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On the antimony-stabilized cubic structure of potassium / ammonium salts of 12-molybdophosphoric acid and its catalytic performance in the oxidehydrogenation of ethane

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Potassium/ammonium salts of 12-molybdophosphoric acid were modified by the addition of an Sb^{5+} salt. The addition of antimony led to a remarkable increase in the thermal structural stability of the compounds obtained. The incipient destruction of the Keggin unit in the mixed potassium/ammonium salt of 12-molybdophosphoric acid was shifted from 400–420°C to 500°C. The potassium salt modified by the addition of one Sb^{5+} atom per KU decomposed at temperatures higher than 600°C. This property allowed the samples to be used as catalysts for high temperature, gas-phase oxidation reactions, such as the oxidehydrogenation of ethane. The compounds did not undergo structural decomposition at temperatures as high as 540°C under reaction conditions, but were poorly active and selective in ethylene formation. Therefore, antimony-stabilized compounds were further modified by the addition of transition metal ions in order to improve the catalytic performance. The addition of small amounts of iron, chromium and cerium ions led to an improvement of the catalytic performance; the compound was apparently monophasic, and characterized by the cubic crystalline structure typical of the salts of 12-molybdophosphoric acid.

Keywords: antimony; 12-molybdophosphoric acid; heteropolycompounds; ethane oxidehydrogenation; ethylene

1. Introduction

Heteropolycompounds have recently found increasing applications as catalysts for gas-phase selective oxidation reactions [1–5]. Among the most important appli-

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cations, heteropolycompounds are efficient catalysts for the oxidation of methacrolein to methacrylic acid [1] and in the oxidehydrogenation of isobutyric acid to methacrylic acid [2–4]. Their polyfunctionality (they are both acidic and multielectron oxidizing systems) makes them potentially interesting for reactions of paraffin activation, such as the oxidation of *n*-butane to maleic anhydride [5] and the oxidation of *n*-pentane to maleic and phthalic anhydrides [6]. Keggin-type heteropolycompounds are those more frequently utilized, and in particular 12-molybdophosphoric acid and 12-tungstophosphoric acid, modified by the addition of different transition metal ions. Among the latter, most studies have been focused on the reactivity of transition-metal-substituted polyoxometalates (TMSP), where ions of metals such as Fe, Co, Ni, Mn, Nb and Cr substitute for W or Mo in peripheral positions in the anion. These catalysts have been utilized for liquid-phase olefin epoxidation with either H_2O_2 or molecular oxygen, and for the hydroxylation of paraffins [7–9]. Other studies have been done where the transition metals act as counterions for the Keggin anion. These systems have been used for the gas-phase oxidation of methacrolein and isobutyric acid to methacrylic acid [10].

Very few studies have dealt with the characterization of heteropolycompounds modified by the addition of post-transition elements, such as antimony.

Many years ago, the polychelating heteropolytungstate complex $(M^{n+}Sb_9W_{21}O_{86})^{(19-n)-}$ (where M^{n+} is an alkali or alkaline earth cation) was studied [11,12]. The $SbW_{11}O_{38}H^{6-}$ (with trivalent antimony) anion also is known to exist [13]. Preparation of the heteropolyacid containing pentavalent antimony $H_3(SbMo_{12}O_{40})\cdot 48H_2O$ also has been reported [14]. However, to our knowledge, no data have been reported about the characterization or reactivity of antimony-modified 12-molybdophosphoric acid.

The main limit in the application of heteropolycompounds as heterogeneous catalysts for gas phase applications is the structural stability. It is known that Keggin-type heteropolyacids decompose at temperatures close to 300°C [15]. The decomposition leads to a progressive worsening of catalytic performance related to MoO_3 loss by sublimation, even though the activity can be partially restored by a surface reconstruction of the heteropolycompound in the reaction medium in the presence of water vapour. This limits the application of these compounds to reactions where the substrate is sufficiently reactive, and can be suitably converted at relatively low temperatures, as in the case of the oxidation of isobutyric acid or methacrolein to methacrylic acid.

The present work reports a surprising effect of increased thermal stability achieved by the modification of potassium/ammonium salts of 12-molybdophosphoric acid with an antimony salt. This made it possible to test the materials as heterogeneous catalysts for the gas phase oxidehydrogenation of ethane to ethylene. The antimony-doped potassium salt of 12-molybdophosphoric acid was found to be poorly active and selective in the synthesis of ethylene. Further doping with transition metal ions, however, gave a compound which was both structurally stable and active and selective.

2. Experimental

The preparation of the potassium/ammonium salts of 12-phosphomolybdic acid was done following the procedure reported in a previous work [16]. The salts were precipitated from a solution containing the various salts, through addition of HNO_3. This method has the advantage of yielding the compound in the salt form without intermediate synthesis of the acid.

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. HNO_3 was added dropwise to the solution obtained. During the addition of the acid, the colour of the solution progressively changed from pale green to blue, green and yellow; at the same time, a precipitate was obtained. The addition of acid was stopped when a stable yellow colour of the slurry was obtained. The solvent was then evaporated. The amount of molybdenum used was proportionally decreased as the amount of antimony was 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 addition of acid was begun. When, on the contrary, K-to-Sb ratios lower than 1.0 had to be prepared, $SbCl_3$ was also added.

The drying and calcination procedure was as follows: drying at 120°C overnight (with solvent evaporation), followed by calcination at 180, 200, 220, 320 and 370°C. The temperature was held for 2 h at each intermediate step and 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. With this procedure the Keggin-type structure is formed in solution under strongly acid conditions (i.e., when the acid is added), and the insoluble ammonium/potassium salt of 12-molybdophosphoric acid (the preparation is done in the presence of excess ammonium) is precipitated [16].

Several samples were prepared with increasing amounts of antimony (from 0 to 2 atoms per each atom of phosphorus). A detailed description of these systems will be reported in another paper [17].

Hereinafter the catalysts will be designated according to their K and Sb content, e.g. K_1Sb_1 stands for the sample with composition $K_1(NH_4)_xPMo_{11}Sb_1O_{40}$.

K_3Sb_1 samples were prepared which contained different types of promoters. In this case a second solution was prepared, which contained either metal nitrates (iron, chromium or cerium salts) or ammonium vanadates. This second solution was added dropwise to the one containing molybdenum, phosphorus and antimony ions; the solvent was then evaporated. The heating procedure was the same as that above reported.

Powder XRD data were obtained with a Philips PW 1050/81 diffractometer, controlled by a PW1710 unit using Ni-filtered Cu Kα radiation. The samples were supported in a sample holder with a depth of 1 mm.

The surface areas were determined by N_2 adsorption at −196°C, using the BET theory and a Carlo Erba Sorpty 1826 apparatus.

The catalytic tests were carried out in a stainless-steel laboratory flow reactor, at atmospheric pressure. Ethane, oxygen and inert diluent were fed with the following concentrations: 3.6% ethane, 10% oxygen; residence time was 2.7 s.

The products obtained were analyzed by gas chromatography. Ethane and ethylene were analyzed with a Carbosieve D column, with the oven temperature maintained at 100°C, and a FID. CO and CO_2 were analyzed by means of a Carbosieve S column with the oven temperature programmed from 40 to 220°C, TCD. No products other than ethylene and carbon oxides were detected, not even in traces.

3. Results and discussion

The X-ray diffraction patterns at 500°C for samples with composition K_1Sb_0 and K_1Sb_1, and at 550°C of K_3Sb_0 and K_3Sb_1 are reported in fig. 1. Shown in fig. 2 is the evolution of the pattern for K_1Sb_1 with increasing temperature.

The mixed potassium/ammonium salts are thermally structurally stable up to 420°C [16], while the potassium salt of 12-molybdophosphoric acid begins to decompose at temperatures as high as 500°C. Figs. 1 and 2 show that K_1Sb_0 is highly decomposed at 500°C, exhibiting the diffraction lines typical of MoO_3 besides those typical of the cubic salt of 12-molybdophosphoric acid. On the contrary, K_1Sb_1 only exhibits slight decomposition at 500°C. Fig. 2 indicates that the decomposition of this salt is complete at temperatures higher than 500°C. The K_3Sb_0 salt is partly decomposed at 550°C, while the K_3Sb_1 salt is still intact at this temperature. It was found that the incipient decomposition of this salt occurred at 600°C.

The addition of antimony clearly induces a structural stabilization to the compound. The incipient formation of MoO_3, indicative of the destruction of the structure of the compound, is shifted towards higher temperatures. The addition of antimony results in a 50–100 degree increase in the range of thermal stability.

Thermal stability up to temperatures higher than 500°C is known to be exhibited by anhydrous potassium or cesium salts of 12-molybdophosphoric acid, all possessing the stable cubic secondary structure, while no stabilization has been observed for salts of divalent or trivalent transition metal ions.

The stabilization effect induced by antimony is a surprising effect. No information is available in literature regarding the addition of either Sb^{3+} or Sb^{5+} as a counterion of the Keggin anion, but it is likely that the observed stabilization effect obtained by the addition of antimony may be similar to that achieved when salts of 12-molybdophosphoric acid are formed with alkali metals. It is known that these ions coordinate to surface oxygen atoms of the Keggin anion, giving rise to a more rigid and hence stable secondary structure for the heteropolycompound. One hypothesis that can be formulated is that the antimony may replace ammonium in

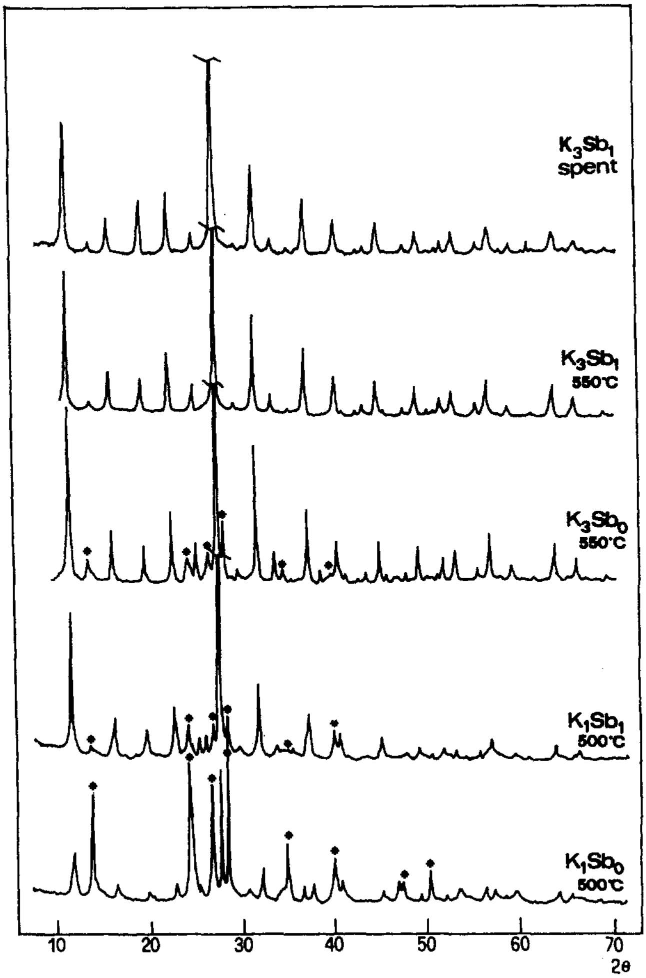

Fig. 1. X-ray diffraction patterns of compounds prepared with and without antimony. (*) MoO_3.

the secondary structure, giving rise to a more stable compound. However, it has to be pointed out that the stabilization effect induced by the addition of antimony also occurs with the K_3 salt, thus with the compound where the heteropolyanion is completely salified by the potassium cations. Therefore, this suggests a more complex role of the antimony.

This thermal stability can be usefully exploited by employing these materials as catalysts for applications that require high temperatures, such as the oxidehydrogenation of light paraffins. The oxidehydrogenation of ethane was used as a test reaction to check the reactivity of these thermally stable, antimony-modified, heteropolycompounds. Table 1 compares the reactivity of the samples displayed in figs. 1 and 2.

At relatively low reaction temperature, i.e. 425°C, K_1Sb_0 is fairly active, but

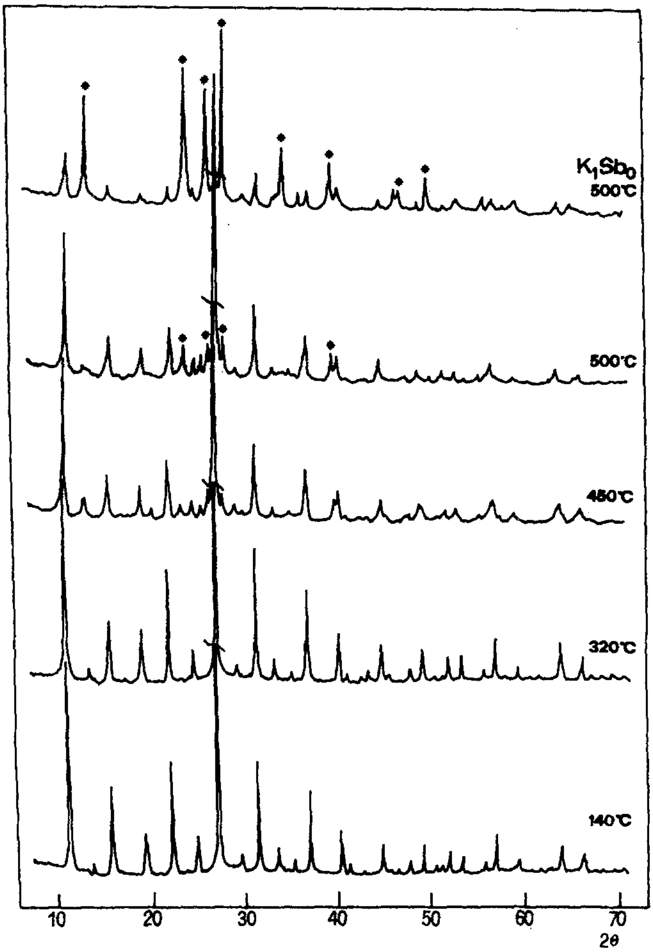

Fig. 2. X-ray diffraction patterns showing the evolution of K_1Sb_1 with increasing temperature. (*) MoO_3.

the activity very rapidly decreases and the unloaded catalyst is highly decomposed. Since 425°C is very close to the temperature of incipient decomposition for the mixed potassium/ammonium salt of 12-molybdophosphoric acid [16], the reaction was carried out at lower temperatures. A considerable decrease in conversion was found, and in addition the stability of the catalytic performance was not substantially improved. This indicates that under reaction conditions, possibly because of local overheating due to the exothermal reaction or to the more reductive conditions, the structural stability of the heteropolycompound is lower than under oxidizing conditions.

The K_3Sb_0 sample was less active at 425°C, and also showed a slightly declining catalytic activity. The catalyst was not decomposed after reaction; at 480°C, instead, the catalyst was progressively decomposed, and the decline in activity was

Table 1
Reactivity of potassium salts of 12-molybdophosphate, modified with Sb^{5+} compared with unmodified compounds

Sample	Temperature (°C)	Time-on-stream (h)	Ethane conv. (%)	Ethylene select. (%)
K_1Sb_0	425	1	5.6	48
	425	3	2.5	43
	400	1	2.0	54
	400	3	1.2	46
K_1Sb_1	425	1	3.5	52
	425	3	3.1	56
K_3Sb_0	425	1	5.6	43
	425	3	3.8	40
K_3Sb_1	425	1	2.8	42
	425	3	2.5	44
	500	1	5.9	38
	540	1	6.7	34
	540	10	6.1	38
	540	40	5.7	41

more rapid. This indicates that the observed deactivation can be due to factors other than structural decomposition. It is worth mentioning that the spent catalysts exhibited a change in colour which is known to be due to overreduction of the catalyst [18].

Different was the behavior of the antimony-containing heteropolycompounds. The addition of antimony led to a decrease in the catalytic activity with respect to the unmodified compound, but the performance was more stable with the time-on-stream. K_3Sb_1 could be utilized at temperatures as high as 540°C, without apparent structural destruction even after 40 h of time-on-stream; the XRD pattern of spent catalyst, shown in fig. 1, was the same as that of the fresh sample.

With increasing reaction temperature, the selectivity to ethylene progressively decreased. However, a slight decline in activity was observed with this sample, despite its structural integrity, as shown in table 1. In this case, too, the deactivation is therefore due to phenomena other than the structural decomposition, i.e. overreduction of molybdenum.

In order to improve the catalytic performance of the structurally stable, antimony-modified compound in ethane oxidehydrogenation, the K_3Sb_1 compound was modified by the addition of different metal salts, which could act as promoters for the ethane activation. Some of the catalysts prepared are reported in table 2. For all of them, X-ray diffraction patterns and IR spectroscopy analysis showed the presence of only the cubic secondary structure for Keggin-type heteropolycom-

Table 2
Reactivity of transition-metal-modified antimony- containing heteropolycompounds

Sample	Temperature (°C)	Time-on-stream (h)	Ethane conv. (%)	Ethylene select. (%)
$K_3V_1Sb_0$	425	1	24.0	22
	425	3	11.2	29
$K_3V_1Sb_1$	425	1	6.8	46
	425	3	6.5	49
$K_3Fe_1Sb_0$	425	1	5.4	59
	425	3	4.7	65
	500	1	9.7	48
	500	3	7.2	51
$K_3Fe_1Sb_1$	425	1	2.6	86
	540	1	6.8	83
$K_3Fe_1Ce_{0.25}Sb_1$	540	1	9.6	65
$K_3Fe_1Ce_{0.25}Cr_{0.5}Sb_1$	540	1	17.2	62
$K_3Fe_1Ce_{0.25}Cr_{0.5}Sb_1$ [a]	500	1	9.2	22
	500	3	<1	25

[a] This compound was prepared without phosphorus, and did not possess the heteropolycompound structure; residence time 10 s.

pounds, without any trace of other metal oxides. For reference, the corresponding compounds without antimony are also given.

The addition of vanadium ions (compare samples K_3Sb_0 and $K_3Sb_0V_1$) led to a remarkable increase in the activity; however, in correspondence the selectivity to ethylene was decreased. In this case also, the performance of the antimony-doped sample was more constant with time-on-stream.

The addition of iron ions to the compound did not increase the catalytic activity, but led to a considerable increase in the selectivity to ethylene. This effect is more important than an increase in activity, and therefore the compound with composition $K_3Sb_1Fe_1$ was chosen as starting composition, and was further doped with other components. Among the various promoters tested, chromium and cerium were found to increase the catalytic activity, without penalization of the selectivity to ethylene [19]. In addition, the addition of cerium led to catalysts which exhibited a more stable catalytic performance; the steady state was also reached in a shorter period of time (approximately 10–20 h). The improvement in catalytic performance was reached when chromium and cerium were added in amounts lower than 1 atom per Keggin unit. As an example, fig. 3 reports the catalytic behavior as a function of the time-on-stream for a catalyst with composition $K_3PMo_{11}Sb_1Fe_1Ce_{0.25}Cr_{0.5}O_x$ [19].

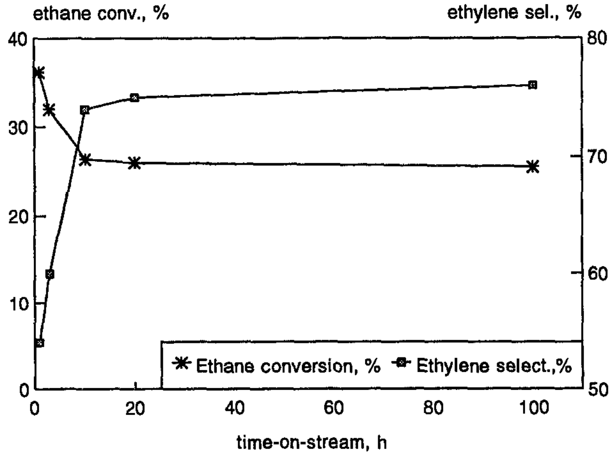

Fig. 3. Catalytic performance with time-on-stream of the $K_3PMo_{11}Sb_1Fe_1Ce_{0.25}Cr_{0.5}O_x$ catalyst; temperature 510°C, residence time 10 s, ethane 3.6%, oxygen 10%.

At the temperature of 510°C and residence time of 10 s, ethane conversion as high as the 26.1% was reached, with 74% selectivity to ethylene, carbon oxides as the only by-products, and maintained for 100 h at least.

The spent catalyst had the same XRD pattern as the fresh catalyst, and only exhibited the reflections typical of the cubic secondary structure of the Keggin-type heteropolycompound.

The importance of the heteropolycompound as the matrix for the catalyst is demonstrated by a reference compound which was prepared with the same metal components, except for the phosphorus, which is the heteroatom in the primary structure of the polyoxometalate. This compound was found to be less active and less selective than the doped heteropolycompound. This suggests that the metal ions added (iron, cerium and chromium) enhance the catalytic performance of the antimony-stabilized potassium salt of 12-molybdophosphoric acid, but that the latter is the catalytic matrix for the activation of the paraffin and its conversion into ethylene.

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