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Effect of Antimony on the Chemical–Physical Features and Reactivity in Isobutyric Acid Oxidehydrogenation of Keggin-Type Heteropolycompounds

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Potassium/ammonium salts of 12-molybdophosphoric acid were modified by the addition of Sb^{3+} salt, and the chemical–physical features as well as the reactivity in isobutyric acid oxidehydrogenation of the compounds obtained were studied. All the salts prepared were monophasic and the secondary structure of the compounds was characterized by a cubic crystallographic cell. The addition of antimony led to a considerable increase in the thermal structural stability of the compounds. A second effect was on the average degree of oxidation of molybdenum, which decreased in proportion to the increase in antimony content. The results of chemical–physical characterization were interpreted by hypothesizing that antimony ions occupy a cationic position in the secondary structure of the heteropolycompound in the case of the salts containing 1 atom of potassium per Keggin unit (KU), and electronically interacts with molybdenum in the Keggin anion, leading to the formation of Mo^{5+} species. In the case of samples containing three atoms of potassium per KU the antimony is present in the form of dispersed salt or oxide. The modification of the molybdenum redox properties led to considerable worsening of the catalytic performance in isobutyric acid oxidehydrogenation, with a decrease in activity (for the samples with one atom of potassium per KU) and also in selectivity to methacrylic acid (for the samples with three atoms of potassium per KU). This effect was interpreted as due to the stabilization of a lower degree of oxidation of molybdenum in antimony-containing samples.

INTRODUCTION

Heteropolycompounds are finding increasing applications as catalysts for both gas-phase and liquid-phase selective oxidation reactions (1–7). They are industrially applied for the oxidation of methacrolein to methacrylic acid and are well known to be efficient also in the oxidehydrogenation of isobutyric acid to methacrylic acid, one of the possible synthetic routes, alternatives to the acetone-cyanohydrin process for methylmethacrylate production (8–16). Their polyfunctionality (they are both acidic and multielectron oxidizing systems) makes them potentially interesting also for reactions of paraffin oxidation (17–32).

The heteropolycompounds more frequently utilized are the Keggin-type ones, and in particular, 12-molybdophosphoric and 12-tungstophosphoric acids, modified by the addition of different transition metal ions. These ions can either be positioned outside the Keggin unit (KU) in the secondary structure in the form of cations, or directly replace molybdenum or tungsten in the anion (as in the case of vanadium). These ions sometimes have a considerable effect on the catalytic behaviour, being directly involved in the oxidation mechanism, influencing the redox properties of the compound (13), or modifying its acid-base properties (33).

A thorough study of the chemical–physical features and reactivity of salts of Keggin-type heteropolycompounds was done by several authors (34–41). For instance, in the case of isobutyric acid oxidehydrogenation, the nature of the cation, when chosen among ammonium, alkali, or alkaline earth metals, was found to have a considerable effect on the catalytic activity and selectivity. Some authors proposed that the observed effects are related to modifications in the microporosity and acidity of the samples (35–41); other authors (13, 14) found a correlation between the oxidizing activity of the compounds and the standard electrode potential of the corresponding cations when these are transition metal ions.

Among the transition metals, the effect of vanadium (in both cationic and anionic position), zinc, chromium, nickel, copper and iron on the catalytic performance of heteropolycompounds in gas-phase oxidation reactions has been studied (20–25, 31–33, 42, 43). Very few studies have been devoted to the effect of antimony on the catalytic properties of heteropolycompounds in reactions of selective oxidation, even though antimony is a well-known component of catalysts for this class of reactions, such as in $VSbO_4$ for propane ammoxidation, for alkylaromatic ammoxidation, and in systems for allylic oxidation. To our

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knowledge, the addition of antimony has been reported only in a few patents (44) for formulations of heteropolycompounds to be used as catalysts for the isobutene selective oxidation to methacrolein.

In previous papers we reported how the addition of antimony ions to the potassium/ammonium salts of 12-molybdophosphoric acid considerably improved the structural thermal stability of the latter compounds and how this effect might be employed for the development of systems active and selective for oxidative transformations which require high temperature, such as the oxidehydrogenation of ethane to ethylene (17, 45, 46). The present work deals with the chemical–physical characterization of antimony-doped Keggin-type phosphomolybdates and with the effect on the catalytic performance in isobutyric acid oxidehydrogenation to methacrylic acid; two classes of catalysts are active in this reaction, iron phosphates and Keggin-type heteropolycompounds.

The study of this reaction is here aimed to verify which are the consequences of the modifications induced by antimony on the reactivity of the heteropolycompound.

EXPERIMENTAL

Preparation of the Heteropolycompounds

Preparation of the potassium/ammonium salts of 12-phosphomolybdic acid was done following the procedure reported in a previous paper (10). The salts were precipitated by the addition of HNO_3 to a solution containing $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $(NH_4)H_2PO_4$, and KCl, in the relative amounts as required by the stoichiometry. With this procedure the Keggin-type structure is formed in solution at acid conditions, and the insoluble ammonium/potassium salts of 12-phosphomolybdic acid are precipitated.

Catalysts containing antimony were prepared utilizing either $K(SbO)C_2H_4O_6$ or $SbCl_3$. The following procedure was utilized: an aqueous solution of calculated amounts of $K(SbO)C_2H_4O_6$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and $(NH_4)H_2PO_4$ was prepared by dissolving the salts in a minimum volume of water, with stirring and heating up to 80°C. During this period, the colour of the solution turned green. HNO_3 was then added dropwise to the solution obtained. During the addition of the acid, the colour of the solution progressively changed from pale green to blue, and then to green and yellow; at the same time, precipitation of the heteropolycompound was obtained. The addition of acid was stopped after a stable yellow colour of the slurry was obtained, at strongly acid pH.

Two series of samples with increasing amounts of antimony were prepared with the above procedure: one containing one atom of potassium per Keggin unit (KU) and one with three atoms of potassium per KU. The amount of molybdenum used was proportionally decreased as the amount of antimony increased. When an amount of K higher than that corresponding to a K-to-Sb ratio of 1 had to be utilized, KNO_3 was also added to the solution before the acid addition. When, on the contrary, K-to-Sb ratios lower than 1.0 had to be prepared, $SbCl_3$ was also added to the solution. Throughout the text the catalysts will be designated according to their K and Sb contents; i.e., K_1Sb_1 stands for the sample containing one atom of potassium and one atom of antimony per KU.

The drying and calcination procedure was the following: drying at 120°C overnight (with solvent evaporation) and then calcination at 180, 200, 220, 320, and 380°C. Before the catalytic tests, the samples were calcined at 380°C. At each intermediate step the temperature was held constant for 2 h. The final temperature was maintained for 24 h. In some cases, higher temperatures were utilized to evaluate the thermal stability of the compound. In all cases, the final temperature was maintained for 24 h.

After the calcination treatment, the samples belonging to the K_1Sb_y series were no longer yellow, but were either green or blue, depending on the calcination temperature and antimony content. On the contrary, samples belonging to the K_3Sb_y series were still yellow after the calcination treatment.

A reference preparation was made by dissolution of Na_2MoO_4 and Na_2HPO_4 in water, kept at 60–70°C. A second solution was prepared, where $SbCl_5$ was dissolved in a H_2O/HNO_3 solution. The latter solution was added dropwise to the first one; no precipitation occurred at this stage. Then, diethylether was added and an etherate phase was obtained which was separated from the aqueous phase; the ether was evaporated and a compound was precipitated which was then characterized.

Characterization of the Compounds and Catalytic Tests

FT-IR spectra were recorded with a Perkin Elmer 1700 spectrometer, using the KBr pressed disk technique. Powder XRD data were obtained with a Phillips PW 1050/81 diffractometer, controlled by a PW1710 unit using Ni-filtered CuK_α radiation. The samples were supported in a sample holder with a depth of 1 mm. The surface areas (BET single point) were determined by N_2 adsorption at 77 K, using a Carlo Erba Sorpty 1826 apparatus. Diffuse Reflectance UV-Vis spectra were recorded at room temperature using a Perkin-Elmer Lambda 19 spectrometer, equipped with a 60-mm integrating sphere coated with barium sulphate reflective paint.

Ionic chromatography was used to determine the absolute amounts per unit weight of K^+ and $(NH_4)^+$ in the samples. Prior to analysis, the samples were heated at 320°C to remove any remaining adsorbed water and excess ammonia. Known amounts of sample were then decomposed with a minimum volume of 1M LiOH. The analysis was carried out using a Waters 501 pump, equipped with a Rheodyne 7125 injector and a Waters 431 conductivity detector. The column utilized was a Vydac 400IC, 5 cm long; the eluent was 2 mM HNO_3, with a flow rate of 2 ml/min. This method was developed for and first applied to the analysis of heteropolycompounds by McGarvey and Moffat (37). For details concerning the confidence of this method of analysis we refer the reader to this paper.

Catalytic tests were carried out in a continuous flow reactor at atmospheric pressure. The standard feed composition was the following: isobutyric acid 2.1 mol% (Aldrich Chemical 99% purity; no further purification was made), oxygen 20%, water 4.3%, and the remainder helium. One gram of catalyst was used for each series of catalytic tests, granulated into particles ranging from 0.3 to 0.5 mm in size. The total flow rate was 60 mL/min, with a residence time of 1 s. The spent catalysts were unloaded by cooling the reactor under helium atmosphere. Reaction temperature was 280°C.

The reactor outlet was kept at 200°C, to prevent product condensation and methacrylic acid polymerization. A volume of the gas phase was sampled on-line by means of a sampling valve and analyzed by gas chromatography. A Carbosieve S column was utilized for CO and CO_2 analysis with a programmed oven temperature from 40 to 240°C (TCD). A GP 10% SP-1200/1% H_3PO_4 on Chromosorb WAW (FID) was utilized for isobutyric acid, acetone, propylene, and methacrylic acid analysis; the oven temperature was programmed from 60 to 120°C.

RESULTS

Characterization of Calcined Samples

Freshly precipitated K_1Sb_y and K_3Sb_y compounds, after drying at 120°C, exhibited X-ray diffraction spectra and FT-IR patterns identical to those of the corresponding mixed ammonium/potassium K_1Sb_0 and potassium K_3Sb_0 salts (10).

Figures 1 and 2 show the X-ray diffraction patterns of the K_1Sb_y and K_3Sb_y samples calcined at 320°C, respectively, for y between 0 and 1.0. In all cases the patterns correspond to that typical of a secondary structure with a cubic crystallographic cell. At this temperature no sample showed any trace of structural decomposition. The latter is in fact usually accompanied by the formation of MoO_3 or of other molybdenum suboxides. In addition, no lines relative to Sb oxide phases were observed. Also the FT-IR spectra showed no differences between samples with different antimony contents, thus confirming the presence of the unmodified primary Keggin unit. The presence of diffraction lines relative to antimony oxide could only be detected in these samples for $y = 2.0$.

The temperature at which structural decomposition begins in the potassium/ammonium mixed salts occurs in air at around 380–400°C (10). Indeed the potassium and ammonium ions fall in the class of those cations that stabilize the primary structure of Keggin-type heteropolycompounds. The addition of antimony further improves the structural stability of the heteropolycompound (17, 45, 46). In the case of the K_1Sb_1 sample, traces of incipient decomposition (evidenced by the presence of MoO_3 diffraction lines) began to appear at temperatures close to 500°C, while the K_1Sb_0 sample at this temperature was completely decomposed. This can also be seen in Fig. 3, where the X-ray diffraction patterns for some samples of the K_3Sb_y series calcined at 550°C are compared. The K_3Sb_1 sample is structurally intact at this high temperature, while $K_3Sb_{0.5}$ shows traces of decomposition and the sample without Sb is highly decomposed. In fact, the potassium-salified compound (K_3Sb_0) begins to decompose at temperatures close to 500°C (10).

FIG. 1. X-ray diffraction spectra of catalysts belonging to the K_1Sb_y series calcined at 320°C. The number refers to the value of y.

Reported in Fig. 4 are the values of specific surface area for the two series of samples calcined at 320°C. In the K_3Sb_y series, the surface area was not modified by the addition of

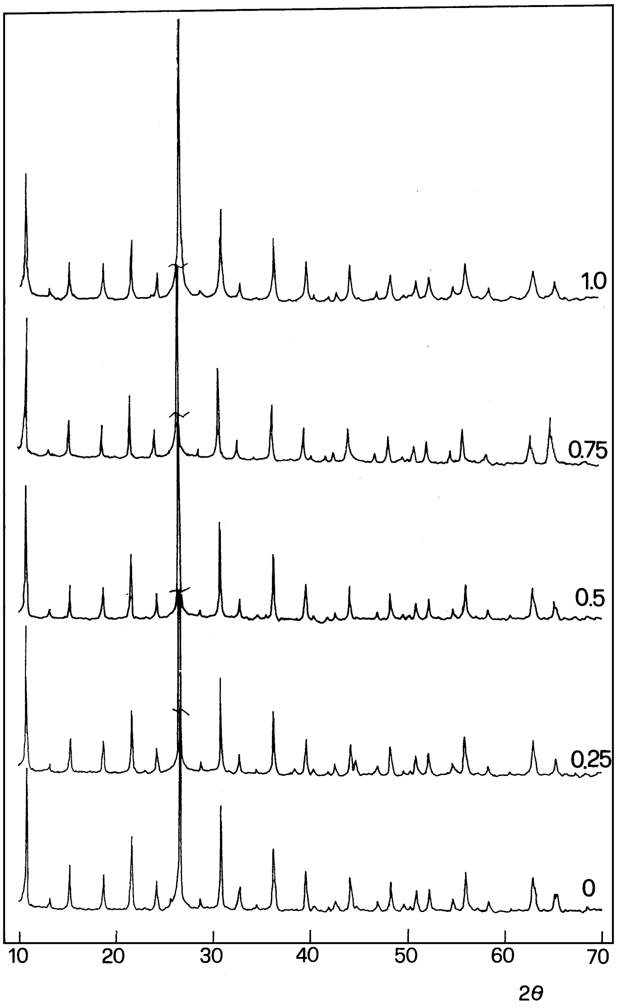

FIG. 2. X-ray diffraction spectra of catalysts belonging to the K_3Sb_y series calcined at 320°C. The number refers to the value of y.

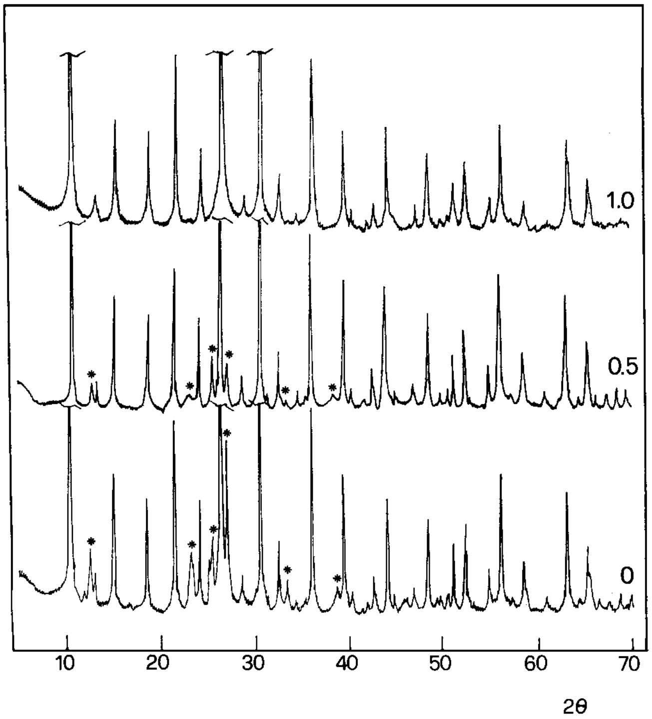

FIG. 3. X-ray diffraction spectra of catalysts belonging to the K_3Sb_y series calcined at 550°C. The number refers to the value of y; $^*MoO_3$ diffraction lines.

antimony up to $y = 1.0$. Higher values of y led, instead, to a decrease in the surface area. In the case of the K_1Sb_y series, the addition of Sb led to a decrease in the surface area. It is worth noting that all the K_xSb_0 salts (mixed potassium/ammonium salts) when calcined at 320°C had surface areas higher than 100 m^2/g (10).

Reported in Table 1 are the amounts of ammonium ions in samples of the K_1Sb_y and K_3Sb_y series calcined at 320°C as determined by ion chromatography. Increasing values of y led to a decrease in the amount of ammonium cation. The amount of potassium (used as a reference) was always found to be close to that employed in the preparation.

Calcination of the compounds in air led to a change in the colour of the samples belonging to the K_1Sb_y series. After drying at 120°C these samples were yellow, thus containing exclusively Mo^{6+}, while after calcination they were green or blue, thus also containing Mo^{5+} species. This is shown in Fig. 5, which reports the DRS-UV-Vis spectra of the K_1Sb_y samples after calcination at 320°C. In these spectra, two ligand–metal charge transfer (LMCT) bands $O^{2-} \rightarrow Mo^{6+}$ (octahedral), due to the different types of metal–oxygen ligands in the structure, are observed at around 280 and 350–370 nm (47–49). It has been reported that the size and position of the lowest-energy CT band is affected by the nature of the counterion, that is by the extent of interaction between polyanions (49). Further bands are observed

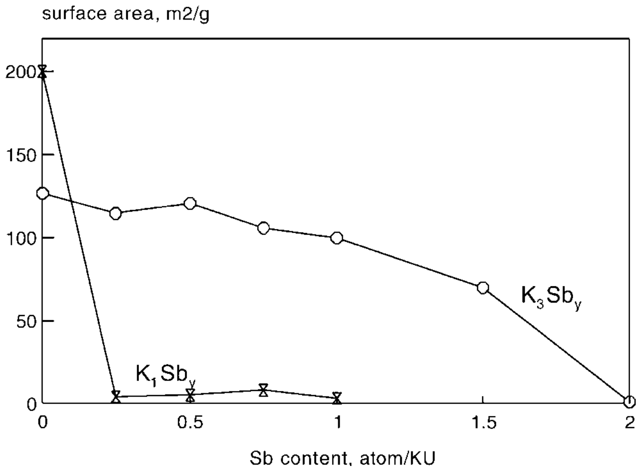

FIG. 4. Specific surface area of catalysts belonging to the K_1Sb_y and K_3Sb_y series calcined at 320°C.

TABLE 1

Amount of Ammonium Cation as Determined by Ionic Chromatography in Samples Calcined at 320°C

Sample	NH_4^+, moles/KU
K_1Sb_0	1.84
$K_1Sb_{0.25}$	0.60
$K_1Sb_{0.5}$	0.46
$K_1Sb_{0.75}$	0.06
$K_1Sb_{1.0}$	0.10
$K_1Sb_{1.5}$	0.24
K_3Sb_0	0.24
$K_3Sb_{0.5}$	0.30
$K_3Sb_{1.0}$	0

in antimony-containing samples. A clear band is present at around 700 nm, which is due to intervalence charge-transfer transitions, e.g. $Mo^{5+} \rightarrow Mo^{6+}$, and is therefore indicative of the presence of octahedral Mo^{5+} (50). The presence of reduced species can also affect the width and position of the lowest energy CT band (50). More than one absorption can occur in the visible spectral region of heteropolyblues, depending on the number of electrons furnished. The absorptivity is proportional to the degree of reduction, and also the width and position of this band is a function of the extent of reduction (47, 48). The figure shows that the extent of molybdenum reduction in these samples is a function of the antimony content, that is the higher the antimony content, the higher the amount of Mo^{5+} species.

On the contrary, the samples belonging to the K_3Sb_y series did not exhibit any change in colour due to the reduction of molybdenum after calcination and, correspondingly, did not show absorptions above 600-nm wavelength.

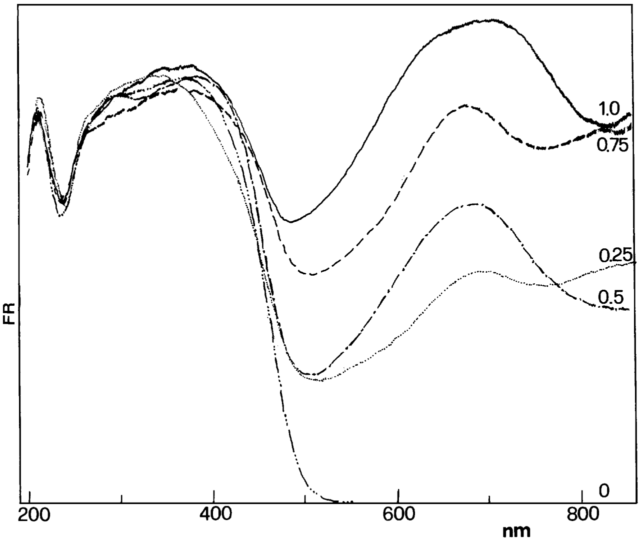

FIG. 5. UV-Vis DRS spectra of catalysts belonging to the K_1Sb_y series calcined at 320°C. The number refers to the value of y.

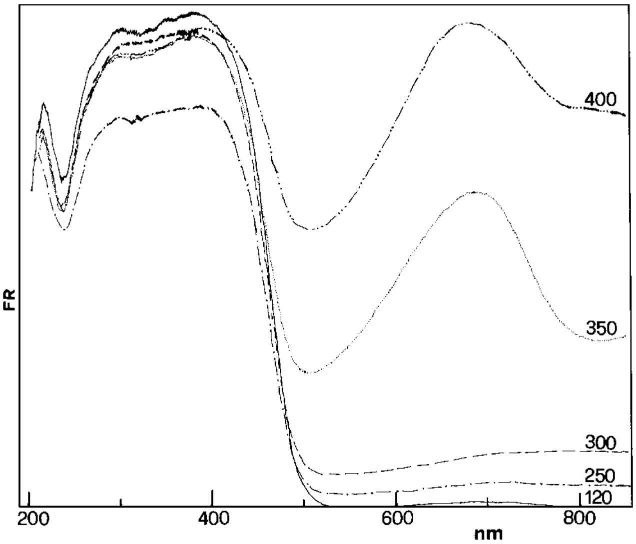

FIG. 6. UV-Vis DRS spectra of catalysts belonging to the $K_1Sb_{0.5}$ catalyst calcined at increasing temperatures (temperatures are indicated in the figure).

The extent of reduction is also a function of the calcination temperature. Figure 6 shows the evolution of the DRS-UV-Vis spectra of the $K_1Sb_{0.5}$ sample as a function of temperature below that of incipient structural decomposition. It is shown that the extent of reduction increases with increasing temperature. After drying at 120°C only LMCT absorptions are observed.

After calcination at 250°C, an increase in the overall absorption above 500 nm wavelength occurs, an absorption centered at around 700 nm becomes visible, and the sample turns a light green colour. For even higher calcination temperatures the band at around 700 nm becomes predominant. The same does not occur for the $K_3Sb_{0.5}$ sample (Fig. 7), where the spectra are not modified after calcination and, correspondingly, the samples retain their original yellow colour.

Activity in Isobutyric Acid Oxidehydrogenation and Characterization of Spent Catalysts

The oxidehydrogenation of isobutyric acid to methacrylic acid was used as a test reaction to verify the effect of the modification of the chemical–physical properties of these compounds as induced by the addition of antimony.

All heteropolycompounds are known to exhibit an initial unstable catalytic behaviour, with a decrease in activity and an increase in selectivity to methacrylic acid; during this period the catalyst is in part reduced (13). The variation of the isobutyric acid conversion with time-on-stream for the K_1Sb_y series, at 280°C and residence time 1 s, is reported in Fig. 8.

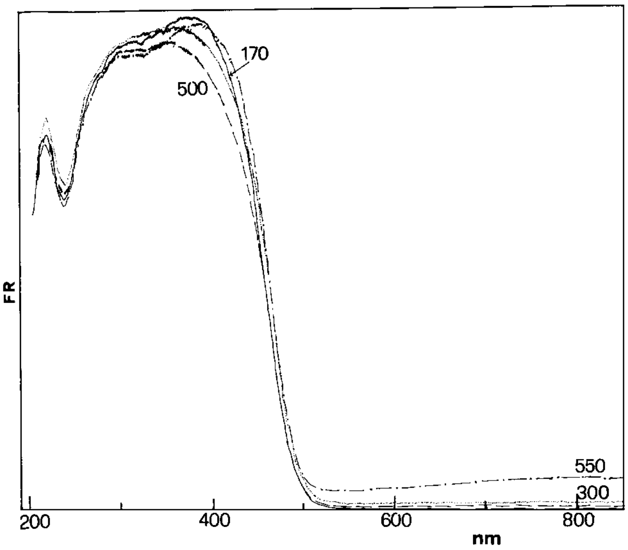

FIG. 7. UV-Vis DRS spectra of the $K_3Sb_{0.5}$ catalyst calcined at increasing temperatures (temperatures are indicated in the figure).

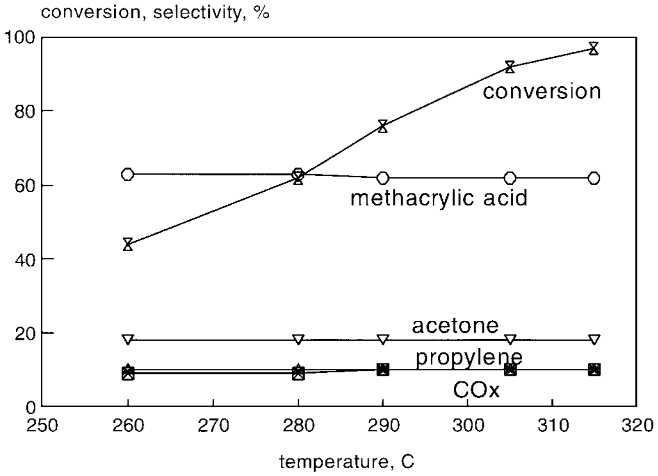

FIG. 9. Isobutyric acid conversion and selectivity to the products as functions of the reaction temperature for the $K_1Sb_{0.25}$ catalyst.

The addition of antimony led to a nonnegligible decrease in the initial activity. Moreover, a clear deactivation with time-on-stream was exhibited, and a few hours were necessary to reach a more stable catalytic performance. Under these conditions the K_1Sb_0 sample did not exhibit any deactivation, and the conditions were in this case sufficient to obtain total isobutyric acid conversion.

Reported in Fig. 9 are the selectivity to the products (methacrylic acid, acetone, propylene, and CO_x) and the conversion as functions of the reaction temperature, under stable reaction conditions (after 20 h time-on-stream) for the $K_1Sb_{0.25}$ sample, the most active among the antimony-containing samples. All the samples of the K_1Sb_y series (including the K_1Sb_0 sample) behaved quite similarly, and the value of selectivity to methacrylic acid was approximately the same for all samples. The figure shows that the selectivity to the different products was rather independent of temperature, analogous to that observed for the $K_x(NH_4)_{3-x}PMo_{12}O_{40}$ compounds (9, 10). Therefore, the presence of antimony only affects the activity, but it does not modify the distribution of the products.

Different, instead, was the behaviour of the K_3Sb_1 sample, for which the distribution of the products as a function of temperature is given in Fig. 10. The sample is compared with the K_3Sb_0 catalyst in Fig. 11. Contrary to that observed with the K_1Sb_y series, in this case not only was the activity lowered by the antimony additions, but also the selectivity to methacrylic acid decreased considerably, due to the increased formation of carbon oxides and propylene. The

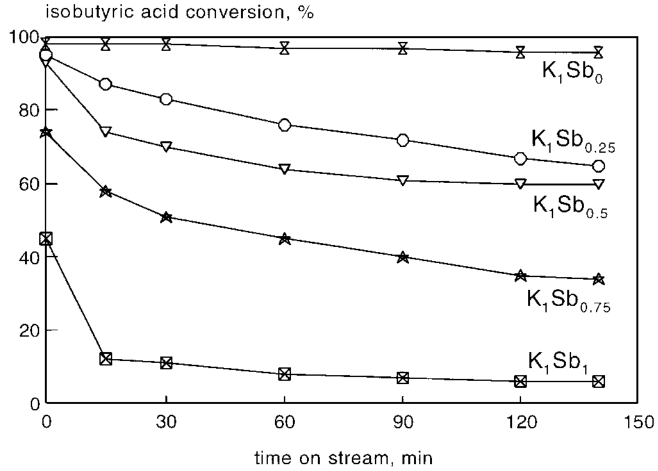

FIG. 8. Isobutyric acid conversion as a function of time-on-stream for catalysts belonging to the K_1Sb_y series. Conditions are given in the Experimental section.

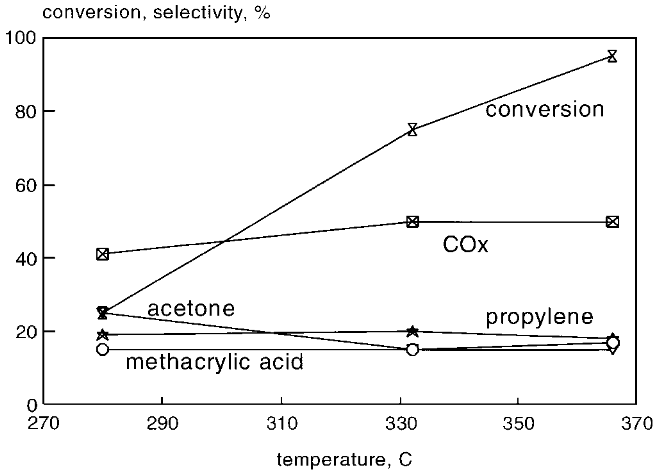

FIG. 10. Isobutyric acid conversion and selectivity to the products as functions of the reaction temperature for the K_3Sb_1 catalyst.

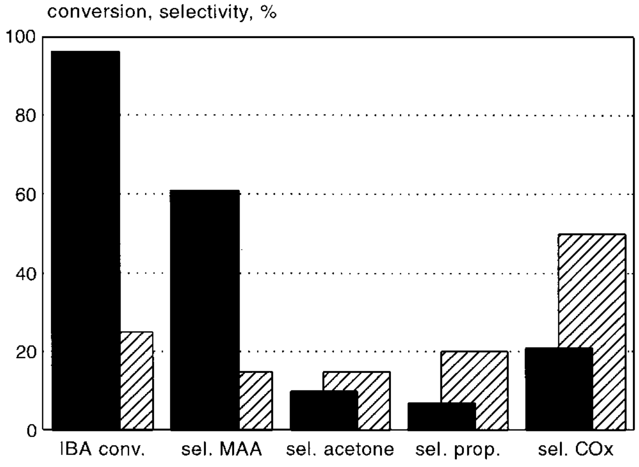

FIG. 11. Comparison of the performance of the K_3Sb_1 (open bars) and K_3Sb_0 (full bars) catalysts at 280°C. Other conditions as described in the Experimental section.

comparison is done for the same level of temperature, and thus in correspondence of different conversion levels; however, the selectivity was practically independent of conversion (9, 10).

The spent catalysts were found to be structurally intact (as shown by both FT-IR and XRD measurements), provided reaction temperatures lower than 350–360°C were used. DRS-UV-Vis spectra of spent K_1Sb_y samples (Fig. 12) indicate a higher extent of reduction than in the corresponding samples before reaction. Once again, the extent of reduction was proportional to the antimony content in the catalysts.

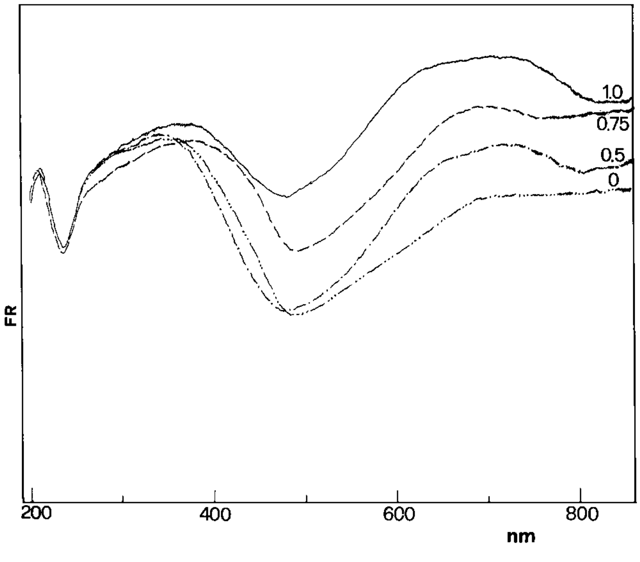

FIG. 12. UV-Vis DRS spectra of catalysts belonging to the K_1Sb_y series after reaction (the number refers to the value of y).

DISCUSSION

The Effect of Sb Additions on the Chemical–Physical Features of the Keggin 12-Molybdophosphates: The K_1Sb_y Series

Antimony has remarkable effects on the chemical–physical features and reactivity of mixed ammonium/potassium salts of 12-molybdophosphates (K_1Sb_y series). The main modifications regard the structural thermal stability (17, 45, 46) and the average oxidation state of molybdenum. These effects suggest a strong morphological and chemical (electronic) interaction between the antimony ions and molybdenum in the heteropolycompound. It is worth mentioning that the FT-IR and XRD diffraction data showed no differences in structure due to the antimony additions with respect to the K_1Sb_0 compound for both the precipitated compounds (dried at 120°C) and the calcined ones (at 320°C). In potassium salts (K_3Sb_y series), instead, the modifications concern only the structural stability, while no effects are induced on the molybdenum valence state. This indicates that the nature of the interaction between antimony ions and molybdenum in the K_3Sb_y series is different than in the K_1Sb_y series, possibly suggesting a different antimony arrangement in the heteropolycompound structure.

It is known that the redox properties of molybdenum-based heteropolycompounds can be remarkably affected by the presence of guest metals, such as vanadium and tungsten, in the primary framework, as well as by the nature of the metal cations in the secondary framework (51, 52). Accordingly, antimony might (i) replace molybdenum in peripheral positions in the Keggin anion, (ii) act as a cation replacing ammonium in the secondary structure, and (iii) even theoretically replace phosphorus as the heteroatom. The latter possibility can be disregarded, because it would lead to IR absorptions different from those typical of 12-phosphomolybdates (1, 51, 52); moreover, no heteropolycompound developed when the preparation was carried out in the absence of phosphorus. The possibility of antimony forming segregated phases, such as dispersed amorphous or microcrystalline phases, is also to be taken into consideration, even though all the heteropolycompounds prepared were monophasic after calcination at 320°C and possessed a very crystalline cubic-type secondary structure. Crystalline phases other than the heteropolysalt were obtained in the presence of antimony only when the value of y in the K_3Sb_y series was 2.0 with the formation of Sb_2O_5.

In our case, it is likely that antimony replaces the ammonium cation in the secondary framework of the K_1Sb_y heteropolycompounds, as suggested by the results obtained. In particular,

(1) The structural stabilization induced by the addition of antimony is evidenced by the data reported (Fig. 3), as well as by previously reported results (17, 45, 46). The

temperature of the initial decomposition is shifted towards higher temperatures. For instance, the temperature at which formation of MoO_3 is observed increases from 400°C to approximately 500°C in the K_1Sb_1 sample (45). The largest increase in thermal stability was found for Sb contents equal to or higher than 1.0 atom per KU. In the K_3Sb_y series, decomposition begins at temperatures close to 550–600°C (45). It is known that the nature of the cation in heteropolycompounds is fundamental in affecting the stability of the Keggin framework, and therefore, the modification in structural stability may arise as a consequence of variation in the cationic composition. The presence of a partially hydrolyzed Sb^{5+} ion, instead of a bare ion (a small ion, 0.62 Å, with a highly positive charge), besides leading to a larger cation which can better interact with the neighbouring oxygen atoms of the Keggin anions, may be more efficient in the compensation of the highly delocalized negative charge of the anion, analogously to what occurs in zeolites.

Moreover, it is known that the surface area of these compounds is greatly affected by the nature of the cation. Indeed, the surface area of antimony-containing K_1Sb_y compounds is much lower than for the K_1Sb_0 sample (Fig. 4).

(2) The amount of ammonium cation, as determined by ionic chromatography (Table 1) corresponds to the theoretical one which is expected in case the Sb^{5+} ion replaces ammonium in the secondary framework (the presence of Sb^{5+} is preferred to Sb^{3+} due to the occurrence of the redox reaction occurring between Sb^{3+} and Mo^{6+}). Indeed, the amount of residual ammonium in the heteropolycompound theoretically depends on the position in the structure. Figure 13 reports the theoretical values which should be expected in the K_1Sb_y series when Sb^{5+} is:

(a) *in a peripheral position in the anion*, replacing one molybdenum ion in the Keggin structure and either keeping a vacancy in the coordination sphere, eventually saturated by a water molecule, $(PMo_{12-y}Sb_yO_{40-y})^{(3-y)-}$, or completing the coordination sphere with an oxo-ligand: $(PMo_{12-y}Sb_yO_{40})^{(3+y)-}$, or with an OH− ligand, $(PMo_{12-y}Sb_yO_{40}H_y)^{3-}$.

(b) *in a cationic position*, thus within the secondary framework of the heteropolycompound; in this case the Sb^{5+} can be either a bare ion, coordinated to the O atoms of neighbouring Keggin anions, or a partially hydrolyzed ion, thus in the form $Sb_y(OH)_{ny}^{(5-n)+}$. In Fig. 13, the different cases for n = 1, 2, and 3 have been considered.

Of course, other possibilities may exist, such as a distribution of antimony in both cationic and anionic positions, as well as the presence of segregated disperse antimony oxide. These theoretical plots have to be compared with the experimental amounts as determined by ionic chromatography (Table 1). The very low amounts of ammonium ion analytically determined in the K_1Sb_y series suggest the presence of antimony in the cationic position in the secondary structure of the heteropolycompound. Excess antimony ions with respect to the amount necessary to act as the counterion may arrange differently, as antimony polynuclear complexes or clusters, or segregated disperse oxide.

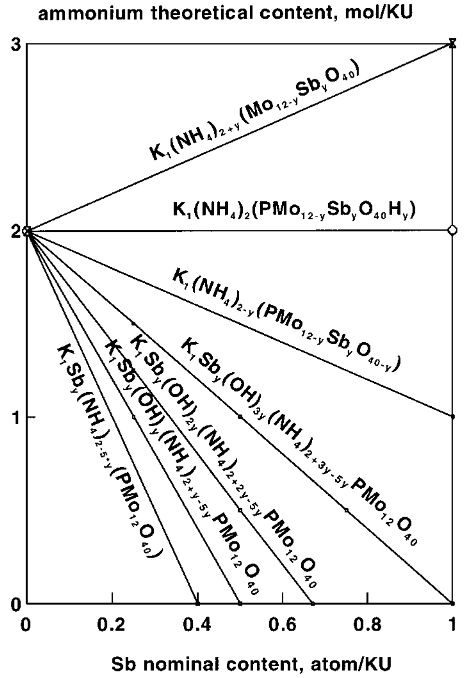

FIG. 13. Theoretical amount of ammonium per Keggin unit as a function of Sb^{5+} content in catalysts belonging to the K_1Sb_y series according to different hypotheses about the position of antimony in the heteropolycompound framework.

Furthermore, the hypothesis of antimony in the primary structure is highly unlikely, since that would lead to differences in the IR spectra of compounds (53); on the contrary, spectra were identical to those of the K_1Sb_0 sample.

A reference preparation was also made in the absence of ammonium cations (see Experimental section), thus under conditions at which the insoluble compound is not formed. The prepared soluble compound was extracted in ether and the heteropolycompound extracted with ether contained no antimony, which remained in the aqueous phase. This indicates that antimony is not included in the primary framework of the Keggin heteropolycompound during the synthesis procedure.

The Effect of Sb Additions on the Chemical–Physical Features of the Keggin 12-Molybdophosphates: The K_3Sb_y Series

In the K_3Sb_y series the potassium alone is enough to balance the anionic charge. The presence of residual ammonium cations would only be justified in the case a $K_3(NH_4)_y(PMo_{12-y}Sb_yO_{40})$ compound were formed. The analysis detected negligible or nil amounts of ammonium in these compounds (Table 1). Therefore in this case Sb^{5+} ions may be in the form of salt or free oxide, dispersed on the surface. In agreement with the hypothesis that the cationic composition is not modified by antimony addition are the values of the surface area, which is the same for all samples of the K_3Sb_y series up to $y = 1.0$ (Fig. 4). The surface areas only decrease in samples containing more than 1.5 Sb atom per KU, thus in those samples where bulk Sb_2O_5 is detected by means of XRD. It is likely that in the latter case the growth of spurious phases can block the porosity of the heteropolycompound, with a consequent decrease in the surface area. Nevertheless, also in this case the antimony interacts with the Keggin anion; in fact, also in K_3Sb_y samples antimony induces structural stabilization to the heteropolycompound (45, 46).

The Effect of Antimony on Molybdenum Redox Properties

The second important effect of antimony is on the degree of molybdenum reduction. During the preparation, antimony favours the reduction of the molybdenum ions in solution. The development of the green colour after addition of the Sb^{3+} salt to the aqueous solution containing molybdenum and phosphorus salts is due to the redox reaction which also occurs in mildly acidic conditions and leads to the formation of the “molybdenum blue” species (corresponding to the contemporaneous presence of Mo^{6+} and Mo^{5+}).

The reduction potential for the redox couple Sb^{3+}/Sb^{5+} ranges from 0.45 to 0.65 V (when the pH is varied from 4 to 0), while the potential relative to the couple Mo^{5+}/Mo^{6+} in heteropolycompounds is a function of the cationic composition and of the type of polyanion, and is known to range from 0.4 to 0.7. A value higher than 0.5 is likely under our conditions in order to justify the occurrence of the redox reaction between Sb^{3+} and Mo^{6+}. However, it is likely that the redox reaction is not complete, due to the very low difference in the reduction potentials between the two couples, and therefore residual Sb^{3+} ions are left in solution. It is worth mentioning that the same redox reaction between Mo^{6+} and Sb^{3+} was also observed in the absence of the phosphorus at pH around 4, even though it was flowing more slowly. Therefore, the reaction also occurs for molybdenum in isopolyanions. The reduction of Mo^{6+} in compounds other than heteropolycompounds usually proceeds up to the formation of Mo^{3+} (the potential relative to the couple Mo^{3+}/Mo^{6+} ranges from 0.1 to 0.3 V for pH ranging from 4 to 0). Only in heteropolycompounds does delocalization of the excess negative charge (on electron being furnished by a reducing agent) through the entire structure allow the reduction process to the formation of Mo^{5+} species to be stopped.

The preparation then consists in the addition of HNO_3. When the pH is then quickly lowered, initially the redox reaction proceeds (the colour of the solution turns blue), due to the reaction between the $(PMo_{12}O_{40})^{3-}$ Keggin anion and the residual Sb^{3+} ions. In this case, however, the reduction of molybdenum occurs at the same time as precipitation of the insoluble ammonium/potassium salt of $(PMo_{12}O_{40})^{3-}$ at low pH; it is likely that the precipitation of the solid may hinder the prosecution of the redox process, which is kinetically favoured only until the heteropolycompound is dissolved.

Finally, the slurry turns yellow, because at very acid pH the molybdenum is reoxidized due to the oxidizing properties of HNO_3. Indeed, when HCl was used instead of HNO_3, the slurry maintained its blue colour; thus Mo^{5+} was not reoxidized.

Since the potassium and the mixed potassium/ammonium salts of 12-molybdophosphoric acid are insoluble compounds, they precipitate at strongly acid pH, while the Sb^{5+} ions remain in solution (the Sb^{5+} species is amphoteric, being soluble either in the form of SbO_3^- or of SbO_2^+, and the region of precipitation is restricted to a very narrow pH range). Thus, the Sb^{5+} only precipitates when the solvent is evaporated. In agreement, no precipitate was obtained when 12-molybdophosphoric acid was first dissolved in water and then $SbCl_5$ was added to the solution.

Then during the heat treatment of the precipitated compounds, the antimony ions may replace ammonium cations, thus migrating into the secondary framework of the heteropolycompound and substituting for ammonium, which is expelled from the structure. Ammonium may be released in the form of molecular nitrogen (10), by redox reaction with Mo^{6+} centers, which are at the same time reduced to Mo^{5+}:

$$K_1(NH_4)_2PMo_{12}O_{40} \rightarrow K_1(PMo_6{}^{VI}Mo_6{}^{V}O_{37}H_2) + N_2 + 3H_2O.$$

The higher the antimony content, the higher the amount of ammonium cation that is expelled from the structure and thus the higher the amount of molecular nitrogen that is formed and the greater the extent of molybdenum reduction. This might explain why the heat treatment leads to a considerable reduction of molybdenum in the K_1Sb_y series and why the extent of reduction is proportional to the antimony content, as shown in Fig. 6. Therefore, the mechanism of formation of these antimony salts may include a solid state reaction at high temperature, with replacement of ammonium cations by antimony ions.

From the above equation it is evident that the complete oxidation of two NH_4^+ species to molecular nitrogen would also require extensive reduction of molybdenum in the Keggin unit, which cannot be withstood by Keggin anions. Therefore, reoxidation of a fraction of reduced molybdenum by molecular oxygen, or a possible participation of Sb^{5+} in ammonium oxidation with the formation of Sb^{3+} can be assumed.

The reduction of molybdenum also proceeds at temperatures higher than 250°C (as shown in Fig. 7), even in those samples which do not have any residual amount of ammonium cations in the framework after calcination (Table 1). Therefore, a possible participation of a solid-state redox reaction between residual Sb^{3+} ions and Mo^{6+} can be postulated to explain the reduction of molybdenum. As mentioned above, this reaction may be hindered in the slurry after precipitation, but it may be kinetically favoured at high temperatures during calcination, thus favouring the solid state interaction between the two cations. It is necessary to consider also that a solid state redox reaction implies a close electronic interaction between the two ions, thus supporting the position of antimony in the secondary structure coordinated to the primary anions.

The case for the K_3Sb_y series is different. In this case molybdenum does not undergo reduction. This may be due to the absence of ammonium cations (which according to the above equation are responsible for the molybdenum reduction), or to the fact that the high-temperature solid state redox reaction between antimony and molybdenum does not occur in this case, because antimony does not replace potassium in the framework, and therefore, the electronic interaction between molybdenum and antimony is not favoured.

Influence of Antimony on the Activity in Isobutyric Acid Oxidehydrogenation to Methacrylic Acid

The addition of antimony leads to considerable deactivation of the potassium/ammonium 12-molybdophosphates, and the decrease in activity is approximately proportional to the Sb content in the K_1Sb_y series (Fig. 8). In fact the conversion of isobutyric acid decreases considerably. Since all spent catalysts did not exhibit any evidence of structural decomposition and all of them were characterized by comparable values of surface area (very low, less than 1 m^2/g) (9, 10), the observed deactivation effect cannot be attributed to morphological or structural differences. The characterization of calcined catalysts (Fig. 5) clearly indicates that the presence of antimony affects the redox properties of molybdenum, and hence, the catalytic properties. The spent catalysts are more reduced than the same samples before reaction, as seen from comparison of the intensities of the bands relative to $O^{2-} \rightarrow Mo^{6+}$ and to intervalence transition $Mo^{5+} \rightarrow Mo^{6+}$ for the samples before and after reaction (Figs. 5 and 12). Also in this case, the extent of reduction is clearly proportional to the antimony content. Since also the spent K_1Sb_0 catalyst is strongly reduced, the reduction is clearly due to the reaction environment, but the presence of antimony stabilizes a higher average degree of reduction, thus an average lower oxidation state for molybdenum, in the reaction environment.

The comparison of the catalytic performance of the K_1Sb_y samples at the very beginning of their lifetime, and after 2 h time-on-stream (Fig. 8), with the corresponding extent of reduction for spent catalysts (Fig. 12), indicates that there exists an inverse relationship between the catalytic activity and the average degree of reduction. The permanence in the reaction environment causes a progressive reduction of molybdenum, to which corresponds a decrease in activity. Therefore, since the more oxidized compounds are more active, it can be postulated that Mo^{6+} ions are likely involved in the activation of the isobutyric acid.

The products distribution of K_1Sb_y samples is not modified with respect to the K_1Sb_0 compound. This suggests that antimony only affects the Mo^{6+} centers responsible for the reactant activation, while the relative rates of the parallel reactions of conversion to the various products are not affected. On the contrary, the K_3Sb_1 sample behaves quite differently from the K_3Sb_0 sample. Under stationary conditions the activity is lower than that of the K_3Sb_0 sample, but the main effect concerns the products distribution (Fig. 11). Indeed, the formation of methacrylic acid decreases, in favour of CO_x, mainly, and of propylene and acetone.

Data reported in the literature suggest that the relative rates of product formation can be affected by the acidity of the heteropolycompound (33, 54), or by the redox potential of the dopant metal in 12-molybdophosphate and 12-tungstophosphates modified by various metal ions (13). In our case, while for the K_1Sb_y series the behaviour can be explained simply by decreased activity, i.e. by modified redox properties of molybdenum, for the K_3Sb_y series the considerable change in the distribution of the products indicates a different change in the physico–chemical properties of the heteropolycompound. Since characterization results indicate that antimony ions are distributed in different ways in the two series of samples, this can explain why antimony does affect the catalytic performance in different ways. While in the K_1Sb_y series the antimony is likely positioned in the secondary framework of the heteropolycompound, modifying the redox properties and reactivity of molybdenum, in the K_3Sb_y series the antimony does not replace potassium and, therefore, is likely dispersed in the form of amorphous or microcrystalline oxide. This additional phase may itself exhibit a nonnegligible activity, leading to a completely different catalytic behaviour with respect to the K_3Sb_0 sample, with a worsening of both activity and selectivity.

CONCLUSIONS

The addition of antimony ions in the preparation of mixed potassium/ammonium salts of 12-molybdophosphoric acid (K_1Sb_y series) has a considerable effect on the physico–chemical features of heteropolycompounds obtained after calcination at 320°C. One effect is the increase in the structural thermal stability of the salts. A second effect is the reduction of molybdenum in the Keggin framework. The characterization of calcined samples suggests that antimony migrates into the secondary framework of mixed ammonium/potassium salts during the calcination treatment. Ammonium is thus released from the structure in the form of molecular nitrogen, with contemporaneous reduction of molybdenum. Molybdenum may also be reduced by direct solid-state redox reaction with Sb^{3+} ions. In potassium salts (K_3Sb_y series), instead, the antimony does not replace the very stable potassium and probably forms segregated dispersed oxide phases. In these samples no modification of the antimony oxidation state occurs as a result of the calcination treatment.

As a consequence of the variation in molybdenum redox properties, the catalytic performance in isobutyric acid oxidehydrogenation (chosen as a test reaction) is affected considerably by the presence of antimony. The activity is generally decreased, and in the case of the potassium salts a decrease in the selectivity to methacrylic acid is also observed.

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