is now negative, that is, poisoning. With barium, on the other hand, the activity and selectivity of the Ba/SiO_2 catalyst, equivalent to silica, were not duplicated by addition of large amounts of Ba on the HPMo catalyst, apparently due to saturation difficulties. This problem may be illustrated by the comparison of samples prepared in different ways. A preparation involving two successive impregnations with barium acetate or a preparation with one impregnation of barium hydroxide produced samples apparently further from saturation (a and b in Fig. 2, left). Even the preparation of a sample with a large excess of barium acetate (8 Ba/KU) gave a less complete saturation than the 4 or 5.2 Ba/KU samples. The first portion of the curve can however provide information on the intensity of the electronic effect. Similar to the results found with the alkali metals, those found for samples containing 2 Ca and 2 Sr/KU are intermediate between those for 2 Mg and 2 Ba, leading to a decrease in the relative activity for 2 cations/KU in the order Ba > Sr > Ca > Mg corresponding again to the increase in electronegativity.

The effects of two trivalent cations, aluminum and bismuth, were also studied (Fig. 3). Aluminum on silica has a net activity and a particular selectivity for the CH_4 oxidation by N_2O. Saturation of the Keggin unit appears to be attained by 3.5–4 Al/KU while the selectivity attains the values expected for the Al/SiO_2 sample. Similarly to the observations for Mg/SiO_2 it is apparent that the HPMo catalyst saturated with Al is equivalent to the Al/SiO_2 catalyst. This suggests that for these cations (Mg and Al) the HPMo has no significant effect on their ability to catalyze the reaction whereas both cations have strong negative effects on the activity of the HPMo sites.

In the case of the bismuth salts the scatter of the data presumably results from difficulties either in the exchange of the protons and/or in the preparation of the samples. It was noted during the preparation that precipitation occurs. However, a tentative curve has been drawn which shows that bismuth decreases the activity of the catalyst in the oxidation reaction while the variation in selectivity clearly shows that some exchange has occurred.

The results of the influence of iron and silver on the activity and selectivity of the

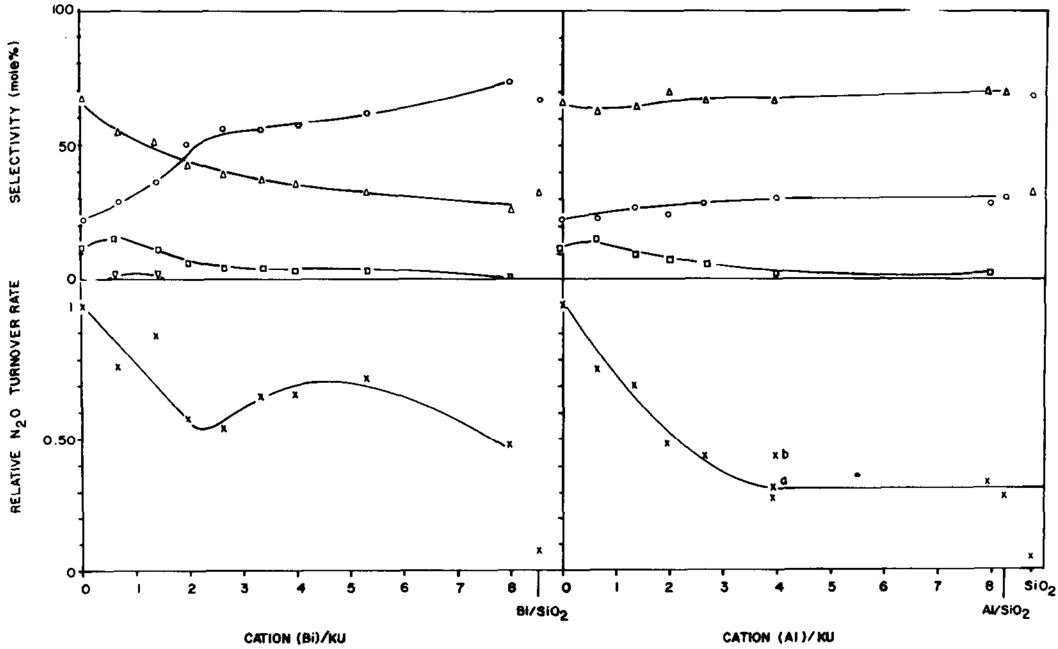

FIG. 3. Relative N_2O turnover rate and selectivity of the $CH_4 + N_2O$ reaction versus the amount of bismuth nitrate (left) or aluminum nitrate (right) on the 16 wt% HPMo catalyst. Same reaction conditions and symbols as those for Fig. 1. (b) Two successive impregnations of 1.5 Al/KU; (a) preparation with aluminum isopropoxide.

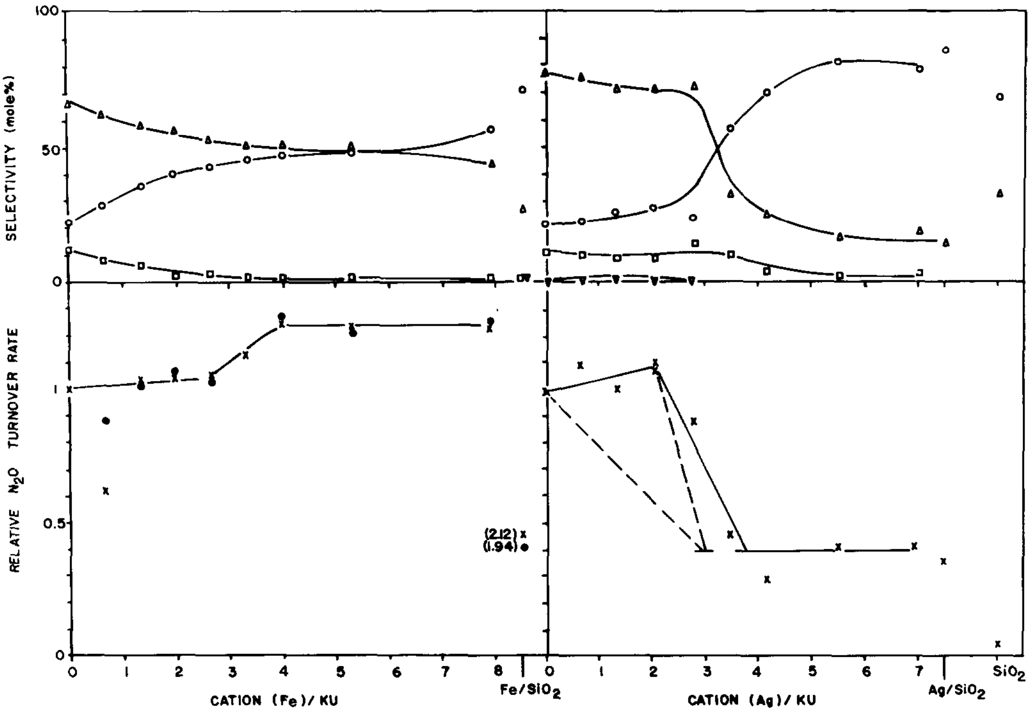

FIG. 4. Relative N_2O turnover rate and selectivity of the CH_4 + N_2O reaction versus the amount of iron oxalate (o) or sulfate (x) (left) or silver nitrate (right) on the 16 wt% catalyst. Same reaction conditions and symbols as those for Fig. 1.

HPMo catalyst are reported in Fig. 4. In both cases we are dealing with a cation giving active species on silica, strongly active in the case of iron and slightly active in the case of silver. Again the same three parts of the curve can be distinguished with an illustration of a negative electronic effect (Fe) and a positive electronic effect (Ag). For this latter cation both the selectivity and the activity reached at high loading are similar to those observed with the Ag/SiO_2 sample. This supports the idea that the exchange of all the H^+ by Ag^+ is readily accomplished. The case of iron is less conclusive. A plateau of the activity is reached but the selectivity of the FePMo catalyst, although tending toward the value of the Fe/SiO_2 catalyst, remains noticeably different whereas the activity level of the plateau is considerably unlike that of the latter catalyst. It is likely that the Keggin unit is not completely saturated although it can be observed that two preparations from two different iron salts (oxalate and sulfate) gave similar results. A more precise look at Fig. 4 (left) shows that at low iron loading a significant perturbation of the system occurred. Whether this is due to the degradation of the KU or a variation of dispersion leading to the formation of large aggregates remains unknown. In addition, the first break in the activity curve appears at 2.5–2.8 Fe/KU which is quite high compared to the 2–2.2 cation/KU obtained for many other cations, and silver in particular. This is likely to result from a nonstoichiometric exchange of the protons.

Although problems related to the structure of the catalyst generated in the preparation are again apparent in the case of iron salts, a negative electronic effect is quite evident and in contrast with the positive ef-

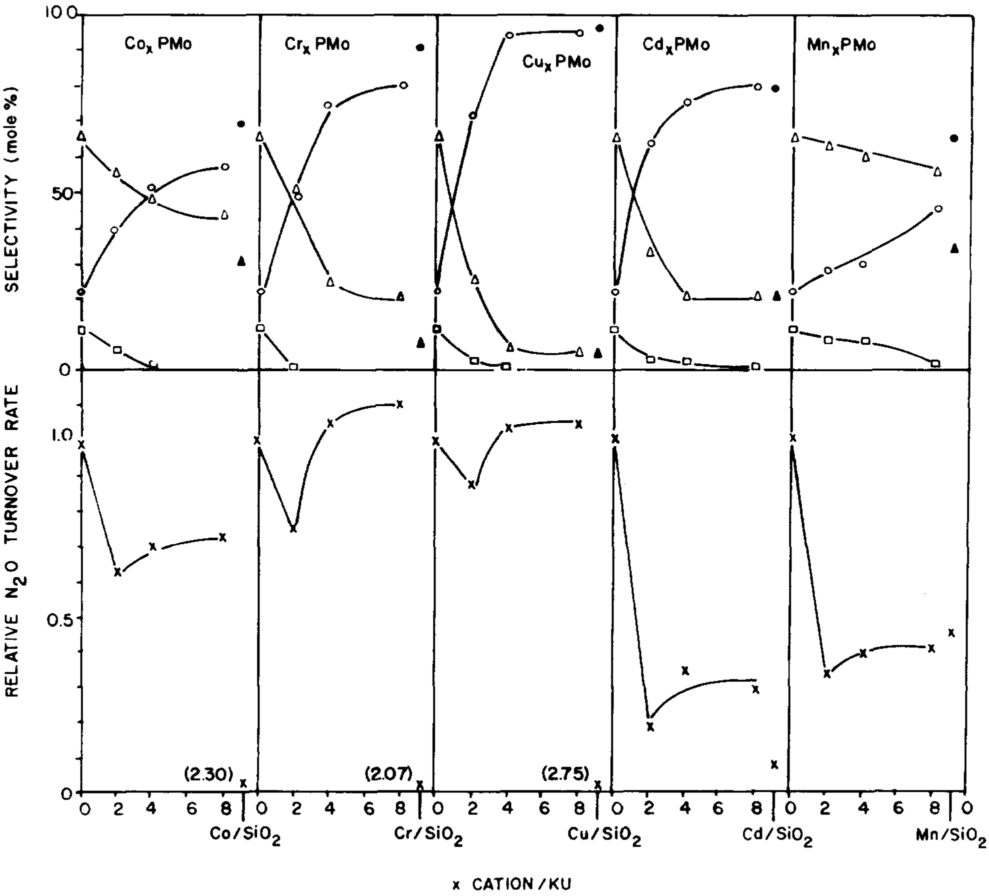

FIG. 5. Relative N_2O turnover rate and selectivity of the $CH_4 + N_2O$ reaction versus the amount of cobalt, chromium, copper, cadmium, and manganese on the 16 wt% HPMo catalyst. Same reaction conditions and symbols as those for Fig. 1.

fect exhibited by silver salts. These results again illustrate the importance of the nature of the cation on that effect.

It can be seen in Fig. 5 that the shape of the curve obtained for the effect of iron on the HPMo activity is not a unique one but occurs with many different cations. As for Fe, the Co, Cr, and Cu cations on silica are very active catalysts for methane oxidation although producing no partial oxidation products for the experimental conditions used. The two other salts, cadmium and manganese on SiO_2 (Fig. 5), are less active catalysts. On the HPMo catalyst these cations, as with Fe, show a large negative electronic effect leading to a pronounced minimum of the relative activity at 2 cations/KU. In Fig. 6, cerium, mercury, nickel, lead, and zinc can also be seen to have a negative electronic effect but to a lesser extent. As the salts of these cations when saturated are only slightly or barely active, the minimum of the relative activities is near the plateau reached after saturation.

The vanadyl salts of the different heteropolyoxometalates HPMo, 12-tungstophosphoric (HPW), and 12-tungstosilicic (HSiW) were prepared from vanadyl sulfate and the activity and selectivity results are reported in Fig. 7. Interestingly these results show that the VO^{2+} cation can re-

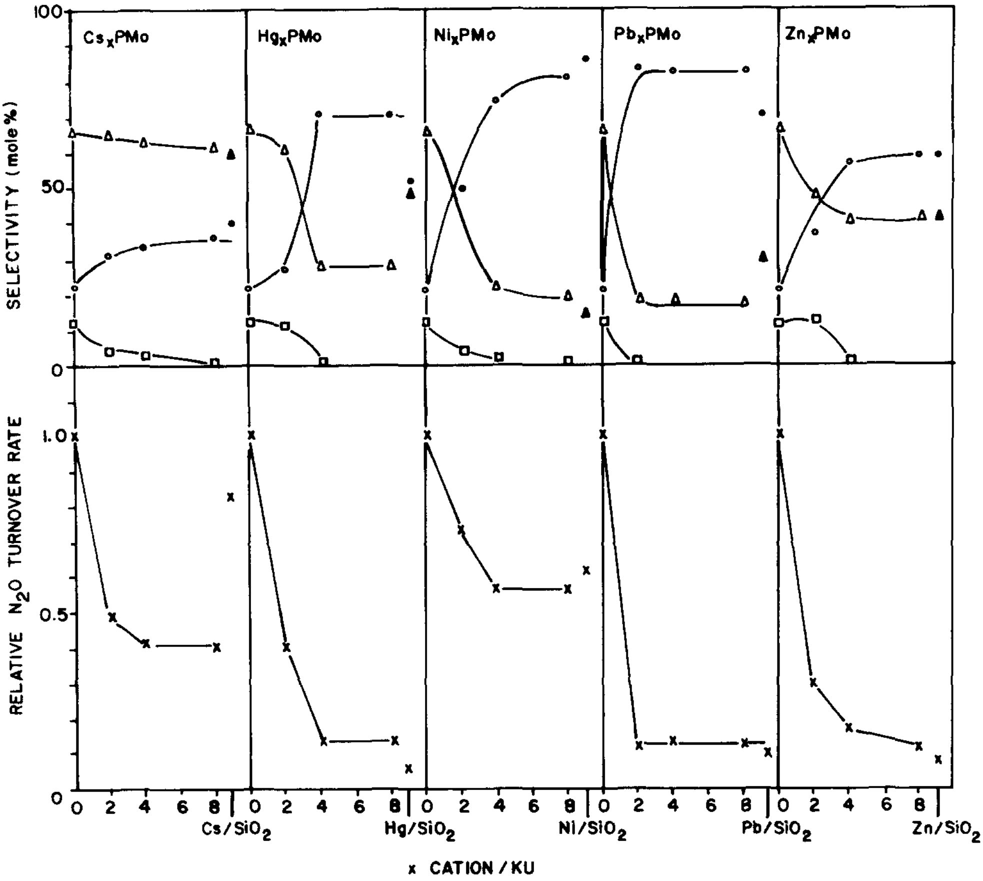

FIG. 6. Relative N_2O turnover rate and selectivity of the $CH_4 + N_2O$ reaction versus the amount of cesium, mercury, nickel, lead, zinc on the 16 wt% HPMo catalyst. Same reaction conditions and symbols as those for Fig. 1.

place the H^+ cation and therefore strongly suggest the existence of vanadyl salts of the heteropolyoxometalates. Except for the HPMo catalyst, these salts are however not completely saturated as no plateau is reached. The inefficiency of the exchange particularly for cation loadings higher than 3 VO/KU is underlined by the difference between the properties of two sets of x VOPW samples resulting from different preparations. A preparation done with a long exchange period (ca. 10 hr) produced more active catalysts than one with a 2-hr period of exchange. In contrast, at low vanadyl loading the results for these time periods were similar, thus demonstrating that the exchange is complete at loadings lower than 2–2.5 VO/KU but becomes nonstoichiometric for higher vanadyl loadings.

Interestingly the breaks appearing in the curves at ca. 1.9 for HPMo and HPW and ca. 2.7 for HSiW are consistent with the expected values from $nH^+ - 1$, i.e., 2 for HPMo, HPW (3 H^+) and 3 for HSiW (4 H^+).

The selectivity in these three cases clearly differs from those of the unpromoted catalyst and of the VO/SiO_2 catalyst. This variation is particularly significant for HPW and HSiW with, in addition, the appearance of partial oxidation products, formaldehyde, and methanol. Although no net

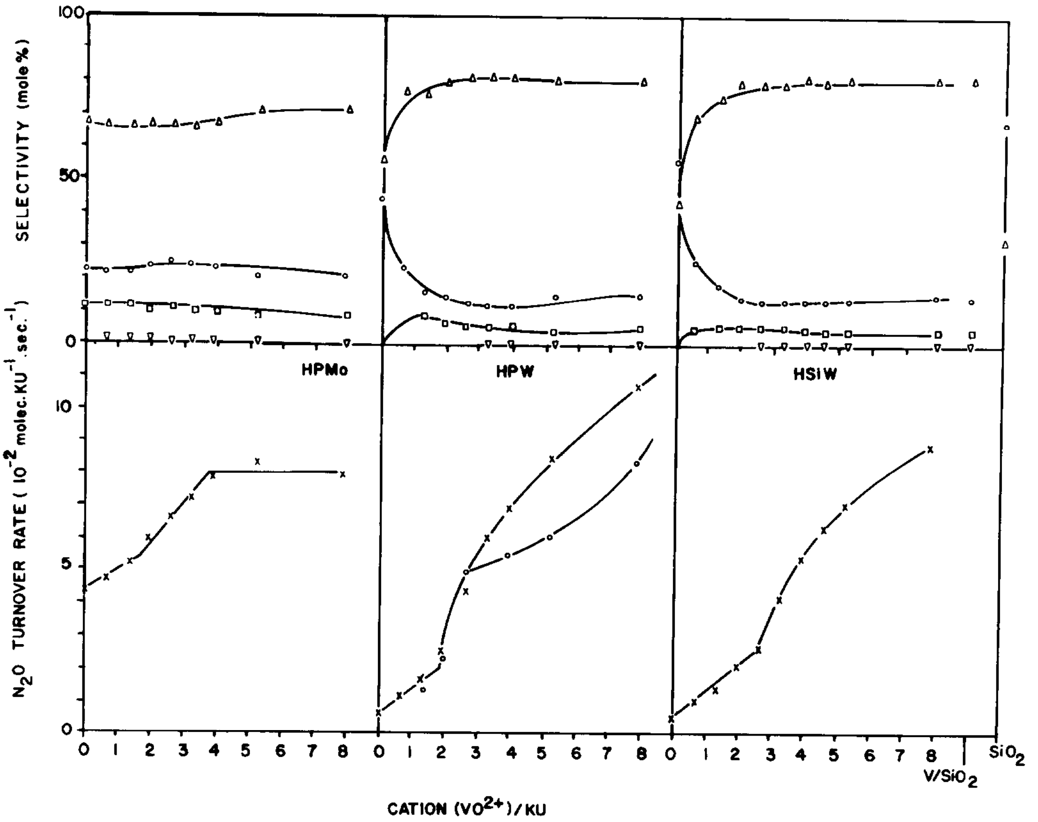

FIG. 7. Relative N_2O turnover rate and selectivity of the $CH_4 + N_2O$ reaction versus the amount of vanadyl sulfate on the 16 wt% HPMo, 23.4 wt% HPW, 23.4 wt% HSiW catalyst. For HPW: (x) first and (o) second preparation. Same reaction conditions and symbols as those for Fig. 1.

improvement of the selectivity relative to V/SiO_2 was found, a tendency to reach a maximum at low vanadyl ion contents (≈1.5 VO/KU) may be distinguished. The electronic effect of the vanadyl cation is clearly negative on the three heteropolyoxometalates. Unfortunately the unsaturation does not allow comparison of the plateau levels which may have shown a possible effect of the elemental composition of the Keggin unit on the activity of the vanadyl cation.

In order to compare the electronic effects exerted by the different cations on the properties of the HPMo catalyst a promotion factor (r) has been computed as the ratio of the turnover number of the HPMo site influenced by two cations, where the effect is maximum, over the turnover number of the original HPMo, i.e.,

$$r = \frac{3A(2) - 2A(s)}{A(0)},$$

where $A(0)$ is the activity of one Keggin unit, $A(2)$, the activity of the Keggin unit saturated with 2 cations, and A(s), the activity of the completely saturated Keggin unit. This latter value should be $A(3)$ for 3 cations/KU but as experimentally observed saturation frequently occurred at higher loading. Therefore the value at the plateau has been taken in most cases whereas in the case of complete poisoning A(s) is evidently equal to the silica activity.

Correlations of this ratio with various cation properties has been examined. That

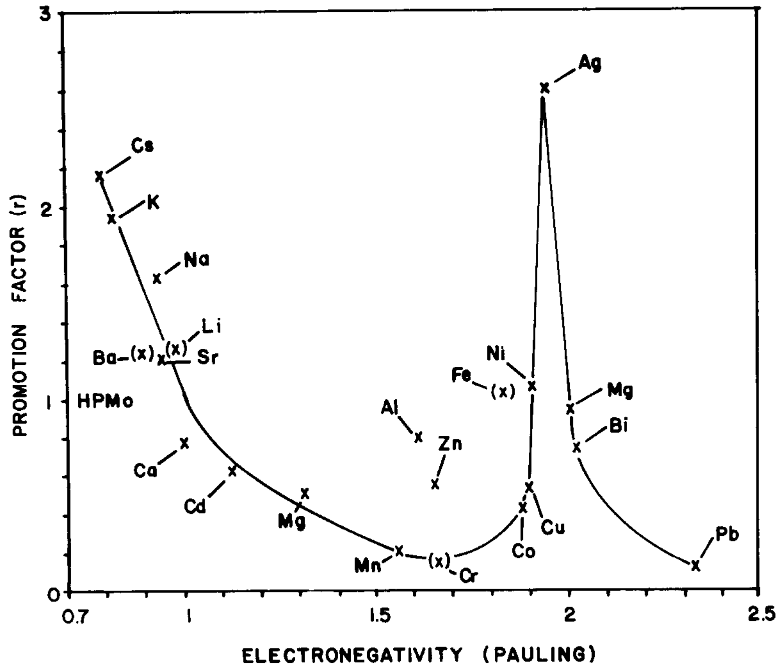

FIG. 8. Promotion factor of the promoted HPMo catalyst at a loading of two cations per KU versus the electronegativity (Pauling's scale). In parentheses, samples likely to be incorrectly exchanged.

with the Pauling electronegativity of the element is shown in Fig. 8. The value of *r* decreases with electronegativity increase except for an apparently sharp peak in values of *r* for electronegativity values in the range 1.8–2.2

DISCUSSION

The results reported in this study support clearly the conclusions and hypotheses advanced in a previous work on the structural and catalytic effects of the cesium cation added to the HPMo catalyst (*12*). In all cases the presence of the cations modify both the activity and the selectivity of the HPMo species.

The first effect of the added cation responsible for the observed changes in the activity and selectivity results from the substitution of the proton by ion exchange. This effect is evidenced particularly clearly for cesium and other cations with no intrinsic activity and for the vanadyl cation on HPMo, HPW, and HSiW. The exchange is likely not complete in some cases (e.g., Li, Ba, Bi). In fact proton substitution is likely to be inhomogeneous (*6*, *7*, *13*) and therefore the reported values should be taken as mean values. In addition the complete exchange often intervenes when a surplus of cations has been provided. However, it can be concluded that formally the saturation of the HPMo Keggin unit occurs at 3 cations/KU regardless of the charge on the cation. The formulae of the partially stoichiometrically exchanged KU can then be proposed as

$$\mathrm{H}^{+}_{3-x}C^{n+}_{x}\ \mathrm{P\ Mo_{12}OP_{40}}A^{m-}_{(n/m)x}$$

with C^{n+} the cation of charge n^+ and A an anion, OH^-, for example, necessary to provide electrical neutrality. Evidently in the case of monovalent cations no compensating anions are necessary.

The observation that the saturation occurs at approximately 3 cations/KU provides strong evidence for the Keggin units as active species and for the role of the proton which is assumed to create the coordinatively unsaturated sites appropriate for the adsorption of the CH_4 and the oxidant. It also suggests that the three protons with HPMo and HPW or four protons with HSiW are not involved in the linkage to the silica surface. It appears then that other modes of interaction between the Keggin unit and the silica surface must exist. Since the Keggin unit is a large negatively charged entity, an electrostatic interaction is one such possibility. Such an interaction is on one hand presumably relatively weak since the supported heteropolyoxometalate was readily stripped from the support by washing with acetonitrile (*12*), but on the other hand sufficiently strong to stabilize the structure of the supported material and increase its thermal resistance, as previously proposed (*12*).

The second effect on the activity produced by the introduction of cations is that interpreted here as an electronic factor. The results reported here suggest that this effect is strongly sensitive to the nature of the cation. The more electropositive or electron-donating cations evidently induce an increase in turnover number whereas electron-accepting cations produce a decrease in the activity. The unexpectedly high value for silver noted in Fig. 8 may be due to the use of the electronegativities for the neutral atoms rather than that for the cations. It can be speculated that the increase in the electron density on the KU and particularly on the KU free sites induced by the electron donor elements such as Cs, K, Na, and Li favors the formation of some active charged oxygen species symbolized previously as O* following the reaction

$$KU\square + K_2O \rightarrow KUO^* + N_2 \qquad (2)$$

where O* may be O^- (*14*) or O^{2-} (*15*) as shown by different authors. Since as previously reported the apparent activation energy of the reaction is not changed by the addition of cesium it appears that the rate but not the mechanism is altered. This supports the contention that reaction (2) is the rate-limiting step of the reaction (*12*).

TABLE 1

Activation Energies for Cation-Exchanged $HPMo/SiO_2$ and Cation/SiO_2 Catalysts

Sample	E_a ($\pm$2 kcal mol^{-1})	Sample	E_a ($\pm$2 kcal mol^{-1})
HPMo	32	Mo/SiO_2	41
3CuPMo	18	Cu/SiO_2	24
3ZnPMo	40	Zn/SiO_2	28
3CrPMo	25	Cr/SiO_2	25
3CoPMo	25	—	
3NiPMo	25	—	
3FePMo	25	Fe/SiO_2	21
3VOPMo	27	V/SiO_2	34

In addition to the two effects of cations discussed above, a third factor may be discerned. With some of the cations an intrinsic activity is observed, with both the cation/SiO_2 and the cation PMo catalysts even after saturation of the Keggin unit, in contrast with the complete poisoning observed for other cation PMo catalysts, e.g., CsPMo. This intrinsic activity apparently results from the generation of additional sites, i.e., the cation itself, presumably operating through a reaction mechanism different from that proposed for the supported heteropoly acids. That is suggested by the variation of the activation energies when the cation on saturated HPMo catalysts is changed (Table 1). Moreover, values of the activation energies found for the cations on $HPMo/SiO_2$ catalysts and the same cations on SiO_2 catalysts are often different. Although such observations could be interpreted as evidence for the effect of the Keggin unit on the catalytic properties of the cation it appears more probable that the structural differences between these two types of catalysts lead to different mechanisms. With the $HPMo/SiO_2$ catalyst the cation is presumably isolated, the KU playing a role similar to that of a support, whereas in the cation/SiO_2 catalysts particles of oxides may form and lead to different catalytic behavior.

Variation of the selectivity with cation loading generally displays three segments similar to those observed with the activity. At low loading (cation/KU = 2) the selectivity changes relatively little, while at higher loading the variations are much more substantial until a stabilization is reached after the saturation of the Keggin unit. It is of interest to note that the cations tend to increase the production of carbon dioxide at the expense of carbon monoxide except in the cases of aluminum and vanadyl cations.

It may be of interest to refer to earlier work on the effect of cations in the application of heteropolyoxometalates as heterogeneous catalysts. However, it is important to note that such previous studies employed various salts of the heteropolyoxometalates as such rather than the cation exchange technique used in the present work. Furthermore the earlier work has been concerned with unsupported heteropolyoxometalates rather than those supported on silica as in the present report. Since it has been shown (*3, 4*) that HPMo supported on silica possesses an enhanced thermal stability in contrast with the unsupported acid, comparisons of the results obtained with the two forms may be difficult. However, Akimoto *et al.* (*16*) were able to show that the conversion of isobutyric acid through oxidative dehydrogenation on unsupported HPMo at 300°C decreased with the increasing electronegativity of the cations in the *prepared* salts and have attributed this observation to a weakening of the Mo–O bond as the cation becomes less electronegative. Unfortunately no previous work, other than that from this laboratory, has been reported on the conversion of methane on heteropolyoxometalates so comparative discussions are difficult, if not impossible. Finally it is useful to recall that, in contrast to the present results alkali doping has been found to be generally advantageous in increasing catalytic efficiency in a variety of catalysts and catalytic processes including, for example, ethylene oxidation (*17*). In such cases, while the effect of the introduction of the alkali has been attributed to a number of sources, an electronic factor has frequently been invoked.

In the conversion of methane on heteropolyoxometalates the introduction of cations generally does not increase the quantities of partial oxidation products. However, small amounts of bismuth, aluminum, and possibly mercury and zinc cations are mildly selective for such purposes. Many other cations, e.g., Cs, Li, Ba, Mg, Ag, Mn, and VO, led to the generation of constant product compositions at low cation loading. It is interesting to note that the introduction of chlorine in the form of a chloromethane has recently been shown to have an advantageous effect in the conversion of methane on heteropolyoxometalates (*18*). Although any conclusions concerning the effect of chlorine would be premature it is tempting to suggest that, while electron-donating elements may generally be disadvantageous, electron-attracting species may induce beneficial shifts in the electron density. However, further work is required to investigate the enhancement of partial oxidation products with the HPMo catalyst in the presence or absence of cations.

ACKNOWLEDGMENTS

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