Oxidative dehydrogenation of isobutyric acid with cupric salts of molybdovanadophosphoric acid (Cu$_x$H$_{4-2x}$PVMo$_{11}$O$_{40}$). Investigation of catalyst activation and deactivation

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Abstract

The oxidative dehydrogenation of isobutyric acid (IBA) to methacrylic acid (MAA) has been studied over cupric salts of undecamolybdovanadophosphoric acid Cu$_x$H$_{4-2x}$PVMo$_{11}$O$_{40}$. The presence of copper as counter cation in heteropoly compounds increases the activity and the selectivity to MAA. The best catalytic performance is obtained for $x=0.5–0.7$.

Samples were characterized by $^{51}$V solid state NMR, EPR, XPS, IR and elementary analysis in order to obtain information on the nature and location of vanadium and copper species in the sample before and after reaction and on the possible changes occurring during the course of the catalytic reaction. It is shown that vanadium localized initially in the heteropolycompound is removed from the Keggin Unit at 593 K. Small clusters of vanadium and copper oxide species with unsaturated coordination are formed. The reduction of V$^{5+}$ into V$^{4+}$ is also evidenced during the catalytic test. Delocalized electrons appear in these conditions inside the small vanadium and copper oxide clusters. This behavior of vanadium and copper is correlated with higher performance of this catalyst, and then appears as a synergic effect.

The stability of Cu$_{0.5}$H$_3$PVMo$_{11}$O$_{40}$ catalyst was also tested. After 250 days of catalytic test, some deactivation was pointed out. This effect is related to a molybdenum loss followed by important surface aggregation of copper. Electronic and ionic exchange are then disturbed in the core of the solid and therefore the reoxidation of the catalytic system is hindered. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Oxidative dehydrogenation; Isobutyric acid; Polyoxomolybdate; Copper vanadium catalyst; Activation; Deactivation
1. Introduction

The oxidative dehydrogenation of isobutyric acid (IBA) leads to the formation of methacrylic acid (MAA), acetone, propene, carbon monoxide, carbon dioxide and water according to the following reactions:

\[
\frac{1}{2} \text{O}_2 \rightarrow \text{MAA} + \text{H}_2\text{O}
\]

\[
\text{O}_2 \rightarrow \text{Acetone} + \text{H}_2\text{O} + \text{CO}_2
\]

\[
\text{IBA} \rightarrow \text{Propene} + \text{CO} + \text{H}_2\text{O}
\]

catalysis

The production of methacrylic acid, a precursor to methylmethacrylate is one of the attractive industrial processes for producing polymethylmethacrylate. Mainly, two kinds of catalysts can activate this reaction: the first ones concern vanadium [1] or iron phosphates [2–6]; the second ones are salts of the 12-molybdovanadophosphate related to the Keggin structure [7–21]. The first class of catalysts presents appreciable stability but requires a large quantity of steam for convenient conversion and selectivity (molar ratios H\textsubscript{2}O/IBA in the feed exceeding 15 are usual). The second series gives excellent MAA yields at low H\textsubscript{2}O/IBA ratio but the catalysts exhibit deactivation and cannot be considered stable enough under industrial experimental conditions. Addition of water and/or molybdenum volatile species in the gas phase was claimed to stabilize the molybdenum content and the activity [18]. The oxidative dehydrogenation process is accomplished through a redox cycle [14–16,19,20] where MAA is formed under the consumption of lattice oxygen [20]. Then, a good reoxidation of the catalyst by air and important lattice oxygen mobility are necessary for high activity and stability. 12-Molybdophosphoric heteropoly acid in which molybdenum atoms are partly substituted by vanadium atoms have been found as effective catalyst candidates. In theory, the vanadium in the Keggin Unit contributes to the reduction of the acid strength and to the enhancement of the performances in the redox reaction [22–32]. So, \( \text{H}_4\text{PVMo}_{11}\text{O}_{40} \) has been found to be a promising catalyst for the conversion of IBA to MAA [26–32]. However, despite their catalytic performance, the low thermal stability of heteropolyacids remains a major drawback in industrial processes. Indeed, these catalysts can deactivate quickly. The mechanism underlying this deactivation is not yet well understood and one of the purposes of this work is to bring more supplementary information on the activation and deactivation processes.

It is usual that mechanistic differences appear depending on whether the counter-ions are transition metal ions, alkali metal or alkaline earth metal ions. Indeed, the transition metal cations may cycle in oxidation state in the course of catalytic oxidation [16,19] and then may stabilize the catalytic system unlike the other two types of ions. From previous work [8,9,13,26–32], it appears that copper is an attractive counter-ion of the Keggin Unit \( \text{PVMo}_{11}\text{O}_{40}^- \). Only few spectroscopic characterization have been reported on this type of catalyst. Intrinsic redox properties of vanadium and counter-ion seem to be responsible of catalytic performance [14,15,19]. In addition, it is necessary to consider complex and often unknown structural (or textural) arrangement of Keggin Units, counter-ion and vanadium. The second purpose of this work is therefore, to compare the catalytic behavior of \( \text{H}_4\text{PVMo}_{11}\text{O}_{40} \) acid with that of cupric salts \( \text{Cu}_x\text{H}_4\text{PVMo}_{11}\text{O}_{40}^- \) and to attempt to deduce information about localization and interaction of copper and vanadium species in the catalyst before and after the test.

2. Experimental

2.1. Preparation of the samples

The pure heteropoly acid \( \text{H}_4\text{PVMo}_{11}\text{O}_{40} \) was prepared using the method proposed by Courtin [33] and modified as following [25,35]: 17.8 g of \( \text{Na}_2\text{HPO}_4 \) were added to a hot aqueous solution (500 cm\textsuperscript{3}) containing 12.2 g of sodium metavanadate \( \text{NaVO}_3 \). After the mixture had been cooled to room temperature, 10 cm\textsuperscript{3} of concentrated \( \text{H}_2\text{SO}_4 \) were added together with aqueous solution (500 cm\textsuperscript{3}) containing 246 g of \( \text{Na}_2\text{MoO}_3 \), 2H\textsubscript{2}O. Then, 400 cm\textsuperscript{3} of concentrated \( \text{H}_2\text{SO}_4 \) were added slowly drop by drop. After the
final mixture had been cooled to room temperature, the heteropolyacid was extracted in ether (400 cm³) as liquid heteropoly etherate. Etherate was completed with half of its volume in water. Excess of ether was then evaporated at room temperature. The crystallization was performed at low temperature (277 K) yielding the 29–30 H₂O hydrate. Acid crystals of the 13–14 H₂O hydrate triclinic phase [36] stable at room temperature were obtained with more than 95% purity. Heteropolyacid samples obtained by this method were used for the catalytic test or for the preparation of heteropolysalts. Cu₂PVMo₁₁O₄₀, 21H₂O catalyst was obtained [37] by simple contact exchange of the H³O⁺ ions in the heteropolyacids (H₄PVMo₁₁O₄₀) solution with Cu²⁺ ions present in a resin Dowex 20–50 (sodium form) previously exchanged using a highly concentrated copper sulfate solution. The heteropolycompounds CuₓH₄₋₂ₓPVMo₁₁O₄₀ (with x=0.3, 0.5, 0.7) were prepared by double decomposition of their corresponding metal sulfate with barium 11-molybdo-1-vanadophosphate in aqueous solution [9,37] of stoichiometric amount. Barium hydroxide was first added slowly to a concentrated solution of H₄PVMo₁₁O₄₀. Copper sulfate was then added to the partly salified HPA solution. At low temperatures, precipitation of barium sulfate occurred. After filtration, crystallization is obtained at 277 K. Purity of the Keggin ion was checked by ³¹P, ⁵¹V NMR, infrared spectroscopy and polarography according to the previous work [34,35]. Elementary microanalysis and thermogravimetry (TG) confirm the composition of the solid. The number of crystallization of water molecules was obtained from TG data. Samples were kept at 278 K in order to avoid any decomposition. The following symbols Cu₀, Cu₀.₃, Cu₀.₇, Cu₂ are used hereafter to refer to the compounds CuₓH₄₋₂ₓPV-Mo₁₁O₄₀ with x=0, 0.3, 0.7, 2.

2.2. Catalytic tests

2.2.1. Tests for comparison of catalysts

These were carried out using a flow fixed-bed quartz reactor at atmospheric pressure with 0.6–1 g of crushed catalyst sample. Nitrogen was used as an inert carrier into which the feed IBA was evaporated. The reaction was performed at 593 K with the following conditions: IBA=2.1%, O₂/IBA=2.5, H₂O/IBA=1.6, total feed rate=9.6 l h⁻¹. All the products were characterized by gas chromatography analysis. A very good accuracy of experimental results is obtained with a careful control of the catalytic bed temperature by a thermocouple set inside it.

2.2.2. Test of catalyst stability for Cu₀.₅H₃PVMo₁₁O₄₀

Test of catalyst stability for Cu₀.₅H₃PVMo₁₁O₄₀, was conducted as near as possible from industrial constraints. It was carried out at 593 K under continuous flow conditions in a stainless steel tube (length: 150 cm, section: 2 cm²) at atmospheric pressure using a mixture of IBA, air, water and nitrogen with the following conditions: IBA=4%, O₂/IBA=2.5, H₂O/IBA=1.6. The total flow rate was 675 l h⁻¹. The reactor was immersed in a dissolved KNO₂–KNO₃ salt bath. The catalyst occupying a volume of 150 cm³ was held in the reactor by a grating. A thermocouple passing through the catalyst bed measured the temperature at different points of the reactor. The sample was crushed with 1% of silicon carbide and sieved. Pellets were ring shaped and diluted with 30% of silica gel in order to reduce exothermic effects. Accuracy of experiments is about 1%, as illustrated by carbon balance (Table 1). All the products were characterized by gas chromatography, in one-line analysis for propene, CO, CO₂ and after liquid condensation for MAA, acetone, acetic acid and IBA. Chemical titration of acidity (NaOH 0.1 mol l⁻¹) and C=C by Br₂ addition confirmed the liquid analysis.

The selectivities are calculated according to

\[ S(X) = \frac{D(X)}{D(\text{IBA})_{\text{CONV}}} \times 100, \]

where \( D(X) \) is the molar flow of X (X=MAA, acetone, propene, acetic acid) and \( D(\text{IBA})_{\text{CONV}} \) is the molar flow of IBA converted.

\[ S(\text{CO, CO₂}) = \frac{D(\text{CO, CO₂})_{\text{Measured}} - D(\text{CO, CO₂})_{\text{From Propene, Acetone Formation}}}{4D(\text{IBA})_{\text{CONV}}} \times 100 \]
S (acetic acid) (<1%) and are very low and their variations are not really significative, then we report in Table 1 only S (MAA), S (acetone) and S (propene).

Differences between carbon balance and the sum of these selectivities correspond to CO, CO₂ and acetic acid.

2.3. Thermal activations

Thermal activations before spectroscopic characterizations were carried out in a fixed flow-bed reactor under dry air or oxygen flow. The flow rate was 10 l h⁻¹ and the heating rate was 200 K h⁻¹.

Rehydration of samples after thermal treatment occurred at room temperature in wet air during 24 h.

2.4. ⁵¹V NMR experiments

Solid state NMR studies were undertaken at 26.289 MHz using a Bruker CXP 100 spectrometer. Wide-line NMR spectra were obtained at room temperature with a single pulse using 1 μs pulse length, a 0.7 s repetition time and a quadrature detection. A special insert (“horse saddle”) was used to allow measurements in vertical 10 mm diameter NMR tubes shut by a greaseless tape allowing measurements in a controlled atmosphere. ⁵¹V NMR spectra were recorded at room temperature. Vanadium oxichloride (VOCl₃) in a sealed tube provided the external reference.

<table>
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<th>Days</th>
<th>θ₁</th>
<th>θ₂</th>
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<th>S(acet.)</th>
<th>S(prop.)</th>
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<td>320</td>
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<td>62.3</td>
<td>11.7</td>
<td>18.5</td>
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θ₁—salt bath temperature, θ₂—“hot point” temperature, C((IBA))—IBA conversion, S(MAA, acet., prop.)—selectivities in MAA, acetone and propene, CB=carbon balance.

① Air flow stopped.
② Removal of the reactor and pause of two months.
③ 15 days standby.
④ % IBA from 4% to 5.34%.
⑤ After water and IBA suppression and readmission.
⑥ Total flow rate =386 l h⁻¹.
2.6. XPS spectra

XPS spectra were performed with a Leybold Heraus LHS-10 spectrometer using Al K$_\alpha$ radiation ($h\nu=1486.6$ eV). Spectra were recorded at room temperature in the fixed retarding ratio mode for which the transmission factor is proportional to the kinetic energy of the emitted photoelectrons. The XPS binding energies were calibrated by using the C$_{1s}$ peak at 285 eV binding energy.

Atomic ratios have been calculated assuming a homogeneous distribution of the different species in the solid from the generally accepted formula [39,40].

$$C_i/C_j = \frac{I_i^k \cdot \sigma_{i,j}^k \cdot \left( \frac{E_{i,j}^k}{E_i^k} \right)^{1.77}}{I_j^k \cdot \sigma_{i,j}^k \cdot \left( \frac{E_{i,j}^k}{E_j^k} \right)^{1.77}}$$

with $C_i/C_j$ the atomic concentration ratio and $I_i^k$, $I_j^k$, $\sigma_{i,j}^k$, $E_{i,j}^k$, respectively, the intensity of photopeak $k$, the photoabsorption cross-section of subshell $k$ and the kinetic energy of peak $k$, for the species $i$ and $j$.

3. Results and discussion

3.1. Test for comparison of catalysts

Fig. 1 displays the variation of the catalytic conversion and selectivity in the oxidative dehydrogenation of IBA for the $\text{Cu}_x\text{H}_{4-2x}\text{PVMo}_{11}\text{O}_{40}$ catalyst series after three days of time on stream in continuous mode. Conversion reaches a maximum (96.7%) for $x=0.3$ and the maximum of MAA selectivity is obtained for $x=0.7$ (78%). The best yield is obtained with $\text{Cu}_{0.6}\text{H}_{2.6}\text{PVMo}_{11}\text{O}_{40}$. These results confirm and complete previous investigations [9,13,41,42] where the best yield in MAA was obtained with $\text{Cu}_{0.5}\text{H}_3\text{PV-Mo}_{11}\text{O}_{40}$ which give an estimation of accuracy for these catalytic results. Moreover, it appears that a total substitution of proton by copper does not improve catalytic performances as already reported. The selectivity to propene increases whereas selectivity to MAA decreases. Therefore, acidic sites are present in the catalytic conditions either for neutral salt as well as for acid [43]. The acidity of neutral salt could be provided by dissociation of water related to metallic cation or by formation of protons through metallic reduction [22–24,44,45]. However, it seems obvious that this acidity should be present as well with acid salts of copper. Another possible assumption could be the reaction of $\text{O}_2^-$ ions from polyanion upon $\text{Cu}^{2+}$ ions leading to the formation of a heteropolycompound with oxygen vacancies and copper oxide aggregates. Then, in the presence of water, this compound could be in equilibrium with the corresponding acid $\text{H}_3\text{PV-Mo}_{11}\text{O}_{40}$ [45]. This hypothesis will be discussed below in $^{51}$V NMR section.

![Fig. 1. Catalytic performances (total activities, selectivities and yields in MAA) of $\text{Cu}_x\text{H}_{4-2x}\text{PVMo}_{11}\text{O}_{40}$ catalysts after three days on stream.](image-url)
3.2. Test of catalyst stability

From previous studies [13,26–32,41,42] it appeared that Cu$_{0.5}$H$_3$PVMo$_{11}$O$_{40}$ was one of the best promising catalysts. This is confirmed by the test of catalyst performances. Then, we have studied the variation of conversion and selectivities for this catalyst during 289 days. Table 1 gives some characteristic results of these evolution. During hundred days, an increase of the conversion and a decrease of selectivity for MAA are observed. Between 100 and 160 days, the temperature of the "hot point" decreases, activity is reduced but selectivity does not change.

After 160 days, the catalytic test was stopped and removed. It was brought into use again after a pause of two months and the catalytic activity was restored.

A decrease in selectivity for MAA and an increase for propene begin after the two hundredth day. Increase in production of propene could be partially due to the presence of reduced sites (oxygen vacancies) and adsorption of water on these sites can induce Brønsted acidic sites [18]. The selectivity to acetone remains constant then the sites of acetone production appear different from sites of MAA production [1,20,46].

Evolution of the thermal profile into the reactor was also checked (Fig. 2) These curves are similar to those given in recent literature [47]. During the first hundred days the catalytic activity is not uniform, the thermal profile shows an optimum at the top of the catalytic bed which mainly works during the first days of the test. Then, this domain broadens and the thermal profile becomes uniform in the last days of the catalytic test. This evolution of thermal profile characterizes a deactivation of the catalyst from the top (introduction of products) to the bottom of the bed. Moreover, the gap between the "hot point" temperature and the salt bath temperature is reduced as the time increases. The decreasing of exothermic effects characterizes the loss in catalytic activity.

The selectivity to MAA and IBA conversion appear quite stable up to 200–240 days and then decreases. The final performance is obtained under higher IBA contact time and/or higher temperature but MAA selectivity exhibits an irreversible drop.

3.3. $^{51}$V NMR results

The $^{51}$V static NMR spectra of H$_4$PVMo$_{11}$O$_{40}$ and Cu$_{0.5}$H$_3$PVMo$_{11}$O$_{40}$ catalysts are given, respectively,
in Figs. 3 and 4. For both of them, vanadium atoms are initially in octahedral symmetry with a slight distortion inside the Keggin Unit. This type of symmetry is characterized in $^{51}$V static NMR by an intense peak at $\Delta$314 ppm with a small peak at $\Delta$971 ppm. Both peaks are named A signal. Such signal is correlated with combination of chemical shift anisotropy (CSA), which is important for the vanadium atom in distorted octahedral symmetry, and first order quadrupolar interaction. Accurate values of CSA and quadrupolar parameters will be published elsewhere from simulation of high speed MAS–NMR spectra [48]. The present study only reports important chemical information from static $^{51}$V NMR experiments. This type of NMR measurements allows easy control of the variable treatment conditions (atmosphere, temperature), and can give phenomenologic comparison of the different samples.

For the acid H$_4$PVMo$_{11}$O$_{40}$ after thermal treatment at 473 K, the A signal is broadened due to an increasing of CSA and quadrupolar constant [48]. A great change appears after a treatment of 1 h at 553 K for H$_4$PVMo$_{11}$O$_{40}$ and at 503 K for Cu$_{0.5}$H$_3$PVMo$_{11}$O$_{40}$. Three new signals are now superimposed with residual A signal. The peak at $\Delta$668 ppm (B signal) relatively symmetrical can be assigned to vanadium in tetrahedral symmetry [49–53]. Highly distorted tetrahedral species should give a second order quadrupolar perturbation and therefore, a modification of the shape of the central transition ($\pm 1/2, \pm 1/2$) (i.e. in NH$_4$VO$_3$) [49, 50, 53–55]. This quadrupolar effect is not observed here and consequently, the tetrahedral species must be only slightly distorted; this conclusion is supported by
the simulation of MAS spectra [48]. So, the vanadium atom has to be ejected from Keggin Units during the thermal treatment and then, a molecular rearrangement of the KU is assumed. The preservation of KU until 673 K seems a reliable hypothesis on the basis of $^{31}$P NMR spectra of $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ [41] which show that no polyphosphates are formed at 593 K. Moreover, these results are in accordance with the results of Fournier et al. [56] from in situ infrared and XRD studies on $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ and on $\text{H}_2\text{PVW}_{11}\text{O}_{40}$ [36] showing that the vanadium atom is out of Keggin Unit at 593 K.

Two peaks, respectively, at 232 ppm (C signal) and $-1581$ ppm (D signal), also appear (Fig. 3) and become very intense after 12 h calcination at 593 K. These signals are much more shifted than common vanadium species reported in [49,53]. A possible interaction of $V^{5+}$ ions with delocalized electrons produced by partial reduction of the solid during the thermal treatment can be assumed. The analysis of this phenomenon appears very difficult because both large downfield (C signal) and large upfield (D signal) shifts are probably related to different and complex magnetic collective interactions of neighboring electrons with particular vanadium nuclei [57,58]. However, the evolution of this phenomenon can be easily followed by comparison of the heteropoly acid and its related copper salts behavior under thermal treatment. The relative intensities of the different signals obtained by integration of the peaks are reported in Table 2 for phenomenologic comparison.

Obviously after similar thermal treatment at 593 K, in $\text{Cu}_{0.5}\text{H}_3\text{PVMo}_{11}\text{O}_{40}$ sample, $\text{Cu}^{2+}$ paramagnetic species induce more intense C and D signals in comparison with $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ although the shift of these signals remain quite similar. Furthermore, at this temperature, no change appear for $\text{Cu}_{0.2}\text{H}_3\text{PVMo}_{11}\text{O}_{40}$ between 1 and 12 h treatment. On the opposite site, for $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ the evolution between vanadium in distorted octahedral environment (A signal) to vanadium in tetrahedral symmetry (B signal) is much more slower, in parallel with C and D slower signals growth.

For samples calcined at 593 K, the evolution of $^{51}$V NMR signals with copper content shows an increase of C and D signals and then it gives another evidence of interaction between $V^{5+}$ ions and paramagnetic species (Table 2). However, this effect appears relatively weak and we can deduce that, probably, only a part of copper(II) ions participate to the collective electronic effect at $V^{5+}$ nuclei evidenced by C and D signals. Reversibility in presence of wet ambient air is partly possible (Fig. 3(f) and Fig. 4(f)). In both cases, C and D signals disappear. Tetrahedral $V^{5+}$ species (B signal) are transformed partially in octahedral $V^{5+}$ species for $\text{H}_4\text{PVMo}_{11}\text{O}_{40}$ (Fig. 3(f)) and totally for $\text{Cu}_{0.2}\text{H}_3\text{PVMo}_{11}\text{O}_{40}$ (Fig. 4(f)). Two important assumptions can be proposed from these rehydration experiments:

1. the tetrahedral $V^{5+}$ species (B signal) could be concerned by oxygen vacancies;
2. the reactivity of these oxygen vacancies would be enhanced in presence of copper.

After the catalytic test, no significant signal of $V^{5+}$ appears in the wide line NMR spectra. Most of the vanadium atoms are in $V^{4+}$ oxidation state.

### 3.4. EPR results

#### 3.4.1. Before the catalytic test

Fig. 5 shows the EPR spectra obtained after calcination of the $\text{Cu}_{0.2}\text{H}_3\text{PVMo}_{11}\text{O}_{40}$ catalyst under a flow of dry oxygen from 293 to 593 K. Apparently, all the spectra are composed of two signals: a normal magnetic field signal with an axial symmetry which can be, without ambiguity, ascribed to $\text{Cu}^{2+}$ ions [59–62] and

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<th>$I_C$ (%)</th>
<th>$I_A$ (%)</th>
<th>$I_B$ (%)</th>
<th>$I_D$ (%)</th>
<th>C(IBA) (%)</th>
<th>S(MAA) (%)</th>
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</thead>
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<tr>
<td>$\text{H}<em>4\text{PVMo}</em>{11}\text{O}_{40}$</td>
<td>4</td>
<td>30</td>
<td>60</td>
<td>6</td>
<td>93.4</td>
<td>62.5</td>
</tr>
<tr>
<td>$\text{H}<em>2\text{PVMo}</em>{11}\text{O}_{40}$</td>
<td>21</td>
<td>24</td>
<td>53</td>
<td>2</td>
<td>91.2</td>
<td>66.6</td>
</tr>
<tr>
<td>$\text{Cu}<em>{0.5}\text{H}<em>3\text{PVMo}</em>{11}\text{O}</em>{40}$</td>
<td>30</td>
<td>10</td>
<td>15</td>
<td>45</td>
<td>95</td>
<td>74.5</td>
</tr>
<tr>
<td>$\text{Cu}<em>{0.2}\text{H}<em>3\text{PVMo}</em>{11}\text{O}</em>{40}$</td>
<td>36</td>
<td>7</td>
<td>–</td>
<td>56</td>
<td>92</td>
<td>64</td>
</tr>
</tbody>
</table>

* $^a$ 12 h treatment.
a low magnetic field signal which is exactly the image of the first one but centered at \( g \approx 4 \). All the measured EPR parameter values of signals are mentioned in Table 3.

When the calcination temperature increases, the parallel hyperfine constant \( A_{\parallel} \) ascribed to \( \text{Cu}^{2+} \) ions increases for a temperature of 373 K and then decreases for higher temperatures. On the contrary, the \( g_{\parallel} \) value decreases and then it increases. From the EPR parameter values, the \( \text{Cu}^{2+} \) ions of the untreated solid (293 K) seem to be surrounded by less ligands than that observed at 373 K but more than those in the solid calcined at 473 and 593 K [63]. The decreasing of copper coordination number at high calcination (473 and 593 K) leads to small diminution of \( \text{Cu}^{2+}–\text{O}^{2-} \) length according to the Debuyst et al. [64] hypothesis.

The resolved lines observed on the right-hand side of the \( \text{Cu}^{2+} \) signal can be attributed to \( \text{V}^{4+} \) species [10,65,66]. The value of \( A_{\parallel}=180 \) G of this corresponding signal can suggest that such ions are located in the octahedral sites outside the Keggin structure [25].

The low field magnetic signal (\( g=4.38 \)) which is produced by a forbidden transition (\( \Delta M_S=2 \)) of a fine structure possesses a well-resolved hyperfine structure particularly for the signal obtained after calcination of the solid at 373 K. The \( A_{\parallel} \) value (70 G) is nearly half of that measured for the normal magnetic signal (138 G). Consequently, such a signal can arise from the presence of a dimer in the solid or from a paramagnetic species possessing a total electron spin \( S=1 \) [67–70]. Since the low magnetic field signal is similar to a \( \text{Cu}^{2+} \) monomer signal (four parallel components), it is then obvious to suggest that the dimer is formed by two non-equivalent paramagnetic species: the first one is the \( \text{Cu}^{2+} \) ion \( (I=3/2) \) whereas the second one could be a paramagnetic species without nuclear spin \( (I=0) \) located near the \( \text{Cu}^{2+} \) ion. Fricke and Ohlmann [71] have observed the presence of \( \text{Mo}^{5+} \) (d⁴) when \( \text{H}_2\text{PMo}_{12}\text{O}_{40} \) is evacuated at 473 K, but their signal is very different from that of reduced \( \text{PMo}_{12}\text{O}_{40}^\text{–} \) [72]. However, Sanchez et al. [72] have shown a great electron mobility in \( \text{PMo}_{12}\text{O}_{40}^\text{–} \) ion even at low temperature (77 K). Such a species, not necessary as main HPA form, can be supposed in interaction with the \( \text{Cu}^{2+} \) ions, then responsible of the dimer signal. That

![Fig. 5. EPR spectra of Cu0.5PVMo11O40 catalyst: (a) freshly prepared and calcined in dry air flow; (b) 1 h at 373 K; (c) 1 h at 473 K; (d) 1 h at 593 K; (e) experiment following (d) after rehydration in air saturated with water.](image)

### Table 3

<table>
<thead>
<tr>
<th>Temperature</th>
<th>( g_{\parallel} )</th>
<th>( A_{\parallel} \text{ (G)} )</th>
<th>( g_{\perp} )</th>
<th>Intensity (arbitrary units)</th>
<th>( g \text{ (triplet state)} )</th>
<th>( A_{\parallel} ) ( \text{ (G)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298 K</td>
<td>2.423</td>
<td>115</td>
<td>2.085</td>
<td>1.4</td>
<td>4.18</td>
<td>–</td>
</tr>
<tr>
<td>373 K</td>
<td>2.386</td>
<td>138</td>
<td>2.066</td>
<td>1</td>
<td>4.23</td>
<td>210, 90</td>
</tr>
<tr>
<td>473 K</td>
<td>2.439</td>
<td>110</td>
<td>2.053</td>
<td>0.8</td>
<td>4.29</td>
<td>180, –</td>
</tr>
<tr>
<td>593 K</td>
<td>–</td>
<td>95</td>
<td>2.059</td>
<td>0.7</td>
<td>–</td>
<td>170, –</td>
</tr>
<tr>
<td>Rehydration at 298 K</td>
<td>2.447</td>
<td>115</td>
<td>2.072</td>
<td>0.8</td>
<td>4.22</td>
<td>–</td>
</tr>
</tbody>
</table>

implies that the coupling between the unpaired $\text{Cu}^{2+}$ electron and the molybdenum unpaired electron occurs through a strong magnetic interaction between $\text{Cu}^{2+}$ ions and partly destroyed Keggin structure.

When the calcination temperature increases from 293 to 593 K, the hyperfine structures of the normal and low magnetic field signals are well-observed at 373 K and progressively disappear with increasing the temperature. This phenomenon is due to the strong dipolar interaction between the copper(II) ions arising from the decrease of their distance. In addition, with the increase of the calcination temperature, the intensity of the signal reaches a maximum at 373 K and then decreases. This phenomenon can also be due to an agglomeration of copper(II) with the formation of large clusters which are undetectable in EPR (Table 3). This phenomenon has been observed in previous studies with variable copper content in the 1-vanadomolybdophosphate [38]. It was showed that agglomeration of copper(II) was important particularly with higher copper contents (i.e. $\text{Cu}_2\text{PV-Mo}_{11}\text{O}_{40}$).

When the $\text{Cu}_{0.5}\text{PVMo}_{11}\text{O}_{40}$ catalyst is treated at 573 K and then rehydrated at 293 K, the EPR spectrum obtained is similar to that observed for the untreated solid but it possesses a better resolved hyperfine structure and the initial intensity is not restored.

### 3.4.2. After the catalytic test

Fig. 6 shows the EPR spectra of $\text{Cu}_{0.5}\text{PVMo}_{11}\text{O}_{40}$ after the catalytic reaction. After three days of running time in the reactor in continuous mode, the spectrum is apparently a superposition of two signals (Fig. 6(a)). The first one is characteristic of $\text{Cu}^{2+}$ ions [13] whereas, the second one with a resolved hyperfine structure can be ascribed without ambiguity to $\text{V}^{4+}$ species [65,66]. However, it is quite evident that small clusters of $\text{Cu}^{2+}$ and $\text{V}^{4+}$ are already present (broad lines are observed with only a poor resolved hyperfine structure). After 10 months of catalytic reaction, the hyperfine structure of the $\text{V}^{4+}$ signal disappears to give a broad symmetric signal (Fig. 6(b)). A similar spectrum was obtained previously [13] on the same catalyst differently prepared and after 40 days of catalytic work. The corresponding $\text{Cu}^{2+}$ and $\text{V}^{4+}$ cluster signals were characterized by $g=2.088$ and $g=1.985$, respectively. The formation of such $\text{V}^{4+}$ clusters occurs during the catalytic reaction. On the contrary, the intensities of the $\text{Cu}^{2+}$ normal and half magnetic signals do not change. When the latter sample is left in contact with air for three months, the intensities of the $\text{V}^{4+}$ clusters signal decreases whereas the $\text{Cu}^{2+}$ clusters signal remains constant (Fig. 6(c)). This decrease is probably due to the oxidation in air of some $\text{V}^{4+}$ species present on the surface of the solid.

### 3.5. Elementary analysis

Elementary analysis of $\text{Cu}_{0.5}\text{H}_3\text{PVMo}_{11}\text{O}_{40}$ gives information on the evolution of the catalyst composition with time (Table 4). The catalyst exhibits an important loss of molybdenum with deactivation and this loss increases with time. Molybdenum is eliminated under gaseous form. After three days in the catalytic reactor, the loss reaches 10% but the catalyst remains perfectly stable. During the first days in the reactors, a rearrangement of Keggin Units occurs (with modification of the vanadium environment). After 10 months of the test, about 30–40% of molybdenum have disappeared and a variation of
copper, vanadium and phosphorus contents is also observed.

From the studies of Watzenberger et al. [18], molybdenum losses exhibit an evolution on all the height of the catalytic bed. This effect is more important at the gas inlet than at the gas outlet. The molybdenum loss leads to a long time deactivation considered as irreversible. In comparison, the short term deactivation is due to the reduction of the catalyst.

3.6. XPS results

XPS results are compiled in Table 5. The O 1s photopeak is well defined and stable before or after the catalytic test at 530±0.1 eV and corresponds to the oxygen present in the polymolybdate structure [73,74]. Deficiency of oxygen in the fresh sample is explained by a superficial reduction of the heteropolycompound in the spectrometer due to vacuum and X-rays. For the catalyst, after three days of catalyst test, no evolution is observed. On the contrary, the deactivated catalyst (after ten months of catalyst test) exhibits important losses of molybdenum and oxygen on the surface. Oxygen losses correspond to losses of molybdenum. Binding energies of Mo3d 3/2 and Mo3d 5/2 are, respectively, 235.2 and 232.1 eV and are in agreement with those obtained by Prevost et al. [74] and Akimoto et al. [75] for Mo6+ on palladium salts.

The V2p photopeak intensity is very weak and it is superimposed with a line due to 1s electrons of oxygen excited by the component. The photopeak position at 517.1±0.3 eV characterizes a vanadium in oxidation state V5+. Before and after the test, atoms of vanadium at the surface of the catalyst are oxidized. For tested samples, the vanadium oxidation state in the bulk is mainly V4+ [11], which is confirmed by our EPR and 51V NMR results. Reoxidation of vanadium at the surface is due to contact with air.

For the fresh catalyst and after three days in the reactor, a photopeak at 935 eV is attributed to Cu2+ ions. The sample tested during 10 months presents a signal relatively more intense with two peaks at 935 and 932 eV, showing the presence of reduced copper (about 16% of the total stoichiometry). Then, the increase of copper species content on the surface of the partly deactivated catalyst (10 months) is very important.

3.7. Infrared results

Infrared results indicate that after three days or 10 months, IR spectra are very similar (Fig. 7) and correspond to previous observations [35,56]. As it was previously shown that a reduced HPA exhibits very poor resolved IR spectra [76], that proves that the Keggin Unit is mainly in its fully oxidized form. Just a small shift (less than 2 cm⁻¹) of some lines is observed (Table 6). The Keggin structure is preserved (lines in the domain 300–400 cm⁻¹ are still present). The shoulder on the P–O band has disappeared and the infrared spectrum is identical to the result obtained with H3PMo12O40. After 10 months in catalytic test a shift from 781 to 785 cm⁻¹ is observed for the vibration due to the Mo–Oc–Mo to bridge accompanied by an increase of intensity.

4. Conclusions and models

Cu0.5H3PVMo11O40 is a good catalyst for the oxidative dehydrogenation of isobutyric acid. A conversion of 92% and a selectivity in MAA of 75% are better than for other HPA (Cu_xH_4-xPVMo11O40, x=0–
2) and a stability of 200 days is promising. Comparative characterizations (before and after the catalytic test) allow to propose models of Cu$_{0.5}$H$_3$PVMo$_{11}$O$_{40}$ behavior before and after deactivation.

After calcination of H$_4$PVMo$_{11}$O$_{40}$ at 593 K during 1 h, vanadium ions are in V$^{5+}$ oxidation state and about 60% of these species are in tetrahedral environment outside the Keggin Unit (B signal in $^{51}$V NMR). After a much longer calcination (12 h), an important part of V$^{5+}$ ions appear in complex interaction with mobile electrons (C and D signals) and when copper is present, it increases this contribution.

From EPR results in dehydration process, copper(II) ions are in a lacunar octahedral environment and this can be correlated with the observed $^{51}$V NMR B signal apparition, more easy in presence of copper. Obviously, the tetrahedral V$^{5+}$ species appear at lower calcination temperature in Cu$_{0.5}$H$_3$PVMo$_{11}$O$_{40}$ and rehydration process is also improved by copper in this compound.

Then, copper seems to enhance the formation of O$^{2-}$ vacancies around vanadium atoms and could improve the mobility of lattice oxygen necessary to obtain a good catalyst for oxidative dehydrogenation process [20].

The lacunar behavior of the system in dehydration and rehydration at 593 K could be described as follows (Fig. 8(a)):

\[
\begin{align*}
POM^{\bullet-} + 2H_3O^+ & \rightleftharpoons POM(n-2)^- \square + 3H_2O \\
VO_2^+ + 2H_3O^+ & \rightleftharpoons VO^{3+} \square + 3H_2O \\
Cu^{2+}O^{2-} + 2H_3O^+ & \rightleftharpoons Cu^{2+} \square + 3H_2O \\
POM(n-2)^- \square + O^{2-} & \rightleftharpoons POM^{\bullet-} \\
VO^{3+} \square + O^{2-} & \rightleftharpoons VO_2^+ \\
Cu^{2+} \square + O^{2-} & \rightleftharpoons Cu^{2+}O^{2-}
\end{align*}
\]

In fact, such lacunar reactive properties could also appear without copper and vanadium. For example, from the studies of Rocchiccioli-Deltcheff et al. [78], it appears that when H$_3$PMo$_{12}$O$_{40}$ is partly decomposed, Mo–O–Mo inter-trimer vacancies in β-MoO$_3$ phase are very sensitive to H$_2$O, leading to Keggin Units reconstruction. However, the O$^{2-}$ ions mobility, and consequently the catalytic performance of H$_2$PMo$_{12}$O$_{40}$ were not so attractive than for catalysts containing copper and vanadium.

Concerning the redox mechanism, V$^{4+}$ ions are produced during the reduction step which probably

![Fig. 7. IRFT spectra of Cu$_{0.5}$H$_3$PVMo$_{11}$O$_{40}$ catalyst after the catalytic test: (a) freshly prepared; (b) three days of test; and (c) 10 months of test.](image)

**Table 6**

Main infrared frequencies (cm$^{-1}$) of Cu$_{0.5}$H$_3$PVMo$_{11}$O$_{40}$ fresh and during the catalytic test

<table>
<thead>
<tr>
<th>Cu$<em>{0.5}$H$<em>3$PVMo$</em>{11}$O$</em>{40}$</th>
<th>P–O$_P$</th>
<th>Mo–O$_i$</th>
<th>Mo–O$_P$–Mo</th>
<th>Mo–O$_i$–Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>1063 +shoulder</td>
<td>962</td>
<td>868</td>
<td>781</td>
</tr>
<tr>
<td>After three days</td>
<td>1065</td>
<td>963</td>
<td>870</td>
<td>781</td>
</tr>
<tr>
<td>After 10 months</td>
<td>1065</td>
<td>962</td>
<td>870</td>
<td>785</td>
</tr>
</tbody>
</table>
involves Mo$^{5+}$/Mo$^{6+}$ catalytic sites in Keggin Units and electronic transfer to vanadium atoms outside the KU. Then, vanadium species play a role of “electron reservoir” [14,15]. From EPR studies conducted after the catalytic test, nearly isotropic signals are observed and can be ascribed to clusters of vanadium and copper oxides containing relatively mobile electrons. In the catalytic stationary state, Mo entities are mainly PMo$_{12}$O$_{40}$$^-$ anions (KU) as evidenced by XRD, IR and XPS. Vanadium and copper entities are either monomeric or small agglomerates (dimeric or more condensed clusters). Molybdenum can also be located outside the KU [77,78]. Monomeric species (V, Cu, Mo) must also play a structural role and they could also participate to the electronic and anionic transfers with KU. The structure of this “active phase” has been also recently discussed as a cubic phase isostructural to the unsubstituted anhydrous alkali-3-HPA salt [79]. In the present case, an XRD analysis of the catalyst after 10 months confirms the existence of a cubic structure ($a=23.25$ nm); however the present study shows that the attribution of this structure to a particular arrangement of the different cations remains quite difficult, and makes suspicious a simple correlation between catalytic performance and such structural characterization.

The synergy between copper and vanadium clusters and HPA domains appears responsible of the increase of $S$(AMA) for Cu$_{0.5}$H$_3$PVMo$_{11}$O$_{40}$ compared to H$_3$PVMo$_{11}$O$_{40}$. This synergy could also be considered as a particular “complementarity” between vanadium and copper. In that way, some comparison could be done with Ballivet et al. [80] study on bronze Cu$_{0.5}$V$_2$O$_5$, who have also reported an important direct activation of vanadium by copper in ODH reactions in correlation with an increase of O$_2^-$ lability.

The model proposed (Fig. 8(b)) is an illustration of the synergic effect of the small clusters of copper and vanadium oxides on the mobility of electrons and O$_2^-$ vacancies into the “bulk” (and surface) during the catalytic test, before deactivation. Furthermore, these clusters may also improve the reoxidation of the catalyst by molecular oxygen.

In addition to the previous chemical Eqs. (1)–(6), the redox mechanism could be described as follows:

**Reduction**

\[
\text{POM}^{n^-} + \text{IBA} + 2\text{H}_2\text{O} \rightarrow \text{MAA} + 2\text{H}_3\text{O}^+ + \text{POM}^{(n+2)-}
\]  
(7)

\[
\text{POM}^{(n+2)-} \rightleftharpoons \text{POM}^{n^-} + 2\text{e}^-
\]  
(8)

\[
\text{VO}_2^+ + 2\text{H}_3\text{O}^+ + \text{e}^- \rightleftharpoons \text{VO}^{2+} + 3\text{H}_2\text{O}
\]  
(9)

\[
\text{Cu}^{2+} + \text{e}^- \rightleftharpoons \text{Cu}^+
\]  
(10)

**Reoxidation**

\[
\text{VO}^{2+} + \frac{1}{2}\text{O}_2 + \text{e}^- \rightarrow \text{VO}_2^+
\]  
(11)

\[
\text{Cu}^+ + \frac{1}{2}\text{O}_2 + \text{e}^- \rightarrow \text{Cu}^{2+}\text{O}^{2-}
\]  
(12)
Then, in the catalytic stationary state, at 593 K, oxygen vacancies and mobile electron concentrations are strongly dependent on POM$^{3-}$, vanadium and copper oxide cluster interactions. Optima results before deactivation correspond approximately to stoichiometry of Cu$_{0.5}$H$_3$PMO$_{11}$O$_{40}$; however, the surface stoichiometry is slightly different, even after three days (Table 5). The local stoichiometry in the bulk in POM$^{3-}$ domains and around them should also be different, but such copper and vanadium content appear as a good compromise to favor oxygen vacancies and electronic transfers, without excessive growing of copper and vanadium oxide clusters, in regard with the POM$^{3-}$ domains.

Catalyst deactivation of Cu$_{0.5}$H$_3$PVMo$_{11}$O$_{40}$ is characterized after ten months working. A drastic loss of molybdenum species appears from XPS and elementary analysis. The loss is much more important on the catalyst surface. The deactivation is accompanied by an increase of copper species content at the surface, both in Cu$^{2+}$ and reduced states. EPR studies also indicate an important agglomeration of copper and vanadium species (total absence of hyperfine structure), with an important decrease of V$^{4+}$ signal intensity. This surface evolution, with a partial deactivation of the catalyst, is in good agreement with Misono’s model for ODH of IBA: AMA and IBA remain at the surface of the catalyst, and the bulk participation only concerns electronic and oxygen diffusion [22–24].

In conclusion, high activity and selectivity to MAA of Cu$_{0.5}$H$_3$PVMO$_{11}$O$_{40}$ catalyst are related to:

1. Formation of vanadium species outside of the Keggin Units which are partly rearranged into PMO$_{12}$O$_{40}^{3-}$ anions.

2. Agglomeration of vanadium and copper atoms into small oxide clusters, which can contribute to oxygen and electronic exchange with Keggin Units in the “HPA phase”. Small clusters of molybdenum oxide in equilibrium with HPA phase through water effect may also participate to the electronic and oxygen mobilities, but synergy with copper and vanadium improve this phenomenon.

The catalyst deactivation is related to the formation of big clusters of copper oxide on the surface of the catalyst, accompanied by a significative destruction of KU characterized by an important loss of molybdenum at the surface. Then, the deactivated catalyst surface is completely destroyed and the bulk appears partly isolated from the surface by clusters of copper, molybdenum and vanadium oxide without synergic properties.

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[33] US Patent 5215952, Ro¨hm, GmbH.