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Palladium Salts of Heteropolyacids as Catalysts in the Wacker Oxidation of 1-Butene

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Palladium salts of heteropolyacids (PdHPAs) of the Keggin series $H_{3+n}PV_nMo_{12-n}O_{40}$ supported on silica, have been used successfully as catalysts in the gas-phase Wacker oxidation of 1-butene. In such catalysts the palladium reaction centre and the redox component are combined in one complex. At 343 K and atmospheric pressure a high initial butanone yield of more than $0.2\ g\ g_{cat}^{-1}\ h^{-1}$, in combination with a very high butanone selectivity of more than 98%, can be obtained. In the steady state, the activity of the catalyst is more than a factor of 10 lower than the initial activity, due to slow reoxidation of reduced palladium–heteropolyanion complexes. The rate of reoxidation depends on the composition of the HPA, the palladium loading, and the reaction conditions. The reaction order of 0.5 in the O_2 partial pressure indicates the dissociation of dioxygen to be rate determining. The degree of hydration of the HPA appears to be important for the activity and stability of the catalysts. Spent catalysts can be regenerated by an oxidation treatment in air at temperatures around 525 K. Regeneration becomes more difficult with high palladium loading of the catalyst. © 1995 Academic Press, Inc.

INTRODUCTION

In our previous article (1), we reported that heteropolyanions (HPAs) of the Keggin 12 series $H_{3+n}PV_nMo_{12-n}O_{40}$ are suitable redox components in heterogeneous Wacker oxidation catalysts. At 343 K these catalysts, consisting of a monolayer of the HPA on silica covered with a submonolayer of palladium sulfate, show initial butanone yields of $0.07\ g \cdot g_{cat}^{-1} \cdot h^{-1}$ with a selectivity of more than 95%. The steady-state activity of the catalysts is lower due to the slow reoxidation of the reduced HPA by dioxygen. The rate of reoxidation can be accelerated by increasing the number of vanadium atoms per Keggin unit, but is also increased when the acidic protons of the heteropolyacid are replaced by transition metal cations, such as Cu^{2+} or Ni^{2+}. The stability of the catalysts is also improved by this exchange (1).

Instead of copper or nickel cations, palladium can be used as a countercation in HPA salts. Application of palladium as a countercation strongly increases the activity of the catalyst as compared to that of the acid-based ones. The application of palladium salts (PdHPAs) in heterogeneous Wacker oxidation catalysts is very attractive, as in this case the palladium centre and the redox component are joined in one complex. This ensures direct contact between the palladium site and the HPA, facilitating the transfer of electrons to the HPA. The application of palladium salts also simplifies the preparation of the catalysts, since both the palladium and the redox component can now be deposited in one impregnation step. When PdHPA salts are applied, the catalytic cycle in 1-butene oxidation can be described by the reactions

$$\mathrm{Pd(II)}\mathbf{HPA} + C_4H_8 + H_2O \rightarrow \mathrm{Pd(0)}H_2\mathbf{HPA} + C_4H_8O \quad [1]$$

$$\mathrm{Pd(0)}H_2\mathbf{HPA} + \tfrac{1}{2}O_2 \rightarrow \mathrm{Pd(II)}\mathbf{HPA} + H_2O, \quad [2]$$

in which $\mathrm{Pd(0)}H_2\mathbf{HPA}$ represents the reduced palladium salt.

The steady-state activity of all heteropolyacid- and heteropolysalt-based catalysts is much lower than the initial activity of these catalysts, due to the slow reoxidation of the reduced HPAs (1). The rate of reoxidation depends not only on the composition of the HPAs but also on the concentration of reactants in the feed and the reaction temperature. By optimizing the reaction conditions, the rate of reoxidation, and hence the steady-state activity, might be improved. The results of a study of the variation of the reaction conditions are presented in this paper. The regeneration of used catalysts by an oxidation treatment is also discussed.

EXPERIMENTAL

Heteropolyacids (HPAs) of the series $H_{3+n}PV_nMo_{12-n}O_{40} \cdot xH_2O$, where n is 2 or 3, were prepared according to the procedure described in a previous paper (1), following the prescriptions of Brauer (2) and Tsigdinos

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and Hallada (3). $H_3PMo_{12}O_{40} \cdot 27H_2O$, obtained from Merck (reagent grade), was used without further pretreatment. The palladium salts from the heteropolyacids were prepared according to the procedure described by Tsigdinos (4). The colour of the product was dark green for $Pd_{1.5}PMo_{12}O_{40}$, pale brown for $Pd_{2.5}PV_2Mo_{10}O_{40}$, and reddish brown for $Pd_3PV_3Mo_9O_{40}$. The protons are not completely exchanged for palladium cations and the fraction of exchanged protons decreases with increasing number of vanadium atoms per Keggin unit (1).

The heteropolyacids and the palladium salts were deposited on a silica support, viz. Davisil-300, BET surface area 287 m^2/g. Two types of catalyst were prepared from the heteropolyacids and palladium salts. The first type consists of a monolayer of heteropolyacid supported on silica, which is, in a second step, impregnated with a palladium sulfate solution (0.02 *M* $PdSO_4 \cdot 2H_2O$ in 0.18 *M* H_2SO_4), as described elsewhere (1). The second type of catalyst is prepared from the palladium salts of the HPAs and consists of a monolayer of the palladium salt on the silica support. All components were deposited by impregnation to incipient wetness with an aqueous solution. The loading of the HPAs was chosen so that a monolayer of Keggin units was arrived at, presuming that the anions are uniformly spread over the surface and that one Keggin unit occupies 1.44 nm^2. Monolayer coverage corresponds to a loading of approximately 42 wt%. The catalysts were dried overnight at 343 K in air and stored at room temperature in a desiccator over calcium chloride.

Catalysts were tested in the oxidation of 1-butene to butanone in conventional microflow equipment under standard conditions: at 343 K, under atmospheric pressure, and with a feed containing 1% 1-butene and 7% water in air, as previously described (1).

Water adsorption experiments were performed in a Stanton Redcroft TG-750 thermobalance. Approximately 20 mg of sample was loaded into a platinum cup and heated to the desired temperature. Then the nitrogen flow was saturated with water by bubbling it through a thermostated vessel filled with water. The weight increase due to the adsorption of water on the surface of the sample was registered at several temperatures and for different water concentrations in the feed. The water coverage was calculated from the difference between the weight of the sample in contact with the saturated stream and its weight in dry nitrogen at 675 K.

Catalysts are coded as described in the preceding paper (1).

RESULTS AND DISCUSSION

Performance in 1-Butene Oxidation

Figure 1 shows a characteristic activity profile of HPA-based catalysts, in this case of the palladium salt of $H_3PMo_{12}O_{40}$, designated $PdPMo_{12}$ (1). The high initial level of activity rapidly declines to a lower steady-state level within 1 h. Initially more than 60% of the 1-butene in the feed is converted to butanone with a selectivity of more than 98%, giving a butanone yield of 0.12 $g \cdot g_{cat}^{-1} \cdot h^{-1}$. After half an hour the activity starts to decline and, after 2 h, reaches a value of 0.013 $g \cdot g_{cat}^{-1} \cdot h^{-1}$. In the next 20 h of operation the activity further declines to a yield of approximately 0.005 $g \cdot g_{cat}^{-1} \cdot h^{-1}$. The selectivity to butanone decreases to 90%, the main side product being butanal.

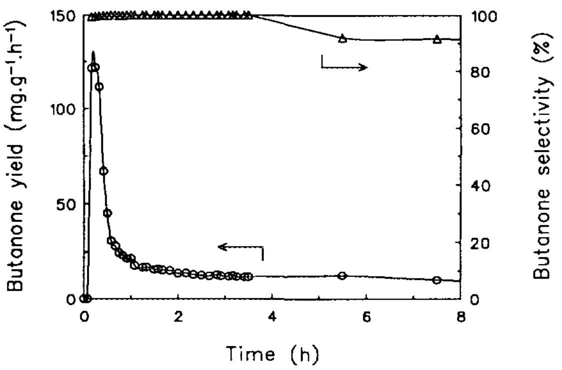

FIG. 1. Butanone yield (○) and selectivity (△) of catalyst $PdPMo_{12}$ at 343 K as a function of time. Feed: 1 kPa 1-butene and 7 kPa H_2O in air.

The initial decrease in activity is a result of reduction of the catalyst under reaction conditions. At the start of the experiment, the rate of butanone formation is determined by the rate of reaction [1]. As the reaction proceeds a larger part of the PdHPAs become reduced and their reoxidation (reaction [2]) becomes rate determining. The rate of reoxidation of the reduced HPAs depends not only on the composition of the HPA, as shown before (1), but also on the reaction conditions.

Kinetics of 1-Butene Oxidation

For heteropolyacid-based catalysts the reoxidation of the reduced HPAs is rate determining under 1-butene oxidation conditions (1). In this section, the kinetics of 1-butene oxidation over palladium salt-based catalysts will be discussed. The influence of the partial pressures of 1-butene, water, and dioxygen in the feed on the activity of the catalysts will be presented and the kinetics will be compared with the kinetics of homogeneous Wacker oxidation with HPAs in the liquid phase, as reported by Matveev *et al.* (5, 6) and Davison (7). All kinetic experiments were performed in the steady state, i.e., the catalyst was first exposed for at least 4 h to the standard reaction conditions and only when the steady state had been reached were the parameters of interest varied.

Variation of the 1-butene partial pressure. Figure 2 shows the butanone yield of catalyst $PdPMo_{12}$ as a func-

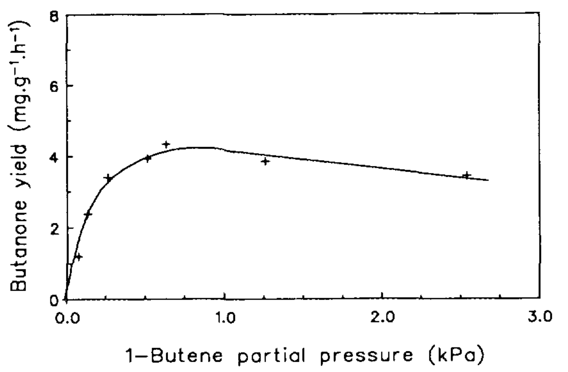

FIG. 2. Butanone yield at 343 K as a function of the 1-butene partial pressure for catalyst $PdPMo_{12}$. Feed: 18 kPa O_2, 7 kPa H_2O, and 76 kPa (C_4H_8 + N_2) of varying composition.

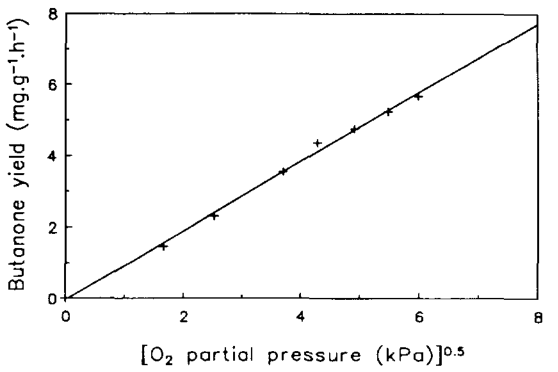

FIG. 3. Butanone yield at 343 K as a function of the square root of the partial pressure of dioxygen in the feed. Catalyst: $PdPMo_{12}$. Feed: 1 kPa 1-butene, 7 kPa water, and 93 kPa of a mixture of N_2 and O_2 of varying composition.

tion of the partial pressure of 1-butene in the feed. The butanone yield initially increases nearly linearly with increasing partial pressure of 1-butene, but it reaches a maximum at 0.6 kPa. Above 0.6 kPa the butanone yield slightly decreases.

Such a maximum in the activity versus alkene-concentration plot was also observed by Matveev (6) in the liquid-phase oxidation of ethene. He attributed this maximum to the formation of different HPA–Pd–ethene complexes with different reactivities. According to Matveev, Pd(0) forms a complex with HPA, which is stabilized by coordination of ethene to the palladium atom. At low partial pressure of ethene, Pd(0) is found in the complexes Pd_2H_2-**HPA**$^{4+}$ (A) and PdH_2**HPA**$(C_2H_4)^{2+}$ (B), whereas at higher ethene pressure the complex PdH_2**HPA**$(C_2H_4)_2^{2+}$ (C) is more abundant. Complexes A and C are less reactive in the reaction with dioxygen and, therefore, high concentrations of one of these complexes lead to a lower overall reaction rate, resulting in a maximum in the activity versus ethene-concentration curve.

The results depicted in Fig. 2 show that the reaction in the heterogeneous case is analogous to the reaction in the liquid phase. This indicates that the reoxidation of the reduced Pd(0)–HPA complex, which is rate determining in the liquid-phase reaction, is rate determining in heterogeneous catalysis as well.

Variation of the dioxygen partial pressure. Figure 3 shows the activity of catalyst $PdPMo_{12}$ as a function of the partial pressure of dioxygen in the feed. The activity of the catalyst steadily increases with increasing dioxygen partial pressure. This supports the supposition that the reoxidation of the reduced Pd(0)–HPA complex is rate determining. The reaction order in dioxygen is approximately 0.5, indicating that the rate-determining step involves the dissociation of dioxygen.

Variation of the water partial pressure. For heterogeneous Wacker oxidation catalysts, based on palladium sulfate impregnated vanadium oxide on titania, a strong influence of the water partial pressure on the activity of the catalysts has been found (8). For the catalysts based on palladium salts of HPAs, described in this paper, the activity is not influenced by the water partial pressure between 4 and 10 kPa. Since the reoxidation of the reduced PdHPA complex is rate determining, only a small influence of the water partial pressure on the reaction rate is to be expected. However, since water is one of the reactants in reaction [1], its presence is essential for the production of butanone.

Figure 4 shows the effect of the removal of water from the feed on the steady-state activity of catalyst $PdPMo_{12}$. After the removal of the water from the feed, after 0.7 h, the activity level drops and becomes almost zero after 1.6 h. The decrease in activity is not instantaneous, however, and the activity remains high for half an hour before it starts to decline. This shows that during this period there has to be an alternative source of water. This source is probably the water from the hydration of the HPA. At

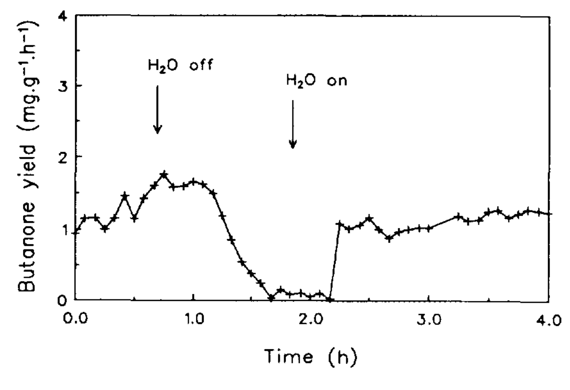

FIG. 4. The influence of the removal of water from the feed on the butanone yield of catalyst $PdPMo_{12}$ at 343 K. Feed: 1 kPa C_4H_8, 18 kPa O_2, 75 kPa N_2, and 7 kPa H_2O, which is removed after 0.7 h and again admitted after 1.8 h.

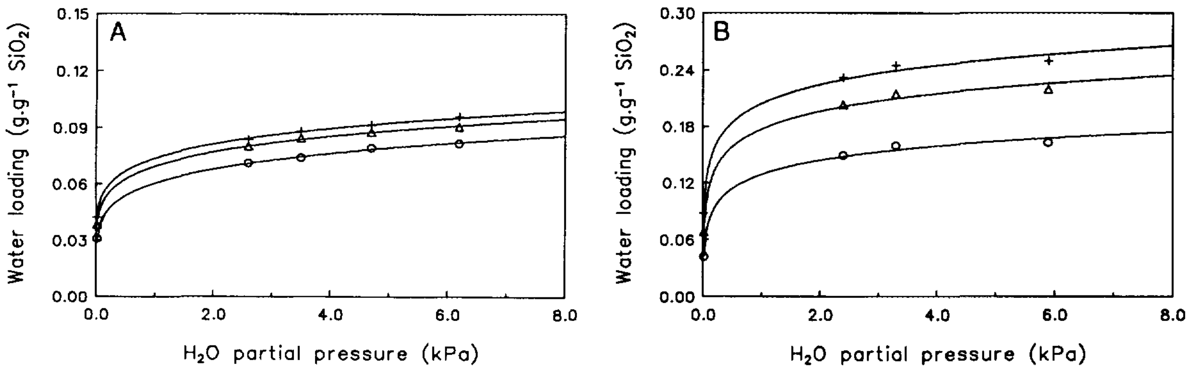

FIG. 5. (A) Physisorption of water (gram water per gram silica) on silica at (+) 331 K, (△) 343 K, and (○) 378 K as a function of the partial pressure of water in the feed. (B) Physisorption of water (gram water per gram silica) on catalyst $PdPMo_{12}$ at (+) 331 K, (△) 343 K, and (○) 378 K as a function of the partial pressure of water.

room temperature the PdHPAs are surrounded by approximately 20 molecules of water (1). TGA profiles show that these water molecules are completely removed only at temperatures above 400 K, indicating that under reaction conditions at 343 K, with water in the feed, the HPAs will possess a high degree of hydration (1). The activity decrease half an hour after water removal from the feed indicates that at that moment all the reactive water molecules surrounding the palladium complex have been removed. When water is again admitted to the feed it takes approximately 0.3 h before the activity of the catalyst is restored, showing that the HPAs must regain a certain degree of hydration before activity is restored. To determine the degree of hydration of HPAs under reaction conditions, the adsorption of water onto the catalyst has been studied at several temperatures and various partial pressures of water.

Figure 5A shows the amount of physisorbed water on the silica support at 331, 343, and 378 K as a function of the partial pressure of water. The amount of physisorbed water is determined from the difference in the weight of the sample at a given partial pressure of water and the weight of the sample in dry air at 675 K. This amount approximately corresponds to a monolayer of water, taking the cross-sectional area of a water molecule to be 0.1 nm^2. The water coverage slightly increases with increasing water partial pressure and with decreasing temperature.

Figure 5B shows the physisorption of water on catalyst $PdPMo_{12}$. The amount of water is given per gram of silica support so that the data can be directly compared with the data in Fig. 5A. Figure 5B shows that in the presence of the PdHPA the amount of water on the catalyst is almost three times as high as on the bare silica support. This indicates that the water is strongly coordinated to the PdHPA. Above 2 kPa the number of water molecules appears to be only slightly influenced by the partial pressure of water. However, a strong influence of the temperature on the degree of hydration of the PdHPA is observed. The degree of hydration of the PdHPA was estimated from the difference in weight between the curves in Figs. 5A and 5B. The degree of hydration strongly decreases with increasing temperature from 24 water molecules per Keggin unit at 331 K, to 20 at 343 K, and to 13 at 378 K. (When the adsorption on silica is neglected then the degree of hydration is 32 water molecules per Keggin unit at 343 K.)

The influence of the reaction temperature. Figure 6 shows the activity of catalyst $PdPV_3Mo_9$ at three different temperatures, viz. at 313, 343, and 373 K. At all three temperatures the activity goes through a maximum and subsequently decreases until the steady-state activity is reached. The initial activity of the catalyst is determined by the rate of reduction of the PdHPA complex (reaction [1]). At 313 and 343 K the conversion is initially 100% and, therefore, the butanone yield is limited by the amount of 1-butene in the feed. When the reaction proceeds, a larger portion of the palladium complexes is reduced and has to be reoxidized by O_2 (reaction [2]). The optimum

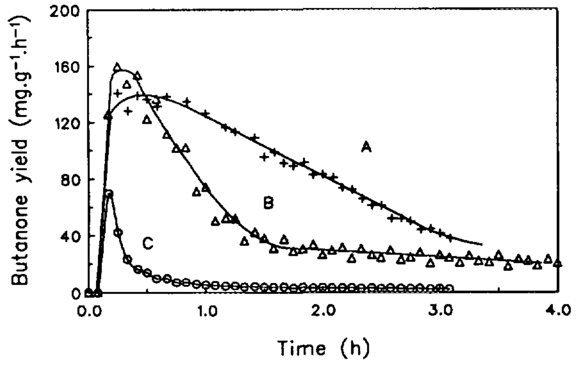

FIG. 6. Butanone yield during the first 3 h of operation of catalyst $PdPV_3Mo_9$ at (A) 313 K, (B) 343 K, and (C) 373 K.

in the activity as a function of the 1-butene partial pressure and the half-order in dioxygen observed above show the rate of reoxidation to be rate determining under 1-butene oxidation conditions. The activity of the catalyst will, therefore, decrease until the rates of reactions [1] and [2] become equal.

Figure 6 shows that the time required to reach the steady-state activity strongly varies with the reaction temperature. When the reaction temperature decreases the initial activity of the catalysts becomes higher and is retained for a longer period of time. This indicates that the rate of reoxidation of the reduced PdHPA increases with decreasing temperature. This was also found by Davison (7) in the liquid phase oxidation of 1-butene.

Since the rate of reoxidation increases with decreasing temperature, the steady-state activity of the catalyst is also expected to increase with decreasing temperature. During the first 3 h this is indeed the case. However, the activity at 313 K steadily decreases and becomes almost equal to the activity at 343 K. The steadily decreasing activity at 313 K might be caused by the high degree of hydration of the HPAs at 313 K. At this temperature, with 7 kPa of water in the feed, the degree of hydration of the PdHPAs is probably more than 50 water molecules per Keggin unit, which might lead to the dissolution of the HPA in its own crystal water. The dissolution of HPAs in their crystal water is also observed during the preparation and drying procedure of these compounds. The dissolution of the PdHPAs on the surface of the catalyst in combination with the reduction during 1-butene oxidation might cause the disintegration of the Keggin units. The low steady-state activity of the catalyst at 313 K might also be caused by deactivation of the catalyst due to accumulation of Pd(0). Further research, however, is required to elucidate this. Still another reason for the low activity might be related to a more extended adsorption of the reaction products on the PdHPAs. Davison (7) reported that the reoxidation of HPAs is inhibited by aldehydes and other oxygen-containing compounds, probably due to coordination of these compounds to the outer oxygen atoms of the HPA. These adsorbed compounds prevent the interaction of dioxygen with the Keggin units, resulting in a lower rate of reoxidation. The low reaction temperature and the high degree of hydration of the PdHPAs at 313 K might result in a slow desorption of the reaction products, thereby inhibiting the reoxidation of the reduced PdHPA.

The much lower initial activity of the catalyst at 373 K as compared to the activity at 313 and 343 K points to a lower rate of reaction [1]. The results of the water adsorption study, described above, show that at 373 K the degree of hydration of the HPA is much lower than at the other temperatures. This possibly explains the lower rate of reaction [1]. The influence of the degree of hydration on the rates of reactions [1] and [2] has to be investigated in more detail to be completely understood. The results obtained thus far, however, indicate that the degree of hydration is very important for the performance and stability of the catalyst.

Regeneration of Catalysts

Since the initial activity of the PdHPA-based catalysts is a factor of 10 higher than their steady-state activity the possibilities for regeneration of the catalysts have been investigated. The results above show that during 1-butene oxidation the catalysts are reduced. Characterization of used catalysts by means of DRIFT and ESR spectra showed that the structure of the Keggin unit is not affected by reduction (1). We did not find any indication that (part) of the deactivation was caused by, for instance, the deposition of carbonaceous deposits on the catalyst. Reoxidation of the catalysts is, therefore, expected to result in complete regeneration of the high initial activity of the catalyst. Since reduction does not lead to the removal of oxygen from the Keggin structure, reoxidation is likely to proceed at relatively low temperatures. Therefore, used catalysts were subjected to several oxidation treatments at different temperatures to study the reoxidation.

Figure 7 shows the activity of catalyst $PdPV_3Mo_9$, fresh and after two different regeneration procedures. Curve A shows the activity of the fresh catalyst, which is characterized by the high initial butanone yield. After 8 h the catalyst was unloaded from the reactor and treated in air. Curve B shows the activity after an oxidation treatment at 475 K for 2 h in air. The activity of the catalyst after this treatment is lower than of the fresh catalyst, showing that the reoxidation is not complete. Curve C shows the activity after a second oxidation treatment at 525 K for 2 h. The activity is now higher than after the first treatment, but still the catalyst is not completely reoxidized. Complete reoxidation of the PdHPAs appears to be difficult to achieve. This is probably related to the high Pd/

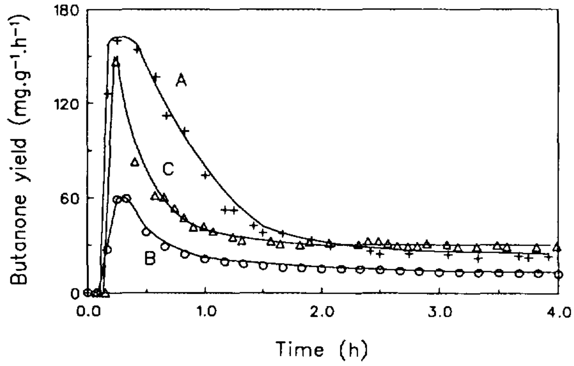

FIG. 7. Butanone yield at 343 K of catalyst $PdPV_3Mo_9$, (A), (+) fresh and after oxidation treatments for 2 h at (B), (○) 475 K, and (C), (△) 525 K. Feed: 1 kPa 1-butene, 7 kPa H_2O, and 93 kPa air.

HPA ratio of these catalysts, which is larger than one in the PdHPAs. The high Pd/HPA ratio might result in segregation of part of the palladium, which is then difficult to reoxidize. Therefore, it would be better to use catalysts with a Pd/HPA ratio smaller than one.

Figure 8 shows the activity of catalyst PV_2Mo_{10}–Pd with a lower palladium loading, prepared by impregnation of silica-supported HPA with a palladium sulfate solution. The Pd/HPA ratio in this catalyst is much smaller than that in PdHPA-based catalysts, viz. 0.1 instead of 1.3. The lower palladium loading results in a lower level of activity but, as shown in Fig. 8, also in an easier reoxidation.

Figure 8 shows the activity of the catalyst, fresh and after several reoxidation treatments. Regeneration at 475 K in flowing air for 0.5 h results in partial reoxidation of the catalyst. Prolongation of the oxidation time to 2 h did not further improve the initial activity of the catalyst. The next oxidation step was, therefore, performed at a higher temperature, viz. at 525 K. As shown in Fig. 8, this treatment resulted in the complete reoxidation of the HPA and the catalyst shows the same activity and selectivity as the fresh catalyst. This shows that the decrease in activity of catalysts with low Pd/HPA ratio is indeed caused by reduction of the HPA and not, for instance, by degradation of the Keggin units. The catalysts can be completely regenerated by a simple oxidation treatment at 525 K and this treatment can be repeated at least five times without any loss of activity. The regeneration temperature necessary to completely oxidize the catalyst was found to vary with the HPA composition; regeneration of PV_3Mo_9–Pd, for instance, is possible at a lower temperature, viz. at 475 K.

The above experiments show that the activity and stability of the catalyst strongly depend on the palladium loading of the catalyst. Higher palladium loadings result in higher initial activity levels but when these become too high, regeneration of the catalyst becomes more difficult. Therefore, the Pd/HPA ratio has to be carefully adjusted to find the optimum composition of the catalyst.

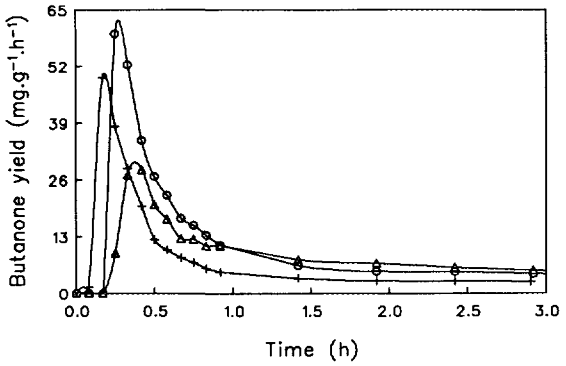

FIG. 8. Butanone yield as a function of time of catalyst PV_2Mo_{10}–Pd, (+) fresh, (△) regenerated at 475 K for 0.5 h, and (○) regenerated at 525 K for 2 h.

CONCLUSIONS

As is the case for acid-based catalysts (1), the initial activity of PdHPA salts is a factor of 5–10 higher than the steady-state activity of the catalysts. The kinetic experiments show that under steady-state conditions the activity of the catalyst is limited by the rate of reoxidation of the reduced PdHPAs. The reaction order of 0.5 in the dioxygen partial pressure points to a rate-determining step involving the dissociation of dioxygen. The rate of reoxidation of the reduced PdHPAs increases with decreasing temperature of reaction.

Under standard conditions, the reaction rate is not much affected by the partial pressure of water in the feed. Water adsorption experiments showed the degree of hydration of the PdHPAs to be almost independent of the partial water pressure above 2 kPa. These experiments show that under standard reaction conditions the PdHPAs are surrounded by more than 20 water molecules per Keggin unit, which are reactive towards Wacker oxidation as well. When water is removed from the feed the reaction carries on for some time, consuming the water of hydration surrounding the Keggin units. There are some indications that a certain degree of hydration of the PdHPAs is required for optimal operation. Although the degree of hydration barely changes with increasing water partial pressure, it strongly decreases when the temperature is raised. The degree of hydration is found to decrease from about 20 to 13 water molecules per Keggin unit when the temperature is raised from 343 to 373 K.

The initial activity level of most HPA-based catalysts is a factor of 10 to 20 higher than the steady-state activity. The high level of initial activity can, as shown above, be regained by a simple oxidation treatment in air at a temperature of 475 to 525 K for catalysts with low Pd/HPA ratio. This observation opens the possibility of applying the catalyst in a two-step process. In such a process the catalyst is alternately exhausted in 1-butene oxidation and reoxidized with air. The two-step process exclusively benefits from the high initial activity of the catalysts giving high conversions per pass combined with a high selectivity.

The results obtained show that Pd salts of HPAs are promising catalysts for heterogeneous Wacker oxidation of alkenes. The initial activity of the catalysts is of the same order of magnitude as the activity of the classical homogeneous Wacker oxidation catalyst. The heterogeneous catalysts, however, possess several important advantages over the homogeneous catalyst, such as a very high butanone selectivity, a low corrosiveness, and the fact that the reaction can be performed in the gas phase, which makes the separation and purification of the products easier. The experiments described are, however, only a first step in the development of a new stable catalyst. Several matters still have to be investigated in more detail to fully understand and optimize the performance. The most important subjects for further research are the effect of temperature and degree of hydration of the Pd-HPA on the activity and stability of the catalysts, the mechanism of reoxidation of the reduced PdHPA, and the optimization of the reaction conditions. The catalyst composition, especially the number of palladium atoms per Keggin unit, has to be optimized and the stability of the catalysts needs to be improved.

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