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Main aspects of the selective oxidation of isobutane to methacrylic acid catalyzed by Keggin-type polyoxometalates

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Abstract

The reactivity of Keggin-type P/Mo polyoxometalates (POMs) as heterogeneous catalysts for the selective oxidation of isobutane to methacrylic acid is reviewed, with reference to both industrial patents and scientific papers published in recent years. The main aspects of the reaction are discussed, and in particular the POM requirements which are necessary to develop an active and selective catalyst are examined for the compound $(NH_4)_3PMo_{12}O_{40}$. Particular attention is given to the importance of the reduction level of the POM in affecting the catalytic performance, and to the generation of the active sites in the reaction environment, in reference to the reaction conditions (either isobutane-rich or isobutane-poor). The discussion about the role of V in P/Mo/V POMs is also included. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Methacrylic acid; Polyoxometalates; Keggin heteropolycompounds; Selective oxidation of isobutane

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1. Generalities of the reaction of isobutane oxidation to methacrylic acid

Methacrylic acid is currently synthesized via the acetone-cyanohydrin (ACH) route, which consists of an initial reaction between acetone and hydrogen cyanide to give the ACH, which is then reacted with excess concentrated sulfuric acid to form the methacrylamide acid sulfate. In a successive stage, the methacrylamide sulfate is treated with excess aqueous methanol. The amide is hydrolyzed and esterified, with formation of a mixture of methylmethacrylate and methacrylic acid. The main drawbacks of this process are the utilization of highly toxic raw materials and the coproduction of 1 mol of NH_4HSO_4 for each mole of methylmethacrylate. This process has recently been improved, as claimed by Mitsubishi [1]: ACH is first hydrolyzed to 2-hydroxyisobutylamide with a MnO_2 catalyst; the amide is then made to react with methylformiate to produce the methyl ester of 2-hydroxyisobutyric acid, with coproduction of formamide (the reaction is catalyzed by CaO). The ester is finally dehydrated with a Na–Y zeolite to methylmethacrylate. Formamide is converted to cyanohydric acid, which is used to produce ACH by reaction with acetone.

Different alternative processes have been proposed since the 1980s to replace the ACH technology; these are shown in Fig. 1. Some of them are close to commercialization, while others, though attractive from the environmental and economic points of view, are still at the research stage. One significant example is the direct oxidation of isobutane to methacrylic acid, which, if developed at the industrial level, would represent a significant improvement with respect to

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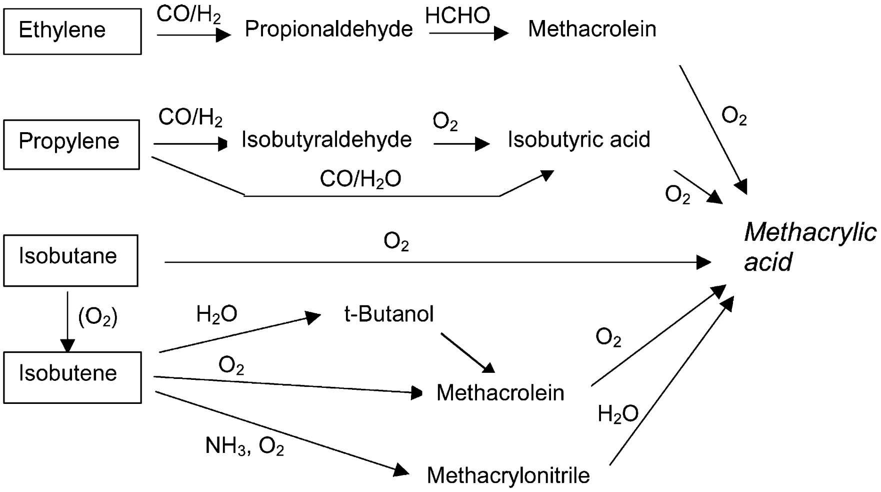

Fig. 1. Synthetic routes for methacrylic acid alternatives to the ACH route.

the other synthetic routes. Several patents have appeared in the 1980s and 1990s claiming the possibility of carrying out the synthesis of methacrylic acid by the one-step oxidation of isobutane in the gas phase, over Keggin-type polyoxometalates (POMs) as heterogeneous catalysts [2–13]. The direct synthesis of methacrylic acid via oxidation of isobutane looks particularly interesting because of (i) the low cost of the raw material, (ii) the simplicity of the one-step process (above all if compared to the complexity of the ACH route), (iii) the very low environmental impact, and (iv) the absence of inorganic coproducts. Rohm and Haas Company was the first, in 1981, to claim the one-step oxidation of isobutane to methacrolein and methacrylic acid [2]. Even though no reference is given in the patent to POMs, the claimed catalyst compositions are clearly Keggin-type compounds. Starting from this patent, a number of patents have followed, mainly from Japanese companies, describing the use of modified Keggin-type POMs as catalysts for the oxidation of isobutane.

Papers which have been published in recent years [14–39] try to establish relationships between catalytic performance and chemical–physical features of the POMs. Specifically, most attention has been given to the possibility of improving the conversion of isobutane and the selectivity to methacrylic acid by developing POMs which contain specific cations. However, it seems that the further development of this process finds major obstacles in the preparation of a POM which on one hand is active and selective, and on the other is structurally stable enough to withstand the reaction conditions necessary for the activation of the paraffin, and the considerable heat of reaction which develops. In this paper, we analyze the main characteristics of this reaction, and the fundamental features which the POM must have in order to perform well in the reaction.

2. Summary of literature results: the main characteristics of the reaction of isobutane oxidation to methacrolein and methacrylic acid catalyzed by Keggin-type POMs

A particular feature of the processes described in patents [2–13] is that almost all of them use isobutane-rich conditions, with isobutane-to-dioxygen molar ratios between 2 (for processes which include a relatively low concentration of an inert component, including the ballast steam) and 0.8, thus closer to the stoichiometric value 0.5 (for those processes where a large amount of inert components is present). This is shown in Fig. 2, which shows in a triangular diagram the feed composition claimed by various companies, with reference to the flammability area at room temperature. In all cases, however, low isobutane conversions are achieved (almost all patents claim isobutane

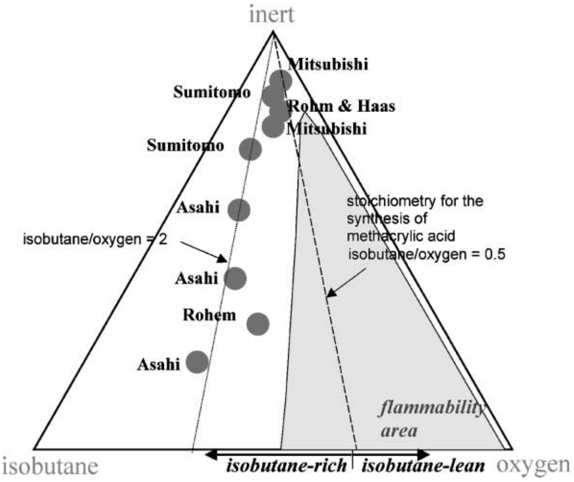

Fig. 2. Triangular scheme of composition isobutane/oxygen/inert, showing the flammability area for mixtures at room temperature, and the feed composition claimed by several industrial companies.

conversions not higher than 25%), and recirculation of unconverted isobutane becomes a compulsory choice. For this reason, Sumitomo Chem. [6,7] claims the oxidation of CO to CO_2 (contained in the effluents from the oxidation reactor) in a separate reactor with a supported Pd catalyst, after the condensation of methacrolein and methacrylic acid. CO_2 can then be removed by absorption in a basic solution.

In all cases steam is present as the main ballast. The role of steam is to decrease the concentration of isobutane and oxygen in the recycle loop and thus keep the reactant mixture outside the flammability region. Water can be easily separated from the other components of the effluent stream, and moreover plays a positive role in the catalytic performance of POMs. Indeed, the presence of water favors the surface reconstruction of the Keggin structure which decomposes during the reaction at high temperature, and promotes desorption of methacrylic acid, saving it from unselective consecutive reactions.

Under the reaction conditions described in patents, methacrolein is a product always present in non-negligible amounts, and therefore a commercial process would require an economical method for recycling not only unconverted isobutane, but also methacrolein. Patents assigned to Asahi Chem. Ind. [12] claim the use of an organic solvent, a mixture of decane, undecane and dodecane, which can efficiently absorb isobutane and methacrolein from the off-gas, with a 99.5% recovery efficiency. Isobutane and methacrolein are then stripped with air and recycled.

There are a few features relative to POMs which seem to be an important condition to obtain the best performance. In all cases, vanadium is present in the framework of the P/Mo Keggin anion, while the cations include different components, i.e., protons, divalent transition metal ions (preferably Cu^{2+}), and alkali metal ions (preferably Cs^{+}). The role of Cu ions is to catalyze the reduction of molybdenum, thus increasing the activity of the catalyst [29,30]; it also affects the surface acidity.

According to Asahi patents [3], in order to be active and selective the POM has to be characterized by the cubic structure, and by a partial degree of reduction (also achieved by in situ treatment with isobutene at 450°C). In Asahi patents, the use of a catalyst suitable for fluidized-bed operation in CFB reactors is also claimed, so as to allow continuous transport of catalyst from the reaction to the regeneration vessel, and vice versa. In addition, alternate feeding of isobutane and of dioxygen on the catalytic bed allows higher selectivities to be obtained [13]. In this case, the catalyst claimed is an ammonium salt of a P/Mo Keggin-type POM. With the CFB reactor, an 8% isobutane conversion with 54% selectivity to methacrylic acid and 17% to methacrolein is obtained. A similar process configuration has also been claimed by Sumitomo Chem. [6], which makes use of isobutane and air (in the two separate steps) which are diluted in steam, and a catalyst analogous to that used under usual cofeeding tests. In this case, a conversion of 11.2% is claimed, with a selectivity of 52.9% to methacrylic acid and 12.8% to methacrolein.

The importance of having the Keggin anion reduced has also been claimed by other authors [14,23–26,38,39]. It is possible that a more reduced catalyst leads to better selectivity to the product of partial oxidation, and is thus less active in total combustion. This might also explain why in most cases isobutane-rich conditions are claimed, since conditions with a high concentration of isobutane are more reducing than those with a low concentration of isobutane (isobutane-poorer conditions with respect to the flammability area). A partially reduced catalyst can be achieved by preparing compounds having organic

Table 1
Summary of results reported in the scientific and patent literature for the oxidation of isobutane to methacrolein and methacrylic acid catalyzed by Keggin-type heteropolycompounds

Catalyst	Reference	T (°C)	τ (s)	$iC_4/O_2/H_2O/N_2$ molar ratios	iC_4H_{10} conversion (%)	Selectivity % MAC + MAA[a]
$H_xPMo_{12}SbO_y$	[2]	340	6.1	10/13/30/47	10	20 + 50
$H_xP_{1.1}Mo_{12}V_{1.1}Cu_{0.1}Cs_{1.1}O_y$	[3]	320	3.6	30/15/20/35	10.3	16.3 + 55.7
$H_xP_{1.5}Mo_{12}V_1Cu_{0.2}Nd_{0.5}Cs_1O_y$	[9]	320	3.6	30/15/20/35	12.8	15.9 + 53.8
$H_xP_{1.5}Mo_{12}VOs_{0.04}Cu_{0.2}Ba_{0.2}K_{0.5}Cs_{0.5}O_y$	[8]	320	2.4	10/16.8/10/63.2	16.3	10.0 + 50.1
$H_4PMo_{11}VO_{40}/Ta_2O_5$	[12]	350	2	4/8/0/88	28.5	41 + 13.3
$H_xP_{1.5}Mo_{12}V_{0.5}As_{0.4}Cs_{1.8}Cu_{0.3}O_y$	[6]	320	3.6	26/13/12/49	11.2	11.5 + 53.6
$H_xP_{1.5}Mo_{12}V_{0.5}As_{0.4}Cs_{1.4}Cu_{0.3}O_y$	[13]	330	5.4	6.5/15.5/15/63	25	42.6 + 2.5
$H_{3.6}Cu_{2.0}Pmo_{11}VO_{40}/SiO_2$[b]	[4]	348	[c]	15.1/29.6/19.7/35.5	13.0	55.6 + 11.5
$H_{1.34}Cs_{2.5}Ni_{0.08}PMo_{11}VO_{40}$	[20]	340	2	17/33/0/50	31	29 + 8
$(Pyr)_3PMo_{12}O_{40}$	[24]	300	[d]	2.2/13.7/33.5/50.6	22.2	51.1 + tr
$H_{2.4}Cs_{1.6}P_{1.7}Mo_{11}V_{1.1}O_{40}$	[27]	349	3.6	26/12/12/50	10.6	37.6 + 7.9

[a] MAC: methacrolein; MAA: methacrylic acid.
[b] 43% of active phase.
[c] W/F 2.1 g h ml^{-1}.
[d] W/F 0.1 g min ml^{-1}.

cations, which during thermal treatment are oxidized at the expense of Mo^{6+} [23,24]. Another possibility is to prepare compounds having cations which can exchange electrons with Mo^{6+} in the anion. It has been found, for instance, that the presence of Sb^{3+} in the compound makes reduction of Mo^{6+} to Mo^{5+} possible even under oxidizing conditions at 350–400°C (i.e., in the presence of air or reaction mixtures at hydrocarbon-poor conditions) [15]. The Mo^{5+} species which develop are stabilized towards reoxidation, thus making it possible to maintain the partially reduced state even under oxidizing conditions.

Some of the best results obtained with the various compositions of heteropolycompound-based catalysts found in the patent and scientific literature are summarized in Table 1.

3. Mechanism of isobutane oxidation to methacrolein and methacrylic acid catalyzed by Keggin P/Mo POMs: analogies with *n*-butane oxidation

The reaction network for isobutane selective oxidation catalyzed by $(NH_4)_3PMo_{12}O_{40}$ consists of parallel reactions for the formation of methacrolein, methacrylic acid, carbon monoxide and carbon dioxide (Fig. 3). Consecutive reactions occur on methacrolein, which is transformed mainly to acetic acid and to carbon oxides. On the contrary, methacrylic acid is stable, and does not undergo consecutive reactions of oxidative degradation [35,36]. Isobutene is never detected amongst the reaction products, despite the large excess of hydrocarbon, which would theoretically favor the desorption of intermediate isobutene due to the lack of oxidizing sites. Indeed, this aspect is one difference with respect to the oxidation of *n*-butane to maleic anhydride, catalyzed by vanadyl pyrophosphate [40]. In this case, intermediate unsaturated hydrocarbons (*n*-butenes and butadiene) can be isolated amongst the reaction products when a very large excess of *n*-butane is fed to the reactor. Also in this case, however, under usual hydrocarbon poor conditions the olefins are not desorbed into the gas phase, but rather quickly transform to the final oxidized product.

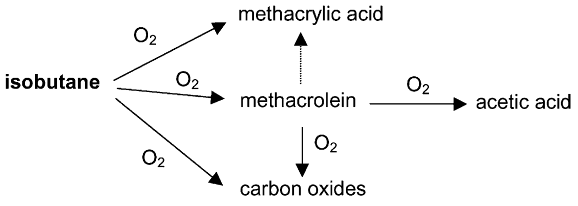

Fig. 3. Reaction scheme for the oxidation of isobutane to methacrylic acid catalyzed by Keggin-type POMs.

One common feature of the two reactions is the very high specificity of the catalysts. In both cases, it seems that acceptable conversions and selectivities are obtained only with a specific catalyst, i.e., Keggin-type POMs in the case of isobutane selective oxidation, and $(VO)_2P_2O_7$ for *n*-butane oxidation. In both cases, the unsaturated hydrocarbon has to be functionalized by insertion of a double bond and by insertion of one (or two) carbonylic/carboxylic groups, and it is likely that specific multifunctional oxidative and acid properties are needed for efficient activation and multielectron transformation of the paraffin to the oxygenated compound [41]. A difference between the two reactions is that in the case of maleic anhydride the two carboxylic groups are condensed; the anhydride should be much more stable in the reaction environment than the methacrylic acid. Despite this, maleic anhydride undergoes consecutive reactions of combustion under both *n*-butane-poor and *n*-butane-rich conditions, while the selectivity to methacrylic acid is not a function of isobutane conversion [35,36].

In order to justify the observed phenomena (i.e., parallel reactions for methacrolein and methacrylic acid formation, and absence of isobutene amongst the reaction products), a mechanism has been proposed (Fig. 4), which is supported by (i) reaction studies on isobutene, methacrolein and methacrylic acid, and (ii) FT-IR measurements of adsorbed intermediate species which develop by interaction of isobutane and reaction products with the catalyst, at different temperatures [35]. The mechanism involves the initial abstraction of a H^- species at the tertiary C atom of the alkane. This is the rate-limiting step of the reaction [28]. An adsorbed alkoxy species is thus formed, which is then converted to an allylic alkoxy species. A dioxyalkylidene species then develops, where the primary carbon atom is connected to the catalyst surface via two C–O–Mo bridges. This intermediate is either transformed to methacrolein (through dissociation of a C–O bond), or to a carboxylate species (via oxidation on an Mo site), which is the precursor for methacrylic acid formation [35]. Therefore, these two products have a common intermediate, and from a kinetic point of view this corresponds to two parallel reactions starting from isobutane, since no intermediate compound is desorbed into the gas phase before the formation of the two oxidized compounds. The reduced catalyst is then reoxidized by oxygen, according to the classical redox mechanism [28].

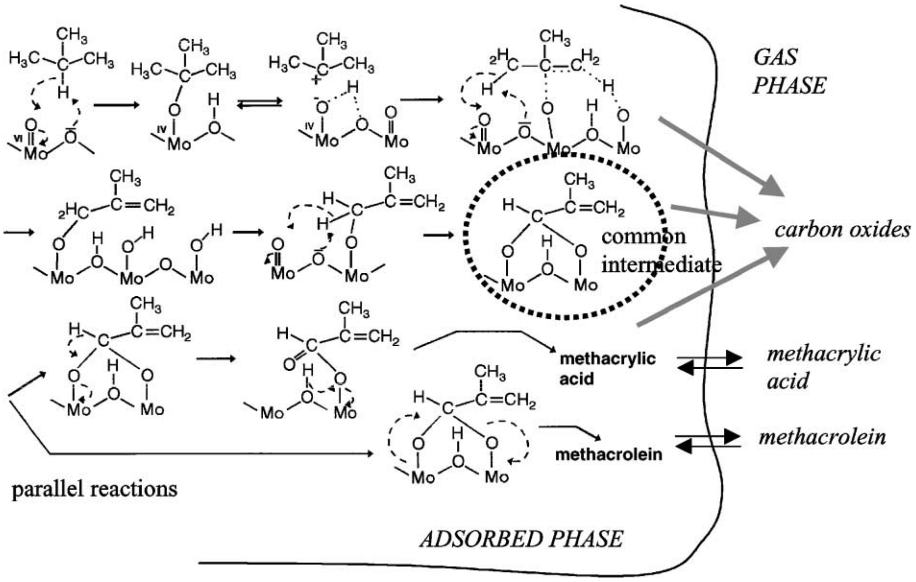

Fig. 4. Mechanism of the oxidation of isobutane to methacrylic acid catalyzed by Keggin-type POMs.

4. Generation of the active species during equilibration under reaction conditions, and importance of the oxidation state of the POM in affecting the selectivity to methacrylic acid

All Keggin-type POMs exhibit an initial unsteady catalytic behavior, which can last from a few hours up to 100 h, depending on the POM composition and on the method employed for its preparation [38,39]. During this period of "equilibration" the following phenomena occur, which lead to a substantial change in the chemical–physical features of the POM:

1. Partial structural decomposition of the POM, as evidenced by (i) the formation of small amounts of crystalline MoO_3, and (ii) the change in the cationic composition. This can be easily detected in the ammonium salt of the Keggin compound: the ammonium content decreases, and possibly is replaced in part by Mo species. This phenomenon has been proposed to occur on the basis of the presence of Mo dimeric species in the unloaded catalysts, made of neighboring Mo cations located in two different positions in the POM framework, i.e., in the Keggin anion and in the counter-anion cationic position [42].
2. Progressive increase in the extent of reduction of the POM, as evidenced by UV–Vis DR spectra of catalysts unloaded after reaction. This is evident in Fig. 5, which shows the ex situ spectra of the $(NH_4)_3PMo_{12}O_{40}$ compound unloaded at different times during the equilibration period [43]. The progressive increase in the intensity of the IVCT band at 700 nm corresponds to the increase in the concentration of the Mo^{5+} species in the POM.

These phenomena, which overlap during the equilibration period, are accompanied by a change in the catalytic performance, with a progressive increase in activity in isobutane oxidation, and with an increase in selectivity to methacrylic acid and, to a lesser extent, to methacrolein, with a corresponding decrease in the selectivity to carbon oxides. Thus, the equilibration time is necessary for the generation of the active and selective sites. These phenomena occur only under isobutane-rich reaction conditions. Indeed, when the reaction is carried out under isobutane-poor conditions (e.g., with 1% isobutane in feed), the above-mentioned phenomena (partial structural decomposition and reduction of the POM) do not occur, and in correspondence the described changes in catalytic performance (considerable increase in activity and increase in

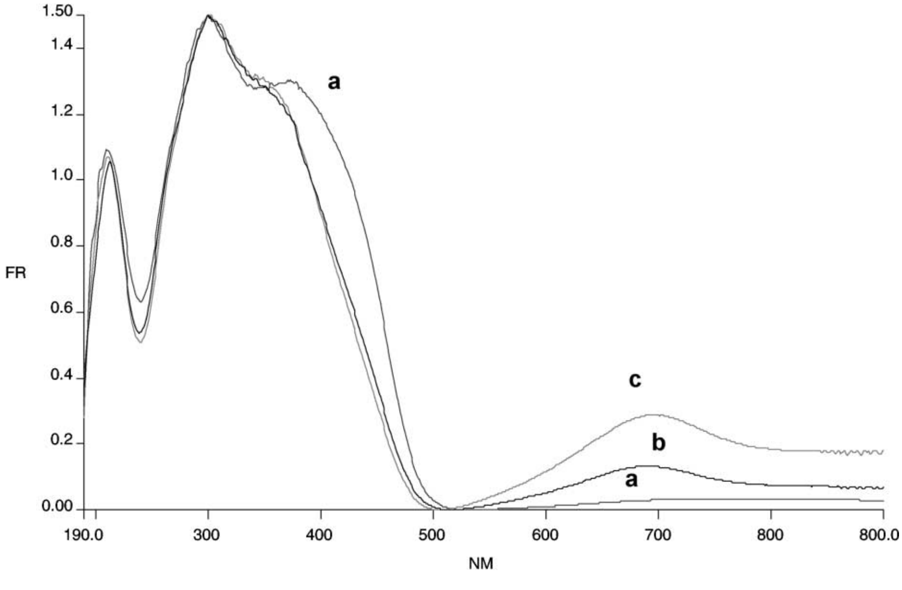

Fig. 5. UV–Vis DR spectra of $(NH_4)_3PMo_{12}O_{40}$ catalyst: (a) after calcination, before reaction; (b) after 25 h time-on-stream under isobutane-rich conditions; (c) after 100 h reaction (equilibrated catalyst).

selectivity to methacrylic acid) are not observed; only a minor change in selectivity to methacrylic acid is observed [38,39]. This means that the reduction of the POM is due to the isobutane-rich conditions (i.e., these conditions are reducing towards a fully oxidized, fresh POM), and that the structural decomposition is due to the higher heat of reaction which develops at the catalyst surface under these conditions. Overheating of the catalyst particles may take place with temperatures which approach that of the incipient structural decomposition of the POM.

The increase in activity during equilibration has been proposed to be related to the formation of new active sites [43], which include the Mo species located in cationic positions in the secondary framework of the POM. The same occurs in the case of V-substituted POMs, in which V^{5+} is originally positioned in the primary anion, but then is transferred during reaction into cationic positions with generation of lacunary or decomposed Keggin units [21,44,45]. This leads to a considerable increase in the catalytic activity. Analogously, it is known that the preparation of POM-based catalysts containing transition metal ions (VO^{2+}, Fe^{2+}, Ni^{2+}, etc.) as the cations are more active than the corresponding undoped compounds [16–20,34,35]. Thus, it seems that one important role for having the active sites for isobutane oxidation is the presence of transition metal ions as cations in the POM. These can be either directly introduced in the secondary structure of the POM during synthesis, or transferred from the Keggin anion into the cationic position during equilibration, as a consequence of the partial structural decomposition of the POM itself [43]. This may explain why very different equilibration times are claimed to be necessary to reach steady performance. Of course, longer periods of time, as well as particular reaction conditions which may favor the above-described phenomena and the generation of the active species, are necessary for freshly prepared POMs which do not include transition metal ions as cations, as in the case of our $(NH_4)_3PMo_{12}O_{40}$ catalyst.

The role played by the two different phenomena occurring in $(NH_4)_3PMo_{12}O_{40}$, i.e., (i) the generation of new, more active sites due to the migration of Mo ions from the Keggin anion into the cationic positions of the POM, and (ii) the reduction of Mo in the POM, are evident in Fig. 6, where the conversion of isobutane and the selectivity to the products are plotted as functions of the reaction time. The data were collected at the reaction temperature of 380°C, with an isobutane-rich feedstock (26 mol% isobutane, 13% oxygen, 12% steam, remainder helium), and residence time 3.6 s. At the very beginning of its lifetime, the fresh POM is completely unselective and inactive. After approximately 100 h reaction time the conversion is 6.5%, with a selectivity to methacrylic acid of 42%

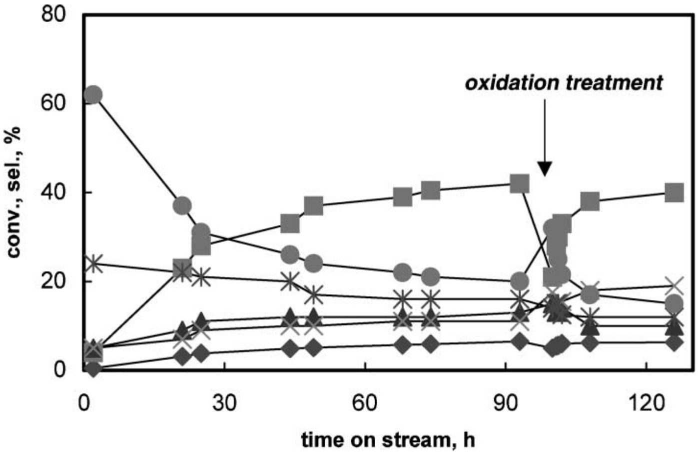

Fig. 6. Catalytic performance of $(NH_4)_3PMo_{12}O_{40}$ prepared by precipitation at pH < 1 as a function of time-on-stream: Reaction conditions: T — 380°C; τ — 3.6 s; feed composition: 26% isobutane, 13% O_2, 12% H_2O, remainder He. Symbols: isobutane conversion (◆), selectivity to methacrylic acid (■), to methacrolein (▲), to acetic acid (×), to carbon monoxide (∗) and to carbon dioxide (●).

and to methacrolein of 13%. The main by-product is carbon dioxide. As mentioned above, during this equilibration period changes in chemical–physical features occur in the POM. After reaching a steady behavior, the catalyst was treated in air at 350°C, and then made to react again under isobutane-rich conditions. The reoxidized catalyst exhibits a selectivity to methacrylic acid which initially is around 20%, and approximately 20–30 h of further equilibration are necessary to reach again the original performance of the equilibrated, reduced catalyst. On the contrary, the activity of the catalyst is almost the same as before the oxidizing treatment. Therefore, the oxidation of the POM which already contains the active sites (generated during the first equilibration period) leads only to a partial loss of selectivity to methacrylic acid. On the other hand, when the two phenomena overlap during the first equilibration period, the progressive increase in activity is mainly due to the generation of the new active sites, while the increase in selectivity is in part due to the latter phenomenon, in part to the reduction of active sites in the POM under isobutane-rich conditions.

5. One way to affect the catalytic performance of the POM: preparation via a lacunary precursor

When the POM is prepared at pH higher than 2, a compound is precipitated which is not the intact insoluble salt $(NH_4)_3PMo_{12}O_{40}$, but rather a so-called lacunary compound, i.e., $(NH_4)_7PMo_{11}O_{40}$ [43]. However, thermal treatment of this precursor at 350°C yields the Keggin compound, and also generates small amounts of MoO_3. The POM obtained is not a fully ammonium salt of the POM, since the analysis reveals a $(NH_4)^+$ content considerably lower than the expected one. This indicates that by transformation of the lacunary compound into the Keggin compound, the electroneutrality in the latter is then guaranteed by some cation other than ammonium. By analogy with what occurs during the equilibration of the POM under isobutane-rich conditions and during the incipient structural decomposition of the Keggin compound (prepared by a thermal treatment of a Keggin precursor precipitated at conventional, strongly acidic pH) [42], it can be hypothesized that the cationic positions are in part occupied by Mo cations, the migration of which occurs during the transformation of the lacunary compound into the Keggin compound. As shown in Fig. 7, which is relative to a catalyst prepared from a lacunary precursor precipitated at pH 4.0, the fresh catalyst is already active from the very beginning of its lifetime, and the only change observed during equilibration (which is shorter than for the POM prepared conventionally, since it lasts only 40–50 h) is an increase in selectivity from the initial 23% to the final 42%. The latter is due to the progressive reduction of the POM, in the same way as it occurred for the equi-

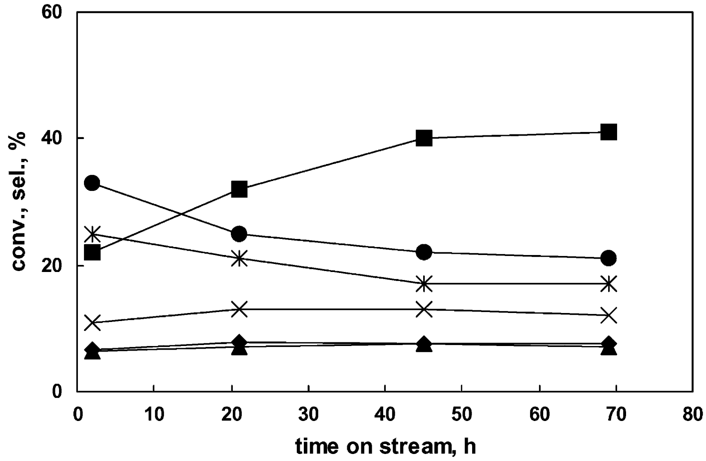

Fig. 7. Catalytic performance of $(NH_4)_3PMo_{12}O_{40}$ prepared by precipitation at pH 4.0 as a function of time-on-stream. Reaction conditions: T — 350°C; τ — 3.6 s; feed composition: 26% isobutane, 13% O_2, 12% H_2O, remainder He. Symbols as in Fig. 6.

librated, but reoxidized, catalyst the behavior of which is described in Fig. 6.

As mentioned above, when the catalyst conventionally prepared via a Keggin precursor at pH < 1 is made to react under isobutane-poor conditions (i.e., low concentration of isobutane in air), neither the generation of active sites nor reduction of the POM occur. In this case, therefore, in order to develop the active sites for operation under isobutane-poor conditions it is necessary to make a pretreatment under reaction conditions which favor the incipient structural decomposition of the POM. Alternatively, data shown in Fig. 7 demonstrate that it is possible to prepare the catalyst via the lacunary precursor, and obtain a catalyst which already contains the active sites, and thus needs no activation procedure. This is also shown in Fig. 8, which compares the catalytic performance under isobutane-poor catalysts for two POMs, prepared with the two different procedures. The selectivity to methacrylic acid is low in both cases, since the reaction conditions are oxidizing, and therefore the equilibrated POM is a fully oxidized one (as confirmed by the electronic spectra of the unloaded catalysts). However, the POM prepared starting from the lacunary precursor is more active and more selective than that prepared by the conventional procedure.

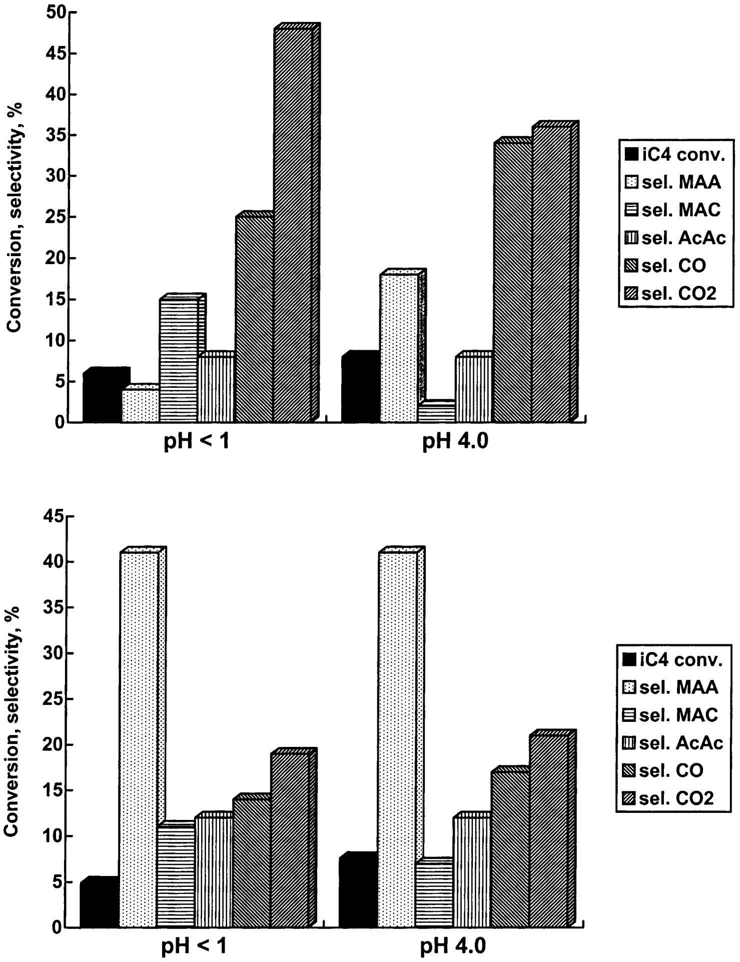

Fig. 8. Comparison of the catalytic performance of $(NH_4)_3PMo_{12}O_{40}$ prepared by precipitation at pH < 1 and pH 4.0 and calcination under isobutane-poor (top) conditions and isobutane-rich (bottom) conditions. Reaction conditions: 1% isobutane or 26% isobutane, 13% oxygen, 12% steam, remainder helium. Residence time 3.6 s, temperature 350°C. MAA: methacrylic acid; MAC: methacrolein; AcAc: acetic acid.

6. Effect of the pH of precipitation on catalytic performance for V-containing POMs

One main difference between the $(NH_4)_3PMo_{12}O_{40}$ POMs prepared at different pH values concerns the activity. POMs which have been prepared via the lacunary precursor are more active, as shown in Fig. 8, which compares the catalytic performance under isobutane-rich conditions for two equilibrated catalysts prepared at $pH < 1$ and at pH 4.0. This difference may be related to the fact that the number of active sites which are generated in the catalyst by thermal treatment of the lacunary precursor is higher than in the case of the catalyst which instead required activation in the reaction environment, and for which the active sites have been generated by incipient structural decomposition of the Keggin units. This is the only difference between the two samples under isobutane-rich conditions, since the selectivity to the products of partial oxidation is comparable in the two cases.

This difference is evident also in the case of the POMs which contain one V atom per Keggin unit, thus having the formula $(NH_4)_4PMo_{11}VO_{40}$. It is known that in P/Mo/V POMs the vanadium atom is readily eliminated from the polyanion structure under reaction conditions, and a vanadyl salt having the cubic structure develops which is the active site in the case of the oxidehydrogenation of isobutyric acid to methacrylic acid [21,44,45]. A dimer structure of two Keggin anions connected by a V–O–V linkage has also been proposed to play an active role in the oxidation of *n*-butane catalyzed by POMs [46]. In the case of isobutane oxidation, all compositions claimed in industrial patents include vanadium. Both Mizuno et al. [20] and Misono and coworkers [21] have demonstrated the improvement in performance obtained by the use of V-containing POMs for isobutane oxidation in activity and in selectivity at high conversion.

In order to try to couple the advantages gained by the use of a catalyst prepared via the lacunary precursor with the activity enhancement effect induced by the addition of vanadium, we prepared a P/Mo/V POM at pH 4.0, and compared the catalyst with that prepared conventionally at $pH < 1$. The effect of time-on-stream at 320°C is shown in Fig. 9, for the reference catalyst prepared at $pH < 1$ and calcined at 350°C. The behavior is very similar to that observed for the P/Mo POM prepared under the same conditions (Fig. 6), with a progressive increase in activity and selectivity to methacrylic acid and methacrolein. The main advantage with respect to the catalyst which does not contain vanadium is in the selectivity to methacrolein, which in this case is around 20% (with an overall selectivity to methacrolein and methacrylic acid which is approximately 70%). This agrees with that reported by Misono and coworkers [21], about the important role of vanadium sites in decreasing the rate of methacrolein and methacrylic acid decomposition to acetic acid and to carbon oxides. Regarding the activity, instead, the conversions achieved with the

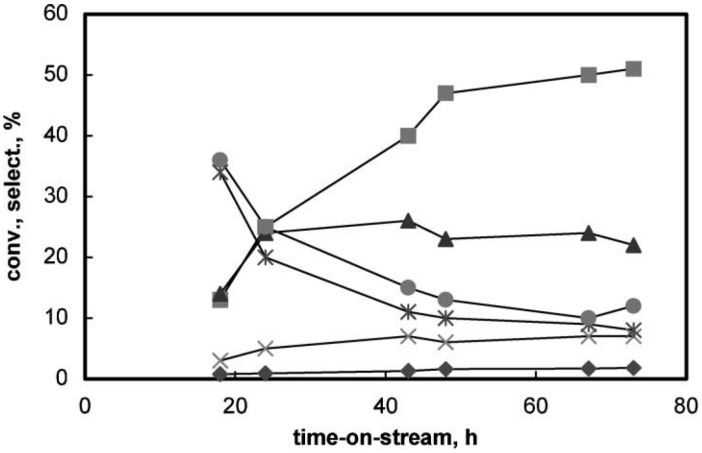

Fig. 9. Catalytic performance as a function of time-on-stream for the $(NH_4)_4PMo_{11}VO_{40}$ compound prepared at $pH < 1$. Reaction conditions: T — 320°C; feed composition: 26% isobutane, 13% oxygen, 12% steam, remainder helium. Residence time 3.6 s. Symbols as in Fig. 6.

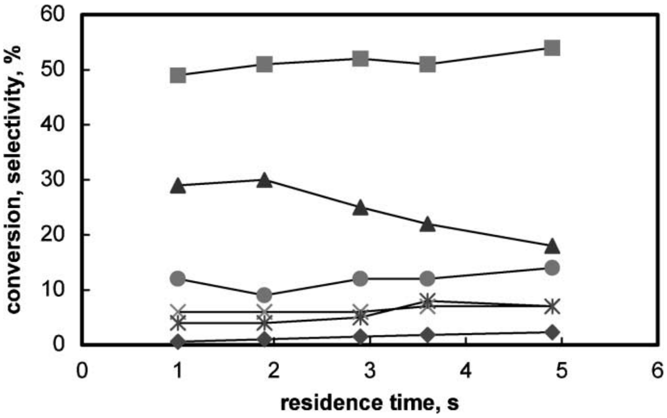

Fig. 10. Catalytic performance as a function of residence time for the equilibrated $(NH_4)_4PMo_{11}VO_{40}$ compound prepared at pH < 1. Reaction conditions: T — 320°C; feed composition: 26% isobutane, 13% oxygen, 12% steam, remainder helium. Symbols as in Fig. 6.

P/Mo POM and with the P/Mo/V POM are similar. This is different with respect to that reported by other authors, who claim that replacement of one Mo atom with one V atom leads to a considerable increase in activity [20].

Just as for the P/Mo POM, the progressive improvement in both activity and selectivity of the P/Mo/V POM during equilibration can be attributed to the generation of the active sites in the reaction environment. One further contribution may arise in this case from the displacement of vanadium atoms from the polyanion into the cationic positions, as has been proposed to occur in acidic POMs and in Cs/H mixed POMs.

The positive role of V on selectivity is even more evident if we plot the results obtained for the equilibrated catalyst when the residence time is varied at 320°C (Fig. 10). The selectivity to methacrolein decreases with increasing conversion of isobutane, but (i) this decrease is less important than in the case of the P/Mo POM [35,36], and (ii) the decrease in selectivity occurs with a parallel increase in the selectivity to methacrylic acid. Therefore, the consecutive reactions which occur on methacrolein are not degradation to acetic acid and to carbon oxides (as in the case of P/Mo POM), but rather selective transformation to methacrylic acid.

When the same P/Mo/V POM catalyst is prepared at pH 4.0, a lacunary precursor develops (as in the case of P/Mo POMs), which if treated at 350°C yields the Keggin-type POM. The catalytic performance as a function of time-on-stream at 350°C for this catalyst is plotted in Fig. 11. The following considerations can be made:

1. In this case, the performance is stable from the beginning of the catalyst lifetime, regarding both the conversion and the distribution of the products (only a low increase of the selectivity to methacrylic acid is observed). In the case of the P/Mo POM prepared at the same pH value, the conversion was stable from the beginning, but the selectivity improved as a consequence of the progressive reduction of the POM under the reaction environment, from the initial 23% up to the final 42% (Fig. 7). Therefore, since the calcined, fresh P/Mo/V POM catalyst is fully oxidized (as was the calcined P/Mo POM), it is possible that the presence of V accelerates the POM reduction, by catalyzing the interaction between Mo and isobutane. Thus, V^{5+} is reduced quickly in the reaction environment, leading to the development of V^{4+} species from the very beginning of the catalyst lifetime, which themselves act as reducing species towards Mo^{6+}, with generation of Mo^{5+} and V^{5+}. This hypothesis is supported by the work of Misono and coworkers [21], who demonstrated that the V ion in P/Mo/V POMs is much more prone to changes in redox state as a consequence of changes in feed composition (thus of changes in reducing potential of the gas phase) than the Mo ion in P/Mo POMs is. The same occurred in our P/Mo/V sample, which if left to react under

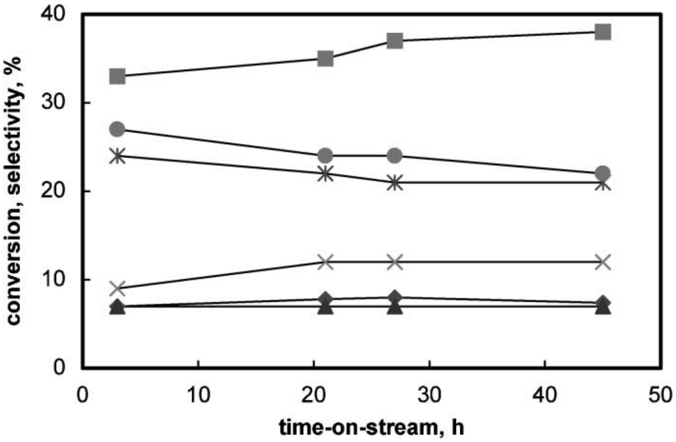

Fig. 11. Catalytic performance as a function of time-on-stream for the $(NH_4)_4PMo_{11}VO_{40}$ compound prepared at pH 4.0. Reaction conditions: T — 350°C; feed composition: 26% isobutane, 13% oxygen, 12% steam, remainder helium. Symbols as in Fig. 6.

isobutane-poor conditions (1% isobutane and 13% oxygen), appeared to be reduced after reaction, with the typical blue color arising from the IVCT band due to the one electron transfer from Mo^{5+} to Mo^{6+}. On the contrary, the P/Mo POM after reaction at the same conditions was as oxidized as the calcined, fresh catalyst [38,39]. This confirms that the redox potential of the POM is greatly affected by the presence of vanadium.

2. Though being more active, the P/Mo/V POM prepared from the lacunary precursor is less selective to both methacrolein and methacrylic acid than the P/Mo/V compound prepared by calcination of the POM precipitated at pH < 1. The lower selectivity may derive both from the higher conversion of isobutane (thus being due to consecutive reactions of oxidative degradation of the products), and the different catalyst features.
3. The performance of the P/Mo/V POM prepared from the lacunary precursor is similar to that of the P/Mo POM prepared starting from the corresponding lacunary precursor. This means that advantages gained by V addition are relevant only when the POM is prepared conventionally at strongly acid pH, in which case improvements mainly concern the selectivity to the products (at least in our ammonium salt of 12-molybdovanadophosphoric acid), and a decrease in the rate of the consecutive reactions of oxidative degradation on methacrolein. On the contrary, when the POM is prepared via the lacunary precursor precipitated at mildly acidic pH, the advantages gained by V addition are surpassed and thus made nil by the advantages achieved through the specific preparation procedure.

7. Conclusion

The present work describes some aspects of the reactivity of POMs as catalysts for the selective oxidation of isobutane to methacrylic acid. This reaction could represent, if developed at the industrial level, an alternative to the current production method via the ACH route. P/Mo Keggin-type POMs are active and selective catalysts for this reaction. In the present study, we analyzed some of the aspects which are associated with the reactivity of the ammonium salt of 12-molybdophosphoric acid, a Keggin-type POM, and of the corresponding compound containing one V atom per Keggin units. These aspects may also help in the interpretation of data published in the patent and scientific literature, and thus may be considered of general validity in reference to the reactivity of POMs in the selective oxidation of isobutane to methacrylic acid.

The following two considerations are of particular importance:

1. The catalytic performance depends considerably on the reaction conditions, and specifically on the isobutane-to-oxygen ratio in the feed. Usually isobutane-rich conditions are claimed to be more selective, and the reason for this is that under these conditions the operative POM is a partially reduced one (i.e., where Mo in the POM has an average valence state lower than 6.00+), and a more reduced POM is intrinsically more selective than a fully oxidized one. This phenomenon is similar to what happens in the case of the synthesis of maleic anhydride via the oxidation of *n*-butane, catalyzed by V/P mixed oxides [40], where the average valence state of vanadium under reaction conditions affects the selectivity of the reaction. In the case of other reactions of selective oxidation catalyzed by transition metal oxides, i.e., the oxidehydrogenation of paraffins to the corresponding olefins, the oxidation state of the metal ion under reaction conditions also plays a fundamental role in determining the catalytic performance [47].
2. The presence of transition metal ions as cations for the Keggin polyanion is necessary in order to develop an active and selective catalyst. This can be achieved in different ways:
    - 2.1. By direct synthesis of POMs which have transition metal ions as the cations in the secondary structure of the POM such as divalent or trivalent ions (e.g., copper, nickel, iron and vanadyl cations). In this case, the development of a stable, equilibrated catalyst requires no more than 20–30 h, as described in the literature.
    - 2.2. By preparation of a P/Mo POM (in the present case an ammonium salt), possibly also containing other metal ions such as V to improve further the performance, where the incipient structural decomposition of the POM under isobutane-rich conditions leads to the partial replacement of ammonium by Mo cations (and by V as well) during the equilibration time. This phenomenon, however, may take up to 100 h of reaction, depending on the reaction conditions, which must be severe enough to start the structural decomposition, but not so severe as to cause extensive decomposition of the POM.
    - 2.3. By preparation of a P/Mo POM via thermal treatment of a lacunary POM precipitated at mildly acidic pH. In this case, a POM is obtained which already contains molybdenum ions in the cationic position in the POM framework. The catalyst prepared by such a procedure is more active than the one prepared at usual, strongly acidic conditions. Furthermore, the necessary equilibration period is much shorter. In this case, the addition of V to the POM composition does not lead to further improvements with respect to the P/Mo POM.

Of course, one fundamental aspect, which has not been examined here, is the long-term stability of the POM under reaction conditions, and thus the ability to give good performance for reaction times which are much longer than the 100 h examined here. This remains one of the major aspects requiring further study.

The future prospects in this field, possibilities for improvement and final commercialization of the process, are related to the development of more active and stable POMs. One way of reaching these objectives may be the development of POMs which are dispersed inside matrices such as silica or other non-reactive oxides. Necessary conditions are that the dispersing material does not worsen the redox properties of the POM, and if possible even stabilizes the compound with regard to long-term deactivation phenomena.

Acknowledgements

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