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# Catalysis of the oxidation of isobutyric acid by vanadyl, copper and mixed vanadyl–copper salts of $H_3[PMo_{12}O_{40}]$ and $H_4[PMo_{11}VO_{40}]$

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## Abstract

Effects of variable amounts of vanadyl or/and copper counter-ions of the heteropolyanions  $[PMo_{12}O_{40}]^{3-}$  and  $[PMo_{11}VO_{40}]^{4-}$  on the catalytic oxidative dehydrogenation of isobutyric acid are reported. For the molybdophosphate, selectivity to methacrylic acid increases continuously with respect to the quantity of vanadyl at the expense of both acetone and propene. On the opposite, copper cations does not modify the selectivity to methacrylic acid. A synergy between the two cations is observed, which is maximal when they are in equal quantities. For the vanadomolybdophosphate, vanadyl alone or vanadyl and copper have a positive effect on the selectivity to methacrylic acid only if there is less than one metal cation per heteropolyanion. This is related to the transformation of the catalyst during the first stage of the reaction: vanadium is reduced by isobutyric acid and expelled from the Keggin unit. For high amounts of vanadyl and/or copper cations, decrease of the activity and selectivity to methacrylic acid could be related to the formation of oxides.

*Keywords:* Polyoxometalates; Molybdophosphate; Vanadomolybdophosphate; Copper; Catalyst

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## 1. Introduction

It has been shown that vanadomolybdophosphoric heteropolyacids  $H_{3+x}[PMo_{12-x}V_xO_{40}]$  ( $x = 1-3$ ) evolve during the catalytic oxidative dehydrogenation of isobutyric acid (IBA) into methacrylic acid (MAA). In the steady state, the vanadium atom does not remain include in the Keggin structure [1,2] and is at the reduced state  $V^{4+}$ . This conclusion was obtained from characterizations and chemical analysis of the catalyst

after reaction [1] and was also drawn from in situ XRD spectra [2]. For example, if the 1-vanado-11-molybdophosphoric acid is utilized, the catalyst at the steady state is made of partly reduced 12-molybdophosphate anions associated with  $V^{4+}$  counter-ions.

Several effects can be expected when the protons of molybdo- and vanadomolybdo-phosphoric acids are substituted by metal cations: (1) a decrease of the Bronsted acid properties of the solid, that can affect considerably the oxidative dehydrogenation of IBA since propene, one of the main by-products, results from an acid catalysis; (2) new chemical properties depending on

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the nature of the metal cations; (3) modifications of the structure of the solid (specific area, porosity) and of the thermal stability of the heteropolyanion. Many works have been devoted to the catalytic properties of acid or neutral salts of heteropolyanions for the oxidative dehydrogenation of IBA. Alkaline or alkaline-earth [3–5], transition metal [6] or lanthanide cations [7] have been studied. Clear conclusions are hardly drawn owing to the lack of precise characterization of the salts and to differences in the experimental conditions (temperature, gas feed composition, pulse or conventional fixed-bed reactor). The reaction can be described by a Mars–van Krevelen mechanism [5,8], and the influence of alkaline cations was discussed considering their interaction with external oxygen atoms of the heteropolyanion and was correlated with their electronegativity [3]. Redox properties of some cations  $M^{2+}$  such as  $Pb^{2+}$ ,  $Hg^{2+}$  and  $Cu^{2+}$  were also considered [6] and an electron transfer between  $Mo^{5+}$  and  $M^{2+}$  could occur in the oxidation step of the reduced catalyst. Vanadyl as a counter-ion of 12-molybdophosphate was studied only recently and the catalytic activity and selectivity of the monovanadyl salt for the oxidation of IBA [1], butane or pentane [9] were compared to those of  $H_4[PMo_{11}VO_{40}]$ . On the other hand, if copper in  $CuH[PMo_{12}O_{40}]$  does not modify the selectivity to MAA [10], its association with vanadyl in  $VO_{0.5}Cu_{0.5}H[PMo_{12}O_{40}]$  increases it.

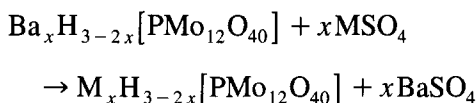
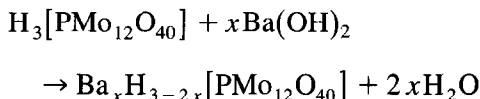
Vanadyl molybdophosphates containing variable quantities of vanadium ( $VO^{2+}/[PMo_{12}O_{40}]^{3-}$  ratio between 0 and 1.5) were synthesized in order to study the influence of the quantity of  $V^{4+}$  on the catalytic properties of the catalyst. Systematic studies of copper and mixed vanadyl–copper salts are presented in the second part in order to define the best catalyst composition for the oxidative dehydrogenation of isobutyric acid. In the last part, the behavior of vanadyl and mixed vanadyl–copper salts of the 1-vanado-molybdophosphoric acid is reported.

## 2. Experimental

### 2.1. Preparation and characterization of the catalysts

All reagents and solvents were purchased from commercial sources and used without further purification. The heteropolyacids  $H_3[PMo_{12}O_{40}]$  and  $H_4[PMo_{11}VO_{40}]$  were prepared according to literature procedures [11,12]

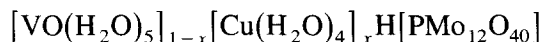
All the vanadyl and copper salts,  $[VO(H_2O)_5]_x H_{3-2x}[PMo_{12}O_{40}]$  and  $[Cu(H_2O)_4]_x H_{3-2x}[PMo_{12}O_{40}]$ , with  $x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1, 1.1, 1.3, 1.5$ , were prepared following the reactions ( $M = VO$  or  $Cu$ ):



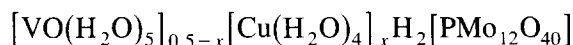
Vanadyl salts  $[VO(H_2O)_5]_x H_{3-2x}[PMo_{12}O_{40}]$ : The heteropolyacid  $H_3[PMo_{12}O_{40}] \cdot 13H_2O$  (10 g; 4.85 mmol) was dissolved in water (10 mL). Solid barium hydroxide  $Ba(OH)_2 \cdot 8H_2O$  ( $1.56 \times g$ ;  $4.85 \times mmol$ ) was added to the stirred solution in several small portions in order to avoid any increase of the pH of the solution which would lead to a partial decomposition of the molybdophosphate anion. Vanadyl sulfate,  $VOSO_4 \cdot 5H_2O$  ( $1.24 \times g$ ;  $4.85 \times mmol$ ) was then quickly added and the stirred solution was kept at room temperature for half an hour. The barium sulfate was filtered off and the resulting solution evaporated to dryness by nitrogen bubbling. The green solid was ground in order to obtain a homogeneous fine powder (diameter about 0.1 mm).

The yellow–green copper salts were obtained by the same procedure, copper sulfate  $CuSO_4 \cdot 5H_2O$  being added ( $1.23 \times g$ ;  $4.85 \times mmol$ ) in place of vanadyl sulfate.

Two series of mixed vanadium–copper salts were prepared:



with  $x = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1$ .



with  $x = 0, 0.1, 0.25, 0.4, 0.5$ .

These salts were obtained by the same procedure using a mixture of vanadyl and copper sulfates in the desired proportions. Vanadyl salts of the 11-molybdo-1-vanadophosphate  $[\text{VO}(\text{H}_2\text{O})_5]_x\text{H}_{4-2x}[\text{PMo}_{11}\text{VO}_{40}]$  and mixed salts  $[\text{Cu}(\text{H}_2\text{O})_4]_{0.5}[\text{VO}(\text{H}_2\text{O})_5]_x\text{H}_{3-2x}[\text{PMo}_{11}\text{VO}_{40}]$  were also prepared from the acid  $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$ .

Purity of all the samples was checked by elementary microanalysis,  $^{31}\text{P}$  NMR spectroscopy and voltammetry in hydroorganic medium, as described below. All the solids are obtained with > 95% purity.

The catalysts before and after reaction were characterized by several methods. It has been previously reported that the heteropolyanions  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  or  $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$  can be easily distinguished by infrared spectroscopy and, after dissolution in hydroorganic medium (water–dioxane v/v +  $\text{HClO}_4$  0.5 mol · L<sup>-1</sup>), by  $^{31}\text{P}$  NMR and voltammetry [1] since they are both stable in this medium. The  $^{31}\text{P}$  NMR spectra were recorded on a Bruker AC 300 apparatus. The anion  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  shows an NMR signal at -2.69 ppm and  $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$  a signal at -2.97 ppm, taking 85%  $\text{H}_3\text{PO}_4$  as reference. The voltammogram of  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  recorder with a glassy carbon electrode shows three bielectronic waves due to the reduction of molybdenum atoms (+0.29, +0.16 and -0.07 V vs. saturated calomel electrode, SCE) and that of  $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$  shows a first wave characterizing the reduction of vanadium (+0.47 V/SCE) followed by three bielectronic waves (+0.25, +0.14 and -0.10 V/SCE).

The amounts of  $\text{V}^{4+}$  and  $\text{Mo}^{5+}$  were determined before and after reaction by titration with  $\text{Ce}^{4+}$  in  $\text{H}_2\text{SO}_4$  0.1 mol · L<sup>-1</sup> and  $\text{Cu}^{2+}$  by

titration with EDTA in the presence of murexide.

Thermogravimetry was carried out under nitrogen flow (50 mL · min<sup>-1</sup>) with a Perkin–Elmer electrobalance at a heating rate of 5°C · min<sup>-1</sup> up to a temperature of 500°C.

## 2.2. Oxidative dehydrogenation of IBA

The vapor phase catalytic oxidative dehydrogenation of IBA was carried out at 593 K with a conventional flow fixed-bed reactor at atmospheric pressure. All reaction products were analyzed by on-line gas phase chromatography. The total feed rate was held constant at 160 mL · min<sup>-1</sup>. The standard feed composition was 2% IBA, 5.2%  $\text{O}_2$ , 3.35%  $\text{H}_2\text{O}$  and  $\text{N}_2$ . Catalysts were pretreated in the reactor under air flow for two hours at 523 K and then heated to 593 K.

The catalytic oxidation of acetone was performed in the same conditions, except acetone replaced IBA.

## 3. Results

### 3.1. Characterization of the catalysts

The thermograms obtained with the copper salts  $[\text{Cu}(\text{H}_2\text{O})_4]_x\text{H}_{3-2x}[\text{PMo}_{12}\text{O}_{40}]$  are reported in Fig. 1. Three kinds of water molecules

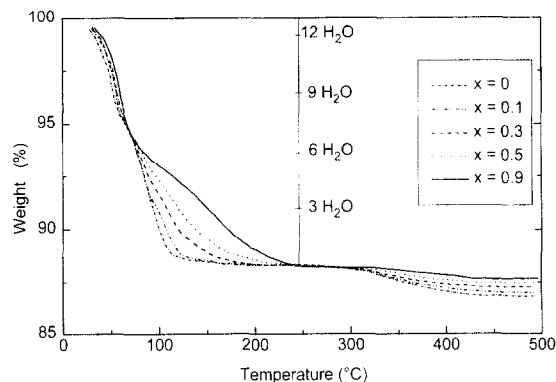


Fig. 1. TGA curves of  $[\text{Cu}(\text{H}_2\text{O})_4]_x\text{H}_{3-2x}\text{PMo}_{12}\text{O}_{40} \cdot 13\text{H}_2\text{O}$ .

are successively lost: crystallization water before 80°C (about  $12 - 4x$  H<sub>2</sub>O), coordination water of Cu<sup>2+</sup> between 80°C and 250°C (about  $4x$  H<sub>2</sub>O), and constitutional water between 300°C and 400°C [ $(3 - 2x)/2$  H<sub>2</sub>O]. The same behavior was observed with vanadyl and mixed vanadyl–copper salts.

X-ray powder diffraction spectra show that all the hydrated salts crystallize, as H<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>] · 13H<sub>2</sub>O, in a triclinic lattice ( $a = 14.10$  Å,  $b = 14.16$  Å,  $c = 13.57$  Å,  $\alpha = 112.0^\circ$ ,  $\beta = 119.7^\circ$ ,  $\gamma = 60.6^\circ$ ). Therefore, the substitution of vanadyl or/and copper cations for protons do not affect the crystal structure. This feature is favorable for the formation of single crystals with a statistic distribution of the cations in the lattice. Moreover, mixture of crystallites were not observed by examination of the crystalline samples, except perhaps for the mixed vanadyl–copper salts containing one cation (VO<sup>2+</sup> + Cu<sup>2+</sup>) per polyanion.

### 3.2. Catalytic activity of the vanadyl salts of [PMo<sub>12</sub>O<sub>40</sub>]<sup>3-</sup>

The catalytic activity of all the samples was studied at high conversion (90% to 94%) of isobutyric acid. In these conditions, a slight

decrease of the conversion (about 5%) was observed at the beginning of the reaction and a steady state was obtained after about 15 hours. Three main products were obtained [13], methacrylic acid (MAA), acetone (ACE) and propene (PRO), with small quantities of acetic acid and CO/CO<sub>2</sub>.

Variations of the activity and selectivities are reported in Fig. 2. The conversion of IBA is not significantly modified (about 92%) but the selectivity to MAA shows a large and progressive increase, from 45% (for H<sub>3</sub>[PMo<sub>12</sub>O<sub>40</sub>]) to 72% (for VO<sub>3/2</sub>[PMo<sub>12</sub>O<sub>40</sub>]), as the quantity of protons substituted by VO<sup>2+</sup> increases. Simultaneously the selectivities to ACE (30% to 18%) and to PRO (24% to 6%) progressively decrease. Amounts of acetic acid and CO/CO<sub>2</sub> remain low.

All the catalysts were characterized after reaction. Infrared spectra were not modified but a strong amorphization occurred during the reaction since the powder X-ray spectra were very poorly defined. All the samples were fully soluble in water indicating that no molybdenum oxide was formed. Oxidation-reduction titration of the solutions of the catalysts showed that the whole vanadium remained as V<sup>4+</sup> and that the molybdophosphate was partially reduced after

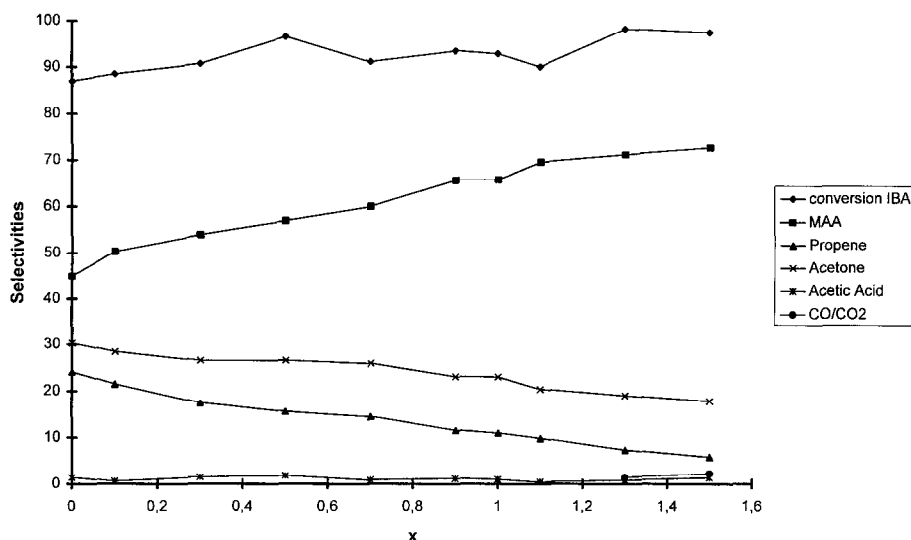


Fig. 2. Conversion and selectivities of the oxidative dehydrogenation of isobutyric acid reaction for (VO)<sub>x</sub>H<sub>3-x</sub>PMo<sub>12</sub>O<sub>40</sub>.

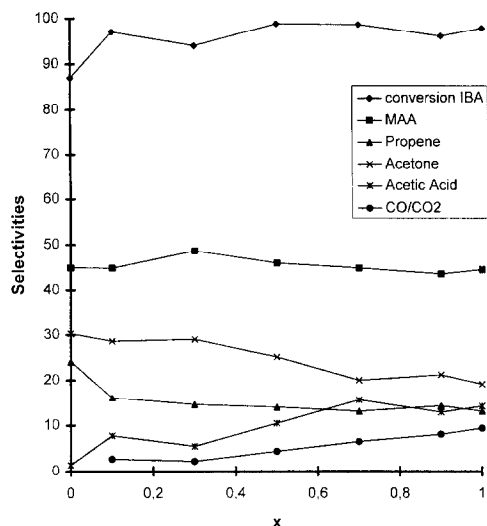


Fig. 3. Conversion and selectivities of the oxidative dehydrogenation of isobutyric acid reaction for  $\text{Cu}_x\text{H}_{3-x}\text{PMo}_{12}\text{O}_{40}$ .

reaction. The amount of  $\text{Mo}^{5+}$  is larger for the vanadyl salts (about  $1 \text{ Mo}^{5+}$  per molybdophosphate for  $x > 0.5$ ) than for the acid (about  $0.5$  for  $x = 0$ ).

### 3.3. Catalytic activity of the copper salts of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$

The variations of the activity and selectivities to the major products are reported in Fig. 3 for  $x < 1$ . The copper salts were significantly more active than the acid since an increase of the conversion of IBA from 87% to 97% was observed even when  $x$  was low. On the opposite of vanadyl salts, the selectivity to MAA was not modified. The decrease of selectivities to PRO and ACE were balanced by the formation of acetic acid and  $\text{CO}/\text{CO}_2$ . Fig. 3 shows that if the formation of ACE regularly decreased when  $x$  is raised from 0 to 1, low quantities of copper reduced the formation of PRO (24% for  $x = 0$  to 16% for  $x = 0.1$ ) which was then little affected by further increasing the amount of  $\text{Cu}^{2+}$  (14% for  $x = 1$ ).

Characterization of the solids after reaction did not show any significant modification of the infrared spectra, which were similar to those of the initial Keggin anion, but the samples were

no more fully soluble in water when  $x$  was greater than 0.5. The insoluble material was separated and the infrared spectrum indicated unambiguously that it was constituted of molybdenum oxide  $\text{MoO}_3$ . The proportion of  $\text{MoO}_3$  was 2% and 9% for  $x = 0.5$  and  $x = 1$ , respectively. The yellow–green color of the catalysts before and after reaction shown that the heteropolyanion was not reduced.

### 3.4. Catalytic oxidation of acetone

The oxidation of ACE was studied in conditions similar to the oxidative dehydrogenation of IBA at  $320^\circ\text{C}$ . Three catalysts were considered:  $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$ ,  $\text{VOH}[\text{PMo}_{12}\text{O}_{40}]$  and  $\text{CuH}[\text{PMo}_{12}\text{O}_{40}]$ , in order to understand the large differences observed between copper and vanadyl salts. The acid and the vanadyl salt have a low catalytic activity (conversions 18% and 12%, respectively, Table 1) but the copper salt is very active (conversion 75%). The main product is acetic acid for the three catalysts following the reaction:



These results explain that large quantities of acetic acid and  $\text{CO}/\text{CO}_2$  were formed when IBA was oxidized in the presence of copper salts.

### 3.5. Catalytic activity of the mixed vanadyl–copper salts of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$

The mixed vanadyl–copper salts were studied in order to associate two effects: the im-

Table 1  
Oxidation of acetone at  $320^\circ\text{C}$  performed in the same conditions as the oxidative dehydrogenation of IBA

	$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	$\text{VOHPMo}_{12}\text{O}_{40}$	$\text{CuHPMo}_{12}\text{O}_{40}$
Conversion of acetone (%)	18.3	12.3	75.2
Selectivity to acetic acid (%)	90.4	81.5	84.3
Selectivity to $\text{CO}/\text{CO}_2$ (%)	9.6	18.5	15.7

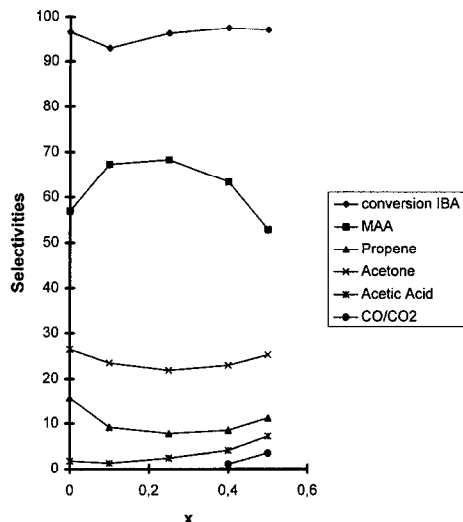


Fig. 4. Conversion and selectivities of the oxidative dehydrogenation of isobutyric acid reaction for  $(VO)_{0.5-x}Cu_xH_2PMo_{12}O_{40}$ .

provement of activity due to  $Cu^{2+}$  and the increase of the selectivity to MAA due to  $V^{4+}$ . Two series of salts were considered: in the first, the sum of vanadyl and copper cations was 0.5 and, in the second, it was 1. So, the number of protons was constant in each series.

The conversion of IBA was always greater or equal to 95% (Figs. 4 and 5). The selectivity to MAA was maximal for equal amounts of vanadyl and copper cations but was higher for  $VO_{0.5}Cu_{0.5}$  (73%) than for  $VO_{0.25}Cu_{0.25}$  (68%).

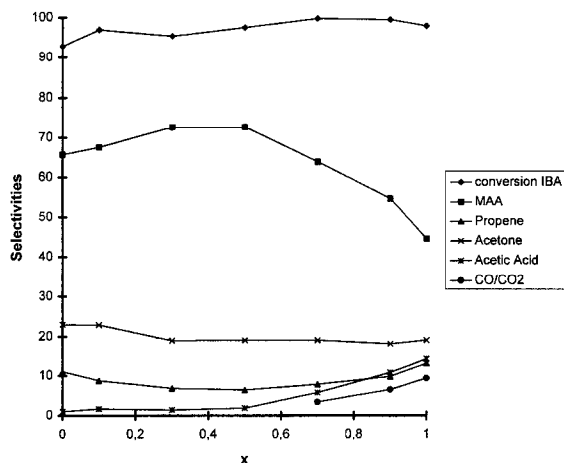


Fig. 5. Conversion and selectivities of the oxidative dehydrogenation of isobutyric acid reaction for  $(VO)_{1-x}Cu_xHPMo_{12}O_{40}$ .

For the two series these values were greater than the best values observed either with vanadyl salts or copper salts alone. The decrease of the MAA selectivity for catalysts with high contents of copper results from the increase of selectivities to all the other products.

The vanadium was  $V^{4+}$  in all the catalysts after reaction and the heteropolyanion was fully oxidized whatever the proportion of copper. Some  $MoO_3$  was formed but in very low quantity (1%) for the best catalyst.

### 3.6. Catalytic activity of vanadyl salts and of mixed vanadyl–copper salts of $[PMo_{11}VO_{40}]^{4-}$

Comparison of the acid  $H_4[PMo_{11}VO_{40}]$  with the salts  $VO_xH_{4-2x}[PMo_{11}VO_{40}]$  is reported in Fig. 6. As for the 12-molybdophosphate, the substitution of  $VO^{2+}$  for  $H^+$  up to  $x = 1$  leads to a drastic increase of the selectivity to MAA from 66% to 75% which can be related to the corresponding decrease of the selectivity to propene from 16% to 5%. Further substitution of protons leads to a decrease of activity and selectivity to MAA to about 70%. The catalysts after reaction are fully soluble in acid water–dioxane solution and their characterizations (in-

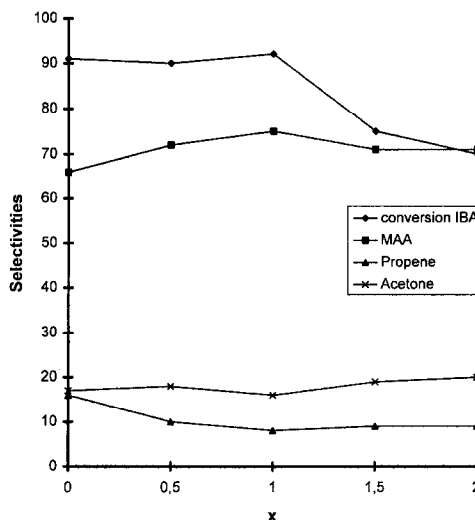


Fig. 6. Conversion and selectivities of the oxidative dehydrogenation of isobutyric acid reaction for  $(VO)_xH_{4-2x}PMo_{11}VO_{40}$ .

frared spectra,  $^{31}\text{P}$  NMR spectra and electrochemical properties of the solutions) showed that they are constituted of partially reduced 12-molybdophosphate anions (about 1  $\text{Mo}^{5+}$  per polyanion) and  $\text{V}^{4+}$  counter-ions.

Vanadyl and copper mixed salts of  $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$  have been studied with a constant quantity of copper and variable quantities of vanadyl cation. The amount of copper has been chosen equal to 0.5 per polyanion in order to not induce too much acetic acid and  $\text{CO}/\text{CO}_2$ . Accordingly, the number of vanadyl cations varied from 0 to 1.5 in the compounds  $\text{Cu}_{0.5}\text{VO}_x\text{H}_{3-2x}[\text{PMo}_{11}\text{VO}_{40}]$ . Results displayed in Fig. 7 show that the highest selectivity is obtained for 0.5  $\text{VO}^{2+}$  (76.5%). A large decrease in the activity was observed with the salt containing  $0.5\text{Cu}^{2+} + 1.5\text{VO}^{2+}$ . Characterizations of catalysts after reaction show always that the solids consisted of partly reduced 12-molybdophosphate anions (about 0.8  $\text{Mo}^{5+}$  per heteropolyanion), the whole vanadium being outside of the Keggin structure at the oxidation state IV. It can be pointed out that the heteropolyanion is always partly reduced whatever the amount of copper cations. All these studies

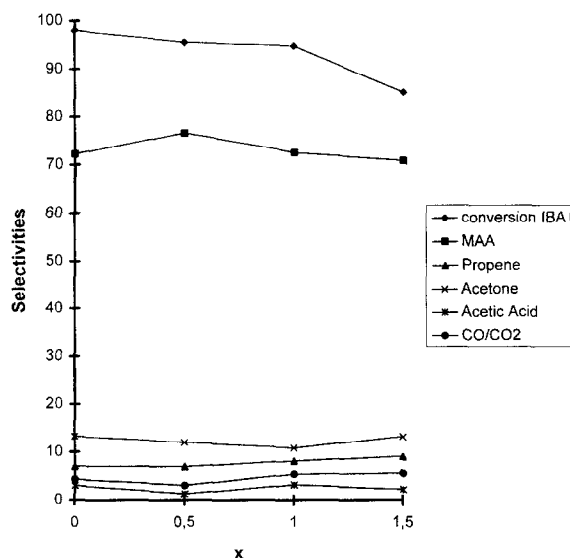


Fig. 7. Conversion and selectivities of the oxidative dehydrogenation of isobutyric acid reaction for  $(\text{VO})_x\text{Cu}_{0.5}\text{H}_{3-2x}\text{PMo}_{11}\text{VO}_{40}$ .

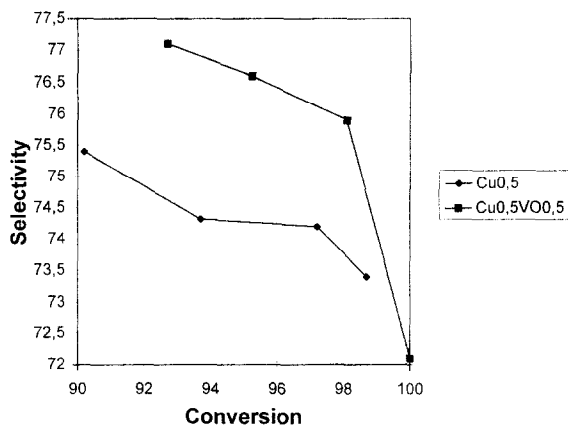


Fig. 8. Effect of the conversion on selectivity to methacrylic acid for  $\text{Cu}_{0.5}\text{H}_3\text{PMo}_{11}\text{VO}_{40}$  and  $\text{Cu}_{0.5}(\text{VO})_{0.5}\text{H}_2\text{PMo}_{11}\text{VO}_{40}$ .

have been performed for conversion of IBA ranging from 90% to 95%. The influence of very high conversion ( $> 95\%$ ) upon the selectivity to MAA has been investigated using variable amounts of catalyst (0.5 to 1.8 g). Results obtained with two catalysts are reported in Fig. 8. The selectivity to MAA decreases only slightly up to a conversion of 97%, but for higher conversion this decrease is more important.

#### 4. Discussion

It is commonly assumed that the presence of vanadium (one to three atoms) in the Keggin structure of the molybdophosphate enhances the heterogeneous catalytic activity of these solids for oxidation reactions and modifies their selectivities. For example, the selectivity to methacrylic acid is higher when  $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$  is used instead of  $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$  for the oxidative dehydrogenation of isobutyric acid. Modification of the catalytic properties have been generally correlated with the strong oxidizing character of vanadium in the oxidation state V [13]. It is now well established that, at the temperature of the reaction (300–340°C), this structure is not stable either after a thermal treatment or

after reaction [1,2,10,14]. So relationships between the catalytic activity, selectivities, chemical and structural properties of vanadium containing heteropolyanions can be reinvestigated from a new point of view, considering  $V^{4+}$  as a counter-ion of heteropolyanions.

The thermograms of copper salts (Fig. 1) and vanadyl salts show the elimination of the coordination water of copper cations between 80 and 250°C (Fig. 1). Two types of vanadyl cations between heteropolyanions have been characterized by ESR [15]. The first one is the aquo complex  $[VO(H_2O)_5]^{2+}$  and the second one is  $VO^{2+}$  bound to external oxygen atoms of the heteropolyanions. These two states can be likely found for all transition metal cations. The stable state at the temperature of the reaction corresponds to cations bound to heteropolyanions but aquo complexes of  $VO^{2+}$  and  $Cu^{2+}$  could be transient species in the oxidation of IBA since water is a product of the reaction and is added in the reaction mixture.

Catalytic effects induced by the  $VO^{2+}/H^+$  and  $Cu^{2+}/H^+$  substitutions in  $H_3[PMo_{12}O_{40}]$  are clearly distinct (Figs. 2 and 3): (1) vanadyl enhances the selectivity to MAA, copper enhances the conversion of IBA without any change in the selectivity to MAA; (2) vanadyl increases but copper decreases the reduction state of the molybdophosphate anion at the steady state. These results suggest that vanadyl cations have an influence on the reduction step of the heteropolyanion by IBA which would be guided to the formation of MAA and that copper enhances the rate of oxidation of the reduced catalyst by  $O_2$  and could be considered as a co-catalyst of the heteropolyanion.

A progressive decrease of the selectivity to MAA would be observed in the two series of mixed vanadyl–copper compounds  $V O_{1-x} C u_x H [P M o_{12} O_{40}]$  or  $V O_{0.5-x} C u_x H_2 [P M o_{12} O_{40}]$  if the effects of the two cations were additive since copper alone has no effect. On the opposite, an increase of the selectivity in each series was observed up to equimolar quantities of the two cations. This

cooperativity can be defined, for example for the first series, following Delmon [16] by:

$$\Delta S = S_x - [(1-x)S_{VO} + xS_{Cu}]$$

where  $S_x$  is the selectivity for the mixed catalyst,  $S_{VO}$  and  $S_{Cu}$  the selectivities for the mono-vanadyl and monocopper salts, respectively.  $\Delta S$  corresponds to the difference between the observed selectivities (Figs. 3 and 4) and the straight line between the two points relative to pure vanadyl and copper salts. Its value is maximal (17% for the two series of compounds) when vanadyl and copper cations are in equal quantities. This synergy between the two cations might be due to their complementary effects on two distinct steps of the catalytic cycle, the reduction (by IBA) and the oxidation (by  $O_2$ ) of the catalyst.

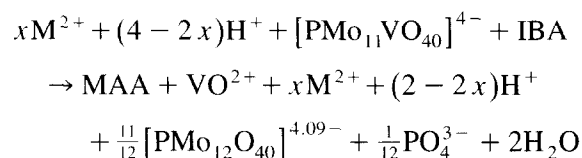
The molybdophosphate is oxidized at the steady state in the presence of  $Cu^{2+}$  and is then very active. Acetic acid, CO and  $CO_2$  are formed when large amounts of  $Cu^{2+}$  are used. They result, at least partially, from the oxidation of acetone, which is efficiently catalyzed by copper salts. This reaction is strongly exothermic and a local increase of the temperature could lead to a rapid decomposition of the molybdophosphate and could explain the formation of molybdenum oxide. Consequently, the quantity of  $Cu^{2+}$  must be low in order to avoid any decomposition of the heteropolyanion.

Understanding of the behavior of salts of  $[PMo_{11}VO_{40}]^{4-}$  must take into account change in the composition of the heteropolyanion during the reaction. Characterization of the catalysts after reaction showed unambiguously that the introduction of vanadyl or/and copper counter-ions in the initial solid does not prevent the reduction and the release of the vanadium from the Keggin structure. The 12-molybdophosphate is always the active species in the conditions of the reaction and utilization of vanadomolybdophosphate is only a convenient way to introduce higher quantities of vanadyl counter-ions in the active catalyst.

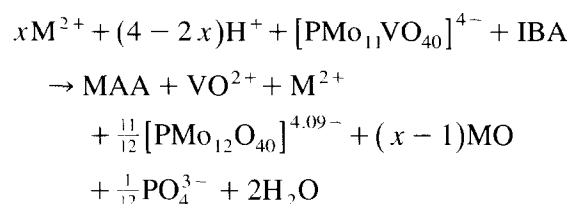
We observed that the activity and selectivity



to MAA are the highest when there is one metal counter-ion per  $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$ , i.e. for  $x = 1$  for the series  $\text{VO}_x\text{H}_{4-2x}[\text{PMo}_{11}\text{VO}_{40}]$  and  $y = 0.5$  for the series  $\text{Cu}_{0.5}\text{VO}_y\text{H}_{3-2y}[\text{PMo}_{11}\text{VO}_{40}]$  (Figs. 6 and 7). The equation of the transformation of the catalyst by reaction on isobutyric acid explains this behavior. Two cases will be considered,  $x < 1$ :



and  $x > 1$ :



M standing for VO or Cu or  $[z \text{VO} + (1 - z) \text{Cu}]$ .

According to these equations, the molybdophosphoric active species must be reduced (1.09  $\text{Mo}^{5+}$  per Keggin unit) after the transformation of  $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$  during the first stage of the reaction. Further reduction of the  $[\text{PMo}_{12}\text{O}_{40}]^{4.09-}$  polyanion by IBA (formally  $2e^- + 2\text{H}^+$  per IBA molecule) into protonated species is possible. On the opposite, oxidation of  $[\text{PMo}_{12}\text{O}_{40}]^{4.09-}$  by  $\text{O}_2$  would lead to the formation of anions  $\text{O}^{2-}$  and consequently of  $\text{H}_2\text{O}$  if protons are available ( $x < 1$ ) or/and metal oxide ( $\text{CuO}$  or  $\text{VO}_2$ ) by association with the metal cations. The maximal oxidation state of the 12-molybdophosphate just depends on the quantity of metal counter-ion if formation of metal oxide is to be avoided. In particular, the heteropolyanion cannot be fully oxidized if  $x$  is greater than 0.5 and oxidation of  $[\text{PMo}_{12}\text{O}_{40}]^{4.09-}$  is impossible if  $x$  is greater than 1 without formation of additional metal oxide.

This explains that the mixed vanadyl/copper salts of  $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$  are always reduced in

the steady state, on the opposite of the behavior of the copper salts of  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  which are fully oxidized. Furthermore, equation (2) shows that metal oxides ( $\text{VO}_2$  or/and  $\text{CuO}$ ) are formed when  $[\text{PMo}_{11}\text{VO}_{40}]^{4-}$  is reduced and transformed by reaction with IBA during the first stage of the reaction if  $x > 1$ . The decrease of both the activity and the selectivity to MAA for high  $x$  values can be likely related to the formation of these oxides. Indeed, formation of  $\text{VO}_2$  and  $\text{CuO}$  have been already postulated in order to explain the ESR signal decrease of these cations after thermal treatment [15] or catalytic reaction [17].

Long-term deactivation of heteropolyanions limits their practical applications. Decomposition of the molybdophosphate with formation of molybdenum oxide in long-time experiments occurs even in the presence of vanadyl and copper cations and vanadium and copper oxides are formed probably simultaneously. On the other hand, it is well known that potassium and cesium salts of the 12-molybdophosphate are stable at high temperature. Maybe the association of vanadyl, copper and cesium counter-ions would lead to catalysts showing a better stability with good catalytic performances. New ways of synthesis of such mixed salts have to be developed in order to obtain an homogeneous dispersion of the counter-ions in the lattice.

## 5. Conclusion

The main conclusions for the present study of the oxidative dehydrogenation of isobutyric acid by heteropolyanions are as follows: (1) vanadyl and copper counter-ions of the 12-molybdophosphate have two different roles, vanadium enhances the selectivity to methacrylic acid and the higher the amount of vanadium the higher the selectivity; (2) copper maintains the heteropolyanion fully oxidized and then enhances its activity but must be in low quantity in order to avoid rapid decomposition of the molybdophosphate and non-selective oxidation;

(3) association of vanadyl and copper cations leads to an increase of the selectivity to methacrylic acid and this cooperative effect is maximal for equal amounts of the two cations; (4) an improvement of the catalytic efficiency of the 1-vanadomolybdophosphate associated to vanadyl and copper counter-ions is obtained only if the total number of metal cations is less than one per heteropolyanion; (5) in any case, the expulsion of the polyanionic vanadium towards the counter-ion position occurs and the 12-molybdophosphate is the active heteropolyanion.

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