Improvement of catalytic performance in isobutane oxidation to methacrylic acid of Keggin-type phosphomolybdates by preparation *via* lacunary precursors: nature of the active sites

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Heterogeneous catalysts for the oxidation of isobutane to methacrylic acid were prepared by precipitation of ammonium salts of P/Mo polyoxometalates (POMs) at pH ranging from strongly acidic (pH < 1) to mildly acidic (pH 4.0), followed by thermal treatment in air at 350 °C. Depending on the pH of precipitation, different types of POMs were obtained (Keggin-type and lacunary-type), the calcination of which, however, in all cases gave rise to a Keggin-type POM, $(NH_4)_3PMo_{12}O_{40}$. Even so, the catalytic performance was different for the catalysts prepared. In particular, the differences mainly concerned the equilibration stage necessary to reach a steady catalytic performance. Based on comparison of the fresh and unloaded catalysts, a hypothesis is formulated concerning the nature of the active sites for isobutane selective oxidation. It is proposed that the active sites are generated as a consequence of the incipient structural decomposition of the POM and migration of Mo from the Keggin anion into the cationic position of the framework. This phenomenon occurs either during the calcination treatment of the lacunary precursor, or during the equilibration stage under reaction conditions for the catalyst prepared starting from the Keggin precursor.

KEY WORDS: Keggin heteropolycompounds; polyoxometalates; selective oxidation of isobutane; methacrylic acid; heterogeneous selective oxidation

1. Introduction

The current industrial production of methylmethacrylate by the "acetone-cyanohydrin" process suffers from a number of drawbacks, which make it environmentally unfriendly. In particular, it makes use of a very toxic reactant (HCN) and intermediate (acetone cyanohydrin), and it coproduces large amounts of impure ammonium sulphate, contaminated with organic compounds. Among the several alternative synthetic routes which have been proposed, particularly interesting from both the practical and scientific points of view is the single-step oxidation of isobutane to methacrylic acid, intermediate in the synthesis of methylmethacrylate. Several research groups have studied this reaction, and it has been established that the most active and selective catalysts are those based on Keggin-type polyoxometalates (POMs), containing phosphorus and molybdenum as the main components [1–15].

The preparation of Keggin-type POMs can be carried out following different procedures, for instance by (i) preparation of the soluble acid ($H_3PMo_{12}O_{40}$) at strongly acid conditions, followed by precipitation of the partly exchanged, unsoluble salt which forms by addition of cations (typically Cs^+), or (ii) direct precipitation of an unsoluble salt at strongly acid pH, *i.e.*, $(NH_4)_3PMo_{12}O_{40}$ if raw materials containing ammonium are used. In all cases, strongly acid conditions are necessary in order to develop the intact Keggin anion, $PMo_{12}O_{40}^{3-}$, since pH values higher than 1–1.5 lead to partial decomposition into the so-called lacunary anions.

The objective of the present work was to analyze the effect of the pH of precipitation of the POMs on their chemical–physical features and catalytic performance in the oxidation of isobutane to methacrylic acid, as a possible parameter to control the reactivity of these compounds. The study of this effect has led us to formulate a hypothesis about the nature of the active sites in Keggin, POMs-based catalysts.

2. Experimental

Ammonium salts of P/Mo Keggin-type POMs and related lacunary compounds were prepared using the following procedure. The compound ("precursor") was precipitated by the addition of HCl (until the desired pH value) to a solution containing dissolved $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and H_3PO_4 (initial pH 4.5), in the relative amounts as required by the stoichiometry. The precipitate was dried at 120 °C overnight (with solvent evaporation), and then calcined up to 350 °C in static air, for 6 h.

The nitrogen content was determined on the solids, using a Carlo-Erba EA 1110 CHNS-O Instrument. Powder XRD data were obtained with a Philips PW 1050/81 diffractometer using Ni-filtered Cu K_α radiation, controlled by a PW1710 unit. The surface areas (BET single point) were determined by N_2 adsorption at 77 K, using a Carlo-Erba

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Sorpty 1826 apparatus. Diffuse reflectance UV-Vis spectra were recorded at room temperature using a Perkin–Elmer Lambda 19 spectrometer, equipped with a 60 mm integrating sphere coated with barium sulphate reflective paint. Raman spectra were recorded with a Renishaw 1000 instrument, Ar laser (2.5 mW).

The catalytic tests were carried out in a stainless-steel continuous-flow reactor, at atmospheric pressure. The feed composition was the following: isobutane 26 mol%, oxygen 13%, steam 12%, remainder helium. Each series of catalytic tests was carried out using 1.5 g of catalyst, granulated into particles. The residence time was equal to 3.6 s. The reactor outlet was kept at 200 °C, to prevent product condensation and methacrylic acid polymerization. A volume of the gas phase was sampled on-line by means of a sampling valve, and analyzed by gas chromatography. A Carbosieve S column was utilized for CO and CO_2 analysis, with a programmed increase in oven temperature from 40 to 240 °C (TCD). A GP 10% SP-1200/1% H_3PO_4 on Chromosorb WAW (FID) was utilized for the analysis of the other products. After the catalytic tests, the catalysts were unloaded by cooling the reactor under a helium atmosphere, and then characterized.

3. Results and discussion

POMs are usually prepared at strongly acid pH (pH < 1), thus at conditions at which the Keggin anion $PMo_{12}O_{40}^{3-}$ is formed; in the presence of ammonium cation, the corresponding unsoluble salt $(NH_4)_3PMo_{12}O_{40}$ precipitates. However, the preparation of POMs can be carried out at higher pH, *i.e.*, between 1 and 7. In this range, lacunary compounds develop, where the atomic ratio between the heteroatom and the oxometal is higher than in the intact Keggin anion. We prepared insoluble ammonium salts at different pH values. Raman spectra of the compounds obtained, after drying at 120 °C (catalyst precursors), are reported in figure 1. With increasing pH, spectra develop where absorption bands are different with respect to those of the intact Keggin unit [16], as a consequence of the decrease in anion symmetry. Limit spectra are those obtained at strongly acid pH (pH $<$ 1) and at pH 4.0; for intermediate values of pH, the spectra correspond to a combination of the limit spectra. According to literature indications, the spectrum of the precursor obtained at pH 4.0 corresponds to that of a lacunary POM having the composition $(NH_4)_7PMo_{11}O_{39}$ [17–19]. Confirmation of this comes from the analysis of the N content of the compound, which is 5.1 wt%, and thus corresponds to 6.7 $(NH_4)^+$ cations per $PMo_{11}O_{39}^{7-}$ formula, close to the theoretical value 7. The difference between the expected value and the experimental one may be due to the presence of small amounts of POMs having different composition. For instance, it has been reported that precipitation at pH 4.3 leads to the development of pure $PMo_{11}O_{39}^{7-}$, while at pH 4.0 contamination by $PMo_{12}O_{40}^{3-}$ is possible [20].

Other interesting features arise from inspection of the UV-Vis DR spectra, shown in figure 2 for compounds precipitated at progressively increasing pH. Big differences are observed for the bands relative to charge transfers (CT) from O^{2-} to Mo^{6+} ions in the Keggin anion. The presence of more than one band in the spectrum of the intact Keggin compound is attributed to different O^{2-} ions [21], but also can be due to inter-anion CT transitions, and therefore may be considerably affected by the size of the cations located in the secondary framework [22]. The intensity of the lowest-energy CT band, which for the intact Keggin anion falls in the range 400–450 nm (depending on several features of the compound itself, such as crystallinity, and nature of the cation [22]), decreases for increasing values of precipitation pH, and in the case of the sample precipitated at pH 4.0 the optical gap is shifted towards higher energy. This reflects the different redox properties of Mo in the intact and in the lacunary compounds. It is known that the particular properties of Keggin anions derive from the electronegativity and hence electron-exchange properties of Mo^{6+}, which are consequences of the high delocalization of charges in the anion and thus of the almost metallic behavior of the single units. When the continuity of the energy bands is interrupted due to the absence of one or more Mo and O ions in the unit, this has consequences on the energy for the electron transfer from the donor to acceptor levels [21].

A similar change in the spectra, with a progressive shift of the lowest-energy CT band towards higher energy was found for $(NH_4)_3PMo_{12-x}W_xO_{40}$ compounds as the value of x increased [23]. Also in this case an increasing amount of

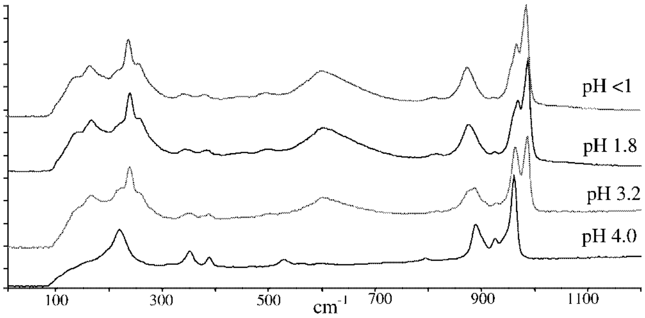

Figure 1. Raman spectra of precursors precipitated at increasing values of pH.

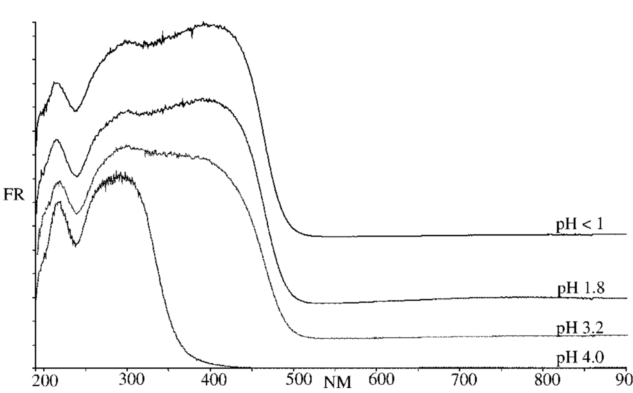

Figure 2. UV-Vis DR spectra of precursors precipitated at increasing values of pH.

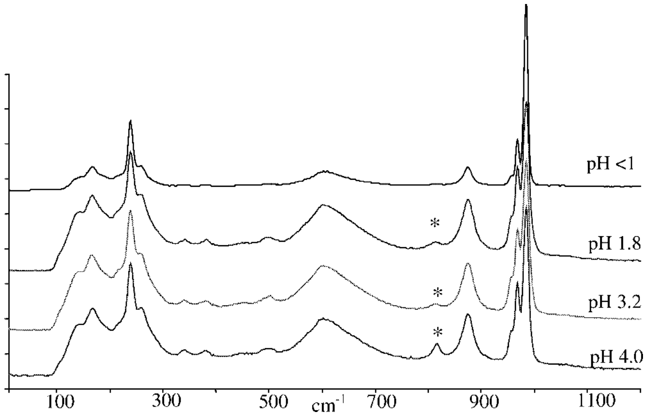

Figure 3. Raman spectra of precursors precipitated at increasing values of pH, after calcination at 350 °C; $*$ MoO_3.

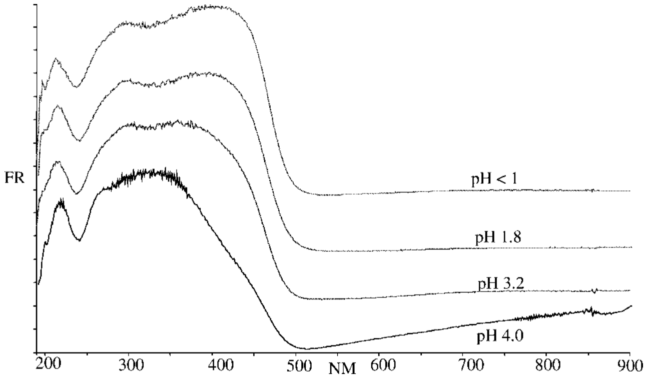

Figure 4. UV-Vis DR spectra of precursors precipitated at increasing values of pH, after calcination at 350 °C.

W in the anion is known to considerably affect the oxidation potential of the POM, and hence the position of the optical gap [21].

Raman and electronic spectra of the samples after calcination at 350 °C are reported in figures 3 and 4, respectively. Raman spectra show that the treatment of the precursors leads in all cases to the formation of an intact, Keggin POM. Therefore, the lacunary compound present in samples precipitated at pH > 1 is transformed into a Keggin compound during the thermal treatment. A small amount of MoO_3 is also observed in the same samples.

The electronic spectra also indicate that transformation of the lacunary precursor into a Keggin compound has occurred. The spectra for all the calcined samples are similar, even though it is possible to distinguish differences in the intensity of the CT band(s) centered above 350 nm. The latter, completely absent in the precursor prepared at pH 4.0 (before calcination), are now evident also in this sample, but they remain more intense in the samples obtained by calcination of precursors precipitated at more acidic conditions.

It has been found by thermal programmed decomposition of $(NH_4)_3PMo_{12}O_{40}$ that the release of ammonia in these compounds begins at 320 °C [24]. Moreover, the release of water by loss of protons and of the O^{2-} ion in the Keggin unit may begin over 350 °C [25]. This phenomenon leads to the partial reduction of Mo, but the temperature at which it occurs is a function of the cation and of the oxometal in the POM. Therefore, it is possible that indeed the compound precipitated at pH < 1 and then calcined is not a fully stoichiometric ammonium salt of 12-molybdophosphoric acid. However, the following experimental results indicate that the amount of impurities, if present, is very low: (i) chemical analysis shows that the N content in the catalyst is close to the stoichiometric, expected value (3.0 ammonium cations per Keggin unit $PMo_{12}O_{40}^{3-}$), and (ii) the calcined POM is a fully oxidized compound [26].

The surface area of calcined samples is a function of the precipitation pH of the corresponding precursor. For the sample prepared at pH < 1 the surface area is close to 200 m^2/g [27], while for the compound precipitated at pH 4.0 it is lower than 5 m^2/g.

The reactivity of the calcined samples in isobutane oxidation to methacrylic acid was followed during time-on-stream. All the POMs exhibit an initial unsteady catalytic behavior, which can last several hours, before reaching the so-called equilibrated state. This is shown in figure 5, for the calcined sample precipitated at pH < 1. In this case, during the equilibration period the main effects are (i) a progressive increase in catalytic activity (which at the beginning of service time is very low), and (ii) a progressive increase in the selectivity to methacrylic acid (which at the beginning of service time is practically nil), with a corresponding decrease in the selectivity to carbon dioxide. Therefore, the catalyst requires a period of activation, during which the active sites are generated.

In the case of the sample prepared by calcination of the precursor precipitated at pH 4.0, instead, the behavior is different (figure 6). The catalytic activity is stable from the very beginning of service life, and therefore the catalyst in this case already contains the sites which are active in isobutane conversion. The initial selectivity to methacrylic acid is 22%, and increases to the stable value of 41%, which is reached in approximately 50 h of time-on-stream.

Comparison of the chemical features of calcined and spent catalysts may help in understanding the nature of the active sites. The surface area of all samples after reaction is very low (less than 5 m^2/g), regardless of the procedure used for preparation; therefore the changes in catalytic performance shown in figures 5 and 6 are not due to changes in surface area. The Raman spectra of samples unloaded after attainment of the steady catalytic performance are shown in figure 7, while the corresponding UV-Vis DR spectra are reported in figure 8. The following effects are visible:

(1) The extent of POM reduction increases for all samples during reaction. This is evident by the appearance of an intense band at around 700 nm (figure 8), which is due to intervalence CT between Mo^{5+} and Mo^{6+} (this band is responsible for the intense blue colour of the so-called heteropolyblues). Therefore, the isobutane-rich gas phase acts as a reducing agent towards the fully oxidized, calcined POM, and progressive reduction of the

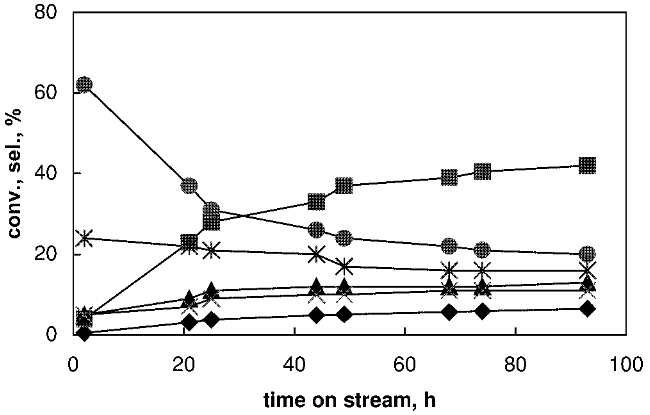

Figure 5. Catalytic performance of the sample prepared by calcination of the Keggin precursor $(NH_4)_3PMo_{12}O_{40}$ precipitated at pH < 1, as a function of time-on-stream at 380 °C and $\tau = 3.6$ s; feed 26% isobutane, 13% O_2, 12% H_2O, remainder He. Isobutane conversion (♦), selectivity to methacrylic acid (■), methacrolein (▲), acetic acid (×), and CO (∗), CO_2 (•).

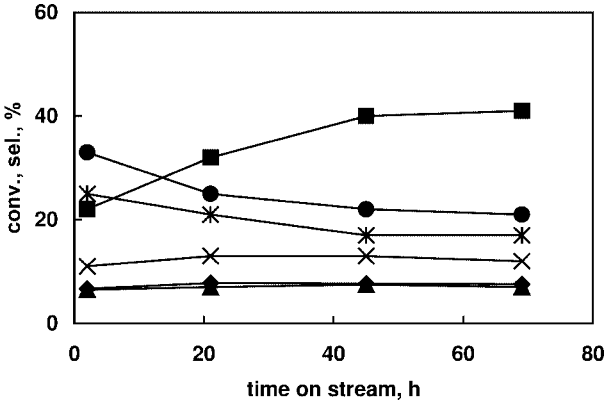

Figure 6. Catalytic performance of the sample prepared by calcination of the lacunary precursor $(NH_4)_7PMo_{11}O_{39}$ precipitated at pH 4.0, as a function of time-on-stream at $T = 350$ °C and $\tau = 3.6$ s; feed 26% isobutane, 13% O_2, 12% H_2O, remainder He. Symbols as in figure 5.

POM occurs during equilibration, until the two rates of (i) oxidized POM reduction by isobutane and (ii) reduced POM reoxidation by oxygen (the two steps in the classical redox mechanism), become equal, and the catalyst reaches an equilibrium situation with the gas phase. This also indicates that the composition of the gas phase affects the redox level of the working POM at steady state. This phenomenon might be, at least in part, responsible for the progressive increase in activity shown in figure 5. However, since the POM reduction occurs in all catalysts, regardless of the pH of precursor precipitation (figure 8), it seems rather to affect another phenomenon which is common to all catalysts, *i.e.*, the progressive increase in selectivity to methacrylic acid (figures 5 and 6). In order to confirm this, a test was done on the catalyst of figure 5, after attainment of the steady performance: the sample was reoxidized *in situ* by treatment with air, and then was made to react again under reducing (hydrocarbon-rich) conditions [26]. It

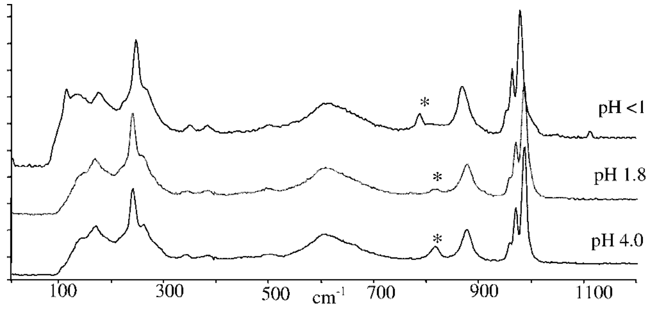

Figure 7. Raman spectra of catalysts prepared by calcination of the precursors precipitated at increasing values of pH, unloaded after reaction; ∗ MoO_3.

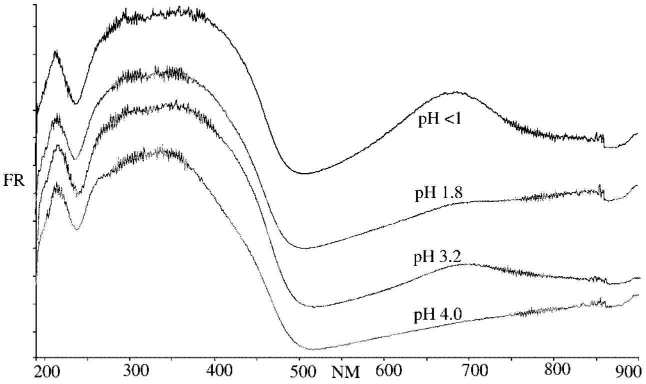

Figure 8. UV-Vis DR spectra of catalysts prepared by calcination of the precursors precipitated at increasing values of pH, unloaded after reaction.

was found that the reoxidation of the POM leads first to a less selective catalyst (with a decrease in the selectivity to methacrylic acid from 42 to 20%); however, the selectivity typical of the equilibrated catalyst is then recovered in 20–30 h, which is the time needed to reduce the POM once again under reaction conditions. A similar change in selectivity to methacrylic acid (from 22% for the oxidized POM to 41% for the reduced POM) is obtained in the case of the catalyst prepared starting from the lacunary precursor (figure 6).

These data point out that the selectivity to methacrylic acid is a function of the degree of reduction (and therefore of the time-on-stream elapsed) of the POM in active catalysts, *i.e.*, in POMs which contain active sites, where the latter have been generated either (i) *in situ* by equilibration under reaction conditions in the case of the calcined catalyst prepared starting from the Keggin precursor (precipitated at pH $<$ 1), or (ii) *ex situ* by calcination of the lacunary precursor (precipitated at pH 4.0). On the other hand, in the former case the initial selectivity to methacrylic acid and the activity are very low (figure 5), and several hours of equilibration are necessary to reach good performance. Therefore, in this case an additional phenomenon overlaps, which is responsible for the increase in activity (*i.e.*, for the *in situ* generation of the active sites) and, at least in part, for the progressive increase in selectivity.

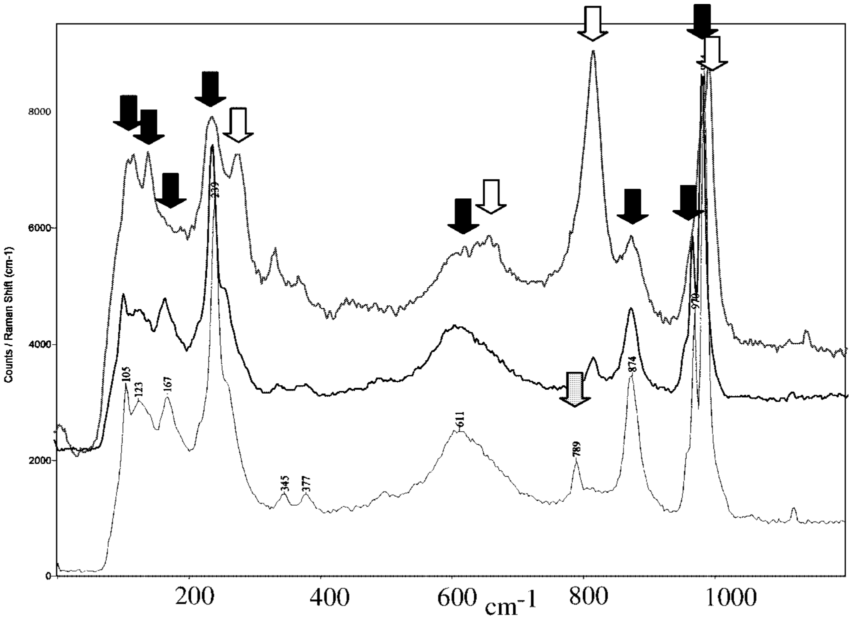

Figure 9. Raman spectra of different particles of the catalyst prepared by calcination of the precursor precipitated at pH < 1, unloaded after reaction. ➡ POM, ⇨ α-MoO_3, ▨ β-MoO_3.

(2) Small amounts of MoO_3, detected by X-ray diffraction (not shown here) and by Raman spectroscopy (figure 7), and indicating partial structural decomposition of the Keggin-type POM, form during reaction for the sample prepared at pH < 1 (which did not contain MoO_3 before reaction, figure 3). The structural decomposition occurring during reaction is likely due to the high surface temperature which develops due to the reaction exothermicity. Indeed, the same decomposition does not occur when the reaction is carried out at isobutane-leaner conditions [26,28]. However, the extent of decomposition is not the same for all the catalyst particles. Figure 9 shows that, depending on the particle on which the beam is focussed, some particles are considerably more decomposed than others; moreover, both β-MoO_3 and α-MoO_3 are the products of decomposition.

(3) The partial structural decomposition is also accompanied by a loss of ammonium cations, which are released from the compound in the form of either ammonia or molecular nitrogen, due to the oxidizing action of the POM. This is clearly evident from the analysis of the N content. The amount of ammonium cation corresponds to 2.3 mole (instead of the theoretical 3.0) per Keggin unit $PMo_{12}O_{40}^{3-}$, for the unloaded sample whose precursor was precipitated at pH < 1, and to 1.7 for the unloaded sample whose precursor was precipitated at pH 4.0. Indeed, it is evident that the decrease in ammonium content, which should theoretically correspond to the fraction of Keggin units which are decomposed, is instead much higher than that expected on the basis of the amount of MoO_3 detected [27,29]. This suggests that a fraction of ammonium is indeed replaced by molybdenum cations in the secondary framework. This hypothesis has been confirmed in past studies by EPR spectroscopy, which indicated the presence of Mo dimers associated with the presence of extra-Keggin-anion Mo ions, probably located in the cationic position in the secondary framework of the POM [27].

(4) A modification occurring in the cationic composition of the POM also is evident from the changes which occur in the ultraviolet part of the electronic spectrum of some of the unloaded samples (figure 8) with respect to the corresponding calcined ones (figure 4). Specifically, in the case of samples prepared by precipitation of the precursor at less acidic conditions (pH 3.2 and 4.0), the spectrum in this region is only slightly changed with respect to the fresh, calcined catalyst. In contrast, in the case of the samples prepared at pH < 1 and pH 1.8, the intensity of the band falling above 400 nm considerably decreases. Therefore, the spectra of all unloaded catalysts are finally similar, regardless of the pH of precipitation of the corresponding precursor.

In conclusion, it is possible to hypothesize that the change occurring in catalyst activity (*i.e.*, in isobutane conversion) for the sample prepared at pH < 1 during the equilibration time (figure 5), is due to a change in the cationic composition of the POM, as a consequence of the structural rearrangement which occurs during reaction by partial decomposition and migration of Mo cations in the secondary framework of the POM. This phenomenon generates sites which constitute the active centres for the oxidation of isobutane to methacrylic acid. The same phenomenon takes a much shorter time to occur for samples prepared at higher pH of precipitation, up to the limit case of the calcined compound whose precursor was precipitated at pH 4.0, which is active from the very beginning (figure 6), because in these cases the active sites are already present in calcined samples. Indeed the active sites form during the structural transformation at 350 °C of the lacunary precursor (the amount of which in the precipitate increases with increasing pH of precipitation) to the Keggin compound.

A possible role might also be played by MoO_3 generated by partial structural decomposition; it has been proposed that the development of a partly decomposed compound leads to a more active catalyst in the oxidehydrogenation of isobutyric acid to methacrylic acid [30].

The *in situ* generation of the active sites (figure 5) also has a positive effect on the selectivity to methacrylic acid, and overlaps with the effect due to the progressive reduction of the POM during the equilibration period. The latter phenomenon instead occurs under reaction conditions for all samples, regardless of the pH of precipitation of the corresponding precursor.

One further aspect concerns the long equilibration time (up to 80 h) needed to reach a stable performance in the case of the calcined sample whose precursor was precipitated at pH < 1 (figure 5). This is in contradiction with that reported in the literature, where shorter times are claimed to be necessary to reach a steady state [8]. This might be due to the fact that all catalysts described in the literature already contain transition metal ions in the secondary framework, like Fe^{2+} or Cu^{2+}. Also, it has been reported that in V-substituted POMs, V^{5+}, originally present in the Keggin anion, during reaction is transferred into the cationic position, generating VO^{2+} sites. Concurrently, the activity increases [31,32]. Therefore, this would seem to confirm the fundamental role played by transition metal ions located in the cationic position of POMs as active sites for the oxidation of isobutane to methacrylic acid. When the POM does not contain these sites (as in our $(NH_4)_3PMo_{12}O_{40}$ catalyst prepared by calcination of the precursor precipitated at pH < 1), the time required for catalyst activation corresponds to the time necessary to initiate the structural decomposition of the POM and the migration of Mo ions from the Keggin anion into the secondary framework of the POM.

In contrast, in the case of the compound prepared at pH 4.0 these active sites form during the calcination treatment, with the transformation of the lacunary precursor into the Keggin compound, and therefore the catalyst is active from the very beginning of the service time. In this case the equilibration time is only necessary to reach a steady reduction level of the POM under hydrocarbon-rich conditions.

4. Conclusions

The pH of precipitation of the POM is one parameter which may affect the performance of the catalyst during the equilibration time. In particular, it is possible to considerably shorten the time-on-stream necessary to reach a steady performance (with better conversion and selectivity to methacrylic acid than during the unsteady period) by preparation of the precursor at mildly acidic conditions (*i.e.*, pH 4.0). The calcination treatment of the lacunary precursor yields a Keggin-type POM that already contains the specific sites active for the oxidation of isobutane to methacrylic acid. When instead the catalyst is prepared conventionally at strongly acid pH (*i.e.*, pH < 1), the generation of the active species occurs during permanence in the reaction environment under isobutane-rich conditions, by partial decomposition of the POM and modification of the cationic composition in the POM framework. An additional phenomenon, the progressive reduction of the POM under reducing, hydrocarbon-rich conditions, occurs with all catalysts, and is also responsible for the improvement in selectivity during catalyst equilibration [26,28].

Acknowledgement

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