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Oxydehydrogenation of Isobutyric Acid with Heteropolyacid Catalysts: Experimental Observations of Deactivation

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The heteropolyacid catalysts $H_5Mo_{10}V_2PO_{40}$ and $H_6Mo_9V_3PO_{40}$ have been used for producing methacrylic acid via the oxydehydrogenation of isobutyric acid. This reaction proceeds via a redox process involving lattice oxygen from the Keggin structure of the catalyst molecules. Changes in the oxidation state of the catalyst produce a deactivation effect which is reversible by fully reoxidizing the catalyst. An irreversible, long-term type of deactivation related to a loss of molybdenum from the catalyst has also been observed. This occurs through the formation of a volatile Mo-containing gas-phase species. Passage of the IBA feed over a bed of molybdenum trioxide prior to entering the reactor eliminates both types of deactivation.

INTRODUCTION

During the last decade, the world demand for methylmethacrylate (MMA) polymers has resulted in MMA production experiencing an annual growth rate of approximately 6–6.5%, with total production capacity reaching 1.4 million tons per year in 1985 (*1*). Over 93% of this production is based on the acetone cyanohydrin process which suffers from the drawbacks of high energy costs and, more importantly of late, environmental problems associated with the disposal of waste ammonium bisulfate. The combination of these drawbacks with the low selling price of MMA ($1.15/kg) relative to the production costs ($1.08/kg) has created interest in producing MMA via alternate routes based on C_4 or C_3 feedstocks, which are estimated to have MMA production costs of $0.89/kg and $0.83/kg, respectively (*1*).

The favorable economics and reduced environmental problems have resulted in approximately 7% of the current world MMA production coming from C_4 feedstocks via the direct two-step oxidation of isobutylene with ternary butylalcohol as an intermediate. Despite enjoying the same advantages, the large-scale production of MMA based on C_3 feedstocks (propylene/syngas route) has yet to occur. One reason for this is due to the difficulties associated with the oxydehydrogenation of isobutyric acid (IBA) to produce methacrylic acid (MAA). The most promising catalysts for the conversion of IBA to MAA have been found to be heteropolyacid catalysts with the overall composition $M_yH_{3+x-y}V_xPO_{40}$ (where $x = 0, 1, 2, \ldots$, and $M = Li^+$, Na^+, K^+, Cs^+, etc.) for which selectivities to MAA of over 70% can be achieved (*2*). Unfortunately, these catalysts can deactivate relatively quickly and this has prevented their use industrially. The mechanism underlying this deactivation is not well understood, and it is the purpose of this work to elucidate the details of the deactivation process with the aim of developing a method to stabilize these catalysts.

REACTION SYSTEM

Detailed descriptions of the chemistry and properties of heteropolyacid (HPA)

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catalysts having the overall composition $H_{3+x}Mo_{12-x}V_xPO_{40}$ have been given by Pope (*3*), Tsigdinos (*4*), and Misono (*5*). These catalysts are not mixtures of the bulk oxides; rather the catalyst molecules have a Keggin structure with a PO_4 grouping at the center surrounded by four Mo_3O_6 (with V possibly substituted for Mo) groupings which are connected together by 12 oxygen atoms. Thus, the oxygen atoms are present in four structurally distinct locations: (1) 4 central oxygen atoms between the four Mo_3O_6 groupings and the central phosphorous atom; (2) 12 oxygen atoms terminally bonded to individual Mo (or V) atoms; (3) 12 oxygen atoms in bridging positions between Mo (or V) atoms within each Mo_3O_6 grouping (three per grouping); and (4) 12 oxygen atoms which connect the corners of the four Mo_3O_6 groupings together. The bridging and corner-sharing oxygen atoms, which are bound quite similarly in the HPA molecule, are believed to be the most important for selective oxidation reactions (*5, 6*).

Shown in Fig. 1 is the overall reaction scheme presented by Akimoto (*7*) for the oxydehydrogenation of IBA on heteropolyacid catalysts. Formation of MAA is assumed to occur via the consecutive homolytic abstraction of hydrogen from adsorbed IBA intermediates. However, the exact details of this process are still uncertain, as an alternate heterolytic reaction scheme has also been proposed by Otake and Onoda (*8*). The formation of MAA is not believed to consume the lattice oxygen atoms directly; instead, the oxygen is needed to remove the two protons (with the commensurate production of water) which result when IBA is converted to MAA.

Two primary alternate reactions can occur when IBA is contacted with HPA catalysts. The first is a decomposition reaction in which IBA is converted to propylene, carbon monoxide, and water (the reverse of the process underlying the synthesis of IBA). This reaction is believed to be catalyzed by Brønsted acid sites on the catalyst, and Otake and Onoda (*9*) have provided a detailed mechanism for the decarboxylation process. According to them, the formation of propylene is initiated by protonation of the carboxylic group, followed by the consecutive splitting off of water and CO. Evidence for the role of Brønsted acid sites has been provided by Haeberle and Emig (*10*) who have shown that the addition of cesium cations to the HPA molecules results in an almost total elimination of the propylene formation reaction. However, the combination of both basic and acidic functions is necessary for MAA formation, because the fully neutralized cesium salt of the HPA is catalytically inert (*10, 11*).

The other alternate reaction involves the formation of acetone by the decarboxylation of the adsorbed IBA intermediate presumably caused by the interaction between IBA radicals and basic lattice oxygen. Other reactions, such as the production of acetic acid or the total combustion of the reactant or product species can also occur,

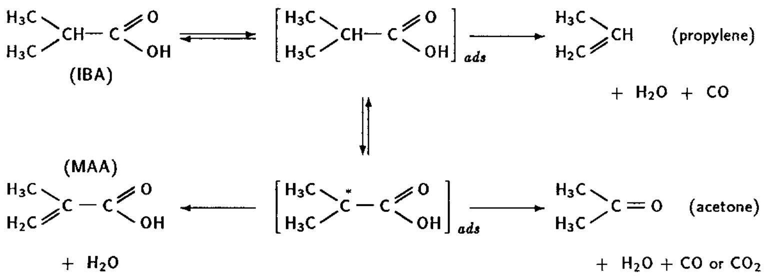

FIG. 1. Overall reactions for the oxydehydrogenation of isobutyric acid.

but these reactions can usually be avoided by the proper choice of reaction conditions. Water is formed in equimolar amounts with each of the three products, propylene, acetone, and MAA. However, from the overall reaction scheme it is seen that only the formation of MAA and acetone consume lattice oxygen. Thus, the rate of propylene formation is not directly influenced by the oxidation state of the catalyst. However, the oxidation state can affect the rate of the dehydrogenation reaction by altering the basicity of the Keggin ions, which can indirectly affect the rate of propylene formation.

EXPERIMENTAL

Two HPA catalysts, $H_5Mo_{10}V_2PO_{40}$ (V_2 catalyst) and $H_6Mo_9V_3PO_{40}$ (V_3 catalyst), were used for examining the reaction kinetics and deactivation behavior. These catalysts were prepared by boiling stoichiometric amounts of molybdenum trioxide, vanadium pentoxide, and phosphoric acid (obtained from Merck GmbH) in water. After vacuum filtration of the solution through a 7-μm quartz filter the solid catalysts were obtained by recrystallization at room temperature, followed by drying and calcination at 340°C for 5 h. The solids were then crushed and sieved, and catalyst particles with a diameter of approximately 0.5 mm were used in the subsequent experiments. XFS analysis showed that the solids produced by this procedure have the correct Mo : P and V : P ratios of 10 : 1 and 2 : 1 or 9 : 1 and 3 : 1, respectively. However, from ^{31}P NMR measurements it was found that the catalysts are not pure substances; instead the V_2 catalyst contains a certain fraction of V_1- and V_3-based compounds. Similarly, the V_3 catalyst contains HPA molecules with other numbers of substituted vanadium atoms. From BET measurements, the specific surface areas of the fresh V_2 and V_3 catalysts were found to be 1.7 m^2/g and 1.4 m^2/g, respectively.

The examination of the kinetic and deactivation behavior was carried out using the equipment shown in Fig. 2. Helium (99.996%), nitrogen (99.999%), and oxygen (99.6%) were obtained from Linde AG, and their flow rates were regulated by electronic flow controllers. Helium was used as an inert carrier into which the feed IBA was evaporated. Nitrogen was used to provide a TCD reference peak. The IBA was reagent grade purity (98%) obtained from Fluka. The flow of the IBA into the evaporator was set using a pulsation-free double recip-

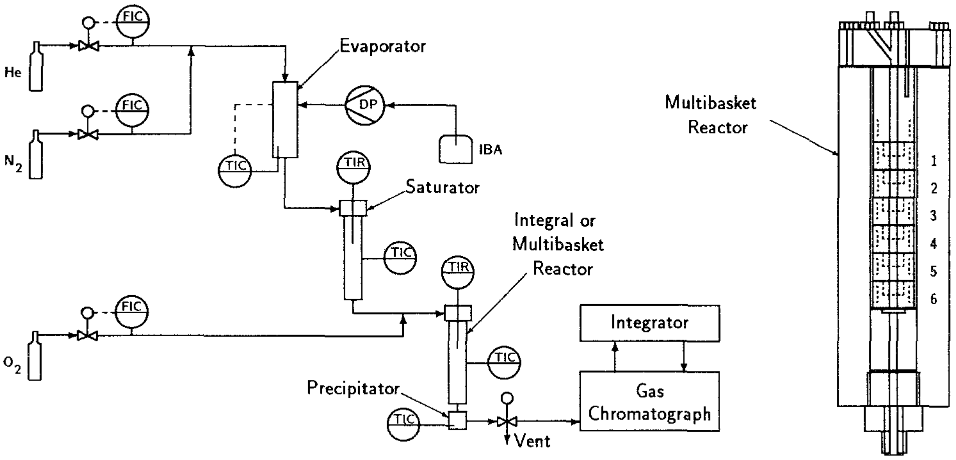

FIG. 2. Schematic of experimental fixed-bed reactor system with molybdenum feed saturator and multibasket reactor (T, temperature, F, flow, I, indicator, R, recorder, C, controller, DP–IBA, pump).

rocating pump, and the temperature of the evaporator was held constant at 220°C. The flow from the evaporator could be passed through the vessel labeled "saturator" in Fig. 2, or alternatively the saturator vessel could be removed, in which case the IBA-containing stream was passed directly to the reactor containing the HPA catalyst. At this point, the IBA-containing stream was combined with the oxygen feed stream just prior to passing over the catalyst bed. The saturator vessel contained MoO_3 and its function will be described later. Except where specifically indicated, the saturator vessel was not used, and thus the IBA stream normally passed directly from the evaporator to the reactor.

Two different fixed-bed reactors were used. The first was of a standard design, constructed from 10-mm-i.d. stainless-steel tubing, and it was heated electrically. Glass pellets were placed above and below the catalyst bed to ensure that the feed stream was well mixed and to preheat the gas to the reaction temperature. The catalyst bed was also diluted with glass pellets (1 : 5) in order to ensure isothermal reaction conditions. From 0.5 to 3 g of catalyst was normally placed in the reactor. This integral reactor was primarily used for kinetic studies. The outlet gas composition was determined using a microprocessor-controlled gas chromatograph with both FID and TCD.

For the experimental investigation of the deactivation behavior, a modified integral reactor (multibasket reactor shown in Fig. 2) was used (*10*). The special segmented inner device consisted of six reactor segments (baskets), each of which could contain approximately 1.5 g of glass pellets and catalyst. The inner diameter of the segments was 10 mm, so as to have flow conditions similar to the standard integral reactor. Following use under reaction conditions, the segments could be separated and the catalyst removed. Each of the six batches of catalyst could then be separately examined (in the standard integral reactor) to determine the variation in catalyst activity with axial location. Following the activity determination, a composition analysis using XFS could be performed to determine the Mo : P and V : P ratios for the catalyst from each basket.

RESULTS AND DISCUSSION

Types of Deactivation

The initial experiments, shown in Fig. 3, were concerned with determining the general reaction and deactivation characteristics of the V_2 and V_3 catalysts using the

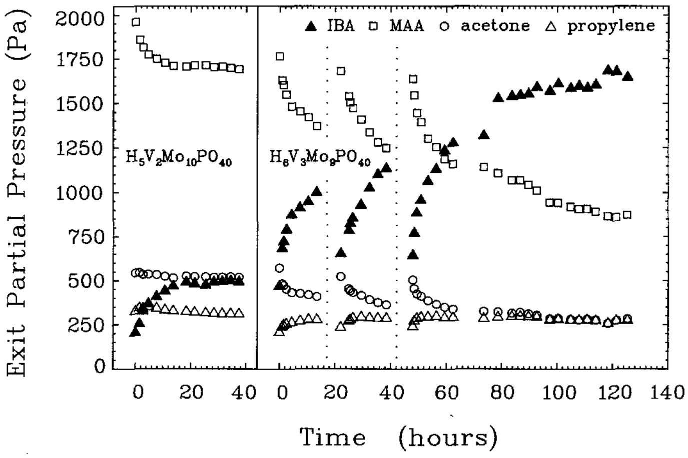

FIG. 3. Typical reaction–deactivation behavior using V_2 and V_3 catalysts (reaction conditions: $T = 590$ K, $P_{IBA,feed} = P_{IBAf} = 3$ kPa, $P_{O_2,feed} = 16$ kPa, 1.5 mol/h total flow rate, 2 g catalyst).

standard integral reactor. Prior to use, each catalyst was pretreated for at least 6 h at the reaction temperature using purified air and then calcined for 1 h under air at 340°C. For both types of catalyst, it is seen that the fully oxidized state has the highest activity for MAA production, and that this initial activity decreases rapidly after the introduction of the IBA-containing feed.

The similarity of the initial decrease for the two catalyst types can be shown by postulating that in both cases the initial activity decreases exponentially according to

$$a = a_r + a_0 e^{-bt}, \qquad (1)$$

where a_r is the "residual" activity remaining after the initial rapid decrease, with overall activity, a, based on the assumption of pseudo-first-order kinetic behavior. In Fig. 4 (first two lines) it is seen that the use of Eq. (1) in a semilogarithmic coordinate system produces straight lines with similar slopes (similar values of b) for both catalysts. Thus, the initial rate of activity decrease is exponentially dependent on the reaction time and is independent of the catalyst composition. Qualitatively similar initial deactivation effects have been observed for HPA catalysts of other compositions (*2, 7, 12, 13*). This leads to the conclusion that the initial deactivation is related to the oxidation state of the catalyst and thus should be reversible if the catalyst is reoxidized. Shown in Fig. 3 are reoxidation experiments using the V_3 catalyst in which three cycles of oxidation (approx. 6 h) with a purified air feed mixture followed by reaction (approx. 16 h) with the IBA/O_2 feed mixture were carried out. It is seen that only a certain fraction of the V_3 catalyst activity was recovered after each reoxidation; however, as shown in Fig. 4, the rate of initial deactivation is the same for all of the cycles. Other experiments have shown that longer reoxidation times do not result in any further recovery of activity.

From the values given in Fig. 4 it is seen that a_r decreases by a constant amount from cycle to cycle; thus, the irreversible loss of activity varies linearly with reaction time. However, this long-term deactivation depends quite markedly on the catalyst composition. As is shown in Fig. 3 for the V_2 catalyst, it is seen that after the first 16 h, the rate of decrease in MAA activity lessens, and only a very slight further decrease occurs over the next 24 h. Longer term experiments with the V_2 catalyst show that the MAA activity continues to decrease very slowly. This is in sharp contrast to the V_3 catalyst where the MAA activity decreases quite noticeably over the 50-h period at the end of the third cycle. Experiments with catalysts of other compositions,

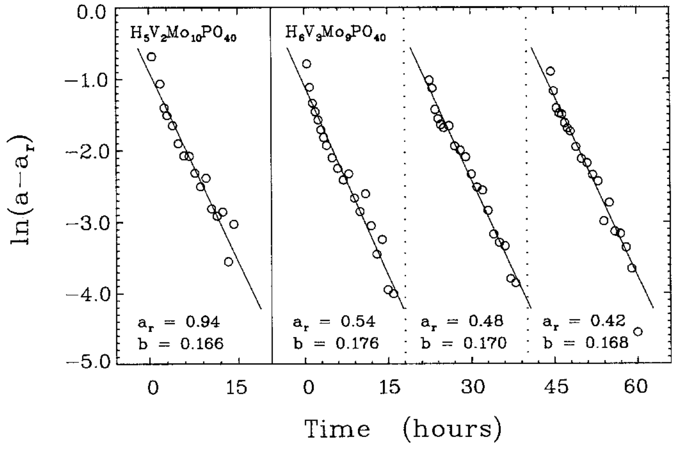

FIG. 4. Exponential activity decrease after reoxidation.

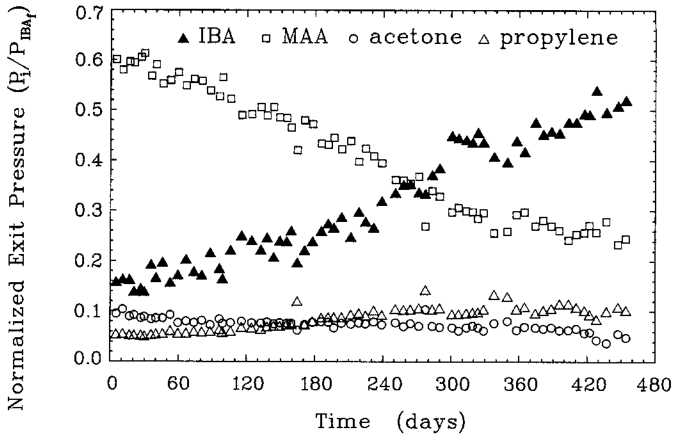

FIG. 5. Long-term linear activity decrease.

similar to those used by Haeberle and Emig (*10*) in which cesium was added to the HPA molecule, have shown that the rate of the long-term linear activity decrease can be reduced but cannot be totally eliminated. This is shown in Fig. 5, where a very stable catalyst was subjected to constant feed conditions for over 450 days. It is seen that a linear decrease in the MAA activity occurred over most of the duration of the experiment.

Effects on Acetone and Propylene

In the foregoing, the discussion has been concerned solely with the MAA activity. However, certain aspects of the activity for acetone and propylene formation are also of interest. In Figs. 3 and 5 it is seen that the decreased activity for MAA production is also accompanied by an activity decrease for acetone production. However, the rate of the decrease for acetone is only a fraction of that experienced by MAA. This indicates that at some point the reaction pathways from IBA to MAA or acetone must involve different types of active sites. When MoO_3 (bulk oxide) is used as a catalyst for this reaction (*14*) it is found that essentially only acetone and propylene are produced (in addition to total oxidation products) with very little MAA being formed, which indicates that differences in the types of Mo species are probably responsible for the differences between MAA and acetone production.

Contrary to that found for MAA and acetone, the production rate of propylene increases during the usage of the catalyst. The increase in propylene formation is mainly due to the increase in the IBA concentration. In addition, increased propylene production could also be partially due to an increase in the number of reduced sites (oxygen vacancies), because the adsorption of product water on reduced sites will increase the number of Brønsted sites. These observations confirm that, unlike the MAA and acetone formation reactions, the production of propylene does not directly involve lattice oxygen. This is consistent with the kinetic model proposed by Haeberle and Emig (*10*), where it was shown that the formation of propylene has a positive-order dependence on the concentration of IBA, whereas the rates of MAA and acetone production are best described by a Mars–van Krevelen-type redox model.

Mechanism of Irreversible Deactivation

A change in the structure of the relatively complex HPA catalyst molecule is the most probable cause of the long-term, irreversible deactivation. The main indication of this was the appearance of a wall coating with various shades of blue near the exit of the integral reactor which indicated that molybdenum-containing compounds had been deposited at this location. The possible loss of Mo from the catalyst was further examined by replacing the standard integral reactor with the multibasket reactor shown in Fig. 2. Following long-term experiments in which the feed and reactor conditions were held constant, the six batches of catalyst were removed and individually tested for MAA activity using the standard integral reactor. In addition to the activity determination, each batch of catalyst was analyzed by XFS so as to determine the ratios of molybdenum and vanadium to phosphorous. Typical activity and composition results for each batch after 50 h of use under reaction conditions are shown in Fig. 6.

It is seen that only about 40% of the original activity is still present for the catalyst at the inlet of the reactor (Sections 1 and 2), whereas the catalyst near the exit of the reactor (Section 6) still possesses close to its original activity. The activity in the first couple of sections has been reduced to approximately that expected from mixtures of the bulk oxides. It is further seen that the reduction in activity is accompanied by a decrease in the amount of molybdenum relative to phosphorous or vanadium in the catalyst. However, activity and catalyst composition are not directly proportional as a loss of only 6% of the Mo is accompanied by a 60% decrease in the activity. If only the HPA molecules near the exterior surface of a catalyst pellet take part in the reaction, then a strong dependence of activity on composition would be expected because a small overall Mo loss would translate into an almost total loss from the molecules near the surface. This loss of Mo (and V) can become much larger than that shown in Fig. 6, as approximately 65% of the molybdenum and 36% of the vanadium were lost from the catalyst in reactor Section 1 following 280 h of use under reaction conditions. Unfortunately, this type of experiment cannot establish a cause–effect relationship, as it is not clear whether the loss of Mo is responsible for the deactivation or if the loss of Mo occurs subsequent to the activity change, perhaps following a breakdown of the Keggin structure.

If it is assumed that the loss of molybdenum occurs via a gas-phase species, then in order to account for the catalyst weight loss the average partial pressure of this compound in the reactor effluent must be in the range 0.05 to 0.39 Pa (data from Fig. 6 plus additional experiments not reported herein). However, the procedure by which

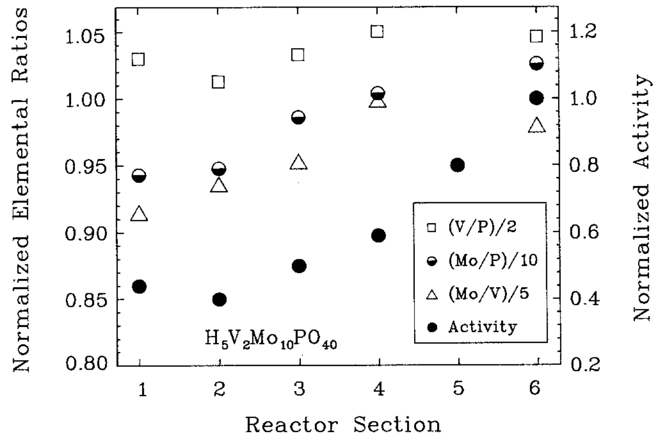

FIG. 6. Axial profiles of activity and catalyst composition after 50 h of reaction (reaction conditions as in Fig. 3).

such a species would be formed is not immediately obvious, as several possibilities exist. For example, oxides of molybdenum are known to sublimate with a relatively high vapor pressure (*15, 16*); molybdenum can under certain conditions readily form a $Mo(CO)_6$ gas-phase species when in the presence of CO (*17*); volatilization of MoO_3 in the presence of water vapor has been reported (*18, 19*); and loss of Mo from Mo/Fe oxide catalysts during methanol oxidation has been observed (*20*). Using the data from the literature, it is possible to estimate the expected exit partial pressure of an Mo-containing gas-phase species under typical reaction conditions for each of the above possibilities. These values are shown in Table 1 where it is seen that only the findings of Popov concerning Mo loss during methanol oxidation (*20*) are in the same range as the observations for the HPA catalysts.

TABLE 1

Partial Pressure of Molybdenum-Containing Gas-Phase Species[a]

	P_{Mo} (Pa)
V_2 catalyst under reaction conditions, experimental (this work)[b]	0.05–0.39
MoO_3 sublimation, calculated (*15*)	2×10^{-8}
$Mo(CO)_6$ formation, calculated for P_{CO} = 0.4 kPa (*17*)	10^{-25}
$MoO_2(OH)_2$ formation, calculated for P_{H_2O} = 2 kPa (*18, 19*)	2×10^{-4}
Volatilization from Fe/Mo catalyst with methanol, calculated (*20*)[c]	0.056
Volatilization from HPA with methanol, experimental (this work)[c]	0.067
Volatilization from HPA with acetone, experimental (this work)[c]	0.008
Volatilization from HPA with isobutyric acid, experimental (this work)[c]	0.06–0.16
Volatilization from HPA with methacrylic acid, experimental (this work)[c]	0.14–0.17

[a] P_{total} = 101.3 kPa, 1.5 mol/h total feed rate, T = 590 K except where otherwise noted.

[b] T = 580–630 K, $P_{IBA,feed}$ = 3 kPa, $P_{IBA,exit}$ = 0.5 to 1 kPa, $P_{MAA,exit} \approx 1.5$ kPa.

[c] P_x = 1 kPa (x = isobutyric acid, methacrylic acid, acetone, or methanol).

The assumption, used in the preceding calculations, that the molybdenum in the HPA molecules behaves similarly to that in MoO_3 or in a Mo/Fe catalyst, was tested by passing methanol (with an inert carrier) at a known, constant flow rate over a measured quantity of HPA catalyst for a fixed period of time. At the end of the experiment the amount of molybdenum in the condensed liquid effluent was determined gravimetrically following evaporation of the liquid with calcination of the precipitate. From this, the partial pressure of a volatile Mo-containing gas-phase species in the effluent stream was calculated. From Table 1 it is seen that the effect of methanol on the HPA catalyst was very similar to that for the Mo/Fe catalyst. Because the action of methanol cannot be used to explain the weight loss during IBA oxydehydrogenation, additional experiments were carried out in which IBA, MAA, or acetone was used instead of methanol. In Table 1 it is seen that the effect of either IBA or MAA is sufficient to account for the experimental weight loss under reaction conditions. The mechanism by which a gas-phase Mo-containing species is formed is not known, but it would appear that the hydroxyl group which is present in methanol, IBA, and MAA probably plays an important role.

Saturation of the Feed with Molybdenum

Further evidence for the existence of a gas-phase Mo-containing species was obtained by using the saturator vessel shown in Fig. 2. This vessel was filled with approximately 24 g of MoO_3 and the IBA feed stream (with an inert carrier) was passed over this bed in order to produce a feed stream containing a gas-phase Mo species. Shown in Fig. 7 are the effects of using this Mo-saturator vessel. Initially the V_2 catalyst had been used under reaction conditions for approximately 130 h without the saturator. A very slight deactivation of the MAA activity can be seen in the 30-h section shown in the initial part of Fig. 7. Following this, the IBA feed was passed

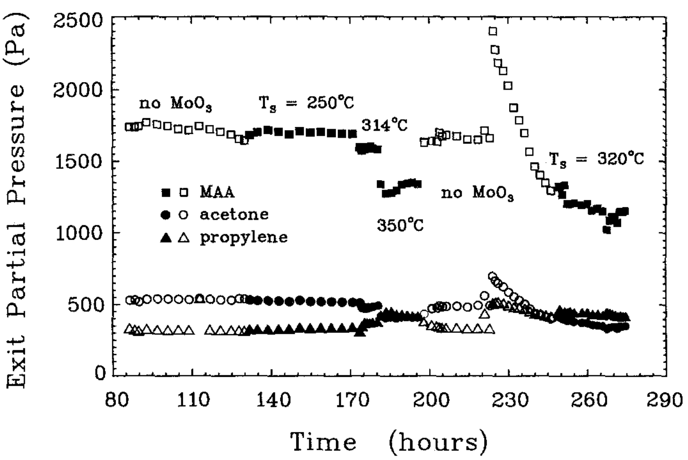

FIG. 7. Effect of molybdenum saturator temperature on activity (reaction conditions as in Fig. 3 except $P_{IBA,feed} = 5$ kPa for final 55 h).

through the saturator which was operated at 250°C. It is seen that the activity is constant for the next 30-h period. Successive increases in the saturator temperature to 314 and 350°C result in rapid changes to lower, but constant, levels of MAA activity. Removal of the saturator results in a rapid increase in the MAA activity back to its original level. These effects are not due to decomposition of the IBA in the saturator vessel because, as shown in Table 2, the IBA conversion in the saturator is quite low. Thus, the presence of a volatile Mo-containing species is confirmed. The effect of using the saturator is further illustrated in the right-most section of Fig. 7, where following approximately 20 h of operation under the earlier conditions, the partial pressure of IBA in the feed was increased from 3000 to 5000 Pa. This results in an instantaneous increase in the exit partial pressure of MAA followed by very rapid deactivation over the next 20 h of operation. As shown in Fig. 7, the rate of deactivation can be reduced by once again passing the IBA feed stream through the saturator, this time at 320°C.

The effect on the deactivation behavior of using the Mo saturator is most clearly shown in Fig. 8. A fresh batch of V_3 catalyst was pretreated and calcined in the standard way. Following this, the IBA feed stream was passed through the saturator (operated at 250°C) and then sent to the reactor. The effluent partial pressures for this mode of operation are shown by the filled symbols in Fig. 8. In contrast to that which occurs when the saturator was not used (open

TABLE 2

Decomposition of IBA in the Molybdenum Saturator

Temperature (°C)	Outlet partial pressure (Pa)				
	P_{CO+CO_2}	$P_{propene}$	$P_{acetone}$	P_{IBA}	P_{MAA}
	$P_{IBA,inlet} = 3000$ Pa				
300	0	0	0	3000	0
320	0	7	0	2980	0
350	51	60	0	2922	13
380	216	211	0	2751	28
	$P_{IBA,inlet} = 5000$ Pa				
320	0	16	25	4961	0
340	5	35	26	4944	0
360	22	88	27	4895	0
380	169	200	31	4747	16

Note. 24 g MoO_3 (0.5- to 2.5-mm pellets), no oxygen in the feed, $P_{total} = 101.3$ kPa, 1.5 mol/h total feed rate, GC resolution ±10 to 20 Pa.

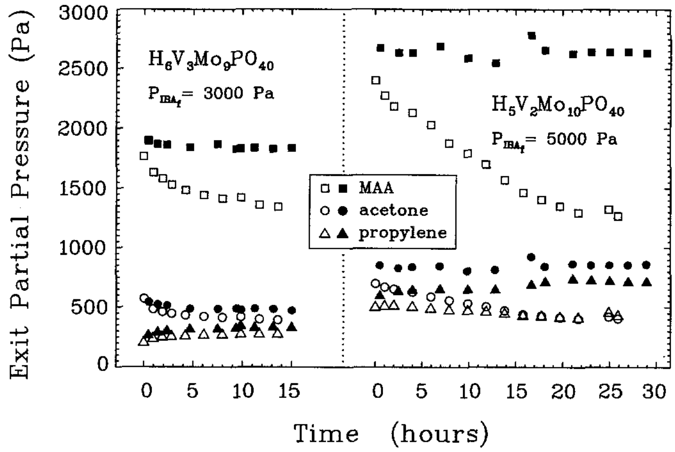

FIG. 8. Effect of molybdenum in the feed using V_3 and V_2 catalysts (reaction conditions as in Fig. 3 except $P_{IBA,feed}$ = 5 kPa for V_2 catalyst).

symbols, data from Fig. 3), the activity is very constant and remains so even beyond the 16-h period shown in Fig. 8. Similar effects were also observed for the V_2 catalyst, as shown by comparing the filled and the open symbols in the right-most portion of Fig. 8. Thus, presaturation of the feed with molybdenum results in an elimination of both the short-term and the long-term types of deactivation.

The elimination of the long-term deactivation is readily understood if, as previously described, the long-term deactivation is due to a loss of molybdenum from the HPA catalyst molecules. If this is the case, then the presence of Mo in the feed would eliminate the driving force for the deactivation. It is worth noting however, that subsequent use of the Mo saturator after deactivation has occurred cannot recover the lost activity. This is clearly shown in the last section of Fig. 7. Thus, the long-term deactivation is not a reversible process.

The elimination of the short-term deactivation is more difficult to understand. If the short-term deactivation is dependent on the oxidation state of the catalyst, then the presaturation of the feed with Mo must in some fashion act to keep the oxidation state of the catalyst at a high level. A possible explanation for this is that the gas-phase Mo-containing species can adsorb onto the catalyst surface and enhance the adsorption of oxygen. One indication that such an adsorption process occurs is the behavior shown in Fig. 7 when the temperature of the saturator was increased from 314 to 350°C. The large decrease in the activity as the temperature was increased is probably due to a blockage of the active sites by an adsorbed Mo-containing species. The speed with which the new constant activity levels are reached is consistent with adsorption/desorption processes which typically proceed quite rapidly relative to other processes. There is apparently an optimal temperature for the saturator, as too low a temperature will permit long-term deactivation to occur due to insufficient molybdenum entering with the feed, whereas too high a temperature results in a stable, but low-activity, catalyst due to blockage of the active sites.

A further indication that Mo presaturation of the feed directly affects the catalyst surface is shown by the BET adsorption curves in Fig. 9. Starting with a fresh catalyst, with the IBA feed passed through the Mo saturator, it is seen that there was a fivefold increase in the surface area of the catalyst after 26 h under reaction conditions. When the experiment was repeated

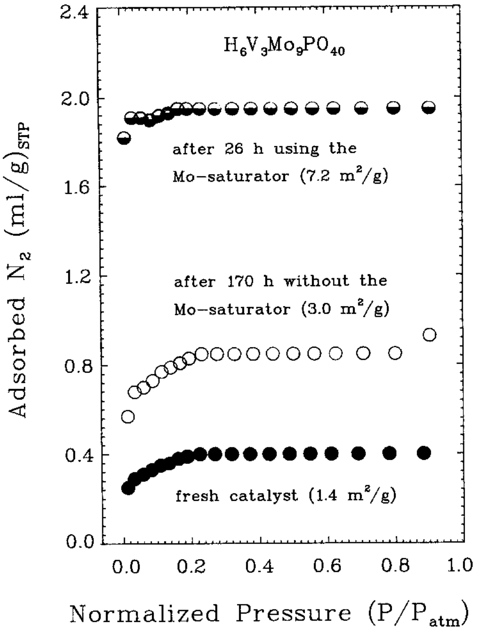

FIG. 9. Effect of deactivation and molybdenum saturation on the BET adsorption characteristics.

without using the Mo saturator, it was found that there was only a slight increase in the catalyst surface area after 26 h of use under reaction conditions (not shown in Fig. 9), with a doubling of the area after 170 h of use. It is also seen in Fig. 9 that the use of the Mo saturator produces a marked change in the pore size distribtion of the catalyst. Relative to the fresh catalyst it appears that the pore size distribution is much narrower and is shifted to smaller pore sizes after using the saturator. This effect was not observed when the saturator was not used.

The blockage of active sites, as shown in Fig. 7, indicates that the adsorbed Mo-containing species is either catalytically inactive, or, at most, is no more active than bulk molybdenum trioxide (*14*). Following the experiment using the Mo saturator, the glass pellets in the reactor were separated from the catalyst pellets. The glass pellets had become visibly covered by a Mo-containing deposit. The catalytic activity of these glass pellets was then tested in the reactor. It was found that only small amounts of propylene and acetone were formed, which confirmed that the heteropolyacid was the active catalyst for MAA formation.

Deactivation caused by the loss of molybdenum has also been reported for methanol oxidation (*20*) and ammoxidation (*21*) catalysts. In the patents concerned with the ammoxidation reaction it has been claimed that Mo-containing catalysts can be stabilized by incorporating excess Mo compounds into the catalyst, or by feeding bulk molybdenum oxide or mixed molybdenum–metal oxides into a fluidized catalyst bed. The mechanism by which these methods serve to stabilize catalyst activity is in all likelihood the same as that described in this study.

SUMMARY

The oxydehydrogenation of isobutyric acid to form methacrylic acid has been examined using heteropolyacid catalysts with the composition $H_{3+x}Mo_{12-x}V_xPO_{40}$ for $x =$ 2 and 3. It has been found that these catalysts display both exponential and linear types of deactivation behavior. The reversible, short-term exponential activity decline is related to the oxidation state of the catalyst, reflecting the fact that the overall reaction proceeds via a redox-type mechanism. The rate of the exponential activity decline is independent of the catalyst composition, and the activity can be recovered by fully reoxidizing the catalyst. The irreversible, long-term linear decrease in the activity has been found to be related to a loss of molybdenum from the catalyst. This occurs via the formation of volatile gas-phase molybdenum-containing species. The gas-phase species form via the interaction of isobutyric acid and/or methacrylic acid with molybdenum. Both types of deactivation can be eliminated by presaturating the feed stream with molybdenum. This can be accomplished by passing the isobutyric acid feed stream over a bed of molybdenum trioxide prior to being sent to the reactor. The volatile Mo-containing species reversibly adsorb onto the surface of the catalyst molecules and prevent the loss of molybdenum from the catalyst and in addition produce an increase in the overall rate of oxygen adsorption. Stable catalyst activity has been found to be achievable even under quite severe reaction conditions.

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