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Effects of NH_4^+, Cs^+, and H^+ Counterions of the Molybdophosphate Anion in the Oxidative Dehydrogenation of Isobutyric Acid

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Mixed ammonium–cesium salts of the molybdophosphoric acid ($Cs_x(NH_4)_{3-x}[PMo_{12}O_{40}]$) have been prepared by solid-state cationic exchange using the ammonium salt impregnated with the suitable quantity of cesium nitrate at incipient wetness. Structural characterization of the solids showed that the exchange is quantitative and that ammonium and cesium cations are randomly distributed in the lattice. Catalytic activity of these salts in the oxidative dehydrogenation of isobutyric acid increases as the amount of cesium increases up to 3 Cs per heteropolyanion. Between 3 and 3.1 Cs, the catalytic activity abruptly falls and, simultaneously, the major product switches from methacrylic acid to acetone. This abrupt change in the activities for $x \approx 3$ corresponds to the strong decrease of the rates of formation of methacrylic acid and propene, whereas the rate of formation of acetone remains almost unmodified. Under the conditions of reaction, departure of ammonia was total for $x \geq 2$ and partial for $x < 2$. Therefore, catalysts formed at steady state have to be considered as acid ammonium–cesium salts when $x < 2$ and acid cesium salts when $2 < x < 3$. So, very few protons are needed in order to obtain an active and selective catalyst in MAA.

Key Words: **catalysis; heteropolyanion; ammonium–cesium molybdophosphate; oxidative dehydrogenation; isobutyric acid.**

1. INTRODUCTION

Utilization of Keggin heteropolyacids $H_n[XM_{12}O_{40}]$ in acid or mild oxidation catalyzed reactions has been largely developed in recent years (1–4). Acidic and redox properties depend on the nature of the constitutive metallic elements, usually tungsten, molybdenum, or vanadium: tungstic compounds are more acid but less oxidizing than molybdenum ones, and partial substitution of vanadium for tungsten or molybdenum enhances the oxidizing ability (5, 6). The Brønsted acidity can be controlled by the substitution of metallic cations for protons. For example, $Cs_3[PW_{12}O_{40}]$ does not show any acid catalytic activity for dehydration of alcohols (4, 7–9). On the other hand, progressive Cs^+/H^+ substitution leads to important modifications of the crystalline structure and of the texture of the solid: $H_3[PW_{12}O_{40}]$ has a low surface area (<10 m^2/g), but the cesium salt has a large surface area (about 200 m^2/g) and is microporous (10, 11). The influence of the counterions on the heterogeneous catalytic activity is then rather complex. Conflicting results have been obtained for the oxidative dehydrogenation of isobutyric acid by cesium salts of the molybdophosphoric acid (12–14). According to Akimoto, cesium can enhance the reactivity of the oxygen atoms of the polyanion (12) and the tricesium salt is very active. But, on the other hand, Ai and Misono have reported a decrease of the activity for acid cesium molybdophosphates with increasing amount of cesium (13, 14) and the tricesium salt is fairly inactive.

McGarvey *et al.* have studied the catalytic activity of ammonium, cesium, and mixed ammonium–cesium molybdophosphates obtained by cationic exchange in aqueous solution in the oxidative dehydrogenation of isobutyric acid (IBA) (15, 16). They concluded that the catalytic behavior depends on the Cs^+/NH_4^+ ratio and that even small quantities of ammonium can activate the catalyst.

In an attempt to understand these large effects and somewhat conflicting results, we prepared the mixed ammonium–cesium and tricesium salts by a different method, with the aim of using true stoichiometric salts, i.e., without residual protons, and we tested them for the oxidative dehydrogenation of isobutyric acid.

2. EXPERIMENTAL

2.1. Preparation of the Samples

$(NH_4)_3[PMo_{12}O_{40}]$. Two solutions were prepared. (A) Ten grams of the molybdophosphoric acid were dissolved in 75 ml of a solution of water/dioxane in equal volumes. Then the heteropolyacid was neutralized by a solution of ammonium hydrogenocarbonate, 0.9 M, in water/dioxane in equal volumes. (B) Five grams of ammonium nitrate were dissolved in 35 ml of the water/dioxane mixture. Solution B was added dropwise to solution A under stirring. A bright yellow precipitate of ammonium molybdophosphate appeared slowly, and the mixture was gently

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stirred for about 2 h. The solid was collected by filtration through a fine frit, washed with cold water, and dried at 120°C for 1 h.

Before characterization and catalytic testing, the ammonium salt was heated under N_2 flow (20 ml/min) using the following procedure: (a) the temperature was raised to 250°C over 1 h (3.83°C/min) and maintained for 20 h at this temperature; (b) the temperature was raised again to 350°C at 0.42°C/min and maintained for 30 h at this temperature; (c) the sample was cooled to room temperature. Analysis, %exp (theor.): Mo 56.97 (57.08), N 2.08 (2.07), P 1.67 (1.54).

$Cs_3[PMo_{12}O_{40}]$. Two solutions were prepared. (A) Ten grams of molybdophosphoric acid were dissolved in 110 ml of a solution of water/dioxane (2/3). Then the heteropolyacid was neutralized by addition of a solution of lithium hydrogenocarbonate, about 0.5 M, until pH 4.5–5.5 (29 ml). The solution of lithium hydrogenocarbonate was obtained by bubbling CO_2 in a solution of lithium hydroxide, 0.5 M, and it was titrated by HCl. (B) Three grams of cesium nitrate were dissolved in 50 ml of the water/dioxane mixture (1/1) at 60°C. Solution B was added dropwise to solution A at 40°C under stirring. A yellow precipitate of cesium molybdophosphate appeared immediately. The solid was collected by filtration through a fine frit, washed with cold water, and dried at room temperature for 2 days.

$Cs_x(NH_4)_{3-x}[PMo_{12}O_{40}]$, ($x = 1, 2, 3, 3.1, 3.3, 3.5$). A series of mixed ammonium–cesium salts was prepared by thermal treatment of a solid mixture of ammonium molybdophosphate and cesium nitrate: five grams of the insoluble $(NH_4)_3[PMo_{12}O_{40}]$ salt ($2.48\ 10^{-3}$ mol), first dehydrated for 1 h at 100°C, was impregnated at incipient wetness by ($x * 2.48 \times 10^{-3}$) mol cesium nitrate dissolved in 5 ml water. The solid was then dried for 90 min at 120°C and ground using a pestle and a mortar. The thermal treatment presented above for $(NH_4)_3[PMo_{12}O_{40}]$ allowed the Cs^+/NH_4^+ cationic exchange with simultaneous decomposition of ammonium nitrate beginning at 210°C. The results of elemental analysis and thermogravimetric analysis agreed with the expected formula and revealed that a quantitative exchange was obtained whatever the x value.

2.2. Oxidative Dehydrogenation of Isobutyric Acid

Reactions were carried out at 320°C using a continuous flow pyrex microcatalytic reactor at atmospheric pressure. The feed gas consisted of 2% IBA, 5.2% O_2, and N_2 balance. The total flow rate was 180 ml/min. The catalyst (1 g) was introduced in the reactor and reached the temperature of reaction in 30 min under an air flux of 180 ml/min. All reaction products were analyzed by on-line gas-phase chromatography with molecular sieves 5A, Porapak Q, and AT 1200 with 1% H_3PO_4 columns. The carbon, oxygen, and hydrogen balances were in the range 90–100%.

2.3. Characterization Methods

Nitrogen adsorption–desorption isotherms were obtained using a Micromeritics ASAP 2010 apparatus. The samples were evacuated at 150°C for 3 h. The results were analyzed by the ASAP 2010 V3.00 program. Morphologies of the catalysts were investigated by SEM using a JEOL JSM-5800LV microscope.

The X-ray diffraction patterns were recorded at room temperature with a Siemens D 5000 diffractometer using Cu $K\alpha$ radiation ($\lambda = 1.5418$ Å) and were fitted by means of the Socabim program PROFILE. The unit cell parameters were determined with the program DICVOL91 (17a) and were refined by means of the program NBS* AIDS83 (17b). X-ray thermodiffractometry was performed under air in an Anton Paar HTK16 high-temperature device of a Siemens D 5000 diffractometer (θ–θ mode) using Co Kα radiation ($\lambda = 1.7903$ Å) and equipped with an M Braun linear position-sensitive detector (PSD). Samples were deposited directly on the heating platinum support connected to a thermocouple. Patterns were recorded from 30 to 610°C every 20°C, with a temperature ramp of 1.8°C min^{-1}. The temperature was stabilized 2 min before every measurement; each data collection lasted 570 s.

Thermogravimetric analysis was carried out under air flow (50 ml/min) with a Perkin–Elmer electrobalance TGA-7 with a heating rate of 5°C/min up to 600°C. The infrared spectra (KBr pellets) were recorded on a Fourier-transformed Nicolet 550 apparatus.

The solution ^{31}P NMR spectra were recorded on a Brucker AC 300 apparatus at 121.5 MHz. Chemical shifts are referenced to 85% H_3PO_4.

3. RESULTS

3.1. Preparations of the Mixed Ammonium–Cesium Salts

Ammonium or cesium 12-molybdophosphates are usually obtained by addition of ammonium or cesium chloride (nitrate) to the solution of the heteropolyacid and filtration of the solid. An alternative method is the addition of ammonium (cesium) carbonate in a stoichiometric amount and evaporation of water. In the first case, it is difficult to eliminate the protons quantitatively, and salts of mean composition $M_{3-x}H_x[PMo_{12}O_{40}]$ ($x \sim 0.3$) are currently obtained (18). In the second method, it is our experience that the basicity of CO_3^{2-} is enough to partially decompose the $[PMo_{12}O_{40}]^{3-}$ anion that is stable only at pH < 2 in aqueous solution. In order to avoid hydrolysis of the heteropolyanion, bases of lower strength can be used. Another way is to utilize mixed water/organic solvent such as water/dioxane since hydroorganic solvents are known to stabilize the heteropolyanions. Hydrogenocarbonate ion was chosen to neutralize acidity, and ammonium or cesium nitrate were then added to obtain the desired salts. The

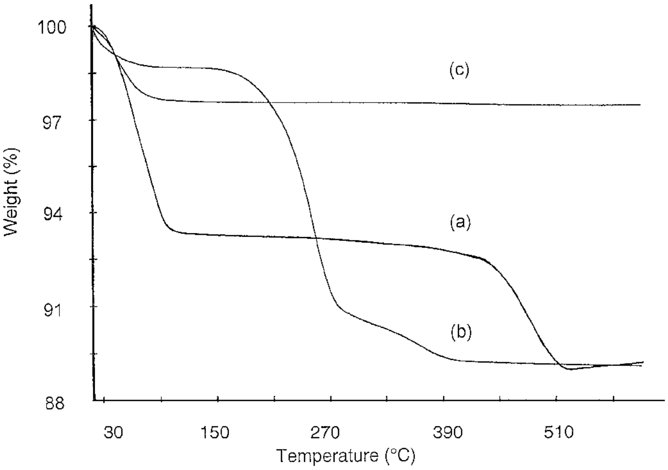


FIG. 1. Thermogravimetric curves recorded under air flow of (a) $(NH_4)_3PMo_{12}O_{40}$, (b) $(NH_4)_3PMo_{12}O_{40} + 3CsNO_3$ dried at 100°C, and (c) $(NH_4)_3PMo_{12}O_{40} + 3CsNO_3$ after thermal exchange.

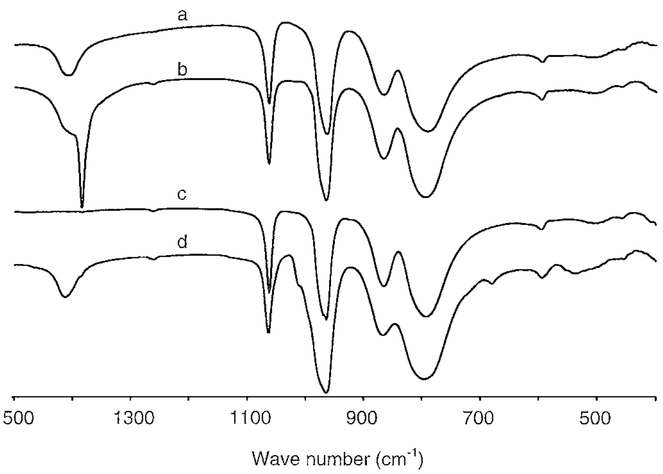


FIG. 2. Infrared spectra of $(NH_4)_3PMo_{12}O_{40}$ (a), $(NH_4)_3PMo_{12}O_{40}$ impregnated by $3CsNO_3$ (b), $(NH_4)_3PMo_{12}O_{40}$ impregnated by $3CsNO_3$ after thermal exchange (c), and $(NH_4)_3PMo_{12}O_{40}$ after reaction (d).

stability of the $PMo_{12}O_{40}^{3-}$ was checked by ^{31}P NMR during the neutralization by $(NH_4)HCO_3$. Its chemical shift slightly increases from −3.10 to −2.99 ppm at the neutralization (3 equivalents). It is only above neutralization (3.5 equivalent) that other weak peaks appear at −0.51 ppm (15%) and −1.85 ppm (2%) when an excess of hydrogenocarbonate was introduced. Therefore it is possible to neutralize the heteropolyacid in this solvent without any decomposition. This method assures the decoupling of neutralization and precipitation steps in order to obtain the required triammonium or tricesium salts without residual protons as indicated by elemental analysis.

The mixed ammonium–cesium salts were obtained by solid-state cationic Cs^+/NH_4^+ exchange which occurred during a thermal treatment of the ammonium salt impregnated by cesium nitrate. The exchange is promoted by the decomposition of ammonium nitrate at temperatures higher than 210°C. Figure 1 shows the thermogravimetric curves of $(NH_4)_3[PMo_{12}O_{40}]$ (a) and of the $(NH_4)_3[PMo_{12}O_{40}] + 3CsNO_3$ mixture (b). Ammonia was eliminated at temperatures higher than 410°C for the pure ammonium salt. The weight loss observed between 150 and 270°C on curve (b) was attributed to the decomposition of ammonium nitrate since the relative intensity of the bands at 1409 ($\delta_d NH_4^+$) and 1385 cm^{-1} ($\nu_d NO_3^-$) on the IR spectrum strongly decreased after a thermal treatment at 270°C. Actually, a treatment temperature of 350°C was required in order to observe a complete Cs^+/NH_4^+ exchange. But, if the treatment was performed directly at 350°C, some lines of molybdenum trioxide appeared on the X-ray powder diffraction pattern, showing a partial decomposition of the heteropolyanion. The treatment was then performed in two steps, first, at 250°C in order to eliminate more than 80% of the ammonium nitrate and, second, at 350°C in order to complete the cationic exchange. Under these conditions, no decomposition of the heteropolyanion was observed and a quantitative substitution of cesium for ammonium can be obtained as shown by infrared spectroscopy (Fig. 2), RX, TGA, and elemental analysis.

3.2. Characterization of the Catalysts before Reaction

Ammonium, cesium, and mixed ammonium–cesium salts crystallize in a cubic lattice, as previously reported for the pure salts (10). Progressive substitution of Cs^+ for NH_4^+ leads to a linear change of the lattice parameter (Fig. 3) according to Végard's law, suggesting a random distribution of the cations in the lattice.

Evolution of the X-ray powder patterns of $(NH_4)_3[PMo_{12}O_{40}]$ with temperature reveals a decomposition in α and β MoO_3 at about 410°C when ammonia is eliminated. In contrast, as is well known, the cesium salt is stable up to 600°C. All the mixed salts $Cs_x(NH_4)_{3-x}[PMo_{12}O_{40}]$ with $x < 3$ present one cubic phase until 410°C. At this

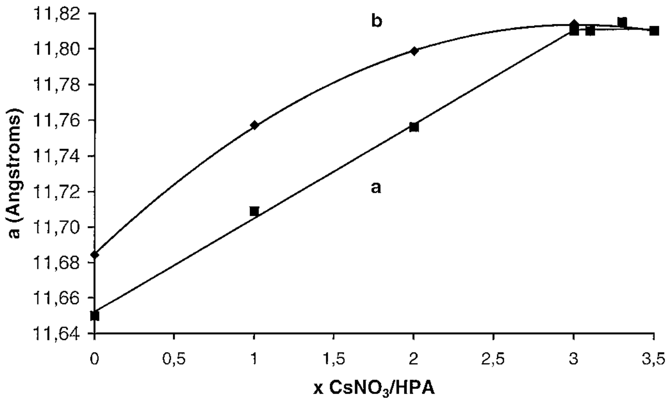


FIG. 3. Lattice parameter of $Cs_x(NH_4)_{3-x}PMo_{12}O_{40}$ as a function of $xCsNO_3$ before (a) and after (b) reaction.

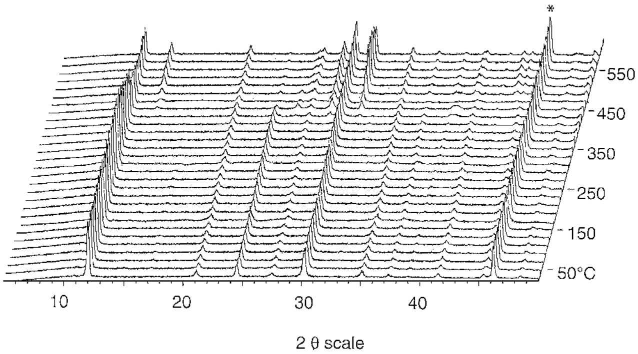


FIG. 4. X-ray diffraction patterns recorded every 20°C from 30 to 590°C under static atmosphere and using Co $K\alpha$ radiation of $Cs_{1.5}(NH_4)_{1.5}PMo_{12}O_{40}$. (The asterisk indicates the line of Pt, 2θ scale.)

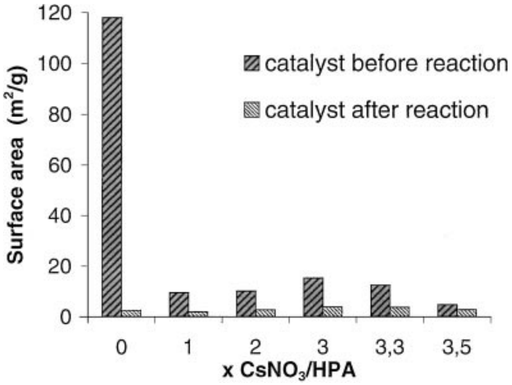


FIG. 5. Surface area of $Cs_x(NH_4)_{3-x}PMo_{12}O_{40}$ as a function of x before and after reaction.

temperature molybdenum oxide phases appear in decreasing proportion as x increases. Therefore, the stability of the heteropolyanion is not increased by the partial substitution of Cs^+ for NH_4^+ (Fig. 4).

The ammonium salt obtained in water/dioxane solvent has a surface area of 120 m^2/g, which is slightly lower than the values observed when this salt was obtained from pure aqueous solution (150 to 180 m^2/g). Thermal treatment at 250°C then 350°C does not modify the surface area. Variation of the surface area of the solids obtained by Cs^+/NH_4^+ thermal exchange with the quantity of Cs^+ is shown in Fig. 5. All the samples have a surface area of 10–15 m^2/g. Therefore, the Cs^+/NH_4^+ exchange, even with small quantities of cesium, leads to a collapse of the porous structure.

The morphology of the catalysts was observed by electron microscopy. The ammonium salt (Fig. 6) is composed of spherical aggregates of 2.5-μm average diameter. After thermal exchange the resulting mixed ammonium–cesium salts and the tricesium salt present the same morphology. The cesium salt obtained by precipitation after neutralization in water/dioxane solution also forms spherical aggregates of 1- to 3-μm diameter. On the other hand, the tricesium salt obtained by precipitation in pure aqueous solution, studied for comparison, shows a quite different aspect: fine particles (0.25 μm) form irregular large plates (>5 μm).

3.3. Catalytic Oxidative Dehydrogenation of Isobutyric Acid

The catalytic activity and selectivities of $(NH_4)_3[PMo_{12}O_{40}]$ and $Cs_3[PMo_{12}O_{40}]$ obtained by precipitation from the water/dioxane solution, reported in Table 1, are in good agreement with those previously reported (14, 16). Conversion of the triammonium salts decreased continuously with time from 60 to 47% after 18 h. For the tricesium salt the conversion remained very low, about 8%. The selectivities of these two salts differed strongly: the major product was methacrylic acid (48%) for the ammonium salts but was acetone (55%) for the cesium salt.

TABLE 1

Catalytic Activities after 18 h of Reaction for 1 g of Hetropolysalts

	IBA conversion	Selectivities				
		MAA	Acetone	Propene	AcOH	COx[a]
$(NH_4)_3[PMo_{12}O_{40}]$	47	48	29	19	1	3
$(NH_4)_3[PMo_{12}O_{40}]$ $+ x CsNO_3$ treated						
$x = 1$	45	48	28	20	1	3
$x = 2$	55	45	29	22	1	3
$x = 3$	73	57	23	16	2	4
$x = 3.1$	18	50	30	15	0	5
$x = 3.3$	15	6	80	8	0	6
$x = 3.5$	20	5	87	6	0	3
$Cs_3[PMo_{12}O_{40}]$	8	14	55	17	0	13

[a] The selectivities to COx are obtained after the subtraction of the contributions of the reaction of formation of acetone propene and acetic acid.

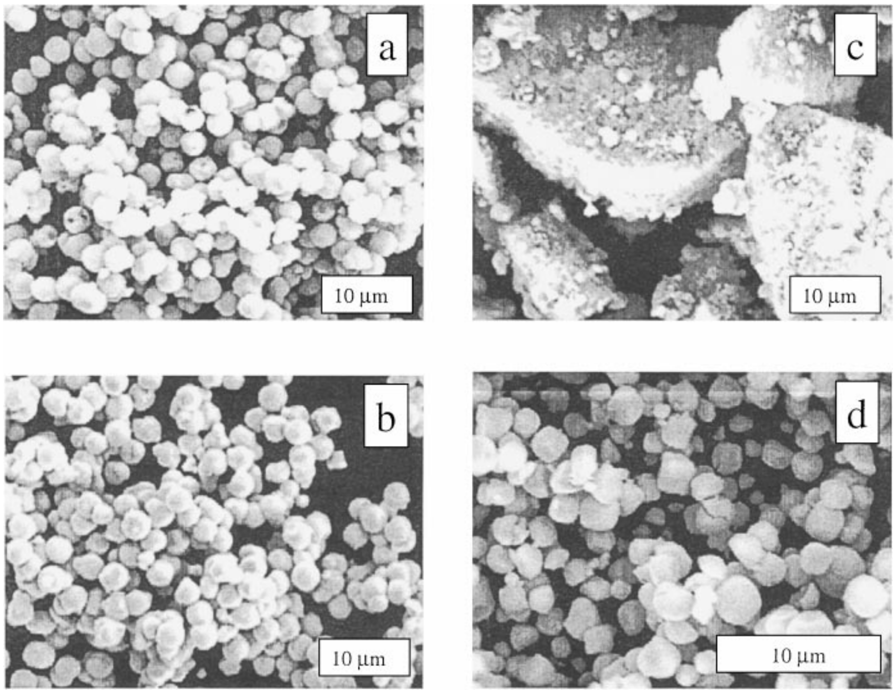


FIG. 6. SEM images of $(NH_4)_3PMo_{12}O_{40}$ (a), $(NH_4)_3PMo_{12}O_{40} + 3CsNO_3$ after thermal exchange (b), $Cs_3PMo_{12}O_{40}$ obtained by precipitation in water (c), and in water/dioxane (d).

The mixed ammonium–cesium salts obtained by thermal exchange reached a steady state after 12 h of reaction. The results obtained after 18 h are presented in Fig. 7. Conversion of IBA, which was 47% for the ammonium salt, was not modified for $x = 1$ but increased to 73% for $x = 3$. Selectivity to MAA was constant (46%) up to $x = 2$ and reached 57% for $x = 3$. Conversely, the selectivity to acetone and propene decreased between $x = 2$ and $x = 3$. Acetic acid and CO_x were obtained in small proportions.

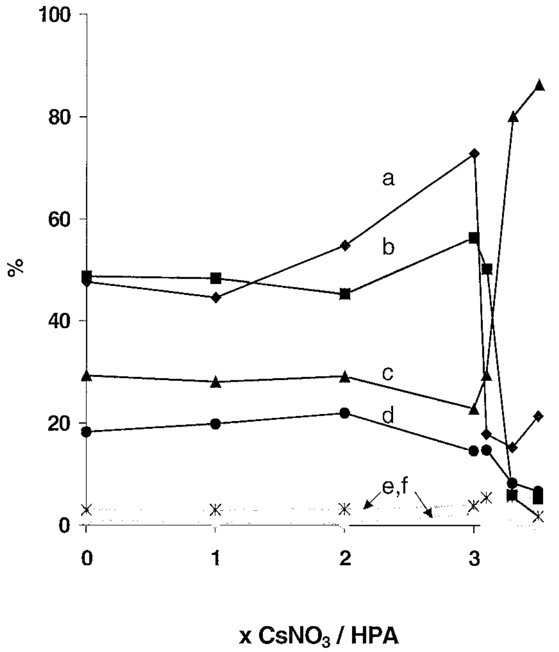


FIG. 7. Catalytic activity at 320°C of $Cs_x(NH_4)_{3-x}PMo_{12}O_{40}$ after 18 h as a function of x: IBA conversion (a) and selectivity to methacrylic acid (b), acetone (c), propene (d), carbone oxides (e), and acetic acid (f).

A drastic decrease in the measured catalytic activity was observed when the composition was close to $Cs^+/[PMo_{12}O_{40}]^{3-} = 3$, corresponding to the stoichiometric salt. The conversion fell from 73% for $x = 3$ to 15% for $x = 3.3$. At the same time, selectivities were strongly modified, 56 to 6% in MAA and 23 to 80% in ACE. Several preparations and experiments were performed to confirm this observation.

3.4. *Characterization of the Catalysts after Reaction*

Elemental analysis showed that the amount of ammonium cations was smaller after catalytic testing than in the initial solids (Table 2). In agreement, the intensity of the NH_4^+ vibration at 1400 cm^{-1} on the IR spectrum decreased (Fig. 2). The loss of ammonia was very important during the reaction since the percentage of ammonia release reached 43% for $x = 0$, 50% for $x = 1$, and 100% for $x = 2$. Catalysts corresponding to $x \geq 2$ did not contain any more ammonium ion at the steady state.

The surface areas of all the samples were between 2 and 4 m^2/g after reaction, whatever the Cs^+/NH_4^+ initial composition (Fig. 5). Electron microscopy showed that the catalytic reaction did not modify the morphology of the

TABLE 2

Composition of $Cs_x(NH_4)_{3-x}[PMo_{12}O_{40}]$ Determined by Elemental Analysis (1), Thermogravimetric Analysis (2), and Elemental Analysis after Reaction (3)

x	0	1	2	3
NH_4^+/HPA (1)	2.92	1.89	0.87	/
NH_4^+/HPA (2)	3.20	2.04	1.00	/
NH_4^+/HPA (3)	1.74	0.87	/	/

Note. (1) Under the limit of analysis.

particles. X-ray diffraction patterns of all the catalysts after reaction showed only the cubic-phase isotype with ammonium and cesium salts, but with a lattice parameter significantly increased, except for x close to 3 (Fig. 3).

The catalysts were blue after reaction when the initial ammonium proportion was high, showing that they were significantly reduced. This color disappeared progressively as the cesium proportion increased, and the active exchanged salt corresponding to $x = 3$ was yellow-green after reaction and was then not reduced at the steady state. The nonactive samples corresponding to $x > 3$ were also yellow-green.

4. DISCUSSION

In a previous study, McGarvey *et al.* (11, 16) studied the catalytic behavior of mixed ammonium–cesium molybdophosphates for the oxidative dehydrogenation of isobutyric acid. These salts were obtained by ionic exchange between ammonium and cesium cations in aqueous solution, starting from the insoluble ammonium or cesium salts. Self-exchanges have been also performed to substitute residual protons of initial ammonium or cesium salts in order to approach the stoichiometric composition in NH_4^+ or Cs^+. Nevertheless protons were still present as shown by elemental analysis (16). A conclusion of this study was that the tricesium salt is a little active but that small quantities of ammonium cations enhance greatly both the catalytic activity and the selectivity to methacrylic acid.

In the present work, ammonium, cesium, and mixed ammonium–cesium salts were obtained by a new method. First, stoichiometric triammonium or tricesium salts were obtained after neutralization of the heteropolyacid by a base of moderate strength in dioxane/water solvent. In this medium, the neutral heteropolyanion is stable and solid triammonium or tricesium salts can be obtained by addition of the suitable nitrate.

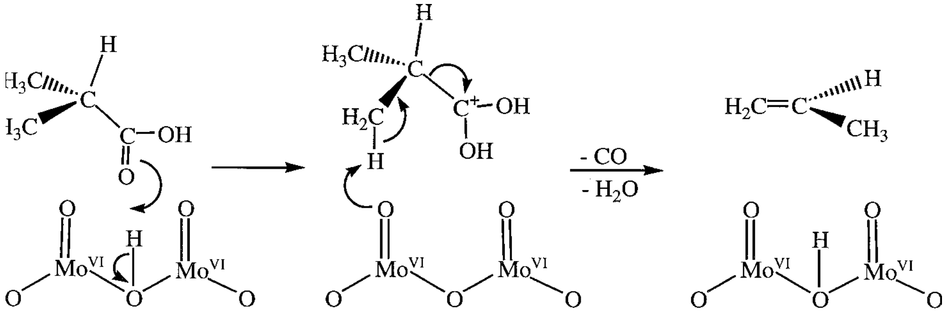
The catalytic activity of the triammonium salt decreases with time, from 60 to 47% after 18 h reaction. Characterization after reaction revealed a release of about 40% of the initial ammonium quantity, a decrease of the surface area, an increase of the unit cell parameter, and a reduced state of the catalyst. The first important point is the loss of ammonium, which could be correlated to the progressive decrease of the conversion of IBA with time. Since protons must remain after the release of ammonia, the catalyst has to be considered either as a mixed NH_4^+/H^+ salt or as a mixture of ammonium salt and acid. X-ray patterns display only the cubic phase characterizing the ammonium salt, but with a slightly greater unit cell parameter, perhaps because of the partial reduction of the heteropolyanion. It should be noted that an acid phase eventually formed could be difficult to identify by X-ray diffraction since acid is often poorly crystallized after catalytic reactions.

It is noteworthy that the loss of ammonium occurs at lower temperature under reaction conditions other than N_2 or air flux. Formation of isobutyronitrile or methacrylonitrile has been reported in the presence of the ammonium salt (16), but none of these products were detected in this work. It is known that ammonium partially reduces the heteropolyanion on evacuation (19), so the loss of ammonia can be due to its oxidation catalyzed by the heteropolyanion itself. Such a redox reaction could explain the deep blue color of the ammonium salt, revealing the reduction of the catalyst.

For the mixed ammonium–cesium salts, the proportion of ammonium lost during the reaction increases from 40% for $x = 0$ to 100% for $x > 2$. So, the catalysts after reaction have to be considered as $Cs^+/NH_4^+/H^+$ salts when $x < 2$ and as Cs^+/H^+ salts when $2 < x < 3$. X-ray patterns show only the cubic phase with a lattice parameter systematically greater than before catalytic test (Fig. 3). This variation corresponds to the increase of the Cs^+/NH_4^+ ratio following the reaction. For $x > 2$, the lattice parameter is that of the tricesium salt. Once again, formation of acid cesium salts or of a mixture of tricesium and acid phases should have occurred.

The oxidative dehydrogenation of isobutyric acid is a bulk type (II) reaction (20). McGarvey *et al.* did not mention any influence of the surface area on the reactivity for mixed ammonium and cesium salts (16). Moreover, a correlation between the catalytic activity and the surface acidity calculated from the value of the surface area before reaction has been established for $Cs^+–H^+$ mixed salts of the $[PMo_{11}VO_{40}]^{4-}$ heteropolyanion (21). The catalysts studied in this work have a low surface area before catalytic test, about 10 m^2/g whatever the Cs^+/NH_4^+ ratio, and a lower surface area at the steady state (~ 2 m^2/g). Since all the catalysts have quite the same low surface area, variations of the catalytic activity and selectivities are essentially dependent on other factors.

A decrease of the reduction state of the catalysts at the steady state was observed as the cesium fraction increased, suggesting that cesium enhances the rate of oxidation of the reduced catalysts. The rate of oxidation by O_2 of acid–cesium molybdophosphates previously reduced by H_2 was studied by Misono (14). The tricesium salt showed the higher rate of oxidation, and the reversibility of the reaction



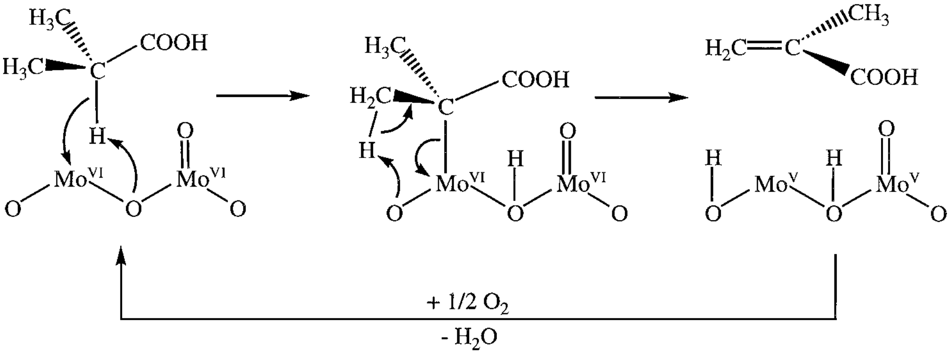
SCHEME 1

reached 97%. In agreement with these results, we observed that the active salt corresponding to $x = 3$ was fully oxidized at the steady state.

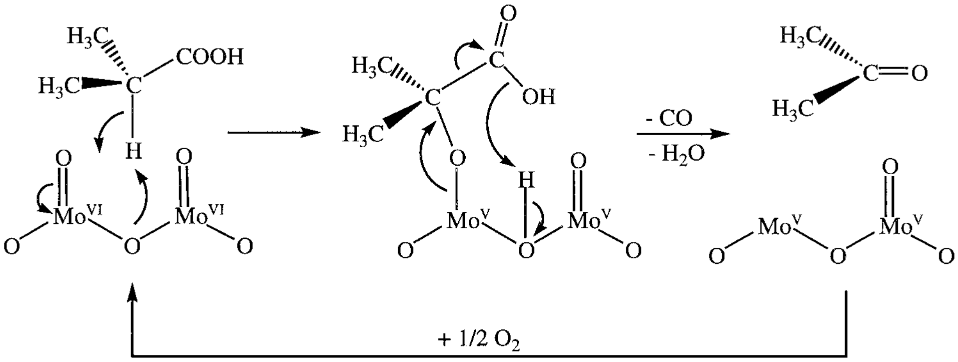
The catalytic activity decreases abruptly when the composition of the catalyst approaches that of the neutral tricesium salt. McGarvey *et al.* (16) have reported that for the mixed ammonium–cesium salts, only small quantities of the ammonium ions are required to maximize the methacrylic acid selectivity. Results of the present study are in agreement with this conclusion if the initial composition of the catalyst is considered. Actually, the cations in the active catalysts are Cs^+ and H^+ since ammonia is quantitatively eliminated during the reaction if $x > 2$. Therefore, the conclusion is that very few protons, not ammonium cations, are sufficient to obtain an active catalyst in the oxidative dehydrogenation of isobutyric acid.

When all the protons are eliminated ($x > 3$) acetone becomes the most abundant product, essentially because of the strong decrease of the rate of formation of methacrylic acid and also of propene, likely due to the disappearance of the corresponding catalytic sites. The decrease of the propene formation rate is evidently due to the lack of Brønsted acid sites since it is obtained by an acid-catalyzed mechanism (Scheme 1). Several redox mechanisms have been proposed in order to explain the concurrent formation of methacrylic acid and acetone. They involve the formation of a common intermediate that can yield either methacrylic acid or acetone. Otake and Onoda have proposed a heterolytic process (23) in which the proton in the α position to the carboxyl group is first eliminated by nucleophilic attack by an oxygen atom of the heteropolyanion. Echigoya has proposed a homolytic process (12). Later, McGarvey *et al.* suggested a heterolytic process involving the initial abstraction of a hydride ion to yield a carbocation (16) which can yield methacrylic acid by abstraction of a proton or acetone by nucleophilic attack of an oxygen atom.

The strong decrease of the rate of formation of methacrylic acid when protons are quantitatively eliminated shows that methacrylic acid formation, but not acetone formation, needs acid sites, as was also previously reported by Ai (24) for the study of the oxidative dehydrogenation of isobutyric acid over the $H_5[PMo_{10}V_2O_{40}]$ heteropolyacid. Thus, two parallel routes of activation of the isobutyric molecule yielding methacrylic acid and acetone can be proposed. It can be observed that, at the temperature of the reaction (320°C), elimination of constitutional water occurs, at least partially, and generates coordinatively unsaturated molybdenum cations. Thus, molybdenum atoms should have both Lewis acid and oxidizing properties. The possibility exists for formation of an organometallic intermediate (Lewis acid properties of Mo, Scheme 2) of limited stability at the temperature of reaction, whereby a concerted transfer of electrons (oxidizing properties of Mo) yields methacrylic acid. In this second step, the formation of



SCHEME 2



SCHEME 3

the double bond involves the attack of the α hydrogen atom by an oxygen atom of the heteropolyanion (basic site). With the tricesium salt, no Lewis acid site could be generated and methacrylic acid would not be obtained. In contrast, in the first step of oxidation of isobutyric acid in acetone (Scheme 3), both oxygen basic sites and oxidizing properties of molybdenum can be implied. The breaking of the Mo–O bond is then assisted by a decarbonylation process in the second step.

The role of cesium counterions of heteropolyanions in acid and redox catalytic reactions has been largely studied. It is generally assumed that cesium enhances the thermal stability of the heteropolycompound. This conclusion is not right for mixed cubic ammonium–cesium salts since crystallized MoO_3 appears always at about 410°C (Fig. 4) whatever the x value if $x < 3$. In addition, owing to their low electronegativity and large size, the interaction of Cs^+ cations with oxygen atoms is likely to be weak, and oxygen atoms keep basic properties which play an important role in the transformation of the isobutyric molecule (Schemes 2 and 3). The last step in the two catalytic redox reactions involves reoxidation of the catalyst. Perhaps the most important role of cesium is to enhance the rate of oxidation of the reduced catalyst by dioxygen, solids being almost fully oxidized at the steady state.

In conclusion, with nearly stoichiometric cesium salts, some heteropolyanions deficient in oxygen would be well dispersed on the surface layer and would be oxidized at the steady state, increasing the selectivity for the oxidation of isobutyric acid to methacrylic acid.

Now it is possible to examine the apparent discrepancy between some results in the literature, keeping in mind that a very small proportion of protons, which are very difficult to detect, can induce high reactivity for cesium salts. The high catalytic activity observed by Akimoto (12) for the tricesium salt would be related to salts with traces of protons. In other works (13, 14), true stoichiometric salts were likely obtained since protons were quantitatively neutralized by cesium carbonate.

An almost linear decrease of the catalytic activity with increasing cesium content has been reported for acidic-cesium salts of $[PMo_{12}O_{40}]^{3-}$ prepared by partial neutralization of the protons by addition of cesium carbonate and evaporation of water to dryness (14). It is now established that this method of preparation leads to the formation of tricesium salt particles embedded in a bulk acid phase for $x < 2$, whereas tricesium salt particles appear to be coated with a thin film of the acid for higher cesium contents (22).

So, it appears that the catalytic activity of such acidic cesium salts decreases as the amount of the surface layer acid phase decreases. A very different behavior was observed with the ammonium-cesium salts obtained by thermal exchange since the catalytic activity increases with cesium content up to 3 and falls just after. The catalysts studied in this work might be at the steady state a solid solution with $NH_4^+/Cs^+/H^+$ cations for $x < 2$ and Cs^+/H^+ cations when $x > 2$. It can be suggested that the particular catalytic behavior of these catalysts is related to the random distribution of the cations in the solid and, likely on the surface.

REFERENCES

1. Misono, M., *Catal. Rev. Sci. Eng.* **29**(2-3), 269 (1987).
2. Misono, M., and Nojiri, N., *Appl. Catal.* **64**, 1 (190).
3. Kozhevnikov, I. V., *Catal. Rev. Sci. Eng.* **37**(2), 311 (1995).
4. Okuhara, T., Mizuno, N., and Misono, M., *Adv. Catal.* **41**, 113 (1996).
5. Pope, M. T., “Heteropoly and Isopoly Oxometalates,” Inorganic Chemistry Concepts, Vol. 8. Springer–Verlag, New York, 1983.
6. Marchal, C., Davidson, A., Thouvenot, R., and Hervé, G., *J. Chem. Soc. Faraday Trans. 1* **89**, 3301 (1993).
7. Okuhara, T., Kasai, A., Hayakawa, N., Yoneda, Y., and Misono, M., *J. Catal.* **83**, 121 (1983).
8. Tatematsu, S., Hibi, T., Okuhara, T., and Misono, M., *Chem. Lett.*, 865 (1984).
9. Ebeid, F., Ali, L., and Ali, A., *Bull. Soc. Chim. Fr.* **128**, 644 (1991).
10. McGarvey, G. B., and Moffat, J. B., *J. Colloid Interface Sci.* **101**, 51 (1988).
11. McGarvey, G. B., and Moffat, J. B., *J. Catal.* **130**, 483 (1991).
12. Akimoto, M., Tsuchida, Y., Sato, K., and Echigoya, E., *J. Catal.* **72**, 83 (1981).

13. Ai, M., *Appl. Catal.* **4**, 245 (1982).
14. Misono, M., Mizuno, N., and Komaya, T., *in* "Proceedings, 8th International Congress on Catalysis, Berlin, 1984," Vol. 5. Dechema, Frankfurt-am-Main, 1984.
15. McGarvey, G. B., and Moffat, J. B., *J. Catal.* **128**, 69 (1991).
16. McGarvey, G. B., and Moffat, J. B., *J. Catal.* **132**, 100 (1991).
17. (a) Boultif, A., and Louër, D., *J. Appl. Crystallogr.* **24**, 987 (1991); (b) Mighell, A. D., Hubbard, C. R., and Stalik, J. K., "NBS*AIDS80: A Fortran Program for Crystallographic Data Evaluation," National Bureau of Standards (U.S). Technical Note 1141, 1981. [NBS*AIDS83 is an expanded version of NBS*AIDS80.]
18. Highfield, J. G., and Moffat, J. B., *J. Catal.* **98**, 245 (1986).
19. Albonetti, S., Cavani, F., Trifiro, F., Gazzano, M., Koutyrev, M., Aissi, F. C., Aboukais, A., and Guelton, M., *J. Catal.* **146**, 491 (1994).
20. Mizuno, N., Watanabe, T., Mori, H., and Misono, M., *J. Catal.* **123**, 157 (1990).
21. Lee, K. Y., Oishi, S., Igarashi, H., and Misono, M., *Catal. Today* **33**, 183 (1997).
22. Langpape, M., Millet, J. M. M., Ozkan, U. S., and Boudeulle, M., *J. Catal.* **181**, 80 (1999).
23. Otake, M., and Onoda, T., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), p. 780. Elsevier, Amsterdam, 1981.
24. Ai, M., *J. Catal.* **98**, 401 (1986).