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The Oxidation of Methane on Heteropolyoxometalates

III. Effect of the Addition of Cesium on Silica-Supported 12-Molybdophosphoric Acid, Molybdena, Vanadia, and Iron Oxide

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The effect, on the oxidation of methane with nitrous oxide, of the addition of cesium to silica-supported 12-molybdophosphoric acid (HPMo), molybdena, vanadia, and iron oxide has been studied. All four catalytic systems show similarities in results with cesium producing a poisoning effect, eventually reducing the solid to a behaviour similar to that of the support. The correspondence of deactivation with the number of available protons in supported HPMo suggests that the protons play a crucial role in the oxidation process. A mechanism is postulated in which the protons abstract oxygen from the Keggin Unit to produce anionic oxygen vacancies which are visualized as vital to the oxidation process on HPMo. The similarity of behaviour of silica-supported molybdena, vanadia, and iron oxide to that of HPMo on addition of cesium suggests the existence of isopolyoxometalate structures on these catalysts. The effect of cesium results from the blocking of the vacancy generation process (dehydration) and from an enhancement of the turnover number resulting from the unblocked sites, this latter effect presumably being electronic in nature. © 1988 Academic Press, Inc.

INTRODUCTION

Previous work from this laboratory (*1, 2*) has shown that the silica-supported heteropolyoxometalates with Keggin structure, for example, 12-molybdophosphoric (HPMo), 12-molybdosilicic (HSiMo), and 10-molybdo-2-vanadophosphoric acids, are effective catalysts for the partial oxidation of methane by nitrous oxide in the temperature range from 793 to 843 K. In contrast, the tungsten-based heteropolyoxometalates, 12-tungstophosphoric acid (HPW) and 12-tungstosilicic acid (HSiW), were found to be relatively inactive in such a process. Further work (*3*) on HPMo supported on silica provided evidence strongly suggesting that the Keggin Unit (KU) $PMo_{12}O_{40}^{3-}$ fixed on the support is the species primarily responsible for the activity and selectivity of the catalyst. In addition it was shown that severe pretreatment conditions, such as calcination in air at 640°C for 16 h or 550°C for 40 h, together with a catalytic reaction at 570°C for 10 h, was not sufficient to destroy all the Keggin Units. However, almost complete thermal degradation occurred after calcination at 730°C for 16 h in air. This remarkable structural stability of the heteropoly anion is apparently due to an advantageous interaction between the support and the Keggin Unit, the latter being dispersed as isolated species grafted on the support surface, up to a loading of 120 μmol KU per gram of support (0.1 KU nm^{-2}) (*3*).

The heteropoly acids are known to contain exchangeable protons (*4–18*), a property suitable for the preparation of a variety of salts. The surface and catalytic properties of the salts of a number of heteropoly acids have been studied (*5–29*), in particular those of 12-molybdophosphoric acid for oxidation (*19, 20*), acid-catalyzed reactions

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(*21, 22*), or redox processes (*20, 23*). The monovalent salts, and particularly those containing alkaline element cations, appear to have been more extensively studied. In particular, it has been shown that partially saturated cesium salts of bulk 12-molybdophosphoric acid had an increased activity in the partial oxidation of butane (*24, 25*). However, such activity enhancement was coincident with an increase in specific surface area. In this laboratory the structural properties of the monovalent salts of 12-molybdo- and 12-tungstophosphoric acids have been studied (*5–18, 26–29*), and the importance of cation size in structural microporosity and secondary bulk structure has been shown. With the aforementioned anions, a cation size in the range 2.5–3.5 Å (Cs^+, NH_4^+, K^+) produced a maximum in micropore volume and surface area.

Since each KU of the silica-supported HPMo catalyst is evidently isolated on the support surface at small loading values, the supported heteropoly acids may be viewed as a system free of bulk structure. Thus it appeared possible to study the effect of the exchange of protons by cesium without the intrusion of surface area effects. The present work examines the effect produced by cesium on both supported heteropolyoxometalates and other partial oxidation catalysts such as supported oxides of molybdenum, vanadium, and iron.

EXPERIMENTAL

Catalysts

The method of preparation of the silica-supported 12-molybdophosphoric (HPMo), 12-molybdosilicic (HSiMo), 12-tungstophosphoric (HPW), 12-tungstosilicic (HSiW), and 10-molybdo-2-vanadophosphoric (HPV_2Mo_{10}) acids has been described previously (*1, 2*). These acids were loaded on the silica support (Grace-Davison, grade 407, 740 $m^2\ g^{-1}$) to provide 0.068 KU/nm^2 of support surface (or 84 μmol KU per gram of support), corresponding to loadings of 16.0, 16.0, 21.2, 21.2, and 16.2 wt% of HPMo, HSiMo, HPW, HSiW, and HPV_2Mo_{10}, 30 H_2O, respectively.

The supported cesium salts of these heteropoly acids were prepared by the impregnation of the calcined supported heteropoly acids with an excess of an aqueous solution of cesium carbonate (Alpha Products 99.9%) acidified with 1 *M* nitric acid. After evaporation to dryness at 80°C the solids were calcined at 200°C for 1 h. No significant quantities of precipitate were produced in the application of this technique to HPMo, HSiMo, and HPV_2Mo_{10} catalysts but precipitation did occur with HPW and HSiW catalysts. Amounts of cesium carbonate to yield zero to eight atoms of cesium per KU were added, and the resulting catalysts are labelled as *x*CsPMo, where *x* represents the number of cesium atoms per HPMo KU.

The preparation of the 3 wt% Mo/SiO_2 and 1.66 wt% V/SiO_2 catalysts has been described previously (*3*). The 1.82 wt% Fe/SiO_2 catalysts were prepared by impregnation of the silica with an excess of an iron oxalate aqueous solution, evaporation to dryness in air at 80°C, and calcination in air at 200°C for 2 h. The three supported metal catalysts were prepared to contain 0.27 atom of metal/nm^2 of support surface (332 μmol metal per gram of support).

Deposition of cesium on the supported oxides (0–1.5 Cs per atom of metal) was accomplished in a manner similar to that with the supported heteropolyoxometalates and is labelled as *x*Cs*M*, where *x* and *M* represent the number of cesium atoms per *M* atoms of supported metal oxide (M = Mo, V, Fe). A sample containing 0.24 atom of cesium/nm^2 of SiO_2 was also prepared by impregnation of cesium carbonate, drying, and calcination in air at 200°C for 2 h.

Catalytic Experiments

The reactor, analytical systems, and operating conditions have been described previously (*1–3*). In the present work one set of operating conditions was primarily employed: reaction temperature, $T_R = 843$ K, catalyst mass $W = 0.5$ g, total flow rate $F = 30$ ml min^{-1}, feed composition, CH_4 (67 mol%), N_2O (33 mol%).

The catalyst samples were pretreated in helium for 1 h at the reaction temperature to remove water. The reaction was allowed to proceed for 3 h to guarantee the attainment of steady state prior to any measurements. The turnover number is calculated per KU for the heteropoly acids or per atom of metal for the supported oxides. For the silica support the rates have been reported per 14.7 nm^2 of support surface, the area occupied by one KU in the supported heteropolyoxometalate catalysts. Selectivities are reported as mole percent CO, CO_2, CH_2O, and CH_3OH produced.

The amount of oxygen which can be extracted by hydrogen has been estimated by a pulse method employing N_2O. The *x*CsPMo samples were reduced in hydrogen at 843 K for 1 h prior to reactions being performed. After a purge with hydrogen 2-ml pulses of N_2O were injected and the amount of nitrogen was measured. This sequence was performed two times in succession on each catalyst sample. The amount of nitrogen produced is equivalent to the number of oxygen atoms consumed in the reoxidation since no oxygen was produced. Fifteen such pulses were required to reoxidize the solid. For comparative purposes a similar experiment was also performed on silica.

Apparent activation energies have been calculated from the results of five to six experiments performed randomly in the temperature range 773–863 K. In all cases, except that of silica where a discontinuity was found at 820 K as previously reported (*1*), a good linearity of the Arrhenius plots was found.

RESULTS

The effect of the amount of cesium on the activity and selectivity of the supported HPMo, HPW, HSiMo, HPV_2Mo_{10} for the $CH_4 + N_2O$ reaction is reported in Figs. 1 and 2. The turnover rates of both methane and nitrous oxide decrease approximately linearly as the amount of cesium is increased up to approximately two cations per KU. With a further increase in the latter the two turnover numbers decrease more precipitously until small values, approximately equivalent to those found for the silica support, are reached when 3.5 to 4 cations/KU are present. Semiquantitatively similar changes may be observed with the selectivities. Small changes are observed up to approximately 2 cations/KU while more substantial changes occur between 2 and 4 Cs/KU until values similar to those for the silica support are reached. Evidently the catalytic properties of the supported HPMo species have been completely poisoned by the addition of 3.5 to 3.8 Cs/KU, a value similar to the 3 H^+ possessed by each KU in the bulk stoichiometric acidic form.

The activities of the HSiMo and HPV_2Mo_{10} acids are completely poisoned and that of HPW is nearly completely poisoned by the addition of cesium (Fig. 2). However, the shapes of the turnover number curves differ from that found with HPMo. With the former catalysts the turnover number decreases monotonically with an increase in the cesium content, reaching values expected for the support for amounts of cesium per KU as small as two for HSiMo and HPW, but approximately four with HPV_2Mo_{10}. Observations during the preparation of these different catalysts may be relevant to these results. It has been noted that a precipitate is formed when cesium carbonate is added to the supported HPW and HSiW catalyst while with the HSiMo and HPV_2Mo_{10} samples no precipitate was observed during the impregnation. With the former catalysts the precipitous decrease in activity may, at least in part, be due to the destruction of the Keggin structure or aggregation of the smaller clusters into larger particles during the impregnation with the cesium carbonate solution. Both the HSiMo and the HPV_2Mo_{10} are

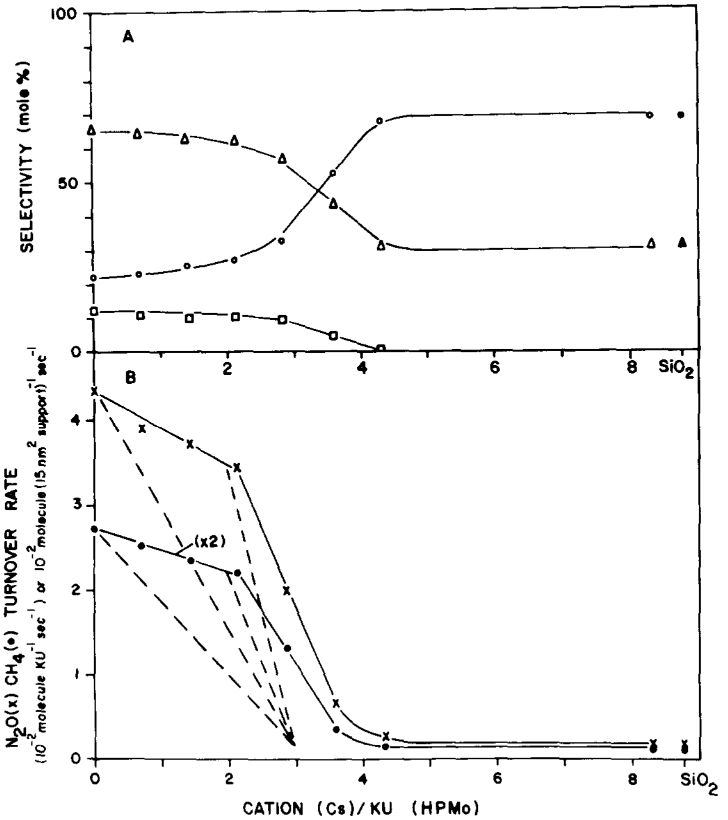

FIG. 1. Turnover rate and selectivity of the CH_4 oxidation by N_2O versus the amount of cesium on the 16 wt% HPMo Catalyst. Turnover rates are expressed as 10^{-2} molecules KU^{-1} s^{-1}. As each KU occupies 14.7 nm^2 of the SiO_2 support surface the equivalent turnover rate for SiO_2 is 10^{-2} molecules (15 nm^2 support)$^{-1}$ s^{-1}. Reaction conditions, T_R = 843 K, W = 0.5 g, F = 30 ml min^{-1}, CH_4 (67 mol%), N_2O (33 mol%). Symbols: (△) CO, (○) CO_2, (□) CH_2O, (×) N_2O turnover rate, (●) CH_4 turnover rate × 2. (Dotted lines are calculated for substitution of H^+ by Cs^+.)

known to be considerably less stable than HPMo. In addition, the aqueous solution of cesium carbonate tends to neutralize the solution which may be detrimental to the stability of the anionic structure of HSiMo and HPV_2Mo_{10}. However, it is apparent from Fig. 2 that whatever decomposition products may be generated, if any, such substances either are inactive or are themselves poisoned by the cesium since both the activity and the selectivity approach that of the support with an increase in the amount of cesium per KU.

The changes in product composition with addition of cesium can also be seen in Fig. 2. With silica-supported HPV_2Mo_{10} the product composition is unchanged after addition of one Cs per KU but with further addition of cesium the proportion of carbon dioxide increases while that of carbon monoxide and formaldehyde decreases, approaching that of silica after addition of four Cs per KU. HSiMo exhibits similar behaviour although the product composition resembles that found with silica after the addition of one Cs per KU. In contrast, with HPW the product composition changes but does not approach that of the support.

Aggregation of the active KU into larger particles on the support surface may also result in a decrease in activity. As alkanes

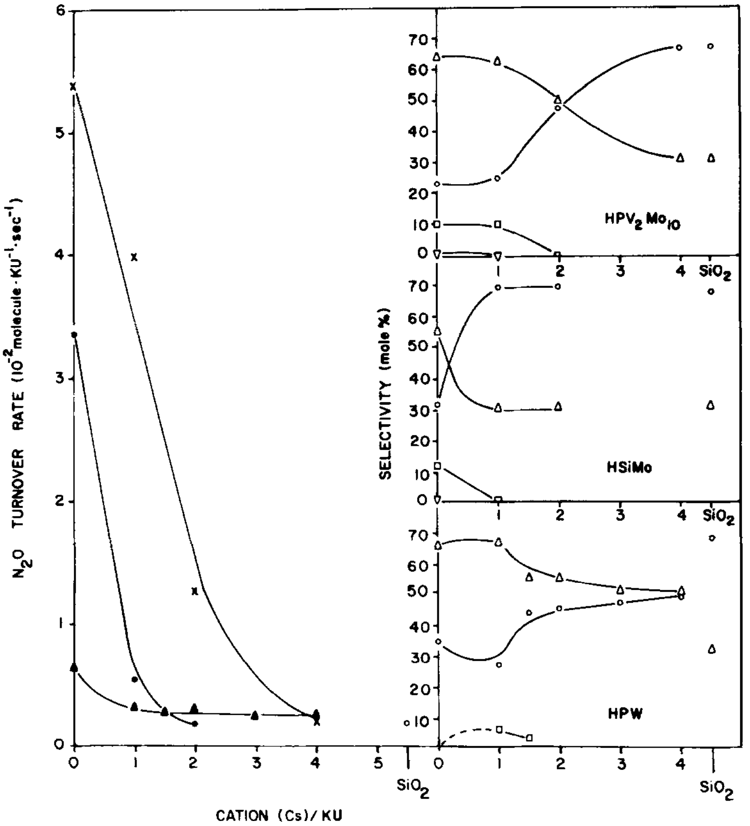

FIG. 2. Turnover rate and selectivity of the CH_4 oxidation by N_2O vs the amount of cesium on the 16.2 wt% HPV_2Mo_{10}, 16 wt% HSiMo, and 21.2 wt% HPW. Same reaction conditions and symbols as those in Fig. 1. Symbols: (△) CO, (○) CO_2, (□) CH_2O; turnover rate: (×) HPV_2Mo_{10}, (●) HSiMo, (▲) HPW.

are unable to penetrate into the bulk of the heteropoly compounds (*15–18, 30*), and consequently reaction of such molecules is confined to the surface of the heteropoly compounds, an aggregation would result in the availability of a reduced number of active sites and an activity and selectivity presumably different from that of the support.

Further investigation of the poisoning by cesium of the activity of the supported HPMo has been undertaken. A study of the reoxidation of samples prereduced by hydrogen was expected to provide information on the poisoning effect when a more powerful reducing agent is used. After reduction by hydrogen at 570°C for 1 h the amount of oxygen necessary to reoxidize the sample was determined by the injection of 15 successive pulses of nitrous oxide and the measurement of the total amount of nitrogen produced. The effect of the amount of cesium on the amount of oxygen consumed may be seen in Fig. 3B. A linear decrease is observed in the number of oxygen atoms per KU necessary to reoxidize the sample as the cesium is increased to approximately three Cs per KU. With additional increases in cesium no further change is evident. It may be seen from Fig. 3B that 19 oxygen atoms per KU are required to reoxidize the reduced HPMo, with no cesium present, but this decreases to approximately 4 oxygen atoms per KU on addition of cesium.

The addition of cesium also reduces the apparent activation energy of the CH_4 +

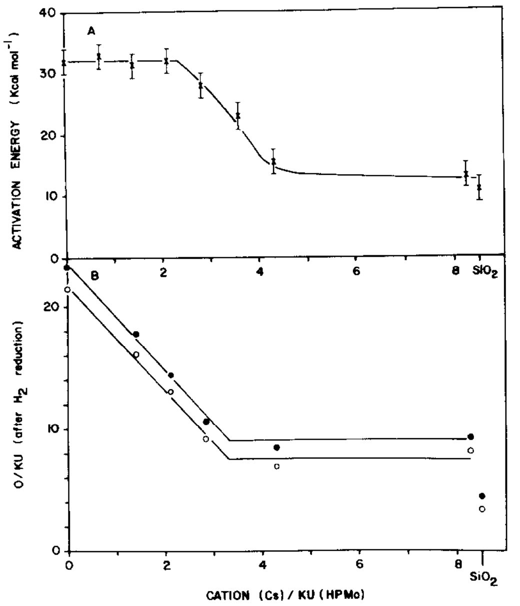

FIG. 3. Variation of (A) the apparent activation energy and (B) the amount of oxygen consumed for reoxidation after H_2 reduction at 843 K for 1 h, versus the amount of cesium on the 16 wt% HPMo. Reaction conditions for (A): $W = 0.5$ g, $F = 30$ ml min^{-1}, CH_4 (67 mol%), N_2O (33 mol%). Symbols: (●) first measure, (○) second measure.

N_2O reaction (Fig. 3A). For amounts of cesium up to approximately two cations per KU the activation energy is unchanged at 32 ± 2 kcal mol^{-1}. Additional increases in the cesium content reduce the activation energy to 12 ± 2 kcal mol^{-1} at approximately four Cs per KU, a value similar to that for the silica support itself.

The ion exchange properties of the heteropoly acids are well known and used extensively for the preparation of numerous salts. Since HPMo contains three protons per KU, a saturation close to three cesium cations per KU was anticipated, provided that other phenomena such as aggregation or decomposition of the KU, or significant adsorption capacity of the support, do not interfere. Since in the case of the Mo-, V-, and Fe-supported oxides the ion exchange capabilities and the number of exchangeable protons are not known, the doping by cesium may provide valuable information.

Both the Mo/SiO_2 and V/SiO_2 catalysts are known to catalyze the partial oxidation of methane (*31–33*). In the pesent work the supported iron on silica has been found more active for the conversion of methane than either Mo/SiO_2 or V/SiO_2, although the selectivities are different (Table 1). The Fe/SiO_2 catalyst produces mainly CO_2 (68 mol%) and CO (30 mol%) with little formaldehyde (≈0.5 mol%) while 2 mol% of methanol is produced.

The effect of the amount of cesium on the conversion and selectivity for the CH_4 +

TABLE 1

Conversion and Selectivity of the Reference Catalysts for the $CH_4 + N_2O$ Reaction

Catalyst	Conversion (mol%)		Selectivity (mol%)			
	CH_4	N_2O	CO	CO_2	CH_2O	CH_3OH
SiO_2	0.12	0.4	32	68	n.d.[a]	n.d.
6 wt% $HPMo/SiO_2$	3.2	10.6	65	23	12	t[b]
3 wt% Mo/SiO_2	0.4	1.2	57	31	12	t
1.66 wt% V/SiO_2	4.1	12.7	73.5	17.5	5	4
1.82 wt% Fe/SiO_2	9.0	30	30	68	0.5	2

Note. Reaction conditions: $T_R = 843$ K, $W = 0.5$ g, $F = 30$ ml min^{-1}, CH_4 (67 mol%), N_2O (33 mol%).

[a] n.d., not detected.

[b] t, trace.

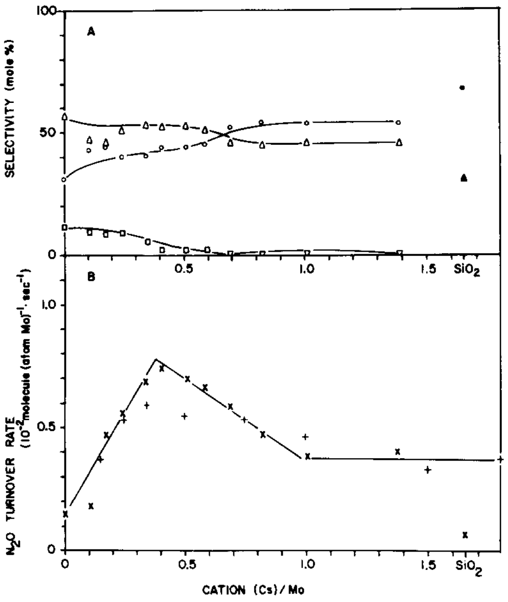

FIG. 4. Turnover rate and selectivity of the CH_4 + N_2O reaction versus the amount of cesium on the 3 wt% Mo/SiO_2 catalyst. Reaction conditions: T_R = 843 K, W = 0.5 g, F = 30 ml min^{-1}, CH_4 (67 mol%), N_2O (33 mol%). Symbols: (△) CO, (○) CO_2, (□) CH_2O, (▽) CH_3OH; turnover rate: samples prepared (×) with cesium nitrate and (+) with cesium carbonate.

N_2O reaction on Mo, V, and Fe catalysts is also shown in Figs. 4–6. Similarly to that found with the HPMo catalysts, the graphs of activity for varying amounts of cesium exhibit three distinct types of behaviour. Both the vanadium and the iron catalysts, which are very active catalysts without cesium, yield curves similar to that found with HPMo. However, in contrast to the observations with the latter, after addition of an amount of cesium sufficient to produce no further changes in activity, the vanadium and iron catalysts have residual activities greater than that of the support itself. It is also evident from the figures that a similar comment applies to the selectivity.

For the Mo/SiO_2 catalyst, which has a low activity in the absence of cesium, small quantities of cesium lead to an initial increase in activity, followed by a decrease, and as with the vanadium and iron catalysts, ultimately an activity level higher than that of the support. The selectivity also fails to reproduce that of the support. In contrast with the results for HPMo, vanadium, and iron catalysts, cesium appears to act as an effective promoter in amounts up to approximately 0.4 Cs/KU on MoO_3/SiO_2.

With the Mo, V, and Fe catalysts the selectivity is altered to favour methanol and carbon dioxide as cesium is added, while the quantities of carbon monoxide and formaldehyde decrease and in the latter case become negligibly small.

DISCUSSION

The effect of the amount of cesium on different supported catalysts provides both structural and catalytic information on these systems. Structurally, the observa-

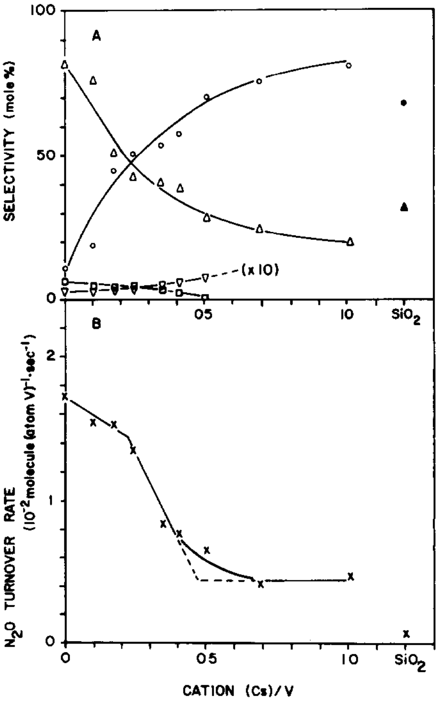

FIG. 5. Turnover rate and selectivity of CH_4 oxidation by N_2O versus the amount of cesium on the 1.66 wt% V/SiO_2 catalyst. Same reaction conditions and symbols as those in Fig. 4.

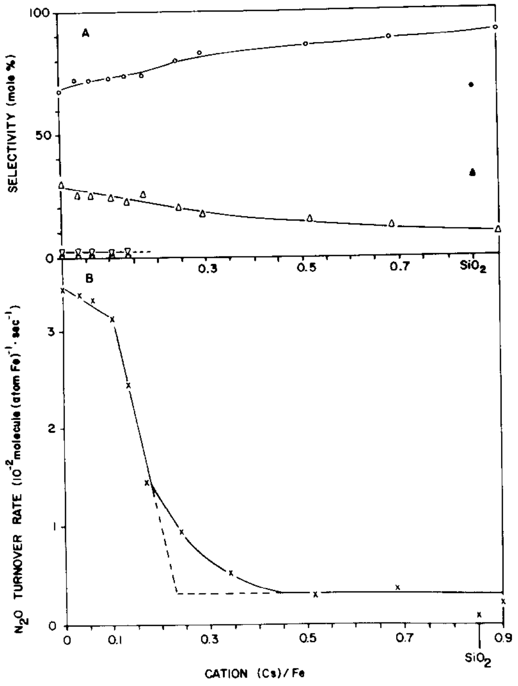

FIG. 6. Turnover rate and selectivity of CH_4 oxidation by N_2O versus the amount of cesium on the 1.82 wt% Fe/SiO_2 catalyst. Same reaction conditions and symbols as those in Fig. 4.

tion that a saturation level is reached can be used to determine the number of exchangeable protons in the system. Since with the HPMo catalyst, three protons are present per Keggin Unit, provided that the Keggin Units are still present in the sample, the saturation should be reached at 3 Cs/KU. The present results show a limit at 3.5 Cs/KU for HPMo. The difference may be attributed to the difficulty in completely exchanging all protons with cesium ions, so that a slight excess is required for that purpose. Since the addition of cesium to silica has no significant effect on the catalytic properties of the support, the measured changes in activity can be referred to hypothetical lines drawn to intersect the activity of the support at 3 Cs/KU (Fig. 1B). Although at sufficiently high temperatures the presence of products of decomposition of the Keggin structures may play a role in fixing some cesium ions, the similarity of the measured saturation value to that expected provides additional evidence that Keggin structures are held on the support, as proposed previously (*3*).

The addition of cesium also produces substantial changes on the supported oxides of Mo, V, and Fe. Fe and V are poisoned similarly to that observed with HPMo while the Mo system shows an initial increase in activity. It will be proposed, however, that such observations are consistent with the same effect of cesium, the difference in the observations with Mo/SiO_2 being attributable to its small activity. The number of H^+ per atom of metal has been reported in Table 2 and compared to the value of that quantity that would be expected if isopolyoxometalate structures are present on the support and are the active

TABLE 2

Comparison of the Experimental and Hypothetical Amounts of Protons per Atom of Metal Formed by Cesium Exchange

Catalyst	Experimental cesium saturation ratio (Cs/atom metal)	Possible polyoxometalate species	Theoretical saturation ratio (H^+/atom metal)
$HPMo/SiO_2$	0.29 (3.5 Cs/KU)	$PMo_{12}O_{40}^{3-}$	3/12 = 0.25
Mo/SiO_2	0.95	$Mo_7O_{24}^{6-}$	6/7 = 0.86
V/SiO_2	0.47	$HV_{10}O_{28}^{5-}$	5/10 = 0.50
		$H_2V_{10}O_{28}^{4-}$	4/10 = 0.40
Fe/SiO_2	0.21	—	—

species for the CH_4 oxidation. Interestingly, the experimental values are similar to those calculated from known isopoly anions. The heptamolybdate anion is a commonly encountered species in aqueous solution and, as proposed for the Mo/Al_2O_3 catalyst, at least in an intermediate range of loading (*34*), could also be the predominant species on the silica support. With the V/SiO_2 catalyst, the values calculated by assuming the presence of the anions $HV_{10}O_{28}^{5-}$ and $H_2V_{10}O_{28}^{4-}$ closely approximate those from experiment (*35*). With iron, the results suggest the existence of a polyoxometalate structure with 0.21 H^+/Fe or approximately 5 Fe/H^+. Whatever the precise structure of the surface species in these systems it is important to recognize here the strong analogy between the $HPMo/SiO_2$ and the Mo-, Fe-, V-supported oxide catalysts.

With the $HPMo/SiO_2$ catalyst the results undoubtedly show that the exchange of all the protons by the cesium is at the origin of the complete poisoning of the CH_4 oxidation process. This demonstrates that the proton has an important role in the oxidation process. Although it could be claimed that the proton is the reactive species activating the methane molecule to produce a carbocation

$$CH_4 + H^+ \rightarrow CH_5^+$$

there is considerable evidence that heterogeneous oxidation on this catalyst proceeds initially through hydrogen abstraction by an active oxygen species O*. While this species can be an O^- reacting with CH_4 to generate a methyl radical (*36*)

$$CH_4 + O^- \rightarrow OH^- + CH_3\cdot \qquad (1)$$

O^{2-} has recently been proposed as capable of reacting with methane (*37*). It can therefore be proposed that protons are required in the oxidation of CH_4 on HPMo to provide for the creation of vacancies by the removal of water as

$$2KUOH \rightarrow KUO + KU\square + H_2O \quad (2)$$

Subsequently N_2O can decompose on these vacancies, replenishing the oxygen in the KU,

$$N_2O + KU\square \rightarrow N_2 + KUO \qquad (3)$$

or a CH_4 molecule, after adsorption on the vacancy, may interact with neighbouring oxygen species. As can be readily understood, substitution of protons by cesium blocks the dehydration reaction (2) and consequently the subsequent reactions are also terminated. Similarly the reduction by H_2, a stronger reductant than CH_4, is also inhibited by the proton substitutions. These results demonstrate that the only vacancy generating process on heteropoly anions is reaction (2).

As can be deduced from reaction (2), the generation of one vacancy results from the loss of two protons. Therefore the number of vacancies that can be created is one-half the number of cesium (or H^+), that is 1.5 per KU. Obviously such a value should be understood as implying that one-half of the anions with Keggin structure have one vacancy each while the other half have two vacancies per anion. In the case of $H_4SiMo_{12}O_{40}$ a complete dehydration should produce two vacancies on every anion. Earlier work from this laboratory (*6, 8–10*) on the temperature-programmed desorption of water from heteropolyoxometalates showed that the water which desorbed from the heteropoly acids at high temperatures resulted from the protons stripping oxygen from the Keggin Units. With $H_3PMo_{12}O_{40}$ and $H_3PW_{12}O_{40}$ the equivalent of 1.5 (±0.1) water molecules per KU was measured as compared with 1.9 (±0.1) H_2O/KU with $H_4SiW_{12}O_{40}$.

The initial effect of the cesium appears therefore to be inhibiting the generation of a vacancy by blocking the dehydration reaction (2). However, this effect alone should produce a linear decrease in the activity (such as that shown by the dotted line in Fig. 1B) as evidenced by Fig. 3B for the reduction of the $HPMo/SiO_2$ catalysts with H_2. The discontinuity in the experimental data at 2.2 Cs/KU demonstrates that a second effect of the cesium is extant. Tentatively, it is suggested that such an additional effect may be electronic in nature since cesium, being very electropositive, may perturb the electron density distribution in the Keggin Unit and therefore also in the sites still free (i.e., not blocked by Cs). Since the remaining sites appear to be more active than expected, the effect of this perturbation is apparently advantageous. The maximum deviation from a purely poisoning relationship can be expected at 2 Cs/KU since for that value only one site (vacancy) can still be generated by a dehydration (reaction (2)) on a Keggin Unit while being under the influence of two cesium ions. It is evident from Fig. 1 that the discontinuity occurs at approximately 2.2 Cs/KU, a value in good agreement with that expected from the aforementioned theoretical considerations. The activity at 2.2 Cs/KU may be estimated as approximately double that which would be expected for a purely poisoning phenomenon, a value which clearly demonstrates a substantial effect.

As can be observed in Fig. 3A, this electronic effect has little or no influence on the activation energy, the increase in rate being apparently related to a change in the preexponential factor. This is also consistent with a retention of the original mechanism since the selectivity in the 0–2 Cs/KU range is relatively constant. Since the reaction of the O^- species with CH_4 (reaction (1)) has been shown to occur readily even at very low temperatures (*24*), it is therefore probable that one of the reactions (2)–(3) is the rate-determining step which is influenced by the cesium. Although Mandelovici and Lunsford (*31*) have proposed that the dehydration step (reaction (2)) may be the energy consuming process, it is possible that, in the present system, the electron transfer process (reaction (3)) is rate limiting.

The similarity of the effect of cesium with the Mo, V, and Fe catalysts and the HPMo catalyst is readily apparent. However, with the supported oxides the activity is not completely eliminated by the addition of cesium but reaches a plateau which in the case of the Mo catalyst is higher than that of the initial catalyst activity. In addition, the selectivities which accompany the activities at their plateau do not reproduce that of the support. This suggests that an oxidation process on the supported oxide saturated by cesium may still be occurring, presumably by a mechanism different from that with the HPMo catalyst, even after exchange of all exchangeable protons. It may be recalled that three types of oxygen exist in the heteropolyoxometalate anions with Keggin structure. One of these bridges the central atom of the anion and the peripheral metal atoms while a second interconnects two of the latter atoms. The third type is attached to the peripheral metal atoms and protrudes from the anion. It is the latter type which is directly associated with any protons present and which is presumably removed to form vacancies. While both the heteropoly- and the isopolyoxometalate structures possess oxygen atoms less directly associated with protons it appears that in the latter species, and under the influence of cesium, these oxygens may be capable of conversion to species appropriate for the oxidation process.

It is, however, conceivable that nonexchangeable protons may remain after introduction of saturation quantities of cesium. It may be relevant in this context to note that, in the three supported oxide systems, the selectivity to methanol increases while that to formaldehyde decreases with increasing quantities of cesium. This may be related to the elimination of protons which could be involved in acid-catalyzed methanol conversion processes. Thus, in the case of the supported molybdenum oxide catalyst, the use of cesium as an additive may increase the activity and enhance the production of methanol.

While postulated reactions (1)–(3) are important steps in the catalytic oxidation process, they obviously represent only a part of the overall mechanism which presumably requires the generation of the methyl radical. While the O^- species involved in these reaction steps is apparently responsible for the abstraction of a hydrogen from the methane molecule it is not necessarily directly involved in the oxidation process itself. The subsequent reaction of the methyl radical with other oxygen species will more probably determine the selective or nonselective path that is followed. Haber *et al.* (*37*) have proposed that reaction of the radical with O^- species will result in complete oxidation whereas that with an O^{2-} species will lead to partial oxidation products. As noted previously both types of oxygen are present in heteropoly- and isopolyoxometalate anions and can evidently play important roles in both oxidation processes.

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REFERENCES

1. Kasztelan, S., and Moffat, J. B., *J. Catal.* **106,** 512 (1987).

2. Moffat, J. B., *in* "Proceedings of a Symposium on the Production of Fuels and Chemicals from Natural Gas, Auckland, New Zealand, April 1987"; "Methane Conversion, Studies in Surface Science in Catalysis" (D. M. Bibby, C. D. Chang, and R. F. Howe, Eds.), Vol. 36, Elsevier, Amsterdam, 1988.

3. Kasztelan, S., and Moffat, J. B., *J. Catal.* **109,** 206 (1988).

4. Pope, M. T., "Heteropoly and Isopoly Oxometalates." Springer-Verlag, Berlin, 1983.

5. Highfield, J. G., and Moffat, J. B., *J. Catal.* **88,** 177 (1984).

6. Hodnett, B. K., and Moffat, J. B., *J. Catal.* **88,** 253 (1984).

7. Highfield, J. G., and Moffat, J. B., *J. Catal.* **89,** 185 (1984).

8. Highfield, J. G., Hodnett, B. K., McMonagle, J. B., and Moffat, J. B., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," p. 611. Dechema, Frankfurt-am-Main, 1984.

9. Moffat, J. B., *in* "Catalysis by Acids and Bases" (B. Imelik, C, Naccache, G. Coudurier, Y. Ben Taarit, and J. C. Vedrine, Eds.), p. 17. Elsevier, Amsterdam, 1985.

10. Hodnett, B. K., and Moffat, J. B., *J. Catal.* **91,** 93 (1985).

11. Highfield, J. G., and Moffat, J. B., *J. Catal.* **95,** 108 (1985).

12. Highfield, J. G., and Moffat, J. B., *J. Catal.* **98,** 245 (1986).

13. Moffat, J. B., and Highfield, J. G., "Catalysis on the Energy Scene, Studies in Surface Science and Catalysis" (S. Kaliaguine and A. Mahay, Eds.), Vol. 19, p. 77. Elsevier, Amsterdam, 1984.

14. Moffat, J. B., *J. Mol. Catal.* **26,** 385 (1984); "Proceedings, 9th Iberoamerican Symposium on Catalysis, Lisbon, 1984"; "Catalysis by Acids and Bases" (B. Imelik, C. Naccache, G. Courdurier, Y. Ben Taarit, and J. C. Vedrine, Eds.), p. 17. Elsevier, Amsterdam, 1985; "Catalysis on the Energy Scene, Studies in Surface Science and Catalysis" (S. Kaliaguine and A. Mahay, Eds.), Vol. 19, p. 165. Elsevier, Amsterdam, 1984.

15. Hayashi, H., and Moffat, J. B., *J. Catal.* **77,** 473 (1982).

16. Hayashi, H., and Moffat, J. B., *J. Catal.* **81,** 61 (1983).

17. Hayashi, H., and Moffat, J. B., *J. Catal.* **83,** 192 (1983).

18. Hayashi, H., and Moffat, J. B., *in* "Catalytic Conversion of Synthesis Gas and Alcohols to Chemicals" (R. G. Herman, Ed.), p. 395. Plenum, New York, 1984.

19. Ai, M., *J. Catal.* **71,** 88 (1981).

20. Misono, M., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," p. V487. Dechema, Frankfurt-am-Main, 1984.

21. Ai, M., *Appl. Catal.* **4,** 245 (1982).

22. McMonagle, J. B., and Moffat, J. B., *J. Catal.* **91,** 132 (1985).

23. Mizuno, N., Watanabe, T., and Misono, M., *J. Phys. Chem.* **88,** 80 (1985).

24. Ai, M., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," p. V475. Dechema, Frankfurt-am-Main, 1984.

25. Ai, M., *J. Catal.* **85,** 324 (1984).

26. McMonagle, J. B., and Moffat, J. B., *J. Colloid Interface Sci.* **101,** 479 (1984).

27. Taylor, D. B., McMonagle, J. B., and Moffat, J. B., *J. Colloid Interface Sci.* **108,** 278 (1985).

28. Moffat, J. B., *Polyhedron* **5,** 261 (1986).

29. Moffat, J. B., *in* "Preparation of Catalysts. IV. Studies in Surface Science and Catalysis" (B. Delmon, P. Grange, P. A. Jacobs, and G. Poncelet, Eds.), Vol. 31. Elsevier, Amsterdam, 1987.

30. Nayak, V. S., and Moffat, J. B., *J. Colloid Interface Sci.* **120,** 301 (1987).

31. Mendelovici, L., and Lunsford, J. H., *J. Catal.* **94,** 37 (1985), and references therein.

32. Khan, M. M., and Somorjai, G. A., *J. Catal.* **91,** 263 (1985).

33. Zhen, K. J., Khan, M. M., Mak, C. H., Lewis, K. B., and Somorjai, G. A., *J. Catal.* **94,** 501 (1985).

34. Kasztelan, S., Payen, E., Toulhoat, H., Grimblot, J., and Bonnelle, J. P., *Polyhedron* **5,** 157 (1986).

35. Meunier, G., Mocaer, B., Kasztelan, S., Le Coustumer, L. R., Grimblot, J., and Bonnelle, J. P., *Appl. Catal.* **21,** 329 (1986).

36. Bohme, D. K., and Fehsenfeld, F. C., *Canad. J. Chem.* **47,** 2717 (1969).

37. Grzybowska, B., Haber, J., and James, J., *J. Catal.* **49,** 150 (1977).