Study of Cesium or Cesium–Transition Metal-Substituted Keggin-Type Phosphomolybdic Acid As Isobutane Oxidation Catalysts

II. Redox and Catalytic Properties

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Cesium and copper- or iron-substituted Keggin-type phosphomolybdic heteropolycompounds with the general formula $Cs_2M_x^{y+}H_{1-xy}PMo_{12}O_{40}$ ($M = Fe^{3+}$ and Cu^{2+} and $0 \leq x \leq 0.43$) have been tested as catalysts in the oxidation of isobutane to methacrylic acid in order to study the effect of the transition metal ion on the catalytic properties. Copper appears to have a positive effect on the activity and a negative effect on the selectivity in methacrylic acid. Iron has almost no effect on the activity but a positive one on the selectivity, although this trend is reversed at higher iron content levels. These results have been correlated to the reducibility and the acidity of the catalysts. © 1999 Academic Press

1. INTRODUCTION

Considerable interest has been shown, in the past decade, in developing a new process for the production of methyl methacrylate. A potential route that has recently received attention is the direct partial oxidation of isobutane into methacrylic acid, followed by a simple esterification. All of the catalysts proposed for the partial oxidation of isobutane into methacrylic acid are based upon Keggin-type heteropolyanions (1–4). Mizuno *et al.* (1) have shown that compounds with the general formula $Cs_{2.5}M_x^{y+}H_{0.5-xy}PMo_{12}O_{40}$ with $M = $ Mn, Fe, Co, Ni, Cu were effective catalysts with an optimal activity obtained with 0.08 Ni^{2+} and the highest selectivity into methacrylic acid with 0.08 Ni^{2+} or 0.08 Fe^{3+} (2). They have shown that the oxidation of isobutane was a surface-type reaction and that the catalytic properties were controlled by both the oxidizing ability of the catalyst surface and its protonic acidity (3).

In the first article of this series, we presented the characterization of catalysts with the general formula $Cs_2M_x^{y+}H_{1-xy}PMo_{12}O_{40}$ with $M = Fe^{3+}$ and Cu^{2+} and $0 \leq x \leq 0.43$ (5). We have shown that these solids had the same microstructure as proposed earlier in the case of potassium-substituted heteropolycompounds (6) and were biphasic

with the acid ($H_3PMo_{12}O_{40}$) covering the cesium salt particles ($Cs_3PMo_{12}O_{40}$). The data obtained showed that the transition metal was doping the supported acid phase. This doping did not change the structure of the acid phase even at high substitution levels, but had an effect on its hydration rate, which decreased (5). The study of the isopropyl alcohol transformation showed that the transition metal ions had an effect on the acidity of the supported acid phase. Copper increased the acidity up to the composition corresponding to $x = 0.2$, whereas iron decreased it. At higher cation contents, the acidity of the copper compounds decreased because of the decrease of the proton content but that of iron remained constant; at high iron content, iron could partially be present as $[Fe(OH)_{3-x}]^+$ species which would act as active sites and compensate for the loss of activity due to the decrease in the number of protons (5).

In this paper we report the study of these solids as catalysts in the oxidation of isobutane into methacrolein (MA) and methacrylic acid (MAA). In order to interpret the catalytic properties and determine the effect of the substitution of transition metal, we have conducted both pre- and postcharacterization experiments focused on the iron and copper countercations as well as a study of the reducibility of the solids.

2. EXPERIMENTAL

2.1. Preparation and Characterization of the Catalysts

Cesium and cesium and iron- or copper-substituted heteropolyacids were synthesized as described previously (5). The same designation according to the metal countercation content of the solids was adopted. For example, $Cs_2Fe_{0.2}$ denotes a solid with the stoichiometry of $Cs_2Fe_{0.2}H_{0.4}PMo_{12}O_{40}$. Four series of compounds have been studied: Cs_2Fe_x, Cs_2Cu_x, $Cs_{2.5}Fe_x$, and $Cs_{3-x}H_x$. Both redox and catalytic properties of the compounds of the two first series have been evaluated, whereas only the catalytic properties of the

third one and the redox properties of the fourth one have been evaluated for comparison.

The characterization techniques used in this study (XRD, LRS, TGA) were described in the first article of this series along with that used to determine the surface areas of the compounds using the BET method (5). In addition to those, EPR spectra have been recorded at 77 K using a Varian E9 spectrometer operating in the X-band mode. DPPH was used as a standard for g-value determinations. XPS measurements were performed as described previously with a VG ESCALAB 200 R spectrometer (5). Binding energies were corrected relative to the carbon $1s$ signal fixed to 284.6 eV. Mössbauer spectra were recorded in air at room temperature, using a 2 GBq ^{57}Co/Rh source and a conventional constant acceleration spectrometer, operated in triangular mode. Isomer shifts were given with respect to to αFe. The relative areas of the observed doublets have been used to quantitatively evaluate the relative ratios of the sites present in the catalysts. This has been done by assuming equal free recoil fraction for all the sites. The validity of the computed fits was judged on the basis of both χ^2 values and convergence of the fitting processes.

2.2. Evaluation of Redox Properties

Reduction and reoxidation of catalysts have been studied in a SETARAM TGA-DTA 92 thermobalance. The catalysts (30–40 mg) were first heated (5 K min^{-1}) to 623 K, cooled to 613 K, and maintained at this temperature under nitrogen (total flow rate 2.4 dm^3 h^{-1}). After a short period of stabilization (0.5 h), the nitrogen flow was shifted to a H$_2$/N$_2$ mixture (1 : 4.88) and the weight variation was recorded. Since hydrogen consumed for reduction evolved as water, we have verified that the water was not readsorbed by checking that no weight variation was observable after a rapid backflush of nitrogen in the course of the reduction. The extent of reduction (ER) was calculated from the measured mass change (dm) by the formula

$$ER = 2 * M_{(HPA)} * dm/(16 * m_{(HPA)}),$$

where $M_{(HPA)}$ is the molar mass of the heteropoly compound and $m_{(HPA)}$ the mass of the analyzed sample. To study the reoxidation of the solids, the nitrogen flow, which was previously replaced by the H$_2$/N$_2$ mixture, was switched to a O$_2$/N$_2$ mixture (1 : 2.33). The experimental precision on the quantitative measurements was considered to be around 10%. An important difference between the iron and copper containing compounds was that the reduction profiles of Cs$_2$Cu$_x$ compounds were characterized by a rapid reduction step, followed by a much slower reduction process. The iron containing compounds, on the other hand, did not exhibit this two-step reduction phenomenon. In the case of the copper containing compounds we tried to evaluate the rate and extent of reduction of the first rapid reduction pe-

TABLE 1

Extent and Rate of the First Rapid Reduction Period of the Compounds Cs$_2$Cu$_x$ by Hydrogen at 613 K, Calculated in Electrons Per Keggin Unit (KU) and Per Copper Ions

Compound	Reduction extent		Reduction rate	
	(e^-/KU)	(e^-/Cu)	(e^-/KU min)	(e^-/Cu min)
Cs$_2$	1.2	—	0.05	—
Cs$_2$Cu$_{0.05}$	1.5	6.5	0.19	3
Cs$_2$Cu$_{0.10}$	1.9	7.0	0.35	3.1
Cs$_2$Cu$_{0.20}$	2.7	7.5	0.81	3.8
Cs$_2$Cu$_{0.30}$	3.2	6.7	1.21	3.9

riod by fitting two straight lines to the nearly linear parts of the curve before and after the sudden slope change. For comparison this procedure was also applied to the Cs$_2$H$_1$ curve, where the point of slope change is at about 30 min. The obtained values are given (Table 1) in electrons per Keggin unit (e^-/KU) and electrons per Keggin unit and minute (e^-/(KU min), respectively. To obtain the reduction extent in terms of electrons per Cu ions, we divided the difference in reduction extent between the copper content and the Cs$_2$H$_1$ sample. In the case of the iron containing compounds, since no nearly linear regions were observed for the curves, the values of the initial reduction rates were calculated by fitting the curves using exponential functions and considering the slope of the reduction curve at time $= 0$ (Table 2). These rates are expressed in electrons per Keggin unit and minute (e^-/(KU min) but also in terms of electron per protons and minutes (e^-/H min). Since no sudden slope change was observed, the extent of reduction values is not compared for the iron containing compounds. The two different ways of evaluation led to sligtly different values for the reduction rate of Cs$_2$H$_1$.

2.3. Catalytic Testing

The oxidation of isobutane (iBu) to methacrylic acid was carried out at atmospheric pressure in a dynamic differential microreactor containing 150 to 300 mg of catalysts.

TABLE 2

Initial Rate of Reduction of the Compounds Cs$_2$Fe$_x$ by Hydrogen at 613 K, Calculated in Electrons Per Keggin Unit (KU) and per Protons (H) and Minutes

Compound	Reduction rate	
	(e^-/KU min)	(e^-/H min)
Cs$_2$	0.058	0.058
Cs$_2$Fe$_{0.05}$	0.044	0.052
Cs$_2$Fe$_{0.10}$	0.028	0.040
Cs$_2$Fe$_{0.20}$	0.020	0.050
Cs$_2$Fe$_{0.30}$	0.013	0.130

Reaction conditions were as follows: $O_2/iBu/He/N_2$: 33.4/17.2/10.1/40.5 kPa; N_2 was the diluent gas and He was used as a reference. The total flow rate was equal to 6 cm^3 min^{-1}; the reaction temperature was 613 K. Prior to the reaction the catalyst was heated in a stream of nitrogen for 0.5 h and kept at 316 K. The gases at the outlet of the reactor were analyzed on line by gas chromatography using an FID and TCD gas chromatograph with Hayesep, AT1200, Porapak Q, and Carbosieve columns. Because all the catalysts were undergoing a deactivation during the first 7 h, the catalytic data were collected after at least 8 h for each catalyst. In order to study the effect of copper and iron on the selectivities, each series of compounds was tested at the same conversion level by varying the mass of the catalysts. Methacrolein, acetic acid (AcA), CO, and CO_2 were the four major by-products formed with methacrylic acid under our reaction conditions. Traces of acetone and acrylic acid have been detected, but they are not considered in the calculations.

3. RESULTS

3.1. Redox Properties

The reduction profiles of the Cu- and Fe-substituted Cs_2 compounds by hydrogen at 613 K are presented in Figs. 1 and 2, respectively. The rate of reduction increased monotonously with the Cu content and decreased with the Fe content (Tables 1 and 2). It is interesting to note that, for the Cu containing compounds, the extent of reduction (at the point of the slope change) was proportional to the copper content, with approximately 7 e^-/Cu. The initial rate of reduction was also proportional to the copper content (Table 1). For iron containing compounds, on the other hand, the initial reduction rate was not proportional to the iron content. Instead it was observed to decrease linearly
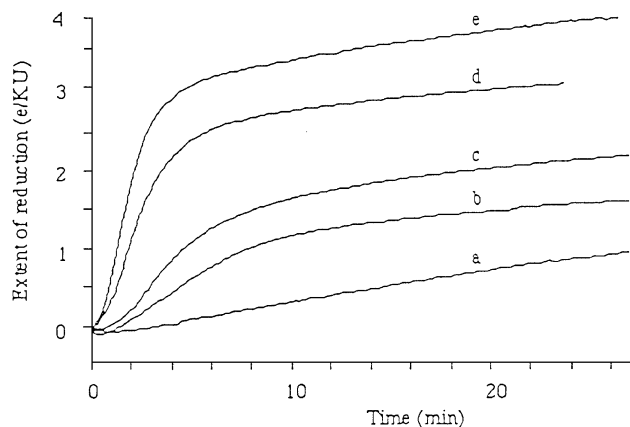

FIG. 1. Extent of reduction at 613 K as a function of time for the Cs_2Cu_x compounds: (a) Cs_2H_1, (b) $Cs_2Cu_{0.05}$, (c) $Cs_2Cu_{0.1}$, (d) $Cs_2Cu_{0.2}$, and (e) $Cs_2Cu_{0.3}$.
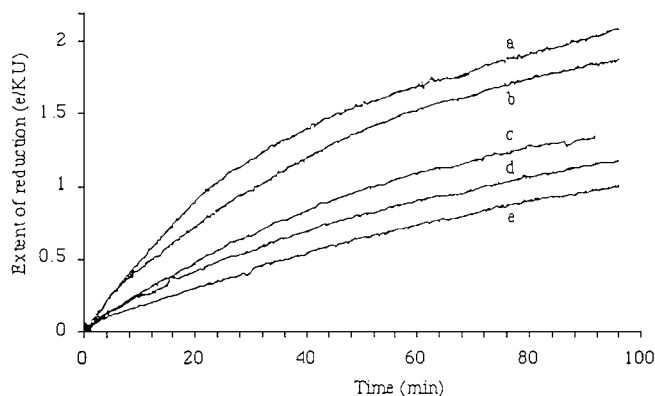

FIG. 2. Extent of reduction at 613 K as a function of time for the Cs_2Fe_x compounds: (a) Cs_2H_1, (b) $Cs_2Fe_{0.05}$, (c) $Cs_2Fe_{0.1}$, (d) $Cs_2Fe_{0.2}$, and (e) $Cs_2Fe_{0.3}$.

with the proton content of the solids at least up to an iron content of 0.2 Fe per KU (Table 2). For comparison, we have studied the initial reduction rate of compounds corresponding to the pure acid supported on the salt (Table 3). We have observed that the initial reduction rate of these compounds decreased linearly with the proton content and that the rate expressed in electrons per protons was approximately the same as that observed for the iron containing compounds (0.05 e^-/H).

We have studied the reoxidation of the compounds using the same technique, but considering in this case the rate of oxidation based on surface area (per m^2) in this case, since oxidation has been shown to be a surface reaction on this type of solids (7). We have observed that the rate of reoxidation depended not only on the composition of the solids, but even more strongly on their initial extent of reduction (i.e., extent of reduction at the beginning of the reoxidation step). We always found an initial period of very fast reoxidation (up to 20% in less than 2 min) followed by a long period of reoxidation with diminishing rate independent on the initial reduction extent. This shows that the curves of reoxidation (i.e., reoxidation rate as a function of reduction extent) were not directly comparable in the case of different initial reduction extents. Since our study did

TABLE 3

Initial Rate of Reduction of the Compounds Cs_xH_{3-x} by Hydrogen at 613 K Calculated in Electrons per Keggin Unit (KU) and per Protons and Minutes

Compound	Reduction rate	
	(e^-/KU min)	(e^-/H min)
Cs_2H_1	0.058	0.058
$Cs_{2.5}H_{0.5}$	0.03	0.05
$Cs_{2.85}H_{0.15}$	0.014	0.07

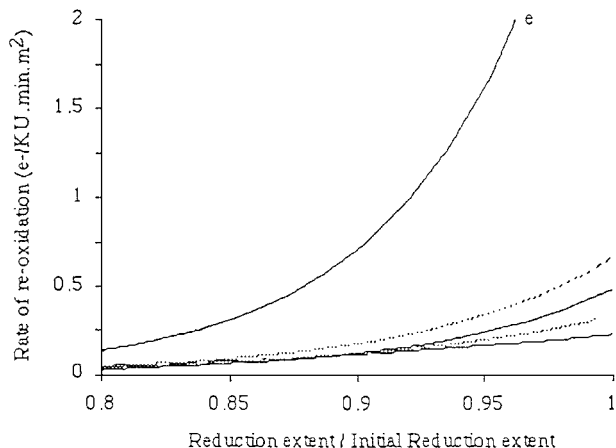**FIG. 3.** Rate of reoxidation as a function of the normalized extent of reduction for the Cs_2Cu_x compounds: (a) Cs_2H_1, (b) $Cs_2Cu_{0.05}$, (c) $Cs_2Cu_{0.1}$, (d) $Cs_2Cu_{0.2}$, and (e) $Cs_2Cu_{0.3}$.

not permit a comparison of samples with exactly the same initial reduction extent, we have introduced a normalized extent of reduction, defined as the ratio of the extent of reduction during the reoxidation process to the initial extent of reduction (Figs. 3 and 4). We observed that the rate of reoxidation increased with the Cu content but decreased with the Fe content. Thus, copper has a positive effect on the reoxidation of the solid and iron has a negative effect.

3.2. Characterization of Reduced Catalysts

We have focused the pre- and postreduction characterization of the catalysts on the two compounds $Cs_2Fe_{0.2}$ and $Cs_2Cu_{0.3}$, both of which had the same proton content. The reduction extents of the Fe and Cu compounds calculated from thermogravimetric data were equal to 0.33 and 1.7 e^-/KU, respectively. The $Cs_2Cu_{0.3}$ compound has been characterized by EPR before and after reduction (Fig. 5). The two spectra at 77 K showed two signals at $g_{eff} = 2.14$

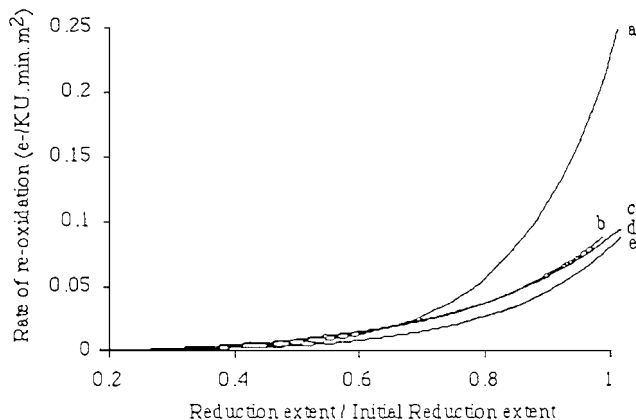**FIG. 4.** Rate of reoxidation as a function of the normalized extent of reduction for the Cs_2Fe_x compounds: (a) Cs_2H_1, (b) $Cs_2Fe_{0.05}$, (c) $Cs_2Fe_{0.1}$, (d) $Cs_2Fe_{0.2}$, and (e) $Cs_2Fe_{0.3}$.

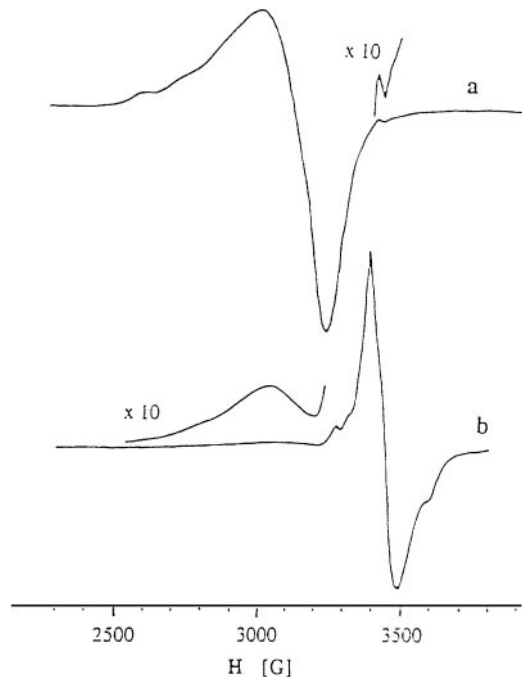**FIG. 5.** EPR spectra recorded at 77 K of the $Cs_2Cu_{0.3}$ compound (a) before and (b) after reduction.

and $g_{eff} = 1.94$, corresponding to Cu^{2+} and Mo^{5+}, respectively. Before reduction, the Mo^{5+} signal was very weak and the Cu^{2+} signal was predominent. After reduction the latter signal was reduced to about 15% of its initial intensity and a strong signal of Mo^{5+} appeared. The reduction of the copper containing compounds involved the reduction of both the copper and the molybdenum. The EPR data showed that around 85% of Cu^{2+} has been reduced. This reduction corresponded to 0.25 e^-/KU. Substracting this contribution from the total reduction of the compound (1.7 e^-/KU), it was possible to determine that 12% of Mo^{6+} was reduced. The XPS analysis data of the compound after reduction showed the presence of Cu^+ and both Mo^{6+} and Mo^{5+} on the surface (Table 4). The Cu^+ was characterized

TABLE 4

Binding Energies and Atomic Ratios Calculated from XPS Data on the Compound $Cs_2Cu_{0.20}$ after Reduction to 1.7 e^-/KU ($X = $ Cu, Cs, P)

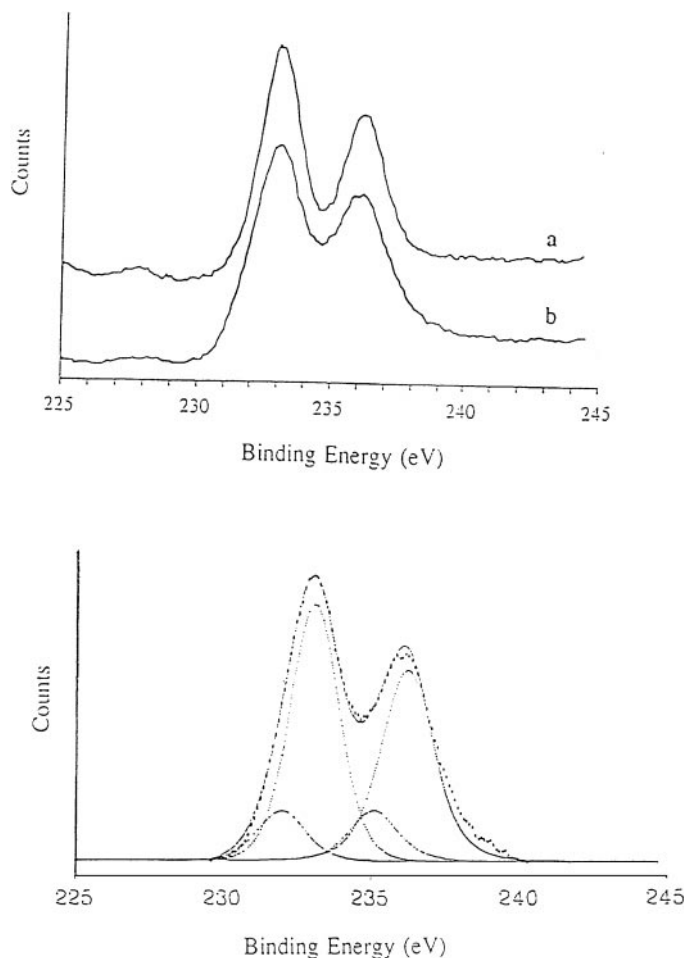| Element		Binding energy (eV)	Atomic ratios 12 X/Mo
Mo3d5/2	Mo^{6+}	233.0	
	Mo^{5+}	231.9	
Mo3d3/2	Mo^{6+}	236.1	
	Mo^{5+}	235.0	
Cu2p3/2		933.2	1.7
Cs2d5/2		724.1	1.4
P2p		134.0	1.3

FIG. 6. Comparison of the Mo$3d_{5/2}$ X-ray photoelectron spectra of the Cs$_2$Cu$_{0.3}$ compound (a) before and (b) after reduction and fitting of the spectrum obtained after reduction.

by a Cu$2p3/2$ peak with a binding energy equal to 933.2 eV, but also by the Auger parameter $\alpha = 1848.2$. The observed Mo$3d5/2$ peak has been fitted into two peaks separated by approximately 1.1 eV, which could be attributed to Mo^{5+} and Mo^{6+} cations (Fig. 6). The relative amount of Mo^{5+} calculated by integrating the peaks was around 22%. This amount was in relatively good agreement with the value calculated from TGA and EPR data, which was equal to 12%.

The Cs$_2$Fe$_{0.2}$ compound has been characterized by Mössbauer spectroscopy before and after reduction. The spectrum obtained before reduction has been fitted with only one ferric doublet, whereas two ferric doublets and one ferrous doublet were needed to fit the spectrum after reduction (Fig. 7, Table 5). In this latter case, the more intense doublet corresponded to the one identified before reduction. The new ferric doublet characterized by $\delta = 0.53$ mm s^{-1} and $\Delta = 0.57$ mm s^{-1} has tentatively been attributed to an iron cation in close proximity of a reduced

TABLE 5

Mössbauer Parameters Calculated from the Spectrum of the Compound Cs$_2$Fe$_{0.2}$ Recorded at 295 K after Reduction to 0.33 e^-/KU

Site	δ	W (mm s^{-1})	Δ	Relative intensities (%)
Fe^{3+}	0.39	0.77	0.80	86
Fe^{3+}	0.53	0.33	0.57	11
Fe^{2+}	1.27	0.46	2.94	2

Note. δ, isomer shift (given with respect to α-Fe); W, line width; Δ, qadrupolar splitting.

molybdenum cation (8). The ferrous doublet, which was not present before reduction, corresponded to only 2% of the iron cations. This result clearly showed that iron cations, unlike the copper cations, were practically not reduced at all and that the reduction of iron containing compounds involved only the reduction of the molybdenum cations.
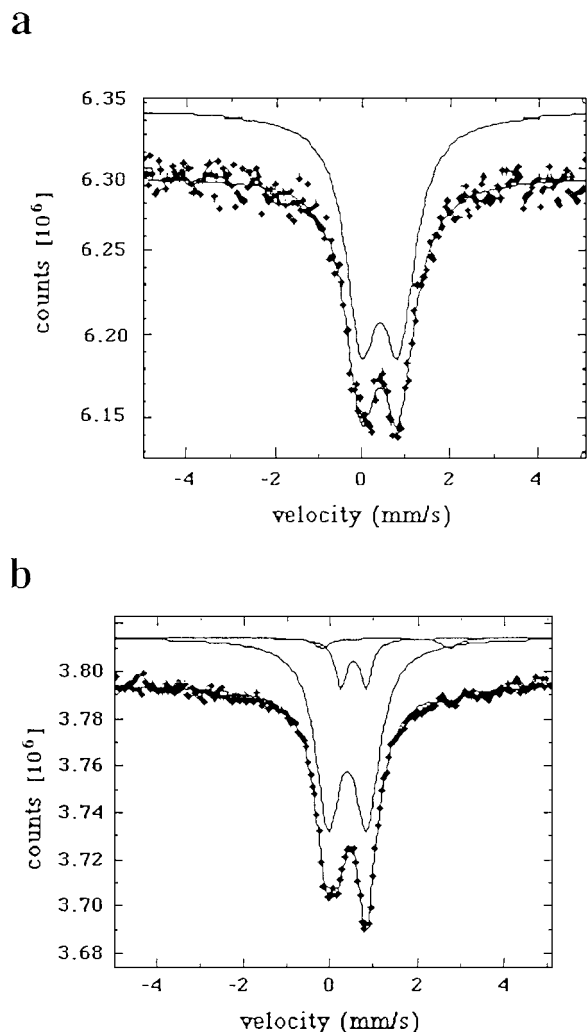
a

b

FIG. 7. Mössbauer spectrum of the Cs$_2$Fe$_{0.2}$ compound (a) before and (b) after reduction.

TABLE 6

Catalytic Properties of the Compounds Cs_2Cu_x in the Oxidation of Isobutane at 613 K

Compound	Conv. (%)	Selectivities (%)					IBu conversion rate (10^{-9} mol s^{-1} m^{-2})
		CO	CO_2	AcA	MA	MAA	
Cs_2	7.2	33	28	11	14	12	41
$Cs_2Cu_{0.05}$	7.0	36	28	13	16	7	48
$Cs_2Cu_{0.20}$	7.5	42	30	7	15	6	48
$Cs_2Cu_{0.30}$	6.6	41	31	5	16	6	51
$Cs_2Cu_{0.43}$	5.9	39	37	4	15	5	53

Note. AcA, acetic acid; MA, methacrolein; MAA, methacrylic acid.

3.3. Catalytic Properties

Results from the catalytic oxidation of isobutane at 613 K on copper and iron containing catalysts are summarized in Tables 6 and 7, respectively. The data are obtained by keeping the conversion level approximately constant and the activity comparisons are made in terms of the iBu conversion rates. We have verified that conversions were linearly changed with weight of catalyst versus flow rate. The substitution of copper cations for protons has a positive effect on the activity, but a negative effect on the selectivity to MAA, which decreased in favor of CO and CO_2. The selectivity to acetic acid followed that of the methacrylic acid, whereas the selectivity to methacrolein remained constant. For the Cs_2Fe_x series of compounds, it is observed that iron has a positive effect on the selectivity to MAA, exhibiting a maximum for the compound $Cs_2Fe_{0.2}$, which corresponds to a minimum for the formation of CO_x. The rate of isobutane conversion did not vary extensively with increasing iron content. Only a broad minimum could be observed. The same enhancement effect in MAA selectivity was observed for the $Cs_{2.5}Fe_x$ compounds, except that there was no maximum with increasing iron content. This could be due to the fact that the iron content of the compounds was

TABLE 7

Catalytic Properties of the Compounds Cs_2Fe_x and $Cs_{2.5}Fe_x$ in the Oxidation of Isobutane at 613 K

Compound	Conv. (%)	Selectivities (%)					IBu conversion rate (10^{-9} mol s^{-1} m^{-2})
		CO	CO_2	AcA	MA	MAA	
Cs_2	7.0	33	31	11	14	12	41
$Cs_2Fe_{0.05}$	6.7	24	29	11	15	21	36
$Cs_2Fe_{0.10}$	6.8	24	27	10	16	21	33
$Cs_2Fe_{0.20}$	6.8	23	27	9	17	24	42
$Cs_2Fe_{0.25}$	6.0	26	26	7	18	17	43
$Cs_2Fe_{0.30}$	6.3	26	26	7	17	18	46
$Cs_{2.5}$	10.3	38	30	9	10	12	41
$Cs_{2.5}Fe_{0.05}$	10.4	35	28	10	10	15	43
$Cs_{2.5}Fe_{0.10}$	10.3	29	29	11	10	19	39

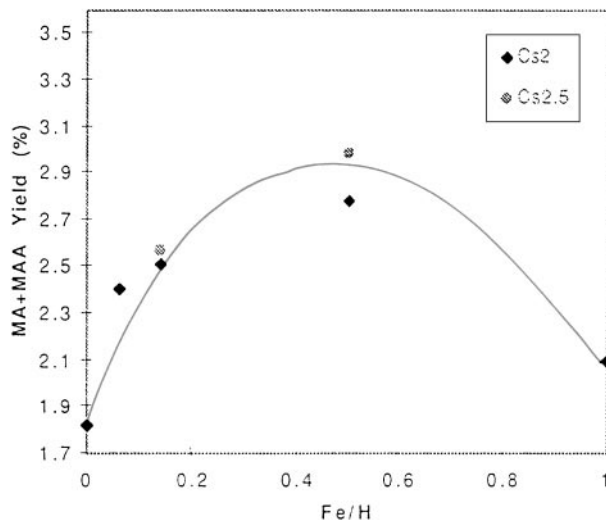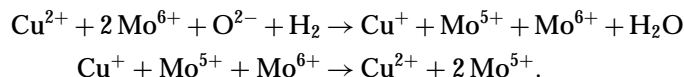*Note.* AcA, acetic acid; MA, methacrolein; MAA, methacrylic acid.

FIG. 8. MA+MAA yield as a function of the Fe/H ratio of the acid phase supported on the cesium salt. MA, methacrolein; MAA, methacrylic acid.

very limited. Similar to the Cs_2Fe_x compounds, the rate of conversion of isobutane did not vary significantly with the iron content. Since both $Cs_{2.5}Fe_x$ and Cs_2Fe_x compounds have the same microstructure and both correspond to the iron-substituted acid phase supported on the cesium salt, we have plotted in Fig. 8 the variation of the MA+MAA yield as a function of the Fe/H ratio of the acid phase. It can be seen that this yield presented a maximum for a Fe/H ratio between 0.3 and 0.5. These results are not inconsistent with those of Mizuno *et al.*, who found experimentally a maximum for Fe/H = 0.31 with the compound $Cs_{2.5}Fe_{0.08}$ (3).

4. DISCUSSION

The observation of two different rates in the reduction process of several samples, a rapid first one and a slow second one, can be explained by the reduction of the acid phase and the pure salt, respectively. This explanation is supported by the fact that the pure salt Cs_3 showed a much smaller reduction rate than the acid containing solids in the series of the undoped samples. In the case of the Cs_2H_1 sample the two reduction periods are not very well seperated, but a faster reduction of the acid phase in the case of the copper compounds showed a better separation. Conversely, a reduced reduction rate in the case of the iron compounds leads to curves without a sudden change in rate. The enhancement of the initial reduction rate and the extent of the first step of reduction shows that copper raises the reduction ability of the acid phase. Taking into account the linearity of this enhancement (the reduction extent is raised by approximately 7 e^-/Cu and the rate by approximately 3.5 e^-/Cu min (Table 1)), it appears that copper takes part directly in the reduction mechanism. This is supported by the results of the characterization of the $Cs_2Cu_{0.3}$ compound

after reduction, which showed that copper was practically reduced completely while molybdenum was only partially reduced. Considering a reduction of 7 e^-/Cu and that one electron corresponds to the reduction of Cu^{2-} to Cu^+, the reduction of 6 Mo^{6+} ions to Mo^{5+} can be attributed to one copper ion. This feature might be explained if the reduction proceeded in the neighborhood of the copper cations with a concerted mechanism between the copper and molybdenum cations. The Cu^{2+} cations could be envisioned to catalyze the reduction of molybdenum cations as follows:

$$Cu^{2+} + 2\,Mo^{6+} + O^{2-} + H_2 \rightarrow Cu^+ + Mo^{5+} + Mo^{6+} + H_2O$$
$$Cu^+ + Mo^{5+} + Mo^{6+} \rightarrow Cu^{2+} + 2\,Mo^{5+}.$$

It is conceivable that copper could function in this capacity until all the adjacent molybdenum ions are reduced. The fact that every Cu^{2+} is involved in the reduction of 6 Mo^{6+} may indicate that the copper countercations have an octahedral coordination in the acid phase with six oxygen atoms of different Keggin heteropolyanions. Contrary to the Cu^{2+} ions, the Fe^{3+} ions were not reduced upon reduction as shown by Mössbauer spectroscopy (Table 5). At the same time, the substitution of iron cations for protons has a negative effect on the reducibility of the compound. The initial reduction rate decreased linearly with the proton content of the solids and can be estimated as approximately 0.05 e^-/H (Table 2). This value corresponds to the one measured for the pure acid supported on the cesium salt. Thus it appears that iron does not participate in the redox mechanism like copper but that it has a negative effect on the reductibility of the adjacent molybdenum ions. A reduction rate proportional to the number of protons means that only the sites not doped with iron participate in the inital reduction.

In Fig. 9 we compare the variations of the initial reduction rate and of the isobutane conversion rate with the transition metal content. It can be seen that these variations correlate relatively well with each other. A similar correlation was observed for Cs_xH_{3-x} compounds and pure alkali phosphomolybdic salts when the proton content and the nature of the alkali ions were varied (9–12). The activity appears to depend upon the reducibility of the solid. In the case of copper containing compounds the reducibility increased continuously with the copper content and so did the activity in isobutane oxidation. In the case of iron containing compounds, the reducibility and the activity did not vary much and went through very broad minima. At high iron content, an increase of activity was observed. A possible explanation for this variation could be that at high iron content $[Fe(OH)_{3-x}]^+$ species were formed as proposed earlier to explain the acidity measurement data (5). These species could, at high temperatures, give rise to more active species.
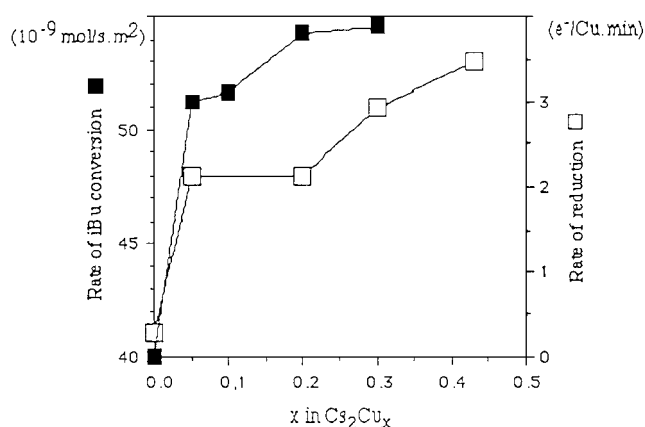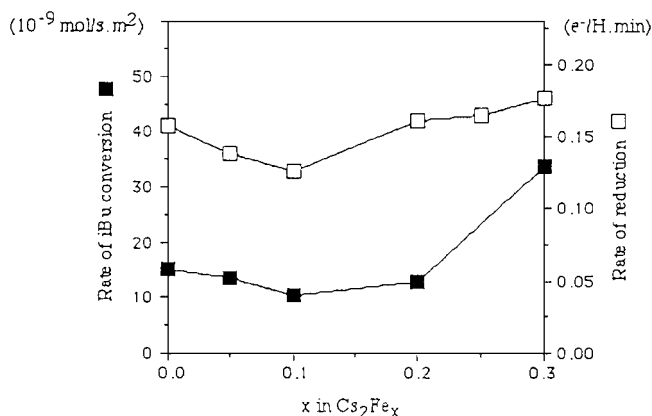

FIG. 9. Variation of the rate of iBu conversion and of the rate of reduction with the transition metal content: (a) Cs_2Fe_x compounds and (b) Cs_2Cu_x compounds.

Figure 10 compares how the selectivity to MAA and the rate of formation of propene vary with the metal content in dehydration of isopropyl alcohol (5). It can be observed that, up to a transition metal content of 0.2 per KU, the selectivity to MAA varies inversely with the acidity. The variations in MAA selectivity were seen to be coupled with the variations in acetic acid and CO_x selectivities. It has been reported that the formation of acetic acid corresponds to the degradation of MAA (4, 10, 13). It can thus be proposed that a high acidity favors the degradation of MAA by a consecutive oxidation reaction. An example of such an effect of high acidity on the stability of an acid molecule has recently been reported in the case of the oxidative dehydrogenation of isobutyric acid on heteropoly compound-based catalysts (14). In this last case the transformation corresponded to the decomposition into propene and CO. In our case the acidity of the pure supported heteropolyacid Cs_2 would already be too high and lead to the partial decomposition of the acids that are formed. A lowering of the acidity by iron substitution would thus have a positive effect on the
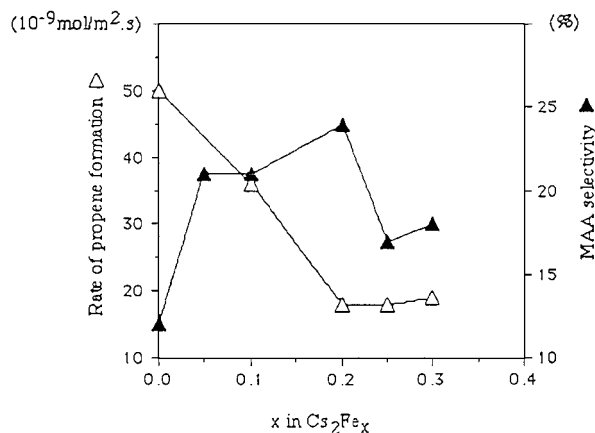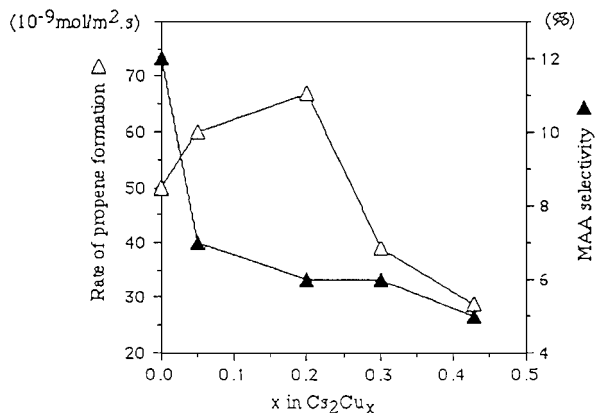
FIG. 10. Effect of transition metal content on the propene formation rate in the reaction of dehydration of isopropyl alcohol and on the MAA selectivity in the oxidation of isobutane: (a) Cs_2Fe_x compounds and (b) Cs_2Cu_x compounds.

selectivity to MAA, and the increase of the acidity by copper substitution would have a negative effect.

At high copper content, it could be observed that the acidity of the solids decreased, but the selectivity in MAA did not increase (Fig. 10). The decrease of the acidity was explained by the opposite effects of the increase in copper content and the decrease in the number of protons (5). It may be proposed that the presence of a certain proton content in the solid is needed to have the formation of methacrylic acid. The same interpretation can be given to explain the data obtained at high iron content, showing that the acidity of the solids remained constant, whereas the selectivity in MAA decreased (Fig. 10). However, in this case, an increase in activity in isobutane oxidation was also observed (Fig. 9). The stabilization of the rate of formation of propene had previously been explained by the presence of $[Fe(OH)_{3-x}]^+$ species which would both act as active sites and limit the loss of activity due to a decrease in the number of protons (5).

The same species may be responsible for both the decrease in MAA selectivity and the increase in activity.

5. CONCLUSION

We have seen that, in the heteropolyacids supported on the cesium salt, the transition metal cations act differently depending upon whether they participate in the reduction process of the heteropolycompound or not. Copper, which is directly involved in the redox mechanism by catalyzing the reduction of the solids, increases the activity. However, it increases the acidity, which has a negative effect on the selectivity to MAA. On the other hand, iron has no direct effect on the reduction rate, but decreases it indirectly by decreasing the number of protons. Therefore, the substitution of iron does not increase the activity, but since it reduces the acidity, it increases the selectivity to MAA. The existence of a maximum for the MA and MAA yield as a function of the Fe content may thus be explained by the superposition of the negative effect on the activity of the catalysts which is decreased and the positive one on the selectivity in MAA. Both the reducibility and the total acidity of the surface of the catalysts are important in the isobutane oxidation reaction. The reducibility seems to influence greatly the activity of the catalysts. The acidity of the compounds seems to affect the selectivity of the catalysts. It appears that an optimum acidity level is needed, one which would be high enough to allow the final desorption of the MAA that is formed, but would not be so high as to affect its further oxidation into AcA and CO_x.

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