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Stability of iron in the Keggin anion of heteropoly acid catalysts for selective oxidation of isobutane

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Abstract

The thermal stability and isobutane oxidation activity of catalysts with Fe selectively placed in the Keggin anion have been studied. For the $Cs_3H_1PMo_{11}FeO_{39}$ salt, Fe was released from the Keggin structure above 570 K, as observed by FT–IR spectroscopy. However, in the presence of NH_4^+ as counter-cation, Fe was released from the Keggin anion at 470 K, simultaneously catalysing the elimination of NH_4^+. Fe-substituted catalysts with Fe contents of 0–1, where ammonium was removed during the heat pre-treatment, showed a negative influence of Fe on the selectivity to methacrylic acid (MAA) and on the isobutane conversion. The influence of the initial position of Fe, inside or outside the Keggin anion, was studied. A catalyst in which Fe was initially as counter-cation, $Cs_{1.5}Fe_{0.5}(NH_4)_{2.0}PMo_{12}O_{40}$, presented a 21% selectivity to MAA at 633 K after 20 h in operation, against a 15% selectivity of a catalyst that had a similar composition but with Fe initially inside the Keggin anion, $Cs_{1.5}(NH_4)_{2.0}PMo_{11.5}Fe_{0.5}O_{39.5}$. Both catalysts showed similar isobutane conversions of ca. 8%. The catalysts underwent changes during the first few hours in a reaction that led to an increase of the selectivity to MAA in both the cases. However, the active sites derived from the lacunary species generated after release of Fe from the Keggin anion were less selective than those derived from 12-molybdophosphoric units. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Heteropoly compound; Fe-substituted; Isobutane oxidation; Methacrylic acid

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1. Introduction

The methacrylic acid (MAA) demand has been constantly increasing in the last years [1]. MAA is the key intermediate in one of the existing processes for the production of methyl methacrylate, industrially applied by various Japanese companies (Japan Methacryl Monomer, Mitsubishi Rayon, Kyodo Monomer) [2]. This process consists of two catalytic oxidation steps — from isobutylene to methacrolein, and then to MAA — and a final esterification with methanol [1–3]. It is very convenient for replacing the conventional acetone–cyanohydrin process, though it shows the inconveniences of being a multi-step process and using a high price feedstock (isobutylene).

The direct oxidation of isobutane to MAA has therefore arisen as a convenient alternative, as a one-step process with a reasonable cost of the feedstock. Several catalysts have been proposed for this reaction, both in journals [4–15] and patents [16–24], most of them based on molybdenum-containing heteropoly acids.

Heteropoly acids with the so-called Keggin structure are amongst the most promising catalysts [25–27]. They consist of a large anion that contains a central atom, typically P, tetrahedrally coordinated to oxygens and surrounded by oxygen-linked hexavalent

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peripheral metal atoms [28]. The structure–activity interaction of these complex systems has not yet been well understood. It has been mentioned that structures in which one or more molybdenum atoms would be substituted by other metal atoms might show an improved performance compared to the heteropoly acids based on 12-molybdophosphoric units [22].

The stability and location of the substituted metal atom in the Keggin anion has been thoroughly studied and discussed in the case of vanadium [10,29–37]. It has been shown that even if vanadium is inside the Keggin anion in the fresh catalyst, it is almost completely removed in reaction conditions. However, studies on the stability and catalytic role of other metal atoms, e.g. iron, in the Keggin unit are scarce.

Iron-substituted Keggin-type polyoxometalates have shown good performance in processes of catalytic oxidation of hydrocarbon in liquid phase [38–40]. Iron has been also mentioned in the patent literature as an additive for Keggin-type heteropoly acid catalysts in isobutane or methacrolein oxidation to MAA [16–21], although it was not disclosed whether Fe was inside or outside of the Keggin unit during the reaction. Furthermore, various works have reported that iron as counter-cation promoted the catalytic performance of Keggin-type heteropoly compounds in the selective oxidation of isobutane [6,8,13,14].

In this work, we study the location and stability of iron-substituted heteropolymolybdate catalysts as a function of heat treatment temperature and type of counter-cations, and investigate the influence on the catalytic performance of the system in the oxidation of isobutane to MAA.

2. Experimental

2.1. Catalysts preparation

The Fe-substituted catalysts have been synthesised from $H_3PMo_{12}O_{40}$ (Nippon Inorganic Colour and Chemical), following a method described elsewhere [41,50]. The pH of 150 ml of 0.1 M $H_3PMo_{12}O_{40}$ aqueous solution was brought to 4.4 (1.0 Fe-substitution) or 1.8 (0.5 Fe-substitution) by addition of Li_2CO_3 (Katayama Chemical Industries). Then 30 ml of $Fe(NO_3)_3$ (Wako Pure Chemical Industries) aqueous solution were added in stoichiometric amount. The resulting Fe-substituted species was precipitated with stoichiometric amounts of CsCl and NH_4Cl (Wako Pure Chemical Industries) (Figs. 1 and 2). After confirming that the catalysts showed the same properties and behaviour if prepared either with chloride or nitrate salts, $CsNO_3$ and NH_4NO_3 (Wako Pure Chemical) were used for preparing the catalysts for the activity tests (Figs. 3–5), as nitrates are more convenient than chlorides from an industrial point of view. The whole procedure was performed at room temperature. In all the cases, a yellow precipitate was formed, which is filtered and dried at 383 K overnight. The yields were above 75% in all cases. In the case of catalysts with Fe as counter-cation, the synthesis was carried out in the same way, but without Li_2CO_3 addition, at pH 1.0. The ammonium salt $(NH_4)_3PMo_{12}O_{40}$ was purchased from Wako Pure Chemical Industries.

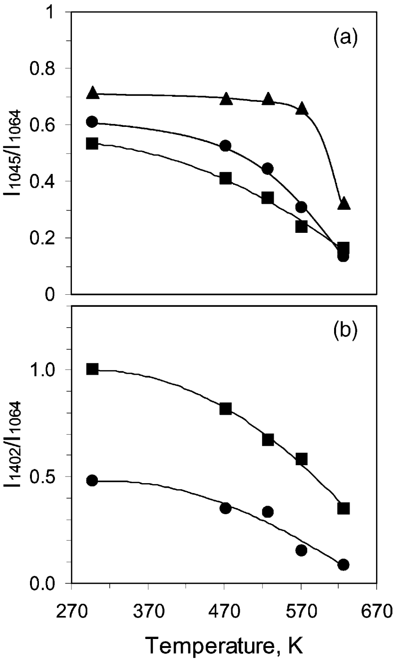

Fig. 1. Influence of temperature on: (a) Fe release from the Keggin anion (P–O stretching secondary band at 1045 cm^{-1}) and (b) NH_4^+ elimination (N–H bending band at 1402 cm^{-1}). (▲) $Cs_3H_1PMo_{11}FeO_{39}$, (●) $Cs_2(NH_4)_2PMo_{11}FeO_{39}$, and (■) $(NH_4)_4PMo_{11}FeO_{39}$. Heat treatment in N_2 during 1 h; temperature increase rate: 10 K min^{-1}.

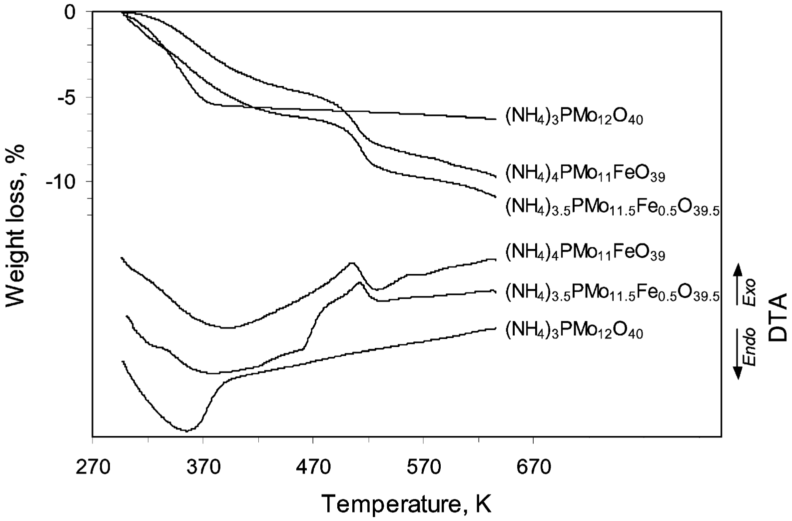

Fig. 2. TG–DTA curves of $(NH_4)_{3+y}PMo_{12-y}Fe_yO_{40-y}$ ($y = 0$–1) in nitrogen.

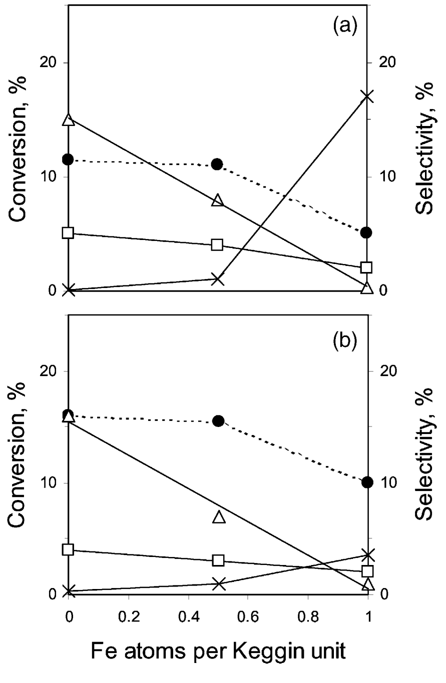

Fig. 3. Variation of (●) isobutane conversion, and selectivity to (×) isobutylene, (□) methacrolein, and (△) MAA of $Cs_2(NH_4)_{1+y}PMo_{12-y}Fe_yO_{40-y}$, as a function of Fe content: (a) $T = 603$ K and (b) $T = 623$ K. Feed composition: [Isobutane] = 25 vol.%, $[O_2]$ = 25 vol.%, $[H_2O]$ = 15 vol.%, $[N_2]$ = balance. Operating conditions: SV = 960 ml/g/h, $P = 152$ kPa.

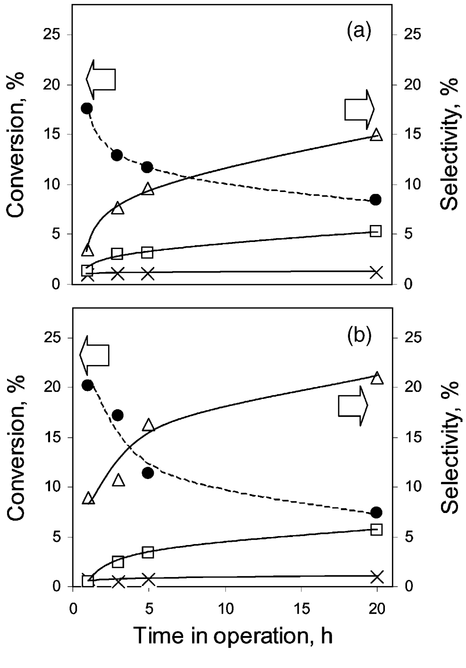

Fig. 4. Variation of (●) isobutane conversion, and selectivity to (×) isobutylene, (□) methacrolein, and (△) MAA, as a function of time in operation: (a) $Cs_{1.5}(NH_4)_{2.0}PMo_{11.5}Fe_{0.5}O_{39.5}$ and (b) $Cs_{1.5}Fe_{0.5}(NH_4)_{2.0}PMo_{12}O_{40}$, pre-treated in N_2 at 623 K for 1 h. Feed composition: [Isobutane] = 25 vol.%, $[O_2]$ = 25 vol.%, $[H_2O]$ = 15 vol.%, $[N_2]$ = balance. Operating conditions: SV = 960 ml/g/h, $P = 152$ kPa, $T = 633 - 588$ K.

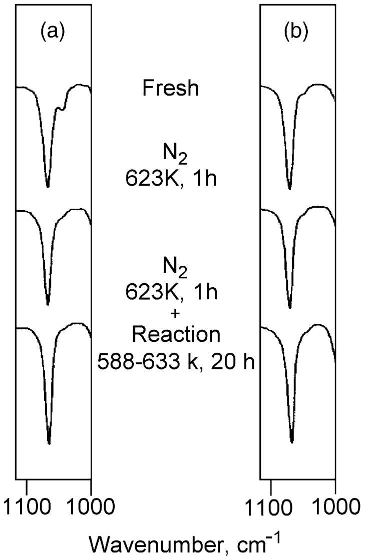

Fig. 5. FT–IR spectra of Fe-containing catalysts fresh, after pre-treatment in nitrogen, and after reaction: (a) $Cs_{1.5}(NH_4)_{2.0}$-$PMo_{11.5}Fe_{0.5}O_{39.5}$ and (b) $Cs_{1.5}Fe_{0.5}(NH_4)_{2.0}PMo_{12}O_{40}$.

2.2. Catalysts characterisation

The composition of the solids was determined by X-ray fluorescence (XRF, Horiba, MESA 500-W), for Cs, P, Mo and Fe, and by thermogravimetry on a platinum crucible (TG–DTA, Shimadzu Scientific Instruments, DTG-50) for ammonia. These results were confirmed by analysis of the filtrate solutions by inductively coupled plasma (Mo, Li, Fe, and P; Shimadzu Scientific Instruments, ICPS-8000), atomic absorption spectrometry (Cs; Hitachi Scientific Instruments, Z6100), and ion chromatography (NO_3^-, NH_4^+; Nippon Dionex, 2000i/sp).

The presence of Fe in the Keggin anion was determined by infrared spectroscopy (FT–IR, Jasco Corporation, Valor III) with KBr supported disks, by measuring the relative intensity of the secondary asymmetric (P–O) stretching vibration band at $1045\,cm^{-1}$ [30–32,41,50]. For ammonium, the intensity of the (N–H) bending band at $1402\,cm^{-1}$ was followed.

The X-ray diffraction (XRD) patterns were recorded on a powder X-ray diffractometer (Rigaku International Corporation, Miniflex) in the 3–60° (2θ) region using Cu Kα radiation.

The surface areas were measured by nitrogen adsorption–desorption at 77 K (Quantachrome Instruments, Autosorb 6), and determined by application of the BET equation [42], taking the area of the nitrogen molecule as $0.162\,nm^2$ [43]. The samples were evacuated overnight at 423 K under a vacuum of <3 Pa to ensure a dry clean surface.

2.3. Activity measurements

The catalytic performance measurements were carried out in a tubular fix bed reactor, into which the reactants were fed by a set of mass flow controllers with the following composition: [isobutane] = 25 vol.%, $[O_2] = 25$ vol.%, $[H_2O] = 15$ vol.%, $[N_2]$ = balance. Operating conditions: GHSV = 960 ml/g/h; $P = 152$ kPa. Water was fed with a mini-pump. Catalysts were pressed into particles of 0.71–1.00 mm diameter, and diluted with SiC particles. Gaseous compounds were analysed by on-line gas chromatography, with detection by TCD (Shimadzu Scientific Instruments, GC-8A). Other products were absorbed in water and analysed by a gas chromatograph with FID detection (Hewlett-Packard, HP 6980 Series). The conversion of isobutane (2-methylpropane), as well as the selectivity to isobutylene (2-methylpropene), methacrolein (2-methyl-2-propenal), and MAA (2-methylpropenoic acid) were measured.

3. Results and discussion

3.1. Influence of Cs^+ on the stability of Fe

The thermal stability of Fe-substituted Keggin heteropoly acids with decreasing Cs^+ contents was studied by FT–IR spectroscopy with $Cs_3H_1PMo_{11}FeO_{39}$, $Cs_2(NH_4)_2PMo_{11}FeO_{39}$ and $(NH_4)_4PMo_{11}FeO_{39}$ treated in nitrogen at different temperatures. In the salts with Cs^+ content lower than three, ammonium was used as co-precipitant.

When transition metal atoms are substituting Mo in the Keggin anion, they induce alterations in the infrared spectrum that allow monitoring the presence of the metal inside the Keggin structure [30–32,41,50]. These previous works show that the substituting metal induces a decrease of the oxoanion symmetry, leading to a split of the asymmetric (P–O) stretching band. As a consequence, a shoulder is observed that is not present in the (P–O) band of the 12-molybdophosporic compound. In case of Fe, this shoulder is very clear, constituting actually a secondary band at 1045 cm^{-1}, being the main (P–O) vibration band at 1064 cm^{-1}.

The Fe presence inside of the heteropoly acid salts and the ammonium content were thus monitored by the relative intensity of the corresponding (P–O) and (N–H) bands at 1045 and 1402 cm^{-1}, respectively. The main (P–O) stretching band at 1064 cm^{-1} was selected as internal reference. However, similar results were observed when the asymmetric (Mo=O) stretching band at 964 cm^{-1} was used as internal reference.

The results are presented in Fig. 1, where the relative intensities of the bands associated with the Fe in the Keggin anion and the ammonium content are shown as a function of the pre-treatment temperature. The data at room temperature, 298 K, correspond to the fresh salt, while the rest were obtained by 1 h treatment in nitrogen.

Initial relative intensities above 0.5 were observed in the three catalysts for the secondary (P–O) band at 1045 cm^{-1} (Fig. 1a). As the treatment temperature increased, the secondary (P–O) band became weaker. This effect began already at 470 K in the case of the ammonium-containing samples, while it was observed only above 570 K for $Cs_3H_1PMo_{11}FeO_{39}$. The ammonium (N–H) band at 1402 cm^{-1} of the ammonium-containing compounds (Fig. 1b) was also intense for samples without treatment and decreased parallel to the Fe band (Fig. 1a). A ratio of 2 between the initial ammonium intensities, 1.0 and 0.5, was in agreement with the corresponding ammonium content, which was 4 and 2, respectively.

The high intensity of the Fe-associated (P–O) band in the fresh catalysts indicated that Fe was initially located inside the Keggin anion. As the temperature of treatment increased, the Fe was gradually released from the Keggin unit. However, the temperature at which this effect took place strongly depended on the Cs^+ content. When Cs^+ was not present, in $(NH_4)_4PMo_{11}FeO_{39}$, the Fe removal began already at 473 K, while with three atoms of Cs^+ as counter-cation, $Cs_3H_1PMo_{11}FeO_{39}$, this phenomenon was retarded up to 573 K. The behaviour of the compound containing two Cs^+ atoms was closer to that of the non-Cs^+ salt.

Parallel to the Fe release, the ammonium elimination began at 473 K, and was almost complete at 623 K, although still some ammonium remained in $(NH_4)_4PMo_{11}FeO_{39}$ after the treatment at 623 K.

As the initial intention was to test catalysts with Fe inside their Keggin unit, the Fe release at low temperature became an undesired effect. On the contrary, the ammonium elimination was wanted, in order to use ammonium as a precursor of H^+ species. This simultaneity of Fe release and ammonium loss suggested that both phenomena might be related to each other. This hypothesis was addressed with further experiments that are presented in the next section.

Concerning the role of Cs^+, the higher stability of Fe in the Keggin anion with higher Cs^+ content showed a stabilising influence of Cs^+. A similar stabilising effect of the metal inside the Keggin anion was previously found for V in Keggin-type $Cs_xH_{4-x}PMo_{11}VO_{40}$ ($x = 0$–4) [37] and $Cs_xH_{3.84-x}Ni_{0.08}PMo_{11}VO_{40}$ ($x = 0$–3) [5,10]. However, in our case this effect was smaller when ammonium was present, as observed by comparing the curves of $Cs_2(NH_4)_2PMo_{11}FeO_{39}$ and $(NH_4)_4PMo_{11}FeO_{39}$ (Fig. 1a), which showed less marked differences. These results indicate that the presence of ammonium diminishes the stabilising effect of Cs^+ on the Fe-substituted Keggin anion.

3.2. *Influence of NH_4^+ on the stability of Fe*

In order to elucidate the possible relation between the Fe release and the ammonium elimination, the thermal behaviour of the commercial ammonium salt of the Keggin anion without Fe, $(NH_4)_3PMo_{12}O_{40}$, was compared with the two corresponding Fe-containing Keggin compounds, $(NH_4)_{3.5}PMo_{11.5}Fe_{0.5}O_{39.5}$ and $(NH_4)_4PMo_{11}FeO_{39}$. The TG–DTA curves of these compounds are shown in Fig. 2, recorded in nitrogen at a heating rate of 10 K min^{-1}. The three compounds showed an initial weight loss that can be attributed to the loss of hydration water [44,45]. This water loss corresponded to six H_2O molecules in the case of $(NH_4)_3PMo_{12}O_{40}$ and $(NH_4)_4PMo_{11}FeO_{39}$, and ten H_2O molecules for $(NH_4)_{3.5}PMo_{11.5}Fe_{0.5}O_{39.5}$.

In the case of $(NH_4)_3PMo_{12}O_{40}$ (Fig. 2), this loss took place rapidly, below 380 K, accompanied by an endothermic peak at 356 K in the DTA curve. After that, no further loss was observed, only detecting a slow decrease that could be due to the loss of residual water. No ammonium was lost, as confirmed by

FT–IR spectroscopy (not shown), with similar relative intensities of the (N–H) bending at 1402 cm^{-1} before and after treatment. This agrees with the ammonium loss temperature of ca. 680 K in nitrogen reported by Marchal-Roch et al. [45,46].

With $(NH_4)_4PMo_{11}FeO_{39}$ (Fig. 2), this water loss was slower, up to a higher temperature of ca. 470 K, accompanied by a broad endothermic peak at 393 K in the DTA curve. In this case, however, a further loss began at ca. 470 K, along with a DTA exothermic peak at 505 K. This exothermic loss can be assigned to ammonium loss, which starts at ca. 470 K, as observed by FT–IR spectroscopy for this compound in Fig. 1(b).

The TG curve of $(NH_4)_{3.5}PMo_{11.5}Fe_{0.5}O_{39.5}$ (Fig. 2) was similar to that of $(NH_4)_4PMo_{11}FeO_{39}$, with an initial weight decrease due to water loss up to ca. 470 K, and then a further decrease assigned to ammonium loss. However, as stated above, the water loss was larger in this case. The DTA curve showed an endothermic peak at 380 K, and an exothermic peak at 512 K. If $(NH_4)_{3.5}PMo_{11.5}Fe_{0.5}O_{39.5}$ would be considered as a mixture of $(NH_4)_3PMo_{12}O_{40}$ and $(NH_4)_4PMo_{11}FeO_{39}$, the expected behaviour would be one influenced by both type of species. That is actually what was observed, with the temperature of endothermic peak of water loss in between those of $(NH_4)_3PMo_{12}O_{40}$ and $(NH_4)_4PMo_{11}FeO_{39}$, and the exothermic peak of ammonium loss similar to $(NH_4)_4PMo_{11}FeO_{39}$, but shifted up by 8 K towards that of $(NH_4)_3PMo_{12}O_{40}$.

Summarising, when the samples contained Fe in the Keggin anion, the temperature of ammonium removal was shifted down to ca. 470 K, from ca. 680 K of the non-iron $(NH_4)_3PMo_{12}O_{40}$. The release of Fe from the Keggin anion at low temperature can thus be attributed to the reaction of Fe^{3+} with the $NH_4{}^+$ counter-ion, which is oxidised to ammonia or nitrogen, and eliminated. There are two possible reasons for this to happen. On the one hand, the oxidation of $NH_4{}^+$ leads to a Fe^{2+} product, which might compromise the stability of the Keggin unit and might therefore be released. On the other hand, the ammonium elimination is an exothermic reaction that might lead to hot spots that would drive to the Fe release. The present results do not allow us to conclude which one of these possibilities, if not both, is responsible for the simultaneity of Fe release and ammonium elimination.

3.3. Effect of Fe on the catalytic performance

The influence of the Fe presence on the catalytic activity has been studied with $Cs_2(NH_4)_{1+y}PMo_{12-y}-Fe_yO_{40-y}$ catalysts, where $y = 0$, 0.5 or 1.0. The catalysts were pre-treated in nitrogen for 1 h at 623 K in order to eliminate the ammonium. As discussed above, this produced the removal of Fe from the Keggin anion as a side effect.

Fig. 3 shows the conversion and selectivity of these Fe-substituted catalysts in the isobutane oxidation as a function of the Fe atoms per Keggin unit at 603 K (Fig. 3a) and 623 K (Fig. 3b). As the Fe content increased, the selectivity to MAA decreased linearly from 15% to close to 0%, either at 603 or 623 K. The isobutane conversion declined only at a high Fe content of $y = 1.0$. The selectivity to methacrolein was below 5% in all cases, and fell slightly to ca. 2% as the Fe content increased. Isobutylene generation increased at Fe contents of $y = 1.0$, especially at 603 K, where a selectivity of 17% was reached (Fig. 3a).

Thus, Fe showed a negative effect on the catalytic performance of the heteropoly compounds. It led to a decrease of the selectivity to MAA, and for contents of 1 Fe per Keggin unit it also induced a lowering of the isobutane conversion.

Taking into account the above-described effect of the pre-treatment on the catalysts structure, it should be pointed out that this was not the catalytic performance of catalysts with Fe inside the Keggin unit, but that of the species resulting from the rearrangement of the starting material after ammonium loss and Fe release from the Keggin anion. The decrease of the (P–O) stretching intensity at 1045 cm^{-1} observed in Fig. 1(a) indicated that Fe was removed from the Keggin anion in $PMo_{11}FeO_{39}{}^{4-}$, resulting in the highly unstable $PMo_{11}O_{39}{}^{7-}$ lacunary species, which rearranged into $PMo_{12}O_{40}{}^{3-}$, showing no shoulder or secondary peak in the (P–O) band. Thus, what remained after the Fe release from the Keggin unit was a rearranged heteropolyanion, where Fe^{3+} worked as counter-cation and the anions were formally $PMo_{12}O_{40}{}^{3-}$ units.

As described in Section 1, Fe has been shown to promote the conversion and selectivity of isobutane oxidation [6,8,13,14]. In these works, Fe had a slightly negative or negligible effect on the isobutane conversion and a positive influence on the selectivity to

MAA. Cavani et al. [6] explained the positive effect of Fe by an increase of the catalysts acidity, while Langpape et al. [14] related it to a charge transfer between the molybdenum cations in the heteropolyanion and the counter-cation. Such a beneficial effect has not been observed in the present work. However, the key difference is that the cited works used Fe directly as counter-cation, while our results were obtained with catalysts that had Fe initially inside the Keggin anion.

In order to investigate the difference between both types of catalysts, two similar catalysts were prepared, with Fe initially inside or outside of the Keggin anion as the only difference. Taking into account that the promoting efficiency of Fe and other metals has been suggested to be higher with metal contents of 0.5 or lower [8,13], the prepared catalysts contained 0.5 Fe atoms per Keggin unit. A Cs^+ content of 1.5 was the highest that could be achieved with the precipitation synthetic method used for these catalysts in the case of Fe as counter-cation. Thus, $Cs_{1.5}(NH_4)_{2.0}PMo_{11.5}Fe_{0.5}O_{39.5}$ and $Cs_{1.5}Fe_{0.5}(NH_4)_{2.0}PMo_{12}O_{40}$ were synthesised, pre-treated at 623 K during 1 h, and their activity was compared. The difference between the syntheses of these catalysts was the pH at which the Fe^{3+} salt was added to the solution.

During the activity tests, the initial peak temperature of the catalyst bed was gradually decreasing. Therefore, the measurements were prolonged for 20 h, at a constant furnace temperature of 580 K. Along the studied time range, the temperature of the catalyst bed went from 633 to 588 K in both the catalysts. Such a phenomenon was previously reported for $K_1(NH_4)_{2-x}Fe_xPMo_{12}O_{40}$ catalysts by Cavani et al. [6] and by us for a Mo–V–P–As–Cs–Cu–O catalyst [15]. In both the cases, an initial changing catalytic behaviour that became stable after 10–15 h was observed, and brought to carry out the measurements after 17–20 h of reaction.

The results are shown in Fig. 4, where conversion and selectivity are shown as a function of time in operation. In both cases, the conversion decreased strongly during the first 5 h, and then continued falling at a lower rate. At the same time, the selectivity to methacrolein and MAA followed an opposite trend, with a strong increase during the first few hours. The initial activity was higher for the catalyst with Fe outside the Keggin anion, but after 20 h both catalysts showed conversions of ca. 8%. The catalyst in which Fe was initially as counter-cation, $Cs_{1.5}Fe_{0.5}(NH_4)_{2.0}PMo_{12}O_{40}$ (Fig. 4b), presented a 21% selectivity to MAA at 633 K after 20 h in operation, against a 15% selectivity of a catalyst that had a similar composition but with Fe initially inside the Keggin anion, $Cs_{1.5}(NH_4)_{2.0}PMo_{11.5}Fe_{0.5}O_{39.5}$ (Fig. 4a). The selectivity to methacrolein after 20 h was similar in both cases.

These results indicate that the active sites derived from the Fe-substituted catalyst, $Cs_{1.5}(NH_4)_{2.0}PMo_{11.5}Fe_{0.5}O_{39.5}$, were different from those obtained with Fe as counter-ion, $Cs_{1.5}Fe_{0.5}(NH_4)_{2.0}PMo_{12}O_{40}$. In both cases, the evolution of the conversion and selectivity, especially during the first 5 h, reflects the changes that are taking place in the catalysts during the reaction, which lead to less active but more selective catalysts. However, despite the evolution that takes place in both catalysts, the active sites resulting when Fe was initially as counter-cation were more selective than those obtained when Fe was initially inside of the Keggin structure.

The BET surface areas of the fresh catalysts, 142 $m^2\,g^{-1}$ for $Cs_{1.5}(NH_4)_{2.0}PMo_{11.5}Fe_{0.5}O_{39.5}$, and 177 $m^2\,g^{-1}$ for $Cs_{1.5}Fe_{0.5}(NH_4)_{2.0}PMo_{12}O_{40}$, decreased to 23 and 13 $m^2\,g^{-1}$, respectively, after use in the reaction for 20 h. This decrease is typical of heteropolyacids in this reaction [6,15], and is related to the evolution of the catalysts performance during the first few hours in operation that was observed in Fig. 4. However, the surface area of the used catalyst was higher with Fe initially inside the Keggin anion, than when Fe was initially as a counter-cation. Thus, the initial position of Fe, which affects the rearrangements that take place during pre-treatment, also influences the evolution of the textural properties during reaction, although in both cases Fe stays as counter-cation.

In order to confirm the position of the Fe atom in the heteropolyacid, the (P–O) stretching bands of the catalysts FT–IR spectra were measured before pre-treatment, after pre-treatment, and after reaction (Fig. 5). The secondary band at 1045 cm^{-1} of $Cs_{1.5}(NH_4)_{2.0}PMo_{11.5}Fe_{0.5}O_{39.5}$ (Fig. 5a) showed that Fe was inside of the Keggin anion in the fresh catalyst, and was not observed after the pre-treatment, indicating that Fe was released from the Keggin unit. In the catalyst prepared with the Fe already as counter-cation, $Cs_{1.5}Fe_{0.5}(NH_4)_{2.0}PMo_{12}O_{40}$ (Fig. 5b), only a negligible shoulder was observed at 1045 cm^{-1} before and after pre-treatment, which might be due to the presence of residual quantities of substituted compound as impurity. This shoulder disappeared after use in the reaction. The absence of secondary (P–O) signals after use in the reaction confirmed that Fe remained outside the Keggin unit in both catalysts after 20 h in operation. The nature of the Fe state remains unclear, as no Fe species was detected by XRD. Attempts to identify the state of the Fe cations were also carried out by XPS, but no Fe signal could be detected either before or after the reaction.

Besides the changes observed in the secondary (P–O) band, the rest of the FT–IR spectrum was not changed after reaction, with characteristic bands at 1064, 964, 860 and 784 cm^{-1}, assigned to (P–O) stretching, (Mo=O) stretching, corner-sharing (Mo–O–Mo) stretching and edge-sharing (Mo–O–Mo) stretching of the Keggin structure, respectively, based on previous assignments for salts of the $PMo_{12}O_{40}{}^{3-}$ Keggin anion [30,47]. The XRD patterns of the catalysts used during 20 h in reaction presented main diffractions at $2\theta\,(\text{relative intensity}) = 26.1\ (100)$ and 30.3 (33), characteristic of 12-molybdophosphoric salts, while no MoO_3 diffractions were observed [48,49].

The results indicate that the Keggin unit remained stable after reaction in the temperature range 588–633 K, even if the structure of the catalyst is changing during the first 5 h in operation. Moreover, by these characterisation techniques the anion nature appeared formally as $PMo_{12}O_{40}{}^{3-}$ in the two used catalysts. On the one hand, in $Cs_{1.5}Fe_{0.5}(NH_4)_{2.0}PMo_{12}O_{40}$ the Keggin unit remains stable. On the other hand, in $Cs_{1.5}(NH_4)_{2.0}PMo_{11.5}Fe_{0.5}O_{39.5}$, firstly Fe is released during pre-treatment in nitrogen, to yield Fe as cation and $PMo_{11}O_{39}{}^{7-}$, and then the highly unstable lacunary species would rearrange into the stable $PMo_{12}O_{40}{}^{3-}$. These differences between both catalysts were reflected in different final surface areas. The results indicate that the active sites derived from the unstable lacunary $PMo_{11}O_{39}{}^{7-}$, generated after release of Fe from the Keggin anion, are less selective than those derived from 12-molybdophosphoric $PMo_{12}O_{40}{}^{3-}$ units.

4. Conclusions

The release of Fe from the Keggin anion is favoured by the reaction of Fe^{3+} with $NH_4{}^+$ present as counter-ion. This leads to the elimination of $NH_4{}^+$ at lower temperatures than in non-substituted 12-molybdophosphoric compounds.

The presence of Cs^+ stabilises Fe in the Keggin anion, increasing the temperature at which Fe is released. However, this stabilisation is partly inhibited by the presence of ammonium as counter-ion.

The results indicate that the release of Fe from the Keggin anion in $PMo_{11}FeO_{39}{}^{4-}$ yields Fe as counter-cation and a highly unstable lacunary $PMo_{11}O_{39}{}^{7-}$, which rearranges into $PMo_{12}O_{40}{}^{3-}$.

The catalysts $Cs_{1.5}(NH_4)_{2.0}PMo_{11.5}Fe_{0.5}O_{39.5}$ and $Cs_{1.5}Fe_{0.5}(NH_4)_{2.0}PMo_{12}O_{40}$ pre-treated in nitrogen undergo changes during the first few hours in reaction that lead to an increase of the selectivity to MAA. However, the active sites derived from the lacunary species generated after release of Fe from the Keggin anion are less selective than those derived from the 12-molybdophosphoric units.

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