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Improved catalytic performance of Keggin-type polyoxometalates in the oxidation of isobutane to methacrylic acid under hydrocarbon-lean conditions using antimony-doped catalysts

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Abstract

Ammonium salt of 12-molybdophosphoric acid $(NH_4)_3PMo_{12}O_{40}$, having the Keggin structure (polyoxometalate, POM) was prepared and tested as heterogeneous catalyst for the selective oxidation of isobutane to methacrylic acid, under both hydrocarbon-rich and hydrocarbon-lean conditions. The same compound was doped with Sb^{3+} ions, in an amount corresponding to 0.23 Sb atom per Keggin unit. Doping with antimony caused a decrease in the oxidation state of molybdenum, due to the electron exchange occurring between Sb^{3+} and Mo^{6+} during the calcination treatment: $Sb^{3+} + 2Mo^{6+} \leftrightarrow Sb^{5+} + 2Mo^{5+}$. This reduced state for molybdenum in the POM was thus stabilized even under oxidizing conditions.

This effect modified the reactivity of the POM-based catalyst in the title reaction with respect to the undoped catalyst, especially under isobutane-lean conditions (i.e. 1% isobutane, 13% oxygen), thus under conditions which are considerably more oxidizing than those at 26% isobutane (isobutane-rich conditions), typically used for the selective oxidation of isobutane catalyzed by POMs. In fact, while in the absence of antimony, the oxidized catalyst was completely unselective to methacrylic acid under isobutane-lean reaction conditions, the Sb-doped catalyst reached a selectivity as high as 40–45% to methacrylic acid. On the contrary, under intrinsically reducing conditions (i.e. under isobutane-rich conditions), a reduced catalyst also developed in the reaction medium in the case of the undoped system. In this case, the advantage in selectivity gained by using a Sb-doped catalyst was much less than that obtained at low concentration of the hydrocarbon in the feed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Keggin structure; Polyoxometalate; Isobutane; Methacrylic acid

1. Introduction

The synthesis of methyl methacrylate is currently carried out using the “acetone-cyanohydrin” process. This 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 methyl methacrylate. Several industrial companies have studied this reaction, and it has been established that the most active and selective catalysts are those which are based on Keggin-type polyoxometalates (POMs), containing phosphorus and molybdenum as the main components. Several patents and papers have been published, dealing with the study of the effect of the POM composition on the catalytic performance and with the effect of the main reaction parameters on isobutane conversion and on the distribution of products [1–18].

An important aspect of this reaction is that in all patents use is made of isobutane-rich conditions, thus with sub-stoichiometric oxygen [1–5]. Under these conditions the conversion of isobutane is necessarily very low (in the best cases, not higher than 25%), and therefore it becomes necessary to recycle the unconverted reactant. It has been proposed that the reason for this is that the catalyst is selective only provided it can be kept at an average reduced state lower than that typical of the calcined POM; this can be achieved only if a reducing, hydrocarbon-rich gas phase is employed as the feedstock to the reactor [17]. Some authors have reported that catalyst preparations which lead to the development of reduced compounds perform better than POMs prepared conventionally [8,10,12,13]. However, in

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all cases very few indications are given about the possibility of maintaining these performances for prolonged lifetimes. Indeed, the main question is whether this reduced state of the POM can be maintained under reaction conditions, or is fated to evolve inside the reactor.

In a previous study, we found that the addition of small amounts of Sb^{3+} to the POM-based catalyst makes possible the occurrence of a redox reaction between Mo^{6+} in the primary POM structure and antimony, with development of a reduced compound which is stable even under oxidizing conditions [19]. Therefore, this Sb-doped POM is a possible good candidate to (i) check the effective improvement gained in catalytic performance in the presence of a reduced POM, and (ii) verify whether the possible improvement obtained is different under reducing (isobutane-rich) and oxidizing (isobutane-lean) conditions.

2. Experimental

POM with the composition $(NH_4)_3PMo_{12}O_{40}$ was prepared using the following procedure: the compound is precipitated by the addition of HCl to a solution containing dissolved $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and H_3PO_4, in the relative amounts as required by the stoichiometry. The Keggin-type anion $PMo_{12}O_{40}{}^{3-}$ is formed in solution at acid conditions, and the insoluble ammonium salt of 12-phosphomolybdic acid is immediately precipitated. In the case of Sb-doped POM, $SbCl_3$/HCl is also added to the solution, in the desired amount. The colour of the solution turns green. HCl is then added dropwise to the solution obtained, and a green precipitate is obtained. The drying and calcination procedure was the following: drying at 120°C overnight (with solvent evaporation), and then calcination up to 350°C in static air, with a heating rate of 2°/min. The final temperature was maintained for 6 h.

The effective content of Sb was determined by dissolution of the sample in basic medium, and by atomic absorption (Phillips PU 9100). The amount was found to be equal to 0.23 atoms per Keggin unit: $(NH_4)_3PMo_{12}O_{40}/Sb_{0.23}O_x$. Carbon and nitrogen contents were determined on the solids, with a Carlo Erba EA 1110 CHNS-O Instrument.

Powder XRD data were obtained with a Phillips PW 1050/81 diffractometer, controlled by a PW1710 unit using Ni-filtered Cu Kα radiation. The samples were supported in a sample holder with a depth of 1 mm. The surface areas (BET single point) were determined by N_2 adsorption at 77 K, using a Carlo Erba 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 continuous flow reactor, at atmospheric pressure. The feed composition was the following: isobutane between 1 and 26 mol%, oxygen 13%, steam 12%, rest was helium. Each series of catalytic tests was carried out using 1.5 g of catalyst, granulated into particles ranging from 0.3 to 0.5 mm in size. 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

3.1. Characterization and reactivity of $(NH_4)_3PMo_{12}O_{40}$

Fig. 1 shows the effect of time-on-stream (tos) on isobutane conversion and on selectivity to the products, for the catalyst of composition $(NH_4)_3PMo_{12}O_{40}$, under isobutane-rich conditions (26% isobutane). In order to reach stable catalytic performance at least 80 h of reaction are required. During this "equilibration" period, the main effect is that of an increase in isobutane conversion, which at the very beginning is less than 1%, and gradually increases to approximately 6.5%. In the same time, the selectivity to methacrylic acid increases from less than 5 to 40% after 80 h tos, with a corresponding decrease in the selectivity to CO_2. On the contrary, the selectivity to CO and methacrolein remain approximately constant during the activation period, and that to acetic acid slightly increases. Under steady-state conditions, the main product is methacrylic acid.

The effect of reaction temperature on catalytic performance for an already "equilibrated" catalyst is shown in Fig. 2. Methacrylic acid is a relatively stable product,

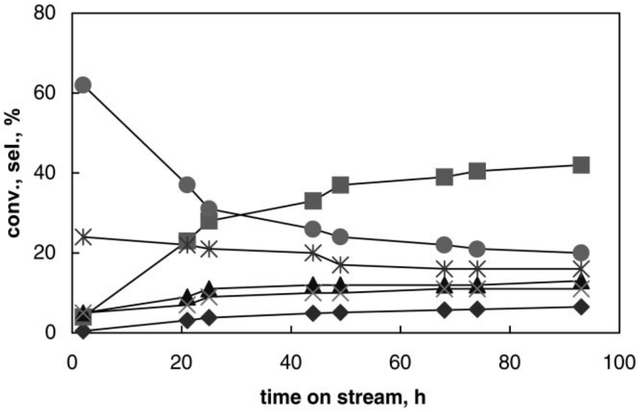

Fig. 1. Catalytic performance of $(NH_4)_3PMo_{12}O_{40}$ as a function of tos at 380°C and τ 3.6 s; feed: 26% isobutane, 13% O_2, 12% H_2O, remainder He. Isobutane conversion (◆); selectivity to methacrylic acid (■); methacrolein (▲); acetic acid (╳); CO (✳); CO_2 (●).

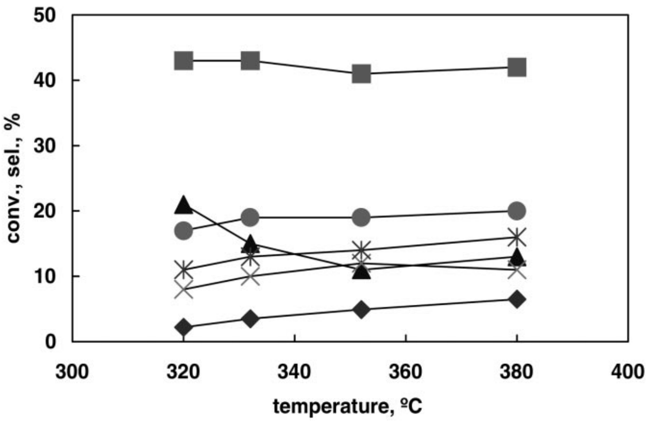

Fig. 2. Catalytic performance of $(NH_4)_3PMo_{12}O_{40}$ as a function of temperature for an equilibrated catalyst at τ 3.6 s; feed: 26% isobutane, 13% O_2, 12% H_2O, remainder He. Symbols as in Fig. 1.

while methacrolein decomposes yielding acetic acid and carbon oxides. In a previous work, a catalyst having the same composition, but calcined at 380°C instead of 350°C [18], showed a slightly different behavior, with a less drastic decrease in selectivity to methacrolein with increasing temperature.

The comparison of the reactivity under isobutane-rich and isobutane-lean conditions, in both cases for "equilibrated" catalysts, is shown in Fig. 3. The catalyst exhibits very low selectivity when the reaction is carried out at 1% isobutane in the feed. This confirms indications from the patent literature, which suggest a general preference for isobutane-rich conditions [1–5].

X-ray diffraction spectra of the catalyst before and after reaction are shown in Fig. 4. The calcined catalyst (spectrum a) only shows the diffraction lines typical of $(NH_4)_3PMo_{12}O_{40}$ (JCPDS 09-0412). On the contrary, a small amount of POM structural decomposition occurs during reaction, as indicated by the appearance of the diffraction lines assigned to α-MoO_3 (Molybdenite, JCPDS 35-0609) in the spectrum of the catalyst unloaded after reaction at isobutane-rich conditions (spectrum b). It is known that for ammonium salts of Keggin-type POMs, structural decomposition begins at temperatures around 400°C, thus higher than those employed in the present study to check the catalytic reactivity [20]. However, local temperatures may develop on the catalyst surface that are higher than those measured in the gas phase, due to the strongly exothermal reactions which occur. This is confirmed by the spectrum relative to the catalyst unloaded after reaction at isobutane-lean conditions (spectrum c in Fig. 4), which is practically the same as that of the fresh (calcined) catalyst, due to the lower heat released with respect to the isobutane-rich conditions.

The partial structural decomposition of the catalyst after reaction at isobutane-rich conditions is also demonstrated by Raman spectra of the corresponding compound. Fig. 5 shows the spectrum of the fresh, calcined catalyst (spectrum a), and of the catalyst unloaded after reaction (spectrum b). The extent of decomposition is not uniform, since the intensity of the bands relative to α-MoO_3 (at 275, 655 and 815 cm^{-1}) greatly changes from particle to particle. In the figure, a spectrum is reported in which the bands attributed to MoO_3 are very intense. The spectrum of the catalyst unloaded after reaction at isobutane-lean conditions is the same as that of the fresh, calcined catalyst.

Electronic UV–VIS diffuse reflectance spectra of the same catalysts are compared in Fig. 6. The following absorption bands can be observed in the spectra:

(a) A large absorption band in the 250–500 nm range. This band is indeed constituted of several components, due to the different energies associated with $O^{2-} \rightarrow Mo^{6+}$ charge-transfers in the Keggin anion. A first component is

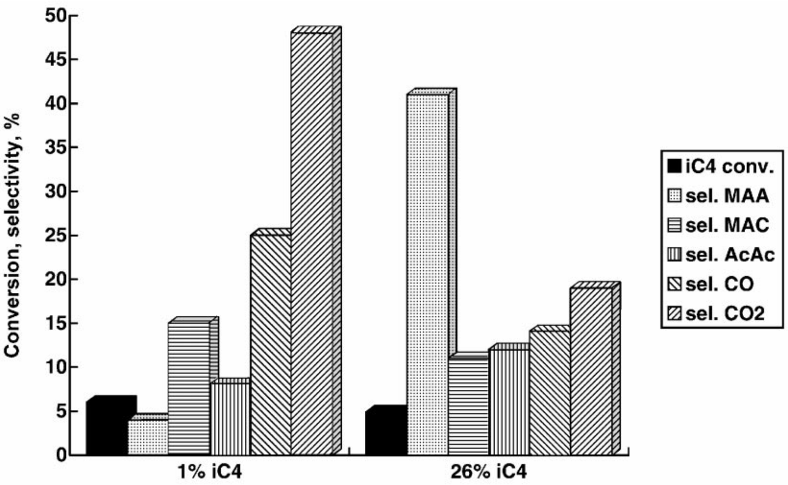

Fig. 3. Comparison of the catalytic performance of an equilibrated $(NH_4)_3PMo_{12}O_{40}$ catalyst under isobutane-lean (1% isobutane, 13% oxygen; residence time 3.6 s; temperature 350°C) and isobutane-rich (26% isobutane, 13% oxygen; residence time 3.6 s; temperature 352°C). MAA: methacrylic acid; MAC: methacrolein; AcAc: acetic acid.

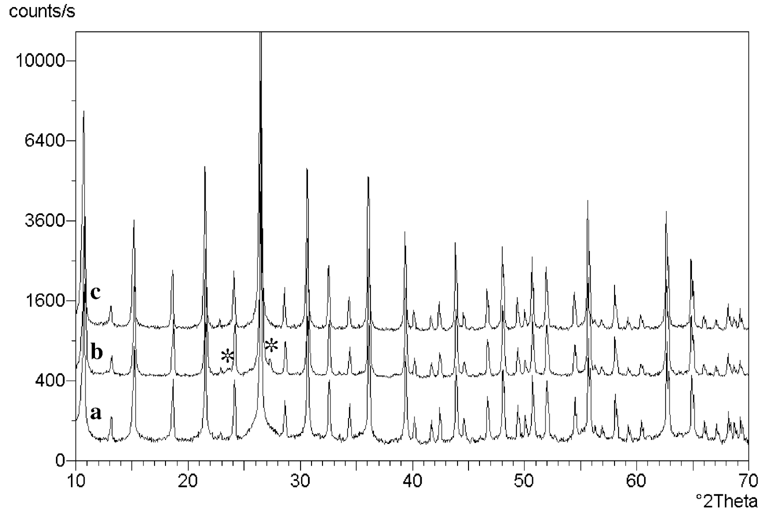

Fig. 4. X-ray diffraction spectra of calcined $(NH_4)_3PMo_{12}O_{40}$ (a) and of the same compound after reaction at isobutane-rich conditions (b) and after reaction at isobutane-lean conditions (c). ✻: α-MoO_3.

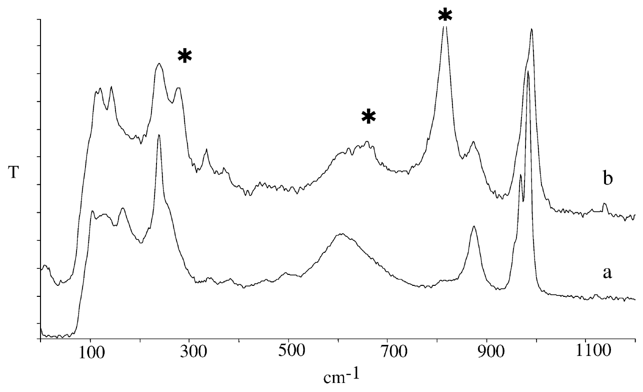

Fig. 5. Raman spectra of calcined $(NH_4)_3PMo_{12}O_{40}$ (a), and of the same catalyst after reaction at isobutane-rich conditions (b). ✻: α-MoO_3.

present in the 270–320 nm range, a second one lies between 330 and 400 nm, and a third one is centred above 400 nm. The bands are strongly convoluted. It has been reported that the energy associated with the absorption band above 400 nm (centred at ≈430–460 nm) is a function of the cationic composition of the Keggin secondary framework, and possibly of other structural and morphological features as well (i.e. the crystallinity of the compound) [21]. Moreover, it has been reported that the low-energy charge-transfer band energy can be affected by the oxidation potential of the oxometal [22].

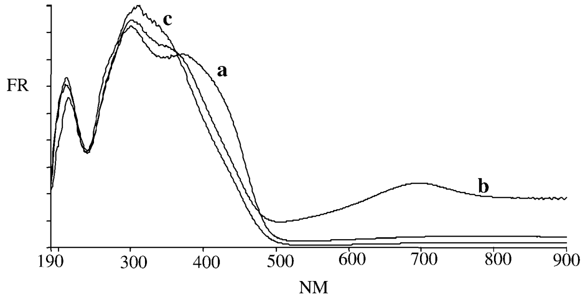

Fig. 6. UV–VIS–DR spectra of calcined $(NH_4)_3PMo_{12}O_{40}$ (a), of the same catalyst after reaction at isobutane-rich conditions (b), and after reaction at isobutane-lean conditions (c).

(b) A broad band is present at around 700 nm, which is due to intervalence charge-transfer transitions, e.g. $Mo^{5+} \rightarrow Mo^{6+}$, and is, therefore, indicative of the presence of octahedral Mo^{5+} [23]. The presence of reduced species can also affect the width and position of the low-energy CT band [23]. More than one absorption band can occur in the visible spectral region of heteropolyblues, depending on the number of electrons furnished. The absorptivity is proportional to the degree of reduction, and the width and position of this band is also a function of the extent of reduction [24]. This band is not present in the calcined sample and in the catalyst unloaded after reaction at isobutane-lean conditions (spectra a and c, respectively, in Fig. 6), whereas it is clearly evident in the spectrum of the catalyst after reaction at isobutane-rich conditions (spectrum b). This suggests that in the latter case the catalyst progressively becomes more reduced under reaction conditions, until reaching a stable redox state that represents the situation of equilibrium with the gas phase. Therefore, at high concentration of the hydrocarbon in the feed, the gas phase can be considered as a reducing one towards the fully oxidized Keggin compound. On the contrary, when operation is carried out at isobutane-lean conditions, the gas phase is not reducing towards the catalyst, and the electronic spectrum of the unloaded catalyst is practically the same as that of the calcined catalyst.

Surface area of the calcined catalyst = 80 m^2/g, while after reaction at both isobutane-rich and isobutane-lean conditions it is considerably lower, less than 5 m^2/g. This effect is not due to accumulation of heavy compounds in the pores;

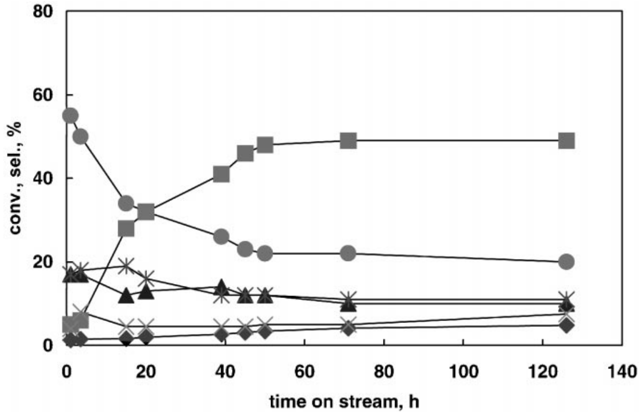

Fig. 7. Catalytic performance of $(NH_4)_3PMo_{12}O_{40}/Sb_{0.23}O_x$ as a function of tos at T 350°C and τ 3.6 s; feed 26% isobutane, 13% O_2, 12% H_2O, remainder He. Symbols as in Fig. 1.

in fact the C content in the spent catalyst was found to be equal to 0.06 wt.%. Fig. 4 shows that neither modification of the POM crystallinity occurs during reaction, which might be responsible for variations in the specific surface area, nor the latter can be attributed to the formation of crystalline MoO_3, which only occur in the case of the catalyst unloaded after reaction at isobutane-rich conditions.

Other modifications in the catalyst composition involve the amount of ammonium cations. While in the case of the calcined catalyst, the N content determined analytically corresponds to 3.0 NH_4^+ cations per Keggin unit, in the catalyst unloaded after reaction at isobutane-rich conditions this amount is considerably lower (2.3 NH_4^+ cations per Keggin unit), while it is practically unchanged in the case of the catalyst unloaded after reaction at isobutane-lean conditions (3.0 cations per Keggin unit). Indeed it is known that the surface area of POMs is greatly affected by the cation type and amount [25]. It is thus possible that a rearrangement of cations is responsible for the decrease in surface area during reaction. This phenomenon, however, still remains basically unclear.

3.2. Characterization and reactivity of $(NH_4)_3PMo_{12}O_{40}/Sb_{0.23}O_x$

The catalytic behavior of the catalyst doped with Sb^{3+} as a function of tos is shown in Fig. 7. The variation in catalytic performance is very similar to that of the undoped catalyst. Also in this case the activity of the catalyst is initially low, and gradually increases with tos. The selectivity to methacrylic acid initially is low and then increases, to a value close to 48%, thus slightly higher than that achieved with the undoped catalyst. The selectivity to methacrolein is around 15% at the beginning of the catalyst service life, and then it slightly decreases.

The effect of the reaction temperature is shown in Fig. 8. Also in this case the selectivity to methacrylic acid is almost independent of reaction temperature. One difference with respect to the undoped catalyst (Fig. 2) is the selectivity to methacrolein, which in the Sb-doped catalyst is stable in the temperature range 340–370°C, while in the case of the undoped catalyst it decreases with increasing reaction temperature, due to consecutive reactions of degradation to acetic acid and to carbon oxides.

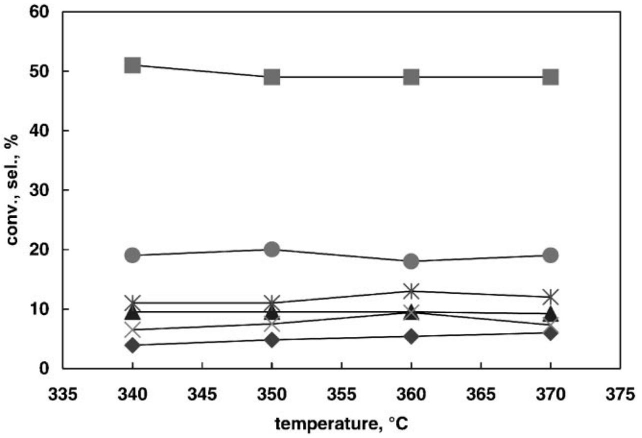

Fig. 8. Catalytic performance of $(NH_4)_3PMo_{12}O_{40}/Sb_{0.23}O_x$ as a function of temperature at τ 3.6 s; feed 26% isobutane, 13% O_2, 12% H_2O, remainder He. Symbols as in Fig. 1.

The most significant effect induced by the presence of antimony is illustrated in Fig. 9, which shows the catalytic performance of the Sb-doped catalyst as a function of the isobutane concentration in the feed. Tests were first carried out at the lower isobutane concentration (1%), letting the catalyst equilibrate in the reaction environment. Tests were then made at progressively increasing concentrations of isobutane, and at each concentration the catalyst was first run for the number of hours necessary to reach stable performance. It is seen that the catalyst is now selective even under low isobutane concentrations. This represents the most impor-

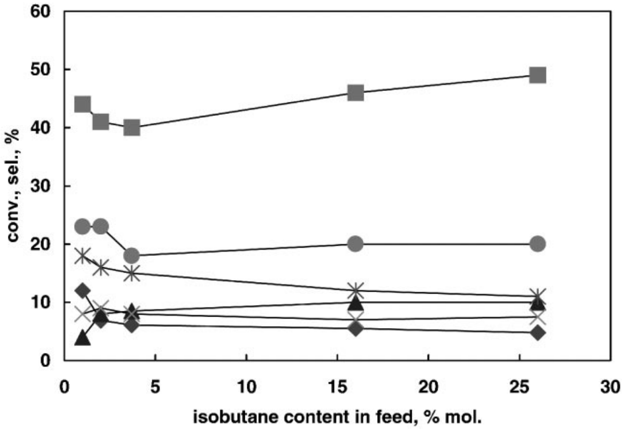

Fig. 9. Catalytic performance of $(NH_4)_3PMo_{12}O_{40}/Sb_{0.23}O_x$ as a function of isobutane content in feed at 350°C; τ 3.6 s, 13% O_2, 12% H_2O, rest He. Symbols as in Fig. 1.

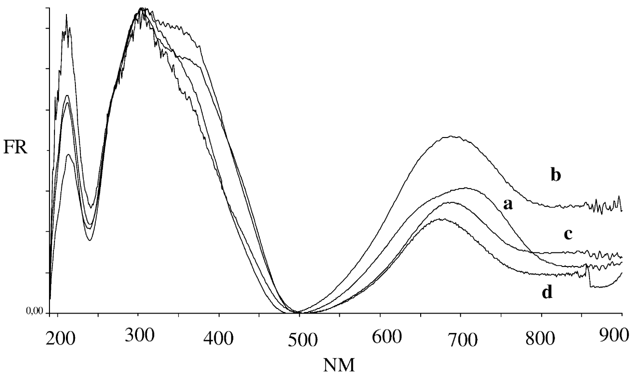

Fig. 10. UV–VIS–DR spectra of fresh (calcined) $(NH_4)_3PMo_{12}O_{40}/Sb_{0.23}O_x$ (a), of the same catalyst after reaction under isobutane-rich conditions (b), after reaction under isobutane-lean conditions (c), and of sample b after reoxidation in flowing air at 350°C (d).

tant achievement, since in the case of the undoped catalyst under isobutane-lean conditions the compound was almost completely unselective (see Fig. 3).

The X-ray diffraction pattern of the calcined catalyst is the same as that of the undoped system. After reaction under both isobutane-rich and isobutane-lean conditions the compound is intact, diffraction lines assigned to MoO_3 are not observed. The same is also observed by Raman spectroscopy. In a previous work [19], it was found that the addition of antimony stabilizes the POM towards structural decomposition; in our case, the improved thermal stability makes the rate of structural decomposition under reaction conditions slower than with the undoped catalyst. Analysis of the N content for the calcined and for the unloaded Sb-doped catalyst after reaction under isobutane-rich conditions indicated that the number of moles of ammonium cation per Keggin unit in the POM = 2.7 for the former catalyst, and equal to 2.2 for the latter one. The amount is lower than 3.0 (the value expected for the calcined catalyst) because a fraction of the ammonium is replaced by antimony ions in the secondary structure of the POM [19]. The decrease in ammonium content during reaction is due either to a partial structural decomposition of the POM (in this case, however, no formation of MoO_3 could be detected by X-ray diffraction and Raman spectroscopy), or by an increase in the extent of replacement of ammonium cations by Sb ions, occurring during permanence in the reaction environment.

Carbon content in the unloaded catalyst is equal to 0.03 wt.%. The surface area of the catalyst is very low (less than 5 m^2/g) in both the calcined and the unloaded catalysts.

The UV–VIS–DR spectra of the fresh (calcined, spectrum a) and unloaded catalysts after reaction under isobutane-rich (spectrum b) and isobutane-lean (spectrum c) conditions are shown in Fig. 10. The catalyst unloaded after reaction under isobutane-rich conditions has then been treated at 350°C in flowing air (spectrum d). It is shown that molybdenum in the POM of the fresh catalyst is in part reduced, as indicated by the broad, intense absorption band centered at around 700 nm. In a previous study [19], it was found that when $SbCl_3$ is added to the acid slurry containing the POM during the preparation procedure, the electron exchange between Mo^{6+} and Sb^{3+} begins, as clearly indicated by the change in colour of the solution. The redox reaction is completed at high temperature during the calcination treatment in air. This has been proposed to be due to the fact that during the thermal treatment a part of antimony replaces a fraction of ammonium in the POM framework in cationic position, and therefore a close electronic interaction between antimony and molybdenum is made possible. The modification of the cationic composition is the reason for the improved structural stability of the catalyst with respect to the undoped one. The development of Mo^{5+} in an oxidizing atmosphere (samples were calcined in static air at 350°C), clearly indicates that the reduced species is stabilized.

The comparison of the spectrum of the fresh (calcined) catalyst with that of the spent catalyst after reaction under isobutane-rich conditions indicates that the permanence in the reaction environment under these conditions further modifies the spectrum of the fresh compound. The intensity of the absorption bands centered at around 700 nm in fact increases, suggesting that molybdenum reduction proceeds during reaction, despite the presence of an already reduced compound in the calcined catalyst.

When the catalyst unloaded after reaction under isobutane-rich conditions (spectrum b) is reoxidized in flowing air at 350°C for 3 h (spectrum d), the intensity of the band at 700 nm decreases. A treatment for longer time does not further modify the spectrum, while higher temperatures of oxidation lead to a further decrease of the band intensity. Therefore, the oxidizing treatment reoxidizes easily the fraction of molybdenum which reduces during reaction, while the fraction of molybdenum reduced during the calcination of the catalyst can be reoxidized only by a stronger oxidizing treatment under flowing air at temperatures higher than that employed for the calcination.

One further aspect concerns the nature of the absorption bands above 500 nm. It is known that absorption spectra of heteropolyblues may change considerably depending on the number of electrons furnished to the POM [26,27]. Spectra in Fig. 10 show the presence of at least two bands in the calcined catalyst (spectrum a), one centered below 700 nm and one above 700 nm. In the case of the spectrum relative to the undoped catalyst after reaction under isobutane-rich conditions (Fig. 6, spectrum b) the presence of either a single band or of two bands can not be easily ascertained. The spectrum of the Sb-doped catalyst after reaction under isobutane-rich conditions (spectrum b in Fig. 10) again seems to consist of two different bands. In the catalyst unloaded after reaction at isobutane-lean conditions (spectrum c) the higher-energy component seems to be the prevailing one, and in the compound which has been in part reoxidized by treatment in flowing air (spectrum d) this band is clearly the only component. These data suggest the existence of at least two different types of reduced sites, (i) one site which can be easily reoxidized by treatment under mild conditions, characterized by a band centered above 700 nm, and (ii) one site which is hardly reoxidizable, characterized by a band centered at wavelength lower than 700 nm. Both species develop during the calcination of the Sb-doped POM by redox reaction between Mo^{6+} and Sb^{3+}, but the relative intensity of the bands is modified as a consequence of the permanence in the reaction environment.

4. Discussion

4.1. The catalytic performance of $(NH_4)_3PMo_{12}O_{40}$: the effect of chemical–physical features on the selectivity to methacrylic acid

The $(NH_4)_3PMo_{12}O_{40}$ catalyst exhibits changes in chemical–physical features during permanence in the reaction environment along the first 80–100 h of service, especially when the reaction is carried out under isobutane-rich conditions. The comparison of the chemical–physical features of the POM, fresh and unloaded, shows that the following modifications occur during the "equilibration" period: (i) a considerable decrease in surface area, (ii) a partial decomposition of the heteropolycompound, with formation of α-MoO_3, (iii) a variation in composition, with a decrease in the amount of ammonium cations, and (iv) an increase in the reduction level of molybdenum, with formation of Mo^{5+} species.

When instead the reaction is carried out under isobutane-lean conditions, the extent of structural decomposition is almost nil, as indicated by the XRD pattern and by the NH_4^+ content of the unloaded catalyst. This difference can clearly be attributed to the lower temperatures which develop at the catalyst surface under isobutane-lean conditions, due to the lower extent of heat production. Moreover, characterization of the catalyst after reaction indicates that the compound is almost as fully oxidized as before reaction (very little reduction is shown, with a very weak absorption band at 700 nm) (see spectrum c in Fig. 6). This confirms that the presence of an oxidizing reaction environment induces much smaller modifications to the catalyst than those occurring under isobutane-rich conditions.

In a previous study, it was proposed that the structural decomposition of POMs occurs via local formation of decomposed Keggin units, with release of Mo cations which in part segregate to form MoO_3, and in part may act as counterions for neighbouring Keggin anions, stabilizing the latter against decomposition [20]. This might explain why the structural decomposition is a slow phenomenon, which does not rapidly propagate after nucleation of the first crystals of molybdenum oxide throughout the entire solid. Moreover, the transfer of molybdenum from the Keggin anion to the cationic position in the secondary framework of the POM can justify the decrease of ammonium content, as determined by chemical analysis. As reported previously [20], the amount of ammonium released from the structure is considerably higher than that expected on the basis of the amount of crystalline MoO_3 detected by XRD.

The variation in catalytic performance occurring with tos during "equilibration" can be reasonably attributed to the mentioned changes in the catalyst features. The main effect is a progressive increase in selectivity to methacrylic acid, with a corresponding decrease in CO_2 formation. This effect can be attributed at least in part to the increase in the extent of molybdenum reduction occurring in the reaction environment. Thus, molybdenum reduction is accompanied by the development of a surface distribution of active sites which is intrinsically more selective to the product of partial oxidation than that in the fully oxidized catalyst. It can be postulated that a discrete extent of POM reduction (under isobutane-rich conditions) leads to a more favourable situation for the formation of methacrylic acid with respect to the case of the fully oxidized catalyst. It is known that electrons furnished to molybdenum are not localized to specific atoms, but are delocalized throughout the entire Keggin anion, and that the electron affinity of the Keggin anion decreases with increasing number of electrons furnished to the POM [25]. Therefore, it is possible that the oxidation potential of a partially reduced Keggin unit is better than that of an oxidized POM for the selective transformation of isobutane to methacrylic acid.

Moreover, the inspection of the catalytic performance for the "equilibrated" catalyst under isobutane-lean conditions (Fig. 3) and for the fresh catalyst under isobutane-rich conditions (Fig. 1, at the beginning of the service life) confirms that an oxidized catalyst (which is present when the reaction is carried out under isobutane-lean conditions, or in any case after the calcination treatment, in a fresh catalyst), leads to poor performance in terms of selectivity to products of partial oxidation, more specifically, to low selectivity to methacrylic acid.

4.2. The catalytic performance of $(NH_4)_3PMo_{12}O_{40}/Sb_{0.23}O_x$: the effect of chemical–physical features on the selectivity to methacrylic acid

In the case of the Sb-doped catalyst, changes in chemical–physical features occurring during reaction at isobutane-rich conditions are less important than for the undoped catalyst. No structural decomposition of the heteropolycompound occurs. However a decrease in the ammonium content implies a modification in cationic composition of the heteropolycompound; therefore, also in this case the amount of ammonium lost does not correspond to the development of a corresponding amount of MoO_3.

The intensity of the visible band at 700 nm increases during reaction. The further increase in the extent of molybdenum reduction by permanence in the reaction environment under isobutane-rich conditions means that either the molybdenum sites involved in the two reduction processes (i.e. the electron exchange process between Sb^{3+} and Mo^{6+}, and the reduction of molybdenum during reaction) are different, or that the nature of the two reduction processes is different. It is worth mentioning that while the fresh calcined catalyst is stable in such reduced state, the spent catalyst can be easily restored to the state of the fresh catalyst by treatment in flowing air at 350°C (see spectrum d in Fig. 10). This can be explained by considering that while the electron exchange between antimony and molybdenum does not lead to the loss of O anions (and for this reason the Mo^{5+} species is stable even in an oxidizing environment, since it does not possess anionic vacancies which can act as preferential sites for O_2 adsorption and dissociative reduction to the O^{2-} species), in the reaction environment the progressive reduction of molybdenum leads to the generation of vacant oxygen sites by O^{2-} insertion onto the organic molecule; these vacancies, however, can be fully replenished in an oxidizing atmosphere. This is also confirmed by the presence of two different signals in the spectral region relative to IVCT transitions, which evolve differently when the samples are treated in flowing air at high temperature.

An alternative hypothesis for the increase of the extent of Mo reduction during reaction is a catalytic effect of the Sb^{3+} species. It is thus possible that under isobutane-rich conditions the Sb^{5+} species (formed by electronic exchange with Mo^{6+} during the calcination treatment) are reduced back to Sb^{3+}, and that the latter again reduce other Mo^{6+} species, being again oxidized to Sb^{5+} and thus possibly repeating the redox cycle until all neighbouring Mo^{6+} atoms in the surrounding Keggin anions have been reduced. However, this hypothesis does not explain the existence of reduced Mo sites having different reactivity towards oxygen.

The comparison of the performance under isobutane-rich conditions for the undoped (Fig. 1) and for the Sb-doped catalyst (Fig. 7) indicates that the stable reduced state induced by the presence of Sb^{3+} is not particularly effective in yielding an appreciable enhancement in the selectivity to methacrylic acid under these conditions. In fact the fresh Sb-doped catalyst, although reduced, is not selective to methacrylic acid (Fig. 7, at the beginning of service life), in the same way as the fresh undoped compound is not selective (Fig. 1). However, the Sb-doped “equilibrated” catalyst appears to be slightly more selective than the “equilibrated” undoped one.

The electronic spectrum of the Sb-doped catalyst after reaction under isobutane-lean conditions (spectrum c in Fig. 10) shows that the catalyst is very similar to the fresh (calcined) one, apart from a different intensity ratio between bands in the spectral region relative to IVCT transitions. This indicates, as expected, that isobutane-lean conditions do not cause further substantial modifications in the degree of POM reduction with respect to the fresh compound. This also means that for conditions which include low concentrations of hydrocarbon, the reduction level induced by the electron exchange between Sb^{3+} and Mo^{6+} during calcination is enough to make the catalyst selective (Fig. 9). It is possible that in the presence of a low concentration of isobutane in the adsorbed state on the catalyst, a non-fully oxidized surface makes possible a better control of the Mo redox properties and of the O-insertion properties of the active sites in the POM. When instead operation is carried out with a high concentration of isobutane in the feed, the selective O-insertion properties and thus the selectivity to the products of partial oxidation are controlled by the effective O availability of the POM, rather than by the redox state of Mo, and thus are related to the in situ evolution of the POM during the reaction (that is to the progressive removal of the O^{2-} species in the reducing environment).

Some differences are observed between undoped and Sb-doped catalysts in the effect of temperature on catalytic performance (see Figs. 2 and 8), especially in the selectivity to methacrolein. In a previous work [15], it was found that the reaction network is made of parallel reactions of isobutane transformation to methacrolein, to methacrylic acid, to carbon oxides and to acetic acid. A consecutive reaction of methacrolein oxidative degradation occurs, while methacrylic acid is stable towards secondary reactions. One possibility is that the presence of a more reduced catalyst (due to the effect of antimony) makes a decrease in the rate of the consecutive reaction of degradation of methacrolein possible.

This can explain the stable selectivity to methacrolein with increasing temperature, but it does not explain the lower selectivity to the aldehyde which is achieved with the Sb-doped catalyst (especially in the low-temperature range). It is possible that with the Sb-doped catalyst methacrolein is in part transformed to methacrylic acid, thus contributing to the higher selectivity to the latter product than with the undoped catalyst (both equilibrated). The existence of a contribution to the formation of methacrylic acid due to the consecutive reaction of methacrolein oxidation was found to occur also in the case of Fe-doped POMs [15,16], especially at the lower reaction temperatures, while in the higher temperatures range (i.e. higher than 350°C), the combustion of the aldehyde to acetic acid and to carbon oxides were the prevailing consecutive reactions.

4.3. The chemical–physical features which affect the isobutane conversion

The effect of Sb-doping on the catalytic activity is similar to the one observed on the selectivity to methacrylic acid. Under isobutane-lean conditions the Sb-doped compound is more active (conversion 12% at 1% isobutane in feed) than the undoped one (conversion 6%). Under isobutane-rich conditions, instead, the two catalysts exhibit comparable activity (conversion 4.8 and 4.9%, respectively, at 350°C and 26% isobutane in feed). Also in this case it is possible to attribute these differences to the extent of molybdenum reduction, and thus to the redox interaction with Sb^{3+}, which plays a non-negligible positive effect only under isobutane-lean conditions. One further evidence which supports the hypothesis of a possible role of the extent of Mo reduction on the isobutane conversion is the progressive increase of activity during equilibration for both undoped and Sb-doped catalysts under isobutane-rich conditions (Figs. 1 and 7), corresponding to an increase in the degree of POM reduction.

However, other hypothesis are possible to explain the variation in activity shown in Figs. 1 and 7. Rocchiccioli-Deltcheff et al. [28] have found that the decomposition of the POM to α-MoO_3 is an irreversible phenomenon, responsible for modifications of textural and morphological features of the catalyst. On the contrary, β-MoO_3 can form again the initial POM in the presence of water vapour. Therefore, another possible explanation is the development of an active surface layer of heteropolyacid over the bulk ammonium salt, as the consequence of the partial structural decomposition of the POM to MoO_3, and of the reconstruction of the acid under reaction conditions. Ilkehans et al. [29] found that in correspondence of the incipient structural decomposition of the POM an increase in activity in the oxidehydrogenation of isobutyric acid to methacrylic acid occurs. This phenomenon was also observed in a previous work [20], and was attributed to the fact that the partial structural decomposition causes the development of a more active compound, containing molybdenum in part as the cation in the POM framework. Both hypothesis (development of an acid POM layer and formation of a Mo-salified POM) can also explain why the amount of ammonium lost during reaction under isobutane-rich conditions is higher than that expected on the basis of the amount of MoO_3 detected by X-ray diffraction, in both undoped and Sb-doped unloaded catalysts.

5. Conclusions

Keggin-type POMs containing P and Mo are catalysts for the oxidation of isobutane to methacrylic acid. These systems operate more effectively under isobutane-rich conditions, thus under conditions where the gas-phase is reducing towards molybdenum in the Keggin anion. Therefore, during reaction a partly reduced state develops, as evidenced by ex situ electronic spectra which clearly indicate the progressive formation of Mo^{5+} with increasing elapsed time of reaction (tos). Under isobutane-lean conditions, instead, the catalyst remains in its fully oxidized state, and is not selective in the transformation of isobutane to methacrylic acid.

The modification of mixed oxide-based catalysts depending on reaction conditions is an important aspect which has often been neglected for selective oxidation reactions. In the present case, it is clear that catalyst changes in the reaction atmosphere and catalytic properties are strongly interrelated. Clearly, any modification in catalyst composition aimed at the stabilization of a situation different from that which would otherwise develop during reaction under specific conditions may result in substantial modifications in catalytic performance. Doping of the POM with Sb^{3+} can indeed stabilize a reduced state for molybdenum in the POM, even under oxidizing conditions (calcination in air) or under oxidizing reaction conditions (isobutane-lean conditions). This leads to a considerable improvement in the catalytic performance under isobutane-lean conditions with respect to the undoped POM catalyst, especially in terms of selectivity to methacrylic acid. The improvement in selectivity instead is much lower under reducing reaction conditions (i.e. isobutane-rich conditions), since in this case the reduced POM is intrinsically more selective to methacrylic acid, and there is no need for a supplementary stabilization of a reduced state by Sb doping. Of course, operation at low hydrocarbon concentration is meaningful only provided conversions of the hydrocarbon higher than those presented here can be obtained. This, therefore, remains one main target for improvement.

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