JOURNAL OF CATALYSIS 146, 491–502 (1994)

Mechanism of Thermal Decomposition of Potassium/Ammonium Salts of the 12-Molybdophosphoric Acid and Effect on the Catalytic Performance in the Isobutyric Acid Oxidehydrogenation

S. Albonetti, F. Cavani, F. Trifirò, M. Gazzano, M. Koutyrev, F. C. Aissi, A. Aboukais, and M. Guelton

Dipartimento di Chimica Industriale e dei Materiali, Viale Risorgimento 4, 40136 Bologna, Italy; CFSM-CNR, Via Selmi 2, 40136 Bologna, Italy; Institute of Chemical Physics, Academy of Sciences, Ul. Kossygina 4, 117334 Moscow, Russia; and Laboratoire de Catalyse Heterogene et Homogene, URA CNRS D04020, 59655 Villeneuve D'Ascq Cedex, France

Received February 3, 1993; revised November 9, 1993

Heteropolycompounds of the composition $K_x(NH_4)_{3-x}PMo_{12}O_{40}$ were prepared by precipitation, through addition of HNO_3 to an aqueous solution of the salts. The precipitated compounds were calcined at increasing temperatures to evaluate the thermal behavior, and were characterized by means of X-ray diffraction, FTIR spectroscopy, surface area measurements, ionic chromatography, EPR spectroscopy, and reactivity in the oxidative dehydrogenation of isobutyric acid to methacrylic acid. A monophasic system was obtained by calcination at 640 K, with patterns characteristic of the Keggin-type cubic secondary structure. The cationic composition was found to be very close to that expected for the complete salification of the Keggin anion. The structural decomposition began at temperatures close to 693 K for the ammonium and ammonium/potassium compounds, with formation of an intermediate heteropolycompound characterized by crystallographic parameters and cationic composition different from the original one and more stable than the latter. The potassium salt remained instead structurally intact up to 753 K. The data were interpreted with the assumption that the decomposition of the heteropolycompound might occur in a stepwise way, with an initial structural collapse of a part of the compound and displacement of some molybdenum ions (originally located in peripheral position in the Keggin anion) in the cationic position of the not yet decomposed compound. The highest amount of this intermediate molybdenum-salified heteropolycompound apparently formed during decomposition of the $(NH_4)_3PMo_{12}O_{40}$ compound. The calcination temperature remarkably affected the catalytic behavior in the oxidative dehydrogenation of isobutyric acid to methacrylic acid. The partial structural collapse occurring by calcination at 693 K led to a decrease in the activity for the potassium/ammonium mixed salts. On the contrary, the ammonium salt increased its activity. It was assumed that this phenomenon could be due to the formation of the intermediate molybdenum-salified heteropolycompound. © 1994 Academic Press, Inc.

INTRODUCTION

Catalytic applications of heteropolyanions have attracted increasing interest in the past decade. Catalysts based on polyoxometallates with the Keggin structure have been particularly studied (1). These compounds have been shown to be efficient in various chemical processes. Heteropolycompounds are particularly interesting as catalysts because their redox and acidic properties, as well as their catalytic performances, may be modified by an appropriate change in their composition (2, 3). However, widespread practical use of these compounds has been hindered by the complexity and poor reproducibility of the methods of synthesis, which usually involve several stages, and by their structural instability. Many studies have been reported in the literature, characterizing Keggin-type heteropolycompounds to be utilized as heterogeneous catalysts (4–15).

Black *et al.* (4) have characterized $K_xH_{3-x}PMo_{12}O_{40}$ catalysts. In this series, no significant solid-solution range was detected and the standard preparation gave stoichiometric mixtures of $K_3PMo_{12}O_{40}$ and $H_3PMo_{12}O_{40}$. The acid phase decomposed at low temperature, even though a stabilization effect induced by an epitaxy between the K_3 phase and the H_3 phase was shown to shift the decomposition towards slightly higher temperatures.

Moffat and co-workers (8, 11, 17, 26, 28–30) have investigated the nature of the formation of microporous heteropolycompounds and the ion-exchange processes which occur in several heteropolyoxometallate salts of 12-tungstophosphoric acid and 12-molybdophosphoric acid. These studies have shown the existence of a single crystallographic phase after calcination at 523–573 K. Moreover, the ion-exchange behavior and pore structure of the heteropolycompounds were found to depend considerably on the nature of the cation introduced in the structure. While heteropolyacids have low surface areas (lower than 5 m^2/g), some of their salts exhibit high surface areas and porous structures largely dependent upon the nature of the cation.

The literature data concerning the characterization and

0021-9517/94 $6.00

properties of heteropolycompounds are sometimes nonhomogeneous and contradictory. The remarkable differences usually found probably depend on the method of preparation utilized. The methods of preparation more widely utilized consist in the synthesis of the Keggin anion in aqueous solution (by dissolution of the right amounts of the salts and control of pH), followed by extraction with ether and precipitation of the acid through solvent evaporation. Then, the acid is exchanged with the desired amount of metal salts (3, 8). Alternatively, the compounds can be prepared by prolonged boiling of stoichiometric amounts of the oxides (7), or by direct precipitation through addition of either stoichiometric (8) or nonstoichiometric (11) amounts of cations in the solution containing the dissolved acids.

Early works (8, 9) have shown that methods involving ion exchange over the heteropolyacid lead to compounds containing varying amounts of residual protons. This introduces a factor of instability in the heteropolycompound. Indeed, it is known that acids begin to decompose at temperatures lower than 623 K. During application as heterogeneous catalysts, the acid form tends to decompose in the reaction environment, releasing MoO_3 and causing a progressive decrease in the catalytic activity with the time-on-stream, as in the case of the isobutyric acid oxydehydrogenation to methacrylic acid (7). Moreover, in the latter case residual acidity can negatively affect the selectivity (3, 10).

Our work has been aimed at the preparation and characterization of heteropolycompounds of the composition $K_x(NH_4)_{3-x}PMo_{12}O_{40}$ (hereafter designated as K_x, with $x = 0$ to 3), prepared with a procedure different from the conventional ones. Our procedure does not involve an acid as intermediate compound, but rather consists in the direct precipitation of the salts.

In the present paper we analyze the thermal behavior of the prepared compounds; in particular, the structural evolution of the K_x salts has been examined by means of different techniques. The samples have been tested in the oxidative dehydrogenation of isobutyric acid (IBA) to methacrylic acid (MAA); the effect of the cationic composition and of the structural thermal evolution on the catalytic performance has been studied.

METHODS

The method employed for the catalyst preparation is the following: 16.95 g of $(NH_4)_3Mo_7O_{24}$ and 0.78 g of H_3PO_4 were dissolved in 40 ml of water kept at 333–343 K. After cooling, KNO_3 was added in order to obtain the desired final composition, and finally 10 ml of HNO_3 was poured into the solution. The addition of HNO_3 led to the precipitation of a yellow compound, which was finally dried at 393 K overnight, then at 423 K for 14 h and at 453 K for 5 h. The solid was then slowly heated (50°/h) to the final calcination temperature (640 K, or higher), which was maintained for 4 h. Besides the temperature of calcination, the heating rate was found to be a key factor to obtain the Keggin structure: higher rates of heating can make it difficult to obtain the desired structure.

The obtained materials were characterized by means of X-ray diffraction, EPR, FTIR spectroscopy, ionic chromatography, and surface area measurement. FTIR spectra were recorded from 4000 to 450 cm^{-1} with a Perkin–Elmer 1700 spectrometer, using the KBr pressed disk technique.

Cationic chromatography was used to determine the absolute amounts per unit weight of K^+ and $(NH_4)^+$ in the materials. Prior to analysis, the samples were heated at 640 K to remove any remaining adsorbed water and excess ammonia. Known amounts of sample were then decomposed with a minimum volume of 1 *M* LiOH. The analysis was carried out using a Waters 501 pump, equipped with a Rheodyne 7125 injector (loop volume 0.2 mL), and a Waters 431 conductivity detector. The column utilized was a Vydac 400IC, 5 cm long; the eluent was 2 m*M* HNO_3, with a flow rate of 2 ml/min. Data were collected utilizing the Millipore Baseline 810 chromatographic data station.

This method was developed for and first applied to the analysis of heteropolycompounds by McGarvey and Moffat (8), and by Jurgensen *et al.* (12). These authors reported that the heteropolycompound can be attacked by a basic medium (i.e., LiOH), which leads to the decomposition of the Keggin anion. For details concerning the confidence of this method of analysis we refer the readers to the mentioned references (8, 12).

Powder XRD data were obtained with a Philips PW 1050/81 diffractometer, controlled by a PW1710 unit using Ni-filtered Cu*Kα* radiation: $\lambda = 0.15418$ nm (40 KV, 40 mA). The samples were supported in a sample holder with a depth of 1 mm. Quantitative evaluation of the amount of decomposed heteropolycompounds was made by preparing a calibration curve using MoO_3/heteropolycompound mixtures of different known compositions; the reference MoO_3 was obtained by complete decomposition of a heteropolyacid.

The surface areas of the salts were determined by N_2 adsorption at 77 K, using the BET theory and a Carlo Erba Sorptomatic 1826 apparatus. EPR spectra were recorded on a Varian E109 spectrometer at 9.3 GHz (X band); a rectangular dual cavity (TE_{104}) was used and the *g* values were measured by comparison with a standard sample strong pitch varian ($g = 2.0028$).

Catalytic tests were performed in a continuous flow reactor at atmospheric pressure; the standard feed composition was the following: IBA 2.1% (Aldrich Chemical, 99% purity; no further purification was made), oxygen

20%, water 4.3%, the rest helium. One gram of catalyst was used for each series of catalytic tests, granulated into particles ranging from 0.3–0.5 mm in size. Total flow rate was 60 ml/min, with a residence time of 1 sec. All the data were collected after approximately 20 h of time-on-stream, under stationary conditions. The temperature of reaction was varied to achieve the desired IBA conversion. The reactor outlet was kept at 473 K in order to prevent product condensation and methacrylic acid polymerization. A volume of the gas phase was sampled and analyzed by gas chromatography; a Carbosieve S column was utilized for CO and CO_2 analysis, with programmed oven temperature from 313–473 K (thermal conductivity detector), while a GP 10% SP-1200/1% H_3PO_4 on Chromosorb WAW (flame ionization detector) was utilized for IBA, acetone, propylene, and MAA analysis; oven temperature was programmed from 333–393 K.

RESULTS

Physicochemical Characterization of Samples Calcined at 640 K

Table 1 shows the amount of K^+ and $(NH_4)^+$ cation, determined by ionic chromatography, in samples calcined at 640 K.

It is shown that the amount of $(NH_4)^+$ and K^+ ions that are present in the precipitated compound closely corresponds to that expected, though a large excess of ammonium ion was initially present in the raw materials utilized. Small differences between experimental and expected amounts (the formed were always slightly lower) could be due to the presence of residual protons, and thus of unsalified heteropolyacid (which in the conditions utilized for the precipitation is soluble) trapped in the precipitated compound. However, it is known that the 12-molybdophosphoric acid decomposes at temperatures lower than 640 K (1).

TABLE 1

K^+ and $(NH_4)^+$ Content of the Heteropoly Salts Prepared, Determined by Ionic Chromatography in Samples Calcined at 640 K

Sample	Expected amount, atom (Keggin unit)		Measured amount, atom (Keggin unit)	
	K^+	$(NH_4)^+$	K^+	$(NH_4)^+$
$(NH_4)_3PMo_{12}O_{40}$	0	3	0	2.83
$K_1(NH_4)_2PMo_{12}O_{40}$	1	2	0.92	1.84
$K_2(NH_4)_1PMo_{12}O_{40}$	2	1	2.01	0.83
$K_3PMo_{12}O_{40}$	3	0	2.92	0.24

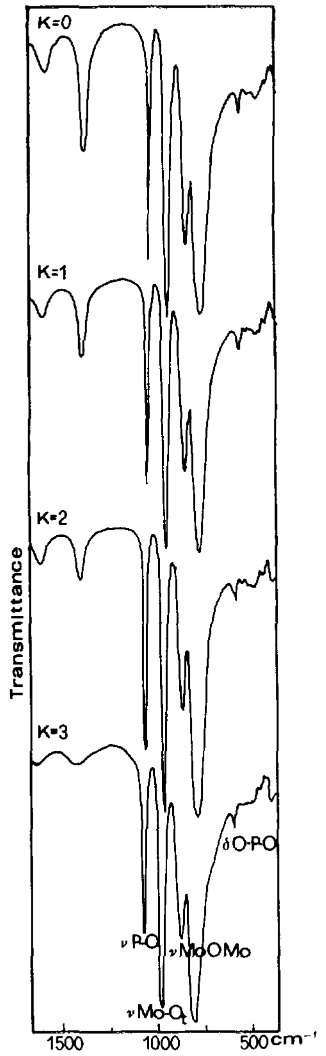

FIG. 1. FTIR spectra of $K_x(NH_4)_{3-x}PMo_{12}O_{40}$ samples calcined at 640 K.

The ammonium in excess, with respect to the stoichiometric requirement, was therefore released at temperatures lower than 640 K. Literature data indicate that the ammonium can be released in the form of gaseous ammonia (13) or as molecular nitrogen (14).

Figure 1 shows the IR spectra of the samples calcined at 640 K. The spectra did not exhibit significant differences. Within the range 600–1100 cm^{-1} the bands characteristic of the Keggin unit were observed. According to Rocchiccioli-Deltcheff *et al.* (15) the bands at about 1070, 965, 870, 790, and 590 cm^{-1} correspond to ν (P–O), ν (Mo=O), ν (Mo–O–Mo), and δ (P–O) vibrations. The peak at 1420 cm^{-1} can be ascribed to the presence of the ammonium ion. The intensity of this absorption was much stronger in samples dried at 443 K than in those calcined at 640 K, confirming the evolution of the ammonium cation.

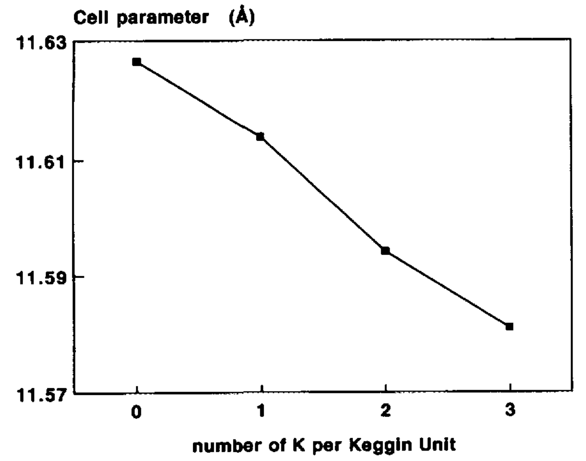

FIG. 2. Lattice parameter of $K_x(NH_4)_{3-x}PMo_{12}O_{40}$ samples calcined at 640 K as a function of x.

Diffraction patterns of all prepared salts were consistent with the existence of a single crystallographic phase, with patterns typical of a cubic phase for the secondary structure (16). It is interesting to consider the changes in the secondary structure as a function of the cation content. Plotted in Fig. 2 is the lattice parameter as a function of the cationic composition; it decreased as the content of potassium ion in the structure increased, in agreement with results reported in the literature (17).

The anionic composition of precipitated compounds was not evaluated by means of ionic chromatography. Nevertheless, both IR spectroscopy and X-ray diffractions clearly indicate the presence of a single phase, with pattern and IR absorptions typical of the Keggin anion.

The catalysts were characterized by means of EPR spectroscopy. This technique is particularly suitable for this kind of compound, because it allows us to easily detect the reduced Mo^{5+} species. Figure 3 illustrates the EPR spectrum (X band) obtained after calcination of the K_1 sample at 640 K. All the other samples gave similar signals, but with different intensities. These spectra were constituted of two parts:

(a) a complex central signal, "α," observed at normal field intensity ($\Delta m_s = 1$) which is a superimposition of monomeric Mo^{5+} and of dimeric species signal. The signal "α," as in all the samples of the K_x series, is asymmetric and characterized by $g_{xx} = 1.961$, $g_{yy} = 1.952$ (both corresponding to $g_\perp$), and $g_{zz} = 1.869$ (corresponding to $g_\parallel$). Furthermore, the signal was accompanied by two satellite lines of weak intensity ($g = 2.035$ and $g = 2.004$, respectively) which are characteristics of the hyperfine interaction between the spin of the $4d^1$ electron of Mo^{5+} and the nuclear spin 5/2 of the isotopes 95 and 97 of molybdenum (18, 19).

The intensity of this signal was rather high in the K_0 sample, and progressively decreased with increasing K content; in the K_3 sample the signal intensity was less than one-tenth that of K_0.

(b) a complex weak signal "β" observed at half normal field intensity, about 1670 Gauss ($\Delta m_s = 2$). The existence of such a signal is characteristic of the presence of one or several types of dimer. The observation of ion pairs is not a systematic phenomenon. Recent literature reports several studies about dimers of copper in heteropolycompounds, in different environments (20, 21). Concerning Mo^{5+} pairs, Meriaudeau *et al.* (22) have revealed their

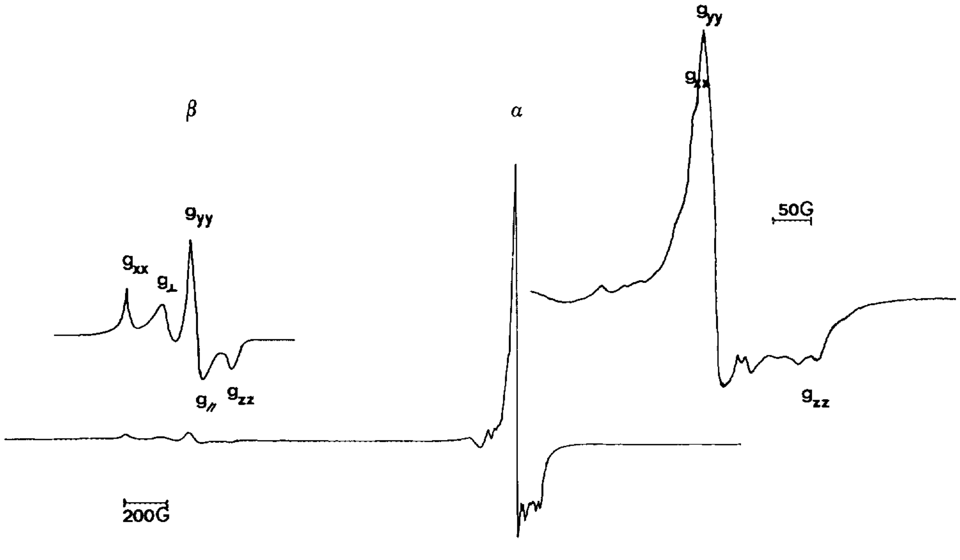

FIG. 3. EPR signal (recorded at 77 K) of the $K_1(NH_4)_2PMo_{12}O_{40}$ sample calcined at 640 K.

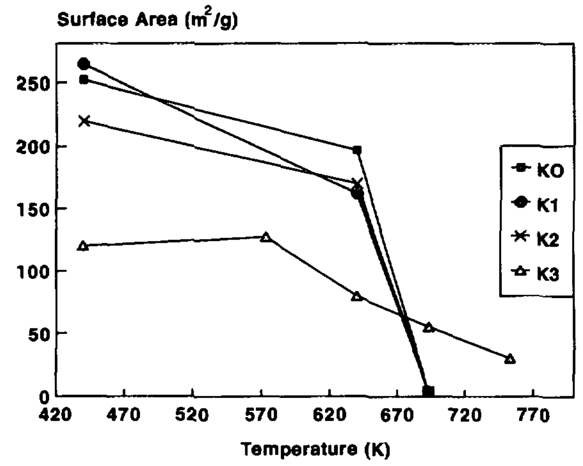

FIG. 4. Surface area of $K_x(NH_4)_{3-x}PMo_{12}O_{40}$ catalysts as a function of calcination temperature.

existence in polycrystalline TiO_2 using a ^{95}Mo-enriched phase.

Structural Evolution at Temperatures Higher Than 640 K

The problem of the thermal stability of the heteropolyanions, which is also important from the catalytic point of view, has been thoroughly studied by many groups (11, 23–25). It is well known in the literature that the decomposition of the Keggin unit in $H_3PMo_{12}O_{40}$ begins at temperatures close to 573–623 K. This phenomenon initially leads to a partial reduction and distortion of the Keggin unit followed by an irreversible collapse of the structure with formation of MoO_3.

The variation in the surface area of the salts with calcination temperature is illustrated in Fig. 4. The surface areas of the solids calcined at 640 K decreased with increasing K^+ content, in agreement with literature data, which report that the ammonium salts had higher surface area than the potassium salts (8, 26).

The samples showed a decrease in the surface area with increasing calcination temperature, as previously reported by Lapham and Moffat (11). The salts K_0, K_1, and K_2, calcined at 693 K, had very low surface area. In contrast, the surface area of the K_3 remained as high as 30 m²/g after heating at 753 K.

The IR spectra of samples after thermal treatment at 693 K are shown in Fig. 5. For the catalysts initially containing ammonium ions, bands relative to molybdenum trioxides appeared, indicating the beginning of the destruction of Keggin unit. The intensity of the bands attributed to MoO_3 decreased with increasing potassium content in the salt: the K_0 and K_1 samples exhibited a high degree of decomposition, the K_2 was much less decomposed, and the K_3 appeared structurally intact. Some shifts in the band frequencies with respect to those of the commercial orthorhombic MoO_3 were observed, as previously reported (23). On the contrary, the structure of K_3 began to decompose only at temperatures higher than 753–773 K.

In all the samples, the band relative to the ammonium cation at 1420 cm^{-1} either completely disappeared or remarkably decreased in intensity after calcination at 693 K. Thus, all the ammonium cations were released from the texture, either in the form of gaseous ammonia or in the form of N_2 (14) at the temperature of incipient decomposition.

The XRD spectra were recorded in order to identify the changes in the structure due to the decomposition of the Keggin unit. All K_x samples of intermediate composition showed clear evidence of progressive decomposition

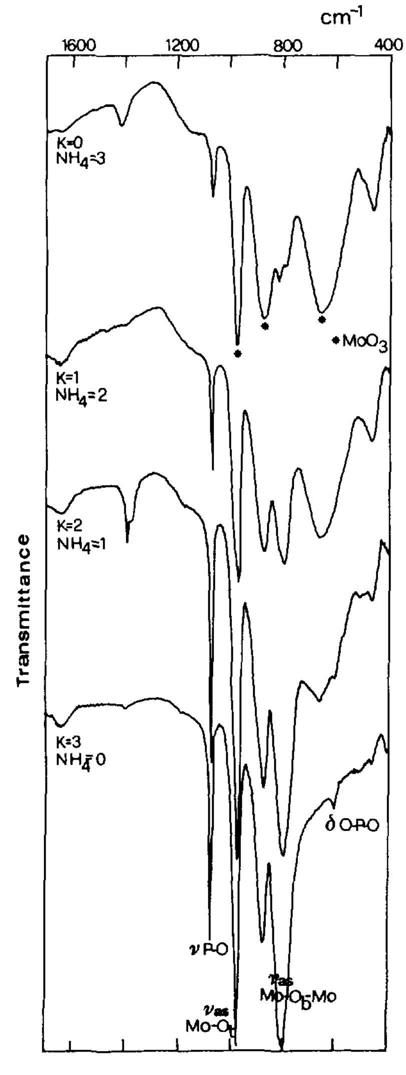

FIG. 5. FTIR spectra of $K_x(NH_4)_{3-x}PMo_{12}O_{40}$ samples calcined at 693 K.

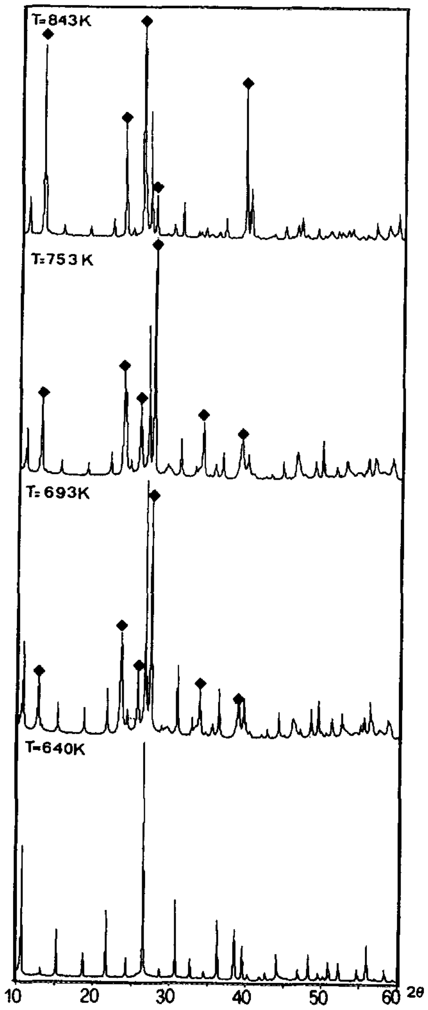

FIG. 6. X-ray diffraction spectra of $K_1(NH_4)_2PMo_{12}O_{40}$ samples calcined at increasing temperatures. (◆) Most intense reflections of MoO_3.

TABLE 2

Change in the Lattice Parameter of the $K_1(NH_4)_2PMo_{12}O_{40}$ Catalyst as a Function of the Calcination Temperature

Temp. of calcination (K)	Cell parameter (Å)
640	11.614 +/− 0.006
693	11.587 +/− 0.002
753	11.567 +/− 0.003
843	11.583 +/− 0.004

with increasing temperature. In contrast, prolonged calcination of K_3 up to 753 K did not alter the powder XRD patterns.

The XRD patterns for the K_1 salt calcined at increasing temperatures are shown in Fig. 6. At 640 K the typical pattern of the cubic secondary structure was obtained without the presence of additional lines relative to spurious phases. The calcination at 693 K led to the appearance of the diffraction lines of MoO_3, in agreement with the IR data. This MoO_3 corresponds, in terms of the relative intensities and positions of the diffraction lines, to that reported in the ICDD data files (16). However, the MoO_3 phase also underwent an evolution. In fact, when calcining at temperatures higher than 750 K, the most intense line relative to MoO_3 (d = 3.26 Å) progressively decreased in intensity, while other diffraction lines, characteristic of MoO_3 but usually less intense than the mentioned one, became the most intense. The data indicate therefore that the MoO_3 formed by heteropolycompound decomposition evolved at a high temperature towards a phase characterized by the preferential exposure of different crystallographic planes.

The changes in lattice parameter of the K_1 salt as a function of the calcination temperature are listed in Table 2. The data clearly indicate a decrease in the lattice parameter of the heteropolycompound with increasing calcination temperature. After the thermal treatment at 693 K, the lattice parameter was close to that of the K_3 sample, while at 753 K it was even lower. At 843 K the parameter for the low fraction of residual heteropolycompound was the same as that of the K_3 sample.

A quantitative analysis was made for the K_0 and K_1 samples calcined at increasing temperatures in order to evaluate the extent of structural decomposition. The results are summarized in Table 3, which gives the calculated weight amount of MoO_3 (approximately corresponding to the fraction of decomposed heteropolycompound)

TABLE 3

Fraction of Decomposed Catalysts as a Function of the Calcination Temperature Calculated by X-Ray Quantitative Analysis

Sample	Temp. calc. (K)	MoO_3 (wt%)
$(NH_4)_3PMo_{12}O_{40}$	640	0
	693	40
	753	100
$K_1(NH_4)_3PMo_{12}O_{40}$	640	0
	693	47
	753	73
	843	>90
$K_2(NH_4)_2PMo_{12}O_{40}$	640	0
	693	<20[a]
$K_3PMo_{12}O_{40}$	640	0
	693	0
	773	Traces

[a] Approximate evaluation made by comparison of the FTIR spectra of the samples.

as a function of the calcination temperature. The fraction of decomposed heteropolycompound at 693 K was approximately 40% for both salts. This amount is remarkably lower than that expected on the basis of IR analysis. The absence at 693 K of the IR band relative to $(NH_4)^+$ cation indicates, in fact, that the evolution of ammonium cations was completed. Protons, residual of ammonium ions evolution, could act as counterions; however, the heteropolyacid is known to be unstable at this temperature, and consequently the fraction of the Keggin anion originally salified by the ammonium cation should decompose.

Therefore, the expected degree of decomposition at 693 K for the K_0 sample is 100%, and for the K_1 67% (with formation, in the latter case, of a residual K_3-like phase) (27), remarkably higher than that experimentally found, especially for the K_0 sample.

A value of decomposition closer to the expected one was found instead after calcination at 753 K. At this temperature, in fact, the K_0 was completely decomposed while K_1 sample was approximately two-thirds decomposed. The decomposition of the K_1 sample continued on further increasing the calcination temperature: at 843 K, the amount of decomposed heteropolycompound was greater than 90%. At this temperature the K_3-like phase (finally formed from the K_1 decomposition) was progressively decomposed, also.

The intensity of the EPR signal "α" is plotted in Fig. 7 as a function of the calcination temperature for the K_0 sample. It is shown that the partial decomposition of the structure at 693 K led to an increase in the degree of reduction of the catalyst. On the contrary, the total collapse of the structure at 773 K led to the disappearance of the signal as a probable consequence of the Mo^{5+} reoxidation.

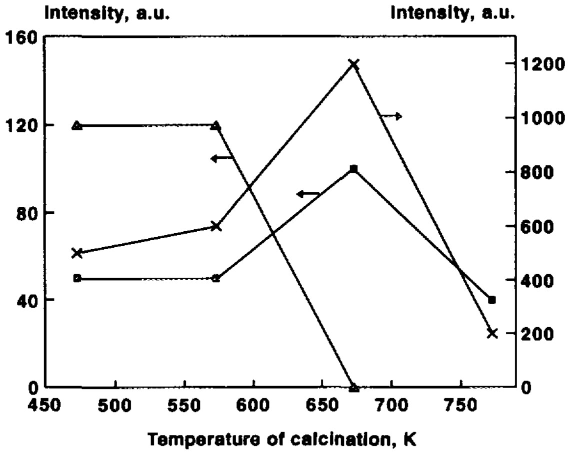

FIG. 7. Intensity of the EPR signals "α" (×), β_1 (▲), and β_2 (■) in $(NH_4)_3PMo_{12}O_{40}$ sample as functions of the calcination temperature.

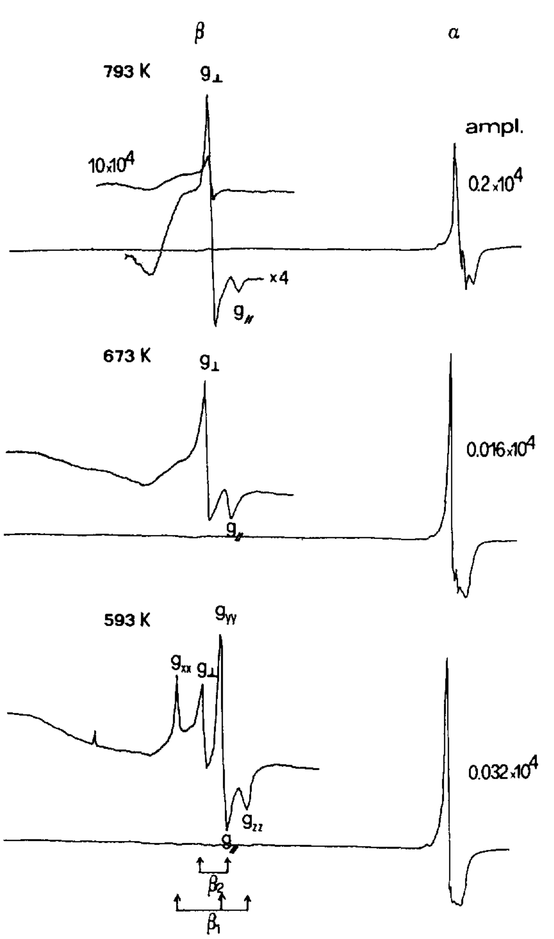

FIG. 8. EPR spectra (recorded at 77 K) of the $(NH_4)_3PMo_{12}O_{40}$ sample at increasing calcination temperatures.

Figure 8 reports the evolution of the EPR spectrum of the K_0 sample as a function of the calcination temperature. At 593 K, two components of the "β" signal can be clearly distinguished (β_1 and β_2). At the temperature of incipient decomposition, 673 K, one series of lines belonging to this complex signal "β" disappeared, and a doublet was left which can be attributed to a Mo^{5+} dimeric species β_2 ($\Delta m_s = 2$) with axial symmetry ($g_\perp = 4.264$, $g_\parallel = 3.820$). The β_2 dimer remained at 793 K but decreased in intensity. The previous series of lines which disappeared at 673 K, but which was observed in the sample calcined at 573 K (and 640 K, also), can be attributed to another dimer of Mo^{5+} species, β_1, in orthorhombic symmetry ($g_{xx} = 4.969$, $g_{yy} = 3.899$, and $g_{zz} = 3.515$).

The evolution of the intensity of signals "α" and "β" gives some qualitative information on the modification of the structure during calcination. The trend of the intensities of the two groups of lines constituting the "β" signal with temperature is plotted in Fig. 7 for the K_0 sample. The intensity of the dimer with axial symmetry β_2 (for

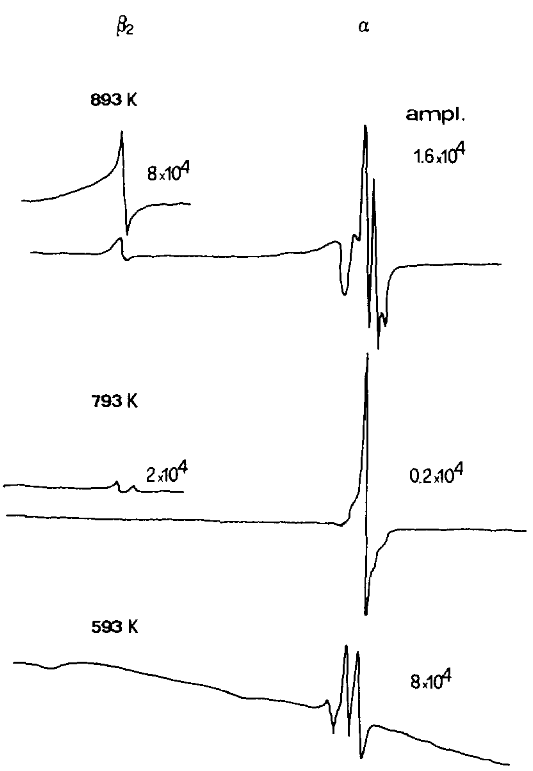

FIG. 9. EPR spectra (recorded at 77 K) of the $K_3PMo_{12}O_{40}$ sample calcined at increasing temperatures.

which the $g_\perp$ component intensity is given) was maximum for calcination at 673 K, and collapsed after this temperature, while the dimer β_1, with orthorhombic symmetry (for which the intensity for the mean value of g_{yy} and g_{xx} components is given), relatively intense at 573 K, disappeared when the sample was calcined at higher temperatures. Simultaneously, the intensity of the "α" signal, constant between 473 and 573 K like the β_1 and β_2, increased until 673 K (temperature of incipient decomposition) before falling (Fig. 7).

The case of the K_3 sample was different. Figure 9 shows the EPR spectra recorded for increasing calcination temperatures. The intensity of the signals for the K_3 sample calcined at 673 K was remarkably lower than that for the K_0 sample; this was due to the very high conductivity of the sample. For higher calcination temperatures the conductivity decreased and the signal intensity increased. The signal at half field was detected only after calcination treatment at 793 K, the temperature at which the structural decomposition began. In addition, only a "β" signal, very weak and corresponding to the dimer with axial symmetry (β_2 signal), was detected. It became more intense after calcination at 893 K.

Catalytic Behavior in Isobutyric Acid Oxidehydrogenation

Figure 10 compares the conversion of IBA at 533 K for the K_x series calcined at increasing temperatures; Figure 11 gives the selectivity to MAA at total IBA conversion.

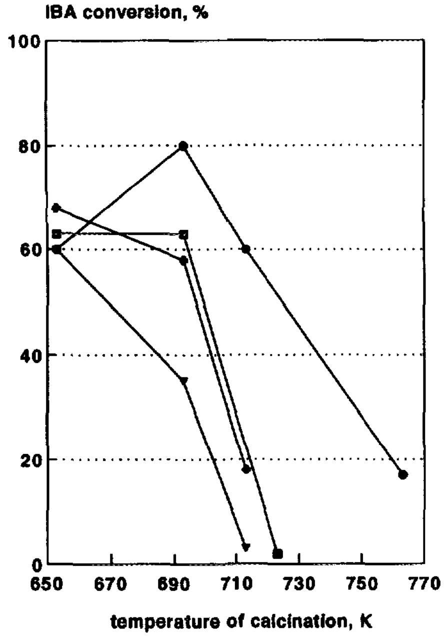

FIG. 10. Conversion of isobutyric acid at 533 K as a function of the calcination temperature for the $(NH_4)_3PMo_{12}O_{40}$ (○), $K_1(NH_4)_2PMo_{12}O_{40}$ (▽), $K_2(NH_4)PMo_{12}O_{40}$ (+) and $K_3PMo_{12}O_{40}$ (☒) samples.

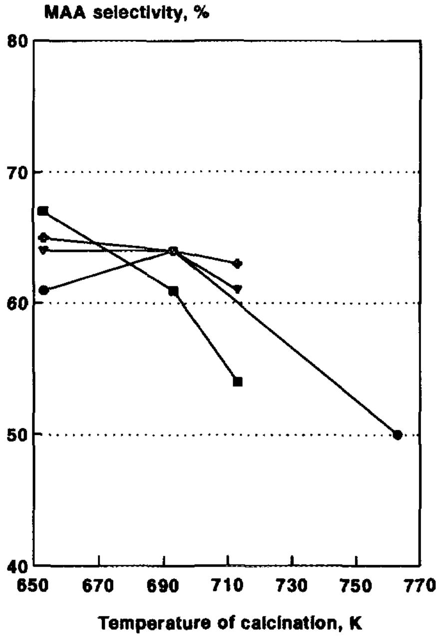

FIG. 11. Selectivity to methacrylic acid at total isobutyric acid conversion as a function of the calcination temperature. Catalysts are the same as in Fig. 10.

Samples calcined at 653 K, a temperature lower than that of incipient decomposition, had similar catalytic performance, both in terms of IBA conversion and selectivity to MAA, despite their different cationic composition. In contrast, a different behavior was observed when the calcination temperature was increased: after treatment at 693 K the K_0 increased its activity, the K_3 maintained it substantially unaltered, while the K_1 and K_2 decreased it. All samples exhibited slight variations in the selectivity to MAA.

After calcination at 713 K all catalysts showed a decrease in activity; however, the activity of the K_0 salt was significantly higher than that of the other catalysts, despite its high degree of structural decomposition. Even after treatment at 763 K (temperature of complete structural decomposition), the K_0 showed a relatively high activity, with a selectivity to MAA close to 50%.

DISCUSSION

Structural Modifications with the Temperature of Calcination

The procedure of preparation described in the present paper is different from the usual ones in that it does not utilize an acid as the starting material. In our case, after the dissolution of the salts, the addition of the HNO_3 led to the formation of the Keggin anion; however, in the presence of K^+ and $(NH_4)^+$ ions (the latter in excess), the insoluble salt immediately precipitated.

All measurements made on the materials calcined at 640 K indicate that a Keggin-type heteropolycompound had been obtained, characterized by the cubic cell for the secondary structure. Moreover, the ionic chromatography results indicate that the amount of cations almost corresponded to that necessary to completely salify the Keggin unit. The presence of small amounts of the free acid cannot, however, be excluded.

X-ray diffraction analysis also indicates the formation of monophasic mixed potassium/ammonium salts when both cations are present.

The decomposition of the ammonium-salified compound (K_0) began at 673–693 K, temperatures higher than that reported in the literature for the free heteropolyacid. In agreement, there is considerable evidence in the literature that salts are generally more stable than the corresponding acids (11, 23–25). Decomposition was complete after calcination at 753 K for 2 h. The decomposition of the K-containing mixed salts (K_1, K_2) also began at temperatures close to 693 K. At 753 K the amount of decomposed heteropolycompound approximately corresponded to the fraction of heteropolysalt originally salified by the ammonium cation. Thus, the K_0 salt was 100% decomposed, and the K_1 two-thirds decomposed.

The progressive decomposition of the K_1 was accompanied by the formation of MoO_3 and a heteropolycompound with crystallographic parameter that progressively decreased, thus indicating the formation of a heteropolycompound with different cationic composition with respect to the original one. The cell parameter was close to that of the K_3 after treatment at 693 K (thus at moderate structural decomposition), but then further decreased for higher temperatures. This suggests a progressive change in the cationic composition, with formation of intermediate phases with cationic composition different from that of the original salt and from that of the K_3 salt. On the contrary, after calcination at 843 K the cell parameter of the residual heteropolycompound was exactly the same as for the K_3 phase.

Another indication arising from the X-ray data is that the amount of decomposed heteropolycompound at 693 K was lower than that expected on the basis of the residual amount of ammonium cation, which at this temperature was practically nil. This can be explained with the assumption that some other cation replaced the ammonium. The most obvious possibility is that the proton was left as a consequence of the ammonia evolution; however, it is known that the heteropolycompound in the acid form is thermally less stable than the salified one, and therefore at the temperature at which the ammonia is released no acid should be left undecomposed. Another possibility consists in the displacement of molybdenum cations from the anionic position during the Keggin unit decomposition; part of the ions form MoO_3, while another part could be instead located in the cationic position of neighboring intact Keggin units, stabilizing them against decomposition at 693 K. This possibility will be further discussed in the following sections.

The Evolution of the Mo^{5+} Species

The EPR characterization adds some further information about the nature of the heteropolycompound evolution with temperature. The "α"-type signal, detected in all the compounds, has been described in the literature to occur in heteropolycompounds that have been subjected to a reducing environment (31, 32).

Upon interaction of some heteropolysalts with acrolein at temperatures higher than 453 K, Serwicka *et al.* (27) found an asymmetric signal (characterized by $g_{xx} = 1.969$, $g_{yy} = 1.960$, and $g_{zz} = 1.857$). Otake *et al.* (31) found a similar signal by reducing the heteropolyacid with H_2 at 553 K.

Upon vacuum treatment at 473 K and reduction of the $H_3PMo_{12}O_{40}$ and H_2, Fricke and Ohlmann (33) found a signal with the parameter $g_{\perp} = 1.958$ and $g_{\parallel} = 1.852$, which the authors correlated with a strong distortion of the Keggin unit, occurring as a consequence of the loss of an O_b atom. The signal obtained as a consequence of the destruction of the Keggin unit (thus related to Mo^{5+} sites in MoO_3) was instead characterized by different parameters ($g_\perp$ 1.930 and $g_\parallel$ 1.873), which are themselves, however, different from those of reduced MoO_3 as well as from those described by Serwicka *et al.* (27) in decomposed heteropolyacids.

Comparison with the literature data allows, therefore, attribution of our "α" signal to Mo^{5+} sites in the Keggin unit, associated with an oxygen-deficient Keggin unit. The EPR parameters for the signal, with $g_\perp > g_\parallel$ and $H_\parallel > H_\perp$, have been proposed to reveal the presence of a strong axial crystal-field component (27).

In our case, the formation of reduced Mo^{5+} sites can be reasonably attributed to the reducing action of NH_3, originally present in excess in the precipitated material. Ammonia is itself oxidized by molybdenum to N_2, which evolves from the catalyst during the heat treatment (14). An increase in the intensity of the "α" signal at 693 K can be related to the reducing action of the ammonium released in correspondence with the structural decomposition. Finally, after calcination at 753 K in air, the signal disappeared, most likely as a consequence of Mo^{5+} reoxidation (at this temperature, no ammonium cation was left in the samples).

The signal at half values of field (signal "β"), on the contrary, has never been described in the literature. Serwicka *et al.* (27) stated that the removal of bridging oxygen atoms (O_b) introduced a significant rhombic distortion of the Mo^{5+} site, thus resulting in a splitting of the $g_\perp$ value into separate g_1 and g_2 values. The same authors postulated, but did not show experimentally, the formation of Mo^{5+}–Mo^{5+} dimers across the oxygen vacancy, trapping two spin-paired electrons in the same molecular orbital. This hypothesis was formulated on the basis of the fact that, although the removal of an oxygen atom should leave two electrons per oxygen vacancy, there was no direct evidence for this, and therefore two electrons in the same Keggin unit are ESR-inactive.

The analysis of the "β" signal indicates the presence of two different types of dimers, with the prevalence of the β_1 signal (with orthorombic symmetry) at low temperature. These dimers likely occur by reduction of two neighboring atoms of molybdenum. The evolution of the signal with increasing temperature is indicative of modifications occurring in the structure. The kind of dimer prevailing at low temperature (thus in the undecomposed Keggin unit) decreased considerably in intensity at the temperatures where the Keggin unit begins to decompose. The dimer with axial simmetry (β_2 signal), on the contrary, increased its intensity along with the Keggin unit decomposition.

The Mechanism of Structural Collapse

The evolution of the EPR signal with temperature, as well as the X-ray analysis results, can be interpreted by assuming that the structural collapse of the $K_x(NH_4)_{3-x}$-based heteropolycompound may occur in two stages, with intermediate formation of a salt, more stable than the ammonium salt, where possibly a fraction of the cationic positions is occupied by molybdenum atoms. The latter could move from the anionic position, replacing ammonium cations (which evolve in correspondence with the Keggin unit decomposition) and hindering the total collapse of the compound. This $K_xMo_{(3-x)/6}$-based heteropolycompound would be characterized by a value of the cell parameter lower than that for the corresponding $K_x(NH_4)_{3-x}$-based solid solution.

For calcination temperatures higher than 693 K the heteropolysalt of intermediate cationic composition is then progressively decomposed. The decomposition is complete at 753 K for the K_0 sample, and almost complete at 843 K for the K_1 sample. At these conditions the residual heteropolycompound is characterized by a lattice parameter for the cubic cell identical to that of the K_3 compound, thus suggesting that at such high temperatures heteropolycompounds with intermediate composition are fully decomposed, and that small amounts of the most stable salt $K_3PMo_{12}O_{40}$ are left.

The modification of the EPR "β" signal with temperature also supports the above-reported hypothesis; the evolution of a dimer with orthorhombic symmetry to one with axial symmetry at 673 K (in correspondence of the incipient structural decomposition) indicates a change in the nature of the Mo^{5+} pairs, for instance a displacement of a molybdenum atom outside the Keggin unit, either in cationic position or inside the formed MoO_3. The latter case is, however, less probable, because the signal at normal fields is very different from that found in reduced MoO_3 (34). In further support of this hypothesis is the modification of the intensity of the signal at normal field occurring during the decomposition. In particular, concurrently to the decrease of the intensity of the β_1 signal at half field (relative to the dimer with orthorombic simmetry), the intensity of the signal at normal field (relative to the Mo monomers) increases. This is in favor of the formation of additional Mo monomeric species, as the consequence of the evolution of the dimer with orthorhombic symmetry.

The attribution of the signal at half field with axial symmetry to a molybdenum ion located in cationic position, to stabilize the Keggin unit against decomposition, is further supported by the absence of this signal in the K_3 sample for calcination temperatures lower than that of incipient decomposition. Only after treatment at 793 K, at which the structural decomposition began, could the signal be detected. Thus, due to the higher thermal stability of the K_3 sample, the formation of the molybdenum species in cationic position is shifted towards higher temperatures.

The Dependence of the Catalytic Performance upon the Structural Evolution

The catalytic performance of heteropolysalts (salified with either ammonium or alkali metals) in IBA oxidehydrogenation was studied by many authors (3, 10, 35, 36), but no one compared the activity of the $K_x(NH_4)_{3-x}PMo_{12}O_{40}$ series.

The salification of the 12-phosphomolybdic acid by ion exchange, or the direct precipitation of the salified compound, leads to materials characterized by remarkable differences in the catalytic performance with respect to the corresponding acid. For instance, the ammonium-salified compound was reported to be more selective to methacrylic acid than the acid form (35). Analogously, potassium-salified compounds were reported to be more active and selective (3), while more contradictory results were given for the cesium-containing compounds (3, 10, 35). The effect of the cation has been related either to its electronegativity (3), thus affecting the redox properties of molybdenum, or to modifications in the acidity (10).

Indeed, our results for mixed ammonium/potassium salts indicate that the activity of the $K_x(NH_4)_{3-x}$ series seems to be rather independent on the cationic composition. All of them give an isobutyric acid conversion in the range 60–70% (Fig. 10), as well as a selectivity to methacrylic acid of 60–70% at total IBA conversion (Fig. 11).

All the samples, after reaction (temperatures were never higher than 600 K), exhibit a remarkably decreased surface area (1–2 m^2/g for the K_0, the K_1, and the K_2 samples, 20 m^2/g for the K_3 one). This occurs without structural decomposition, and is likely due to the blocking of pores by heavy compounds formed during reaction. Since the initial activity only slightly decreases within the first hours of reaction (then stabilizing and remaining constant for at least 50 h), the outer surface of the heteropolycompound is the really active surface.

More interesting is the effect of the calcination temperature on the activity of the compounds. The catalytic performance is in this case a function of the cationic composition. Three different behaviors can be distinguished, which reflect remarkable differences in the thermal evolution of the compounds:

(a) the ammonium-salified compound is activated by a treatment at 693 K; at even higher temperatures the activity falls but nevertheless remains rather high. These results have been confirmed by repeating the calcination treatment and the catalytic tests on the K_0 sample.

(b) the ammonium/potassium mixed salts decrease their activity by calcination at 693 K, in correspondence with the partial structural decomposition; more pronounced is the deactivation of the K_1 sample. Higher temperatures lead for both the K_1 and the K_2 compounds to a further, more significant fall in activity.

(c) the potassium-salified compound maintains the activity up to 693 K (it does not decompose at this temperature); at higher temperatures the activity falls.

The anomalous behavior of the K_0 sample at 693 K can be explained by assuming the formation of an intermediate compound, characterized by a reactivity different from that of both the initial ammonium-salified heteropolycompound and the completely decomposed compound.

It is worth noting that if we assume that the intermediate compound is constituted of a molybdenum-salified Keggin anion, the highest amount of the latter should form in the K_0 sample. In the K_1 and K_2 samples, in fact, the presence of potassium can justify the presence of undecomposed heteropolycompound at 693 K. This could explain why the activation effect achieved by calcination at 693 K is observed with the K_0 sample only.

Calcinations at temperatures higher than 693 K lead to a fall in the activity for all the samples. This phenomenon is expected for the ammonium- and potassium/ammonium-containing salts, in consideration of the increase in the fraction of decomposed heteropolycompound, but is indeed surprising for the K_3 catalyst, which at 723 K still is structurally intact, and whose surface area is about 50 m^2/g (see Fig. 4).

The activity of the K_0 sample is higher than that of the other samples even after calcination at 723 and 763 K, despite the complete structural decomposition and the fall of surface area occurring at these temperatures. The selectivity to MAA decreases, but at 763 K is still approximately 50%. This behavior might be attributed to the formation in the reaction environment (at moderate reaction temperature and in the presence of water vapor) of a shell of heteropolyacid on the surface of the MoO_3/P_2O_5 mixture formed as a consequence of the structural decomposition. In the case of the K^+-containing heteropolycompounds this surface reconstruction of the acid might be possibly hindered by the preferential formation of stable compounds of either molybdenum or phosphorus with potassium.

CONCLUSIONS

Heteropolysalts of mixed composition, $K_x(NH_4)_{3-x}PMo_{12}O_{40}$, exhibited a thermal evolution that depended on the cationic composition. The method of preparation utilized led to monophasic systems, characterized by a

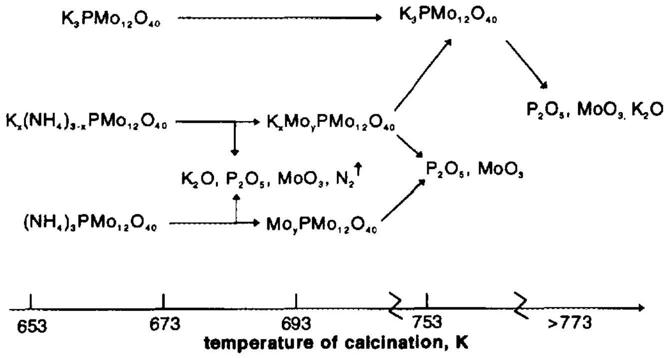

FIG. 12. Scheme representing the thermal evolution of the $K_x(NH_4)_{3-x}PMo_{12}O_{40}$ samples.

cubic cell for the secondary structure, and by a cationic composition very close to the theoretical one. The evolution of excess ammonia at 640 K (i.e., temperatures lower than that of incipient decomposition) led to a partial reduction of molybdenum, with formation of Mo^{5+} dimers inside the structurally intact Keggin unit. The K_0, K_1, and K_2 salts began to decompose at temperatures around 693 K, with complete evolution of structural ammonium cations. The progressive decomposition of the Keggin unit was accompanied by a change in the EPR signal of Mo^{5+}, by a variation of the intensity of signals relative to Mo pairs, and by a decrease in the value of the crystallographic parameter of the cubic cell for the residual heteropolycompound. In addition, the amount of structurally intact heteropolycompound did not correspond to the amount of potassium ions. The data have been explained by hypothesizing that a fraction of the molybdenum atoms located in the Keggin unit could move (during decomposition of the latter) to the cationic position of neighboring undecomposed anions, thus stabilizing them. The thermal evolution of the different K_x compounds with temperature is summarized in Fig. 12.

The preferential formation of the molybdenum-salified heteropolycompound in the partly decomposed ammoniacal salt $(NH_4)_3PMo_{12}O_{40}$ led to a catalyst characterized by an activity in IBA oxidehydrogenation higher than that of the original heteropolycompound. In the other catalysts, instead, where a minor fraction of the molybdenum-salified heteropolycompound formed with decomposition, the structural collapse led to a fall in the activity.

ACKNOWLEDGMENTS

This work was partly sponsored by the Ministero dell' Universita' e della Ricerca Scientifica (60%). Dr. Sergio Zappoli is gratefully acknowledged for the ionic chromatography measurements.

REFERENCES

1. Misono, M., and Nojiri, N., *Appl. Catal.* **64,** 1 (1990).
2,. Misono, M., Mizuno, N., Katamura, K., Kasai, A., Konischi, Y., Sakata, K., Okuhara, T., and Yoneda, Y., *Bull. Chem. Soc. Jpn.* **55,** 400 (1982).
3. (a) Akimoto, M., Tsuchido, Y., Sato, K., and Echigoya, E., *J. Catal.* **72,** 83 (1981); (b) Akimoto, M., Shima, K., Ikeda, H., and Echigoya, E., *J. Catal.* **86,** 173 (1981); (c) Akimoto, M., Ikeda, H., Okabe, A., and Echigoya, E., *J. Catal.* **89,** 196 (1981).
4. Black, J. B., Clayden, N. J., Gay, P. L., Scott, J. D., Serwicka, E. M., and Goodenough, J. B., *J. Catal.* **106,** 1 (1987).
5. Ai, M., *J. Catal.* **71,** 88 (1981).
6. Ai, M., *J. Catal.* **85,** 325 (1984).
7. Watzenberger, O., Lynch, D. T., and Emig, G., *J. Catal.* **124,** 247 (1990).
8. McGarvey, G. B., and Moffat, J. B., *J. Catal.* **128,** 69 (1991).
9. Kutyrev, M. Yu., Staroverova, I. N., Thiep, N. Z., and Krylov, O. V., *in* "New Developments in Selective Oxidation, Studies in Surface Science and Catalysis 55" (G. Centi and F. Trifirò, Eds.), p. 869. Elsevier Science Amsterdam, 1990.
10. Haeberle, Th., and Emig, G., *Chem. Eng. Technol.* **11,** 392 (1988).
11. Lapham, D., and Moffat, J. B., *Langmuir* **7,** 2273 (1991).
12. Jurgensen, A., McGarvey, G. B., and Moffat, J. B., *J. Chromatogr.* **602,** 173 (1992).
13. Thiep, N. Z., Shiryaev, P. A., Koutyrev, M. Y., Krylov, O. V., and Staraverova, I. N., *Kinet. Catal. (Engl. Transl.)* **32,** 634 (1991).
14. Hodnett, B. K., and Moffat, J. B., *J. Catal.* **88,** 253 (1984).
15. Rocchiccioli-Deltcheff, C., Thouvenot, R., and Franck, R., *Spectrochim. Acta, Part A* **32,** 587 (1976).
16. ICDD Powder Diffraction File number 9-408, 9-412, 5-508.
17. McGarvey, G. B., and Moffat, J. B., *J. Catal.* **130,** 483 (1991).
18. Howe, R. F., and Leith, I. H., *J. Chem. Soc., Faraday Trans. I* **69,** 1967 (1973).
19. Che, M., Mac Atteer, J., and Tench, A. J., *J. Chem. Soc., Faraday Trans. I* **74,** 2378 (1978).
20. Abou-Kais, A., Bechara, R., Ghoussoub, D., Aissi, C. F., Guelton, M., and Bonnelle, J. P., *J. Chem. Soc., Faraday Trans. I* **87**(4), 631 (1991).
21. Abou-Kais, A., Bennani, R., Aissi, C. F., Wrobel, G., and Guelton, M., *J. Chem. Soc., Faraday Trans. I* **88**(4), 615 (1992).
22. Meriaudeau, P., Clerjaud, B., and Che, M., *J. Phys. Chem.* **87,** 3872 (1983).
23. Rocchiccioli-Deltcheff, C., Amirouche, M., Hervé, G., Fournier, M., Che, M., and Tatibouet, J. M., *J. Catal.* **126,** 591 (1990).
24. Bielanski, R., Malecka, A., and Kubelkova, L., *J. Chem. Soc., Faraday Trans. I* **85,** 2847 (1989).
25. Orita, H., Hayakawa, T., Schimuzu, M., and Takehira, K., *Appl. Catal.* **77,** 133 (1991).
26. McMonagle, J. B., and Moffat, J. B., *J. Coll. Inter. Sci.* **101,** 479 (1984).
27. Serwicka, E. M., Black, J. B., and Goodenough, J. B., *J. Catal.* **106,** 23 (1987).
28. Moffat, J. B., *J. Mol. Catal.* **52,** 169 (1989).
29. McGarvey, G. B., and Moffat, J. B., *J. Colloid Interface Sci.* **125,** 51 (1988).
30. Taylor, D. B., McMonagle, J. B., and Moffat, J. B., *J. Colloid Interface Sci.* **108,** 278 (1985).
31. Otake, M., Komiyama, Y., and Otaki, T., *J. Phys. Chem.* **77,** 2896 (1973).
32. Komisai, Y., Sakata, K., Misono, M., and Yoneda, Y., *J. Catal.* **77,** 169 (1982).
33. Fricke, R., and Ohlmann, G., *J. Chem. Soc., Faraday Trans. I* **82,** 283 (1986).
34. Che, M., Louis, C., and Sojka, Z., *J. Chem. Soc., Faraday Trans. I* **85,** 3939 (1989).
35. McGarvey, G. B., and Moffat, J. B., *J. Catal.* **132,** 100 (1991).
36. Desquilles, G., Bartoli, M. J., Bordes, E., and Courtine, P., *in* "Proceedings, DGMK Conference on Selective Oxidation in Petrochemistry," p. 69. Goslar, September, 1992.