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Heteropolyanions as Redox Components in Heterogeneous Wacker Oxidation Catalysts

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Heteropolyanions (HPAs) of the Keggin type have been successfully applied as redox components in heterogeneous Wacker catalysts. The catalysts consist of a silica support covered with a layer of HPA of the series $H_{3+n}PV_nMo_{12-n}O_{40}$ on which a submonolayer of palladium sulfate is deposited. The initial butanone yield in the oxidation of 1-butene at 343 K is approximately 0.10 g butanone per gram of catalyst per hour. The steady-state activity is, however, a factor of 10 lower due to the slow reoxidation of reduced HPA. The rate of reoxidation and hence the steady-state activity increases with increasing number (n) of vanadium atoms per Keggin unit and when the protons of the HPA are replaced by Cu^{2+} or by Ni^{2+}. Even higher activity is obtained with palladium salts of heteropolyacids. In these palladium salts the palladium reaction centre and the redox component are combined in one complex. The butanone selectivity of the catalysts with $n > 0$ is high, viz. >95%, and increases with increasing values of n to more than 98%. The butanone selectivity also increases when the protons are exchanged for metal cations, such as Cu^{2+}, Ni^{2+}, Pd^{2+}, or Cs^+. The stability of the Keggin units under reaction conditions is high. Under Wacker oxidation conditions the HPAs are partly reduced, but DRIFT and ESR spectroscopy and TPR analysis of used catalysts show that the Keggin structure remains intact. Reoxidation of the reduced HPAs is, however, slow under reaction conditions.

INTRODUCTION

To overcome the disadvantages of the classical homogeneous Wacker oxidation process, such as the corrosiveness of the system and the formation of chlorinated side products, various types of heterogeneous Wacker oxidation catalysts have been developed (1–4). In our previous articles (5–7), heterogeneous catalysts based on palladium sulfate supported on a monolayer of vanadium oxide on several types of support have been described. Titania-supported catalysts show the best results in the oxidation of 1-butene to butanone. The rate of butanone production, however, appears to be limited by the efficiency of the vanadium oxide redox layer. In particular, the dispersion and the reducibility of the vanadium oxide layer are determining for the activity of the catalysts (7).

In homogeneous Wacker oxidation reactions several other redox components have been used besides the Cu(II)/Cu(I) couple of the classical Wacker–Hoechst process. The redox component should possess a reduction potential between approximately 0.59 and 1.2 V. The lower limit is determined by the reduction potential of the Pd(II)/Pd(0) couple and the upper limit by the potential of the O_2/H_2O couple (8). Compounds which meet this requirement are, for instance, Fe^{3+}, *p*-benzoquinone, and several heteropolyacids. *p*-Benzoquinone is often used as a redox compound in kinetic studies (9, 10). Reoxidation of the hydroquinone by dioxygen, however, is extremely slow, which renders this compound unsuitable for application in a continuous process. Shitova *et al.* (11) tried to apply the Fe(III)/Fe(II) couple, but this couple turned out to be kinetically unfavourable since both the reoxidation of Pd(0) by Fe^{3+} and the reoxidation of Fe^{2+} by dioxygen are slow under Wacker oxidation conditions. Heteropolyanions (HPAs), on the other hand, gave very promising results in the homogeneous Wacker oxidation of ethene (12).

Matveev *et al.* (8, 12) showed the oxidation of ethene to acetaldehyde in the $PdSO_4$–HPA system to be approximately 100 times faster than in the classical chloride-containing ($PdCl_2/CuCl_2$) system. The increased reaction rate in HPA systems results from a change in rate-determining step. In the classical chloride-containing system the rate of reaction is determined by one of the stages in the reduction of the Pd(II) complex to Pd(0); in chloride-free systems, for instance with HPA or benzoquinone, the rate-determining step involves the reoxidation of Pd(0) by dioxygen (8, 12).

Davison (13) showed HPAs of the Keggin type to be suitable redox components in the liquid-phase Wacker oxidation of 1-butene as well. Especially HPAs of the

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series $H_{3+n}PV_nMo_{12-n}O_{40}$, with $n = 2$ to 6, gave very good results: palladium is rapidly reoxidized by the HPAs and the reduced HPAs can be reoxidized by dioxygen. Both Matveev (8, 12) and Davison (13) showed the reoxidation of the reduced HPAs by dioxygen to be rate determining under Wacker oxidation conditions. For HPA systems the catalytic cycle can be described by the reactions

$$Pd^{2+} + C_4H_8 + H_2O \rightarrow Pd(0) + C_4H_8O + 2\,H^+ \quad [1]$$

$$Pd(0) + 2\,H^+ + HPA \rightarrow Pd^{2+} + H_2HPA \quad [2]$$

$$H_2HPA + \tfrac{1}{2}\,O_2 \rightarrow HPA + H_2O, \quad [3]$$

in which H_2HPA represents the reduced form of HPA.

In the past decade, the application of heteropolyanions as catalysts in either acid-catalyzed or redox reactions has been studied extensively (14–16). The fact that the acidic and redox properties of these compounds can easily be modified makes them very attractive as catalysts in both fundamental and applied studies. HPAs of the Keggin 12 series are especially widely used because of their favourable redox properties and their good stability. HPA catalysts are often used in liquid-phase processes but they can be used in gas-phase reactions as well, for instance, supported on silica or on active carbon (14, 15, 17).

In this article the application of HPAs of the series $H_{3+n}PV_nMo_{12-n}O_{40}$, with $n = 0, 2, 3, 8$ as redox components in heterogeneous Wacker oxidation catalysts is described. They are deposited on a silica support and impregnated with palladium sulfate. To study the existence and persistence of the Keggin unit on the silica support, fresh and spent catalysts have been investigated by TPR and by ESR, DRIFT, and NMR spectroscopy. The catalysts have been tested in the oxidation of 1-butene to butanone. The influence of the number of vanadium atoms in the Keggin unit on the activity and selectivity in 1-butene oxidation is discussed. The performance of catalysts based on Cu^{2+}, Ni^{2+}, and Cs^+ salts of the heteropolyacids in the oxidation of 1-butene is compared with the performance of those based on the actual heteropolyacids. Pd^{2+} can also be used as a countercation for heteropolyanions. The application of such palladium salts (PdHPAs) in heterogeneous Wacker oxidation catalysts would be 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. The performance of catalysts based on palladium salts is compared with the performance of the heteropolyacid-based ones.

EXPERIMENTAL

Preparation of Heteropolyacids and Their Salts

$H_3PMo_{12}O_{40} \cdot 27H_2O$ was obtained from Merck (reagent grade) and was used without any further pretreatment. $H_5PV_2Mo_{10}O_{40}$ and $H_6PV_3Mo_9O_{40}$ were prepared according to the method described by Tsigdinos (18). Since it is difficult to prepare acids with $n > 6$, the sodium salt of $H_{11}PV_8Mo_4O_{40}$ was prepared according to the method described by Davison (13).

Preparation of $H_5PV_2Mo_{10}O_{40} \cdot xH_2O$. $NaVO_3$ (24.4 g) (Fluka) was dissolved in 100 cm^3 boiling demineralized water. A solution of 7.1 g $Na_2HPO_4 \cdot 2H_2O$ (Baker) in 100 cm^3 water was added. After cooling to room temperature and upon addition of 5 cm^3 of concentrated sulfuric acid the solution turned red. Subsequently, 121 g $Na_2MoO_4 \cdot 2H_2O$ (Merck), dissolved in 200 cm^3 water, was added to the solution. The reaction mixture was vigorously stirred while 85 cm^3 of concentrated sulfuric acid was added dropwise. Then the solution was cooled and 500 cm^3 diethyl ether was added to extract the HPA product. Upon addition of diethyl ether three layers were formed; the darkest layer contained the HPA–etherate complex. This layer was separated and the diethyl ether was removed in a rotary evaporator. The resulting product was recrystallized from water in a desiccator above concentrated sulfuric acid, giving large orange-red crystals.

Preparation of $H_6PV_3Mo_9O_{40} \cdot xH_2O$. $H_6PV_3Mo_9O_{40} \cdot xH_2O$ was prepared according to the same procedure as $H_5PV_2Mo_{10}O_{40} \cdot xH_2O$, but the relative amounts of starting materials were different. During the preparation of this acid the following solutions were used: 36.6 g $NaVO_3$ in 200 cm^3 water, 7.1 g $Na_2HPO_4 \cdot 2H_2O$ in 50 cm^3 water, 5 cm^3 H_2SO_4 (96%), 54.5 g $Na_2MoO_4 \cdot 2H_2O$ in 150 cm^3 water, and 85 cm^3 H_2SO_4 (96%). The product was extracted in 400 cm^3 diethyl ether and recrystallized from water, giving red crystals.

Preparation of $Na_{11}PV_8Mo_4O_{40} \cdot xH_2O$. $Na_{11}PV_8Mo_4O_{40} \cdot xH_2O$ was prepared according to the procedure described by Davison (13), which was slightly modified. $Na_3PO_4 \cdot 12H_2O$ (5.7 g) MoO_3, (8.64 g), V_2O_5 4.74 g, Na_2CO_3 (2.41 g) were dissolved in 75 cm^3 water and refluxed for 1 h. The resulting dark solution was filtered hot over celite to remove undissolved residues. After cooling the volume of the solution was minimized in a rotary evaporator and the resulting solution was crystallized above concentrated sulfuric acid.

Preparation of Cu^{2+}, Ni^{2+}, Cs^+, and Pd^{2+} salts. The copper, nickel, and caesium salts of $H_5PV_2Mo_{10}O_{40} \cdot xH_2O$ were prepared according to the method described by Tsigdinos (19). A stoichiometric amount of the metal carbonate was added to an aqueous solution of the HPA.

$CuCO_3 \cdot CuOH$ and $3NiCO_3 \cdot 2Ni(OH)_2$ were used to prepare, respectively, the copper and nickel salts of $H_5PV_2Mo_{19}O_{40}$. Addition of the metal salts to the acidic solution of the HPA and heating of the solution to 340 K resulted in the evolution of carbon dioxide. The water from the solution was subsequently removed in a rotary evaporator.

The caesium salt of $H_5PV_2Mo_{10}O_{40}$ was prepared by addition of Cs_2CO_3 to a solution of the HPA. The insoluble caesium salt immediately precipitates on addition of the caesium carbonate. The precipitate was washed three times with water and dried.

The palladium salts from the heteropolyacids were prepared according to the procedure described by Tsigdinos (19). Approximately 8 g of the HPA was dissolved in 100 cm^3 water. A stoichiometric amount of $BaCO_3$ was added and the solution was heated to 353 K to remove carbon dioxide. Subsequently a stoichiometric amount of a solution of 2 g $PdSO_4 \cdot 2H_2O$ (Alfa Products) dissolved in 100 cm^3 water was added, resulting in the precipitation of barium sulfate. The barium sulfate precipitate was removed from the solution by filtration over celite. Then, the water was removed from the solution in a rotary evaporator to give the palladium salt. 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 P : V : Mo ratios of the products were determined by ICP analysis. The degree of hydration of the products was determined thermogravimetrically in a Stanton Redcroft TG-750 thermobalance. Approximately 10 mg of sample was placed in a platinum cup and heated in flowing air (0.17 cm^3/s) at a rate of 0.17 K/s. The composition of the HPAs, as deduced from the results of ICP and TGA analysis, is listed in Table 1. Below, the HPAs will be coded, giving the average number of vanadium and molybdenum atoms per Keggin unit and, for salts, the type of metal cation. For instance, $H_6PV_3Mo_9O_{40}$ will be coded as PV_3Mo_9 and $Cu_{2.5}PV_2Mo_{10}O_{40}$ as $CuPV_2Mo_{10}$.

TABLE 1

Catalyst Codes and Composition as Determined by ICP and TGA Analysis

Code	Real composition of HPA[a]	Pd loading (wt%)
PMo12–Pd	$H_3PMo_{12}O_{40} \cdot 27\ H_2O$	0.2
PV_2Mo_{10}–Pd	$H_5PV_{2.2}Mo_{9.8}O_{40} \cdot 28\ H_2O$	0.2
PV_3Mo_9–Pd	$H_6PV_{3.2}Mo_{8.8}O_{40} \cdot 25\ H_2O$	0.2
$NaPV_8Mo_4$–Pd	$Na_{6.1}H_{4.9}PV_{8.5}Mo_{3.5}O_{40} \cdot 19\ H_2O$	0.2
$CuPV_2Mo_{10}$–Pd	$Cu_{2.9}PV_{2.1}Mo_{9.9}O_{40} \cdot 21\ H_2O$	0.2
$NiPV_2Mo_{10}$–Pd	$Ni_{2.7}PV_{2.1}Mo_{9.9}O_{40} \cdot 30\ H_2O$	0.2
$CsPV_2Mo_{10}$–Pd	Not determined	0.2
$PdPMo_{12}$	$Pd_{1.1}H_{0.8}PMo_{12}O_{40} \cdot 20\ H_2O$	2.3
$PdPV_2Mo_{10}$	$Pd_{1.6}H_{1.8}PV_2Mo_{10}O_{40} \cdot 21\ H_2O$	3.4
$PdPV_3Mo_9$	$Pd_{1.3}H_{3.4}PV_{2.9}Mo_{9.1}O_{40} \cdot 21\ H_2O$	2.6

[a] *P* is arbitrarily set to 1.

Figure 1A shows a characteristic TGA profile of the heteropolyacid PV_2Mo_{10}. The dehydration of heteropolyacids proceeds in two steps; the first between 290 and 410 K, which results in the formation of the anhydrous acid, and the second above 550 K, which coincides with the destruction of the Keggin unit. The first weight loss is used to calculate the degree of hydration, the second step to determine the number of protons of the acid.

Figure 1B shows a characteristic TGA profile of heteropolysalts, in this case $PdPV_3Mo_9$. For the salts the two dehydration steps are not as clearly separated as for the acids. Again, the first weight loss is caused by dehydra-

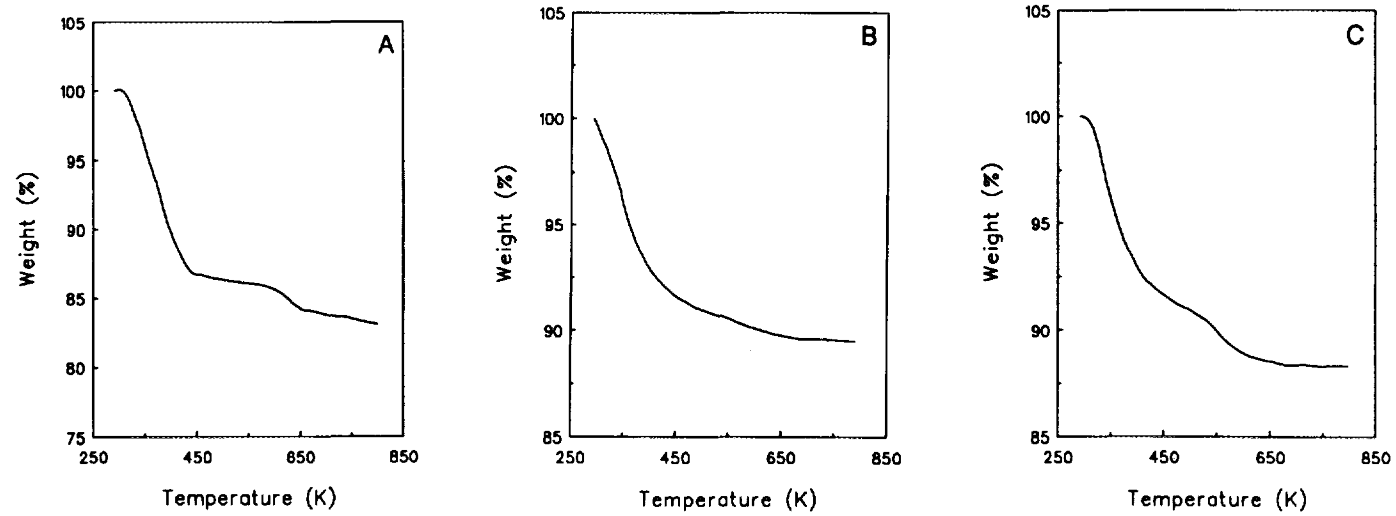

FIG. 1. TGA profiles of (A) PV_3Mo_9, (B) $PdPV_3Mo_9$, and (C) $PdPV_3Mo_9$ after 16 h of 1-butene oxidation. Profiles are recorded in a flow of 0.17 cm^3/s air at a heating rate of 0.17 K/s.

tion. The high-temperature weight reduction is due to the loss of water coordinated around the metal cations (19).

Catalyst Preparation

The heteropolyanions were deposited on silica (Davisil-300), BET surface area 287 m^2/g, by impregnation to incipient wetness of an aqueous solution of the HPA. The loading of the HPAs was chosen such that a monolayer of Keggin units was achieved, 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 about 40 wt%. The supported samples were dried overnight at 343 K in air and stored at room temperature. Dried samples were subsequently impregnated to incipient wetness with a 0.02 *M* solution of $PdSO_4 \cdot 2H_2O$ (Alfa Products) in 0.18 *M* H_2SO_4. Sulfuric acid was added to aid palladium sulfate dissolution. The palladium sulfate impregnation step results in a palladium sulfate loading corresponding to 0.2 wt% Pd. The molar HPA/Pd ratio in the catalysts is approximately 10. Catalysts were dried overnight at 343 K in air and stored at room temperature in a desiccator over calcium chloride. Palladium sulfate impregnated catalysts will be coded with Pd. For instance, PV_2Mo_{10}–Pd means silica-supported PV_2Mo_{10} impregnated with palladium sulfate. Catalysts based on palladium salts were *not* impregnated with palladium sulfate.

Catalysts were tested in the oxidation of 1-butene to butanone in conventional flow equipment (5). Approximately 0.7 g of catalyst was mixed with glass beads and loaded into the stainless steel reactor. Catalysts were tested under standard conditions, which are summarized in Table 2. The reaction products were analyzed by means of a Delsi-Nermag DN-200 gas chromatograph equipped with a 25 m capillary FFAP column (internal diameter 320 μm). The products were detected with a flame ionization detector (FID). The butanone yield is expressed in grams of butanone produced per gram of catalyst per hour.

Diffuse reflectance infrared Fourier transform (DRIFT) spectra of HPAs and catalysts were recorded on a Nicolet Magna-IR Spectrometer 550. Samples were mixed and ground with KBr and loaded into the sample holder. Electron spin resonance (ESR) spectra were recorded at 77 K on a Jeol JES-RE 2X ESR spectrometer, operated at the X-band frequency.

TABLE 2

1-Butene Oxidation Test Conditions

Feed	1 kPa 1-butene 7 kPa water 18 kPa dioxygen 75 kPa dinitrogen
Feed rate	0.83 $cm^3(STP) \cdot s^{-1}$
Amount of catalyst	0.5–0.7 g
Particle size	230–700 μm
Temperature	343 K
Pressure	101 kPa

Temperature programmed reduction (TPR) experiments were performed in the equipment described in detail elsewhere (20). TPR–TPO experiments were performed in a similar equipment, with an additional option for temperature programmed oxidation (TPO). About 100 mg of sample was loaded in the quartz reactor tube and heated at a rate of 0.17 K/s under a flow of reducing or oxidizing gas. In the TPR mode a 50% H_2 in argon mixture was fed through the reactor at a rate of 0.5 $cm^3(STP) \cdot s^{-1}$, whereas in the TPO mode a 67% O_2 in helium mixture was fed at a rate of 0.75 $cm^3(STP) \cdot s^{-1}$. Water produced during the reaction was removed in a molecular sieve trap. Dihydrogen and dioxygen consumptions were detected by means of thermal conductivity detectors (TCD). The sensitivities of the TCDs for dihydrogen and dioxygen were calibrated by measuring the response upon injection of pulses of dihydrogen and dioxygen, respectively, of known volume and pressure.

RESULTS AND DISCUSSION

Catalyst Characterization

In order to determine whether the prepared HPAs indeed possess the characteristic Keggin structure, the reaction products were characterized as follows. Figure 2 shows the DRIFT spectra of pure PV_3Mo_9 (A) and of the silica-supported palladium sulfate-impregnated catalyst (B). Both spectra show the characteristic bands of HPAs with the Keggin structure, in the 700 to 1100 cm^{-1} region. In Figure 2, curve A, absorption bands are observed at 790 + 880, 957, and 1055 cm^{-1} to be ascribed to vibrations

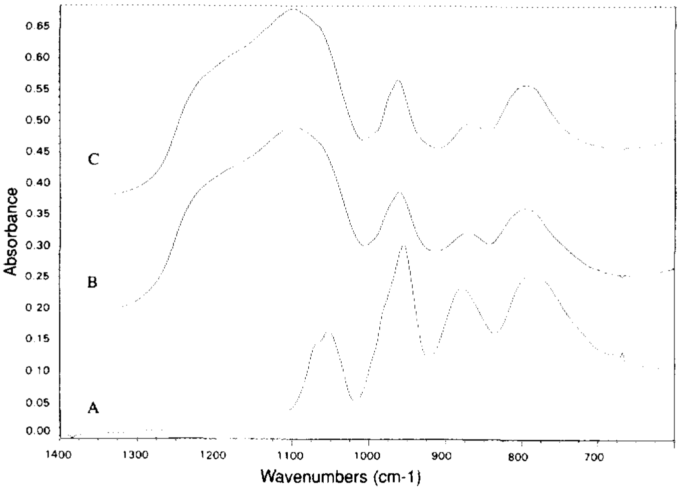

FIG. 2. DRIFT spectra of (A) pure PV_3Mo_9, (B) fresh silica-supported PV_3Mo_9–Pd, and (C) PV_3Mo_9–Pd after 20 h of 1-butene oxidation.

of the *M*–O–*M*, *M*=O, and P–O bonds in the Keggin unit (*M* = V or Mo), respectively (15, 21). In the spectrum of the fresh catalyst (B), the P–O vibration is masked by the broad features in the 1000–1300 cm^{-1} region of the silica support. Neither of these spectra shows peaks indicative of the presence of any degradation products or contaminants, such as MoO_3 or V_2O_5. Exchange of the acidic protons of the HPA for metal cations does not change the features in the DRIFT spectra.

Figure 3, curve A, shows the ESR spectrum of PV_2Mo_{10}–Pd, recorded at 77 K. The spectrum shows the anisotropic signal and hyperfine splitting of isolated V^{4+} in axial symmetry, characterized by $g_\perp = 1.989$, $A_\perp = 8.02$ mT, $g_\parallel = 1.939$, and $A_\parallel = 20.2$ mT. The spectrum strongly resembles the spectra of pure and silica-supported PV_2Mo_{10} published by Otake *et al.* (31) and Serwicka and Grey (22).

The formation of a heteropolyanion structure is also confirmed by TPR. Figure 4, curves A and B, shows the TPR profiles of the starting materials $NaVO_3$ and $Na_2MoO_4 \cdot 2H_2O$, respectively. Sodium metavanadate (see curve A) reduces in two steps, viz., at 840 and 964 K. The oxidation state of the vanadium after reduction is approximately V^{3+}. The sodium molybdate reduction starts at temperatures above 975 K. The area of the reduction peak indicates that the molybdate is almost completely reduced to metal.

PV_2Mo_{10} prepared from these two compounds gives a totally different reduction pattern (see curve C) and the reduction starts at 650 K. The pattern shows a sharp peak at 790 K, preceded by a small shoulder and a broad low peak at 940 K. The results of Davison (13) and Wang *et al.* (23) concerning reduction of vanadium-containing HPAs in solution, show that the reduction starts with the reduction of the vanadium atoms in the Keggin unit from V^{5+} to V^{4+}; i.e., there is a two-electron reduction step for PV_2Mo_{10}. The reduction profile in Fig. 4, curve C, however, shows no separate two-electron reduction step. Possibly, the shoulder preceding the large peak at 790 K results from the reduction of the vanadium atoms. The total area under curve C is about equal to the sum of the areas under curves A and B, indicating that ultimately the metals in the Keggin unit are reduced to the same extent as those in the starting materials, viz. $Mo^{6+} \rightarrow Mo(0)$ and $V^{5+} \rightarrow V^{3+}$.

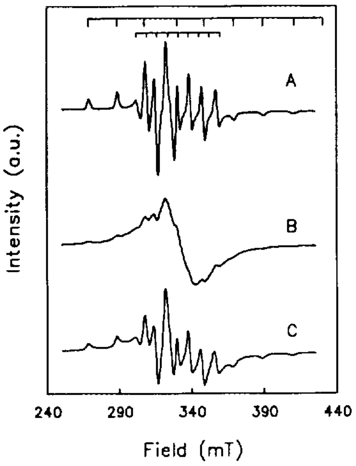

FIG. 3. ESR spectra recorded at 77 K of catalyst PV_2Mo_{10}–Pd, (A) fresh, (B) after 20 h of 1-butene oxidation, and (C) after reduction and oxidation at 475 K.

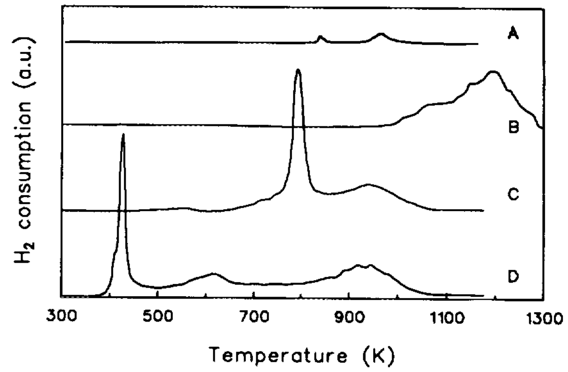

FIG. 4. TPR profiles of (A) $NaVO_3$, (B) $NaMoO_4 \cdot 2H_2O$, and (C) PV_2Mo_{10} supported on silica, and (D) PV_2Mo_{10}–Pd. The heating rate is 0.17 K/s. Profiles are normalized to 20 μmol Keggin units.

Curve D in Fig. 4 shows the reduction profile of PV_2Mo_{10}–Pd. The catalytic activity of palladium upon reduction with dihydrogen, as observed before for vanadium oxide-based catalysts (5, 7), is also found for the reduction of HPAs; the sharp peak at 790 K in curve C is shifted to a much lower temperature, viz. 430 K. An increased reducibility in the presence of palladium was also reported by Ziemecki (24) and Katamura *et al.* (21). The peak at 940 K appears not to be affected by the presence of palladium. The peak at 620 K in the profile of the palladium sulfate impregnated catalyst is probably caused by the reduction of sulfate. This sulfate reduction was also observed for the palladium sulfate-based heterogeneous catalysts with vanadium oxide as the redox component (5, 7).

The large reduction peak at 430 K in curve D (Fig. 4) shows that in the presence of palladium the HPA is easily reduced at temperatures around 400 K. The area of the peak roughly corresponds to a reduction of 20 electrons per Keggin unit, instead of the 2-electron reduction expected in the absence of palladium on the basis of literature data (8, 13, 23). A reduction with the transfer of 20 electrons leads to the reduction of the two vanadium atoms to the V^{3+} state, of half of the molybdenum atoms to the Mo^{4+} state, and of the other half to the Mo^{5+} state. This very deep reduction is likely to result in the destruction of the Keggin unit, which would be unfavourable for application in the heterogeneous Wacker catalyst. However, the reduction of the HPAs under 1-butene oxidation conditions possibly does not proceed as far as in the TPR experiment, since the reaction runs at lower temperature and in an atmosphere containing dioxygen.

The Performance in 1-Butene Oxidation

In homogeneous Wacker oxidation HPAs have been proven to be good reoxidants for palladium (8, 12, 13), but they have, to our knowledge, never been used in heterogeneous Wacker catalysts. To determine whether or not the HPAs themselves possess any activity, silica-supported PV_2Mo_{10} was tested in 1-butene oxidation. PV_2Mo_{10} shows no activity for butanone production. However, a small fraction of the 1-butene in the feed is converted to 2-butanol over the supported HPAs. This is the result of the acid-catalyzed hydration of 1-butene (25).

If palladium sulfate is applied without a redox component some initial activity is found, but the butanone production ceases after a few hours. In the absence of a redox compound only a stoichiometric amount of butanone is produced, according to reaction (1).

Figure 5 shows the activity and butanone selectivity of catalyst PV_2Mo_{10}–Pd. More than the stoichiometric amount of butanone is indeed produced over this catalyst. Initially a conversion of more than 50% is observed and within 1 h of operation more than 20 times the stoichiometric amount has been formed, indicating that Pd(0) is indeed quickly reoxidized by the HPA. The butanone selectivity is high, viz. 90%, and the main side product is 2-butanol. Minor amounts of other compounds, such as butanal, crotonaldehyde, and acetaldehyde, are also detected.

Figure 6 shows the activity of catalyst PV_3Mo_9–Pd in the absence of dioxygen in the feed. Initially a high conversion and butanone yield is observed, but the activity strongly decreases after 1 h on stream. This can be easily understood since in the absence of dioxygen only reactions [1] and [2] can proceed, resulting in the reduction of both the palladium sulfate and the HPA. The absence of dioxygen makes the reoxidation of the reduced HPA impossible and the catalyst is depleted of oxygen. When both the palladium sulfate and the HPAs are in the reduced state the reaction stops, as can be seen in Fig. 6. When dioxygen is again admitted to the reactor the activity of the catalyst is partly regained, indicating that partial reoxidation of the reduced HPAs by dioxygen under Wacker oxidation conditions is possible. Hence, these results show that HPAs of the Keggin type can be applied as redox components in heterogeneous Wacker catalysts and that the reaction cycle can indeed be represented by Eqs. [1] to [3].

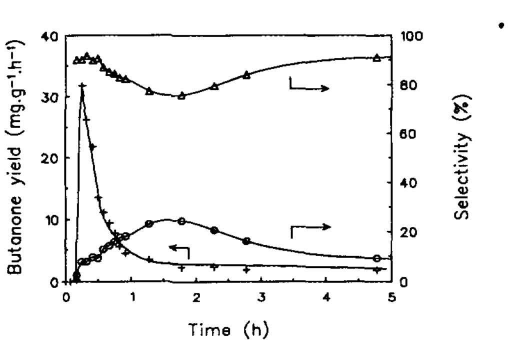

FIG. 5. Butanone yield (+) and selectivity to butanone (△) and 2-butanol (○) of catalyst PV_2Mo_{10}–Pd at 343 K.

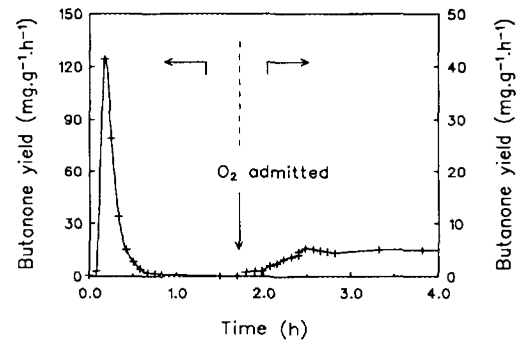

FIG. 6. Butanone production at 343 K in the absence of dioxygen in the feed. The catalyst is PV_3Mo_9–Pd. After 1.8 h dioxygen is admitted to the reactor.

The total amount of butanone produced in the absence of dioxygen (see Fig. 6) can be used to estimate the degree of reduction of the Keggin unit under Wacker oxidation conditions. The results in Fig. 4 show that in the presence of palladium and under TPR conditions each Keggin unit accepts approximately 20 electrons in the first reduction step. Each molecule of butanone produced in the oxidation of 1-butene gives two electrons and these are, in the absence of dioxygen, all incorporated by Pd and the HPAs. This results in the reduction of every Keggin unit with approximately 4 electrons. Apparently, under 1-butene oxidation conditions the Keggin units are not reduced to the same extent as they are under TPR conditions. The consumption of about 4 electrons per Keggin unit roughly corresponds to the reduction of the three vanadium atoms in PV_3Mo_9 to the tetravalent state. Reduction of V^{5+} to V^{4+} was also found by Davison (13), who applied HPAs in the liquid-phase oxidation of 1-butene. These results indicate that, at least in vanadium-containing HPAs, the redox activity of the HPAs appears to be mainly related to the vanadium atoms in the Keggin unit. However, the catalyst based on PMo_{12} also shows a good amount of activity in the oxidation of 1-butene. Obviously, in the absence of vanadium atoms in the Keggin unit, molybdenum atoms can act as redox centres as well. In the presence of vanadium the reduction of molybdenum appears to be absent but can not be excluded.

Reoxidation of Reduced HPAs

The results in Fig. 5 show that initially the activity of HPA-based catalysts in the oxidation of 1-butene is very high; conversions of more than 50% per pass are obtained during the first hour of operation. However, the activity starts to decline almost directly until a steady state is reached after approximately 4 h. For some catalysts the initial activity is more than a factor of 10 higher than the steady-state activity. The activity only starts to decrease when every palladium atom has been used more than once, indicating that the reoxidation of palladium by the HPA is fast. Therefore, the reason for the declining activity might be that the reoxidation of the reduced HPA is too slow.

From the change in colour of the catalyst it is clear that the HPAs are reduced under reduction conditions; due to the formation of reduced HPAs, which are dark blue, the colour of the catalyst changes from orange-red to almost black. The degree of reduction of the HPA in the steady state can be estimated by TPR. Figure 7 shows the TPR profiles of catalyst PV_3Mo_9–Pd (A) when freshly prepared and (B) after 8 h under standard reaction conditions. The profiles of the fresh and used catalyst are comparable, except for the sharp peak at 430 K, which is smaller for the used catalyst, showing that the catalyst is partly reduced. The degree of reduction of the used catalyst cannot be determined very accurately, but the difference in peak area indicates that the degree of reduction is at least 4 electrons per Keggin unit. This is the same degree of reduction found in the absence of dioxygen, indicating that the HPA is almost completely reduced under steady-state conditions.

The above results indicate that the reoxidation of the reduced HPAs (reaction [3]) is indeed rate determining under 1-butene oxidation conditions. This conclusion is supported by the fact that the reaction rate appeared to be zero order in the palladium sulfate coverage. Davison (13) and Matveev (8) reported the reoxidation of the reduced HPAs to be rate determining in the liquid-phase oxidations of 1-butene and ethene as well.

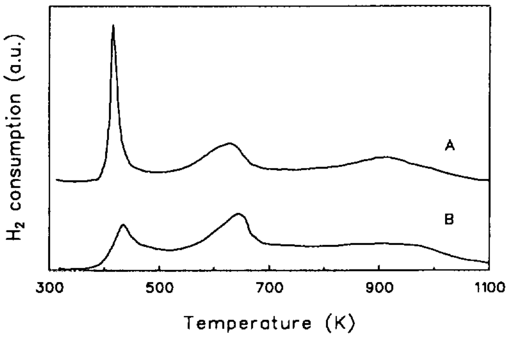

FIG. 7. TPR profiles of catalyst PV_3Mo_9–Pd, fresh (A) and after 8 h under 1-butene oxidation conditions (B). The heating rate is 0.17 K/s.

The slow reoxidation of the reduced HPAs results in a strong decrease in butanone production after 1 h of operation. It would, of course, be attractive to improve the rate of reoxidation of the reduced HPAs so that the initial high level of activity of the catalysts can be retained. The redox properties of heteropoly compounds can easily be modified, for instance by substituting Mo for V or W, or by replacing P by Si. Davison (13) and Mateev *et al.* (8, 12, 16) reported that the rate of reoxidation of the reduced HPAs of the series $H_{3+n}PV_nMo_{12-n}O_{40}$ increases with increasing *n* values. The reoxidation rate is also increased when the protons of heteropolyacids are exchanged for transition metal cations, such as Cu^{2+} or Ni^{2+}, or for alkali metal cations, such as K^+ or Cs^+ (23, 26–28). The alkali metal salts are insoluble in water and possess some microporosity, which makes them suitable as support materials. In the next section the dependence of the rate of reoxidation of the reduced HPA on the composition of the HPA will be discussed. Both the number of vanadium atoms in the Keggin unit and the type of counterions will be varied.

Variation of the Number of Vanadium Atoms per Keggin Unit

Since the reoxidation of the reduced HPA becomes rate determining in 1-butene oxidation, the steady-state activity of the catalyst is determined by this reoxidation rate. Davison (13) and Matveev *et al.* (8, 12) reported that in liquid-phase Wacker oxidation reactions the rate of reoxidation increases with increasing number (*n*) of vanadium atoms in the Keggin unit.

Figure 8A shows the initial and steady-state activities of heterogeneous Wacker catalysts as a function of *n*. Both the initial and the steady-state activity increase with increasing *n*, up to $n = 3$. Since the steady-state activity is determined by the rate of reoxidation of the HPA it can be concluded that also in heterogeneous catalysts reoxidation is enhanced by an increasing number of vanadium atoms in the Keggin unit. The activity of $NaPV_8Mo_4$–Pd is initially lower than the activity of PV_3Mo_9–Pd. This lower activity might be the result of the fact that in this catalyst part of the protons are replaced by sodium cations. For the acid-based catalysts with $n = 0, 2, 3$ a very high initial activity is observed, which strongly declines during the first 2 h of the operation, whereas for $NaPV_8Mo_4$–Pd the difference between initial and steady-state activity is smaller.

Figure 8B shows that the selectivity to butanone also increases with increasing number of *n*. The HPAs with $n > 0$ all show a high selectivity of more than 90%. The selectivity of PMo_{12}–Pd is, however, much lower due to

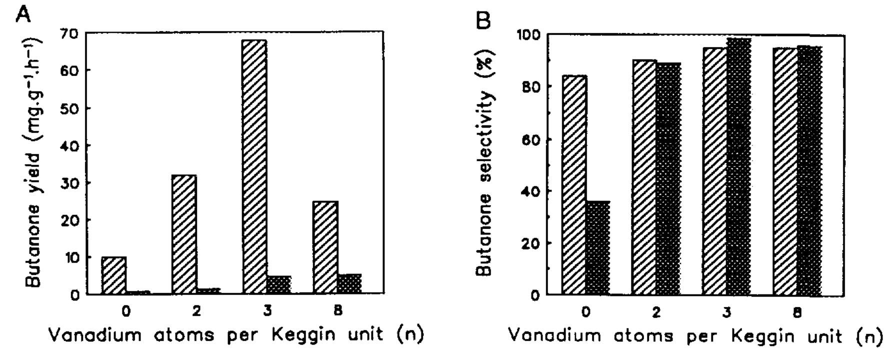

FIG. 8. Initial (dashed) and steady-state (black) activity (A) and butanone selectivity (B) in the oxidation of 1-butene at 343 K of catalysts of the series PV_nMo_{12-n}–Pd, with n = 0, 2, 3 and 8.

the formation of a considerable amount of 2-butanol. As discussed above, the formation of butanol is catalyzed by strongly acidic protons (25) and therefore the selectivity in 1-butene oxidation can be regarded as indicative of the acidity of the HPA. When n increases the number of protons per Keggin unit also increases, but since the butanol production decreases the acidity of these protons appears to become weaker. Serwicka *et al.* (30) also reported that the acidity of the HPA decreases with increasing number of n.

The difference between the initial and steady-state selectivity of PMo_{12}–Pd is caused by the decreasing rate of butanone production. The 2-butanol production remains approximately constant over the period of the experiment, whereas the butanone production decreases.

The initial activity of the catalysts is determined by the rates of reactions [1] and [2], whereas the steady-state activity is determined by the rate of reaction [3]. Therefore, the differences in initial activity must be related to the reducibility of the HPA, whereas the steady-state activity is related to the reoxidizability of the reduced HPA. Figure 9 shows the TPR profiles of the catalysts PMo_{12}–Pd, PV_2Mo_{10}–Pd, and PV_3Mo_9–Pd. The three catalysts show comparable reduction profiles with three reduction steps at approximately 400, 600, and 900 K. The peak at 600 K stems from the reduction of sulfate in the catalyst. The reduction peaks at 400 and 900 K are characteristic for the HPA and change with the changing composition of the HPA. The peak at 400 K strongly increases when vanadium is present in the Keggin unit. This shows that the hydrogen uptake of the HPA increases when molybdenum is replaced by vanadium; i.e., the number of electrons accepted in the first reduction step strongly increases. The onset temperature and the temperature of maximum reduction rate (T_{max}) do not change. Since the initial rate of butanone production is determined by the ability of the HPA to accept electrons from Pd(0) (reaction [2]) an increased reducibility of the HPA is expected to give rise to a higher initial activity. This is indeed observed for the catalyst of the series PV_nMo_{12-n}, with n = 0, 2, or 3.

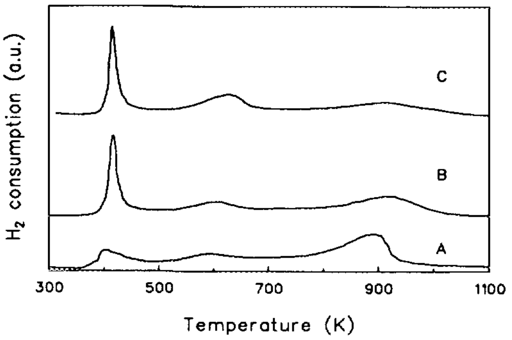

FIG. 9. TPR profiles of catalysts of the series PV_nMo_{12-n}–Pd. (A) PMo_{12}–Pd, (B) PV_2Mo_{10}–Pd, and (C) PV_3Mo_9–Pd. The heating rate is 0.17 K/s.

A similar relation is expected between the oxidizability of the reduced HPA and the steady-state activity. Therefore, several experiments were performed to determine differences in the rates of reoxidation. The catalysts were first reduced by dihydrogen at 475 K in the TPR equipment and cooled to 200 K under helium. Then the reduced samples were reoxidized during a TPO experiment. A problem encountered with these experiments was the extensive physisorption of dioxygen on the catalyst at 200 K. When the temperature program of the TPO experiment was begun a strong broad negative peak due to the desorption of dioxygen was observed, which only ceased above 250 K. This desorption of dioxygen and the fact that only a broad low dioxygen consumption peak is observed make it impossible to compare the onset temperatures for reoxidation or the degree of reoxidation of the different samples. The samples were, however, completely reoxidized in the TPO experiment, since the reduction profile in a second TPR experiment was identical to the profile in the first one.

The Influence of the Counterion on the Activity

Cu^{2+}, Ni^{2+}, Pd^{2+}, and Cs^{+} salts of PV_2Mo_{10} were prepared to study the influence of the counterion on the performance of the catalysts in the oxidation of 1-butene. Copper and nickel cations are presumed to participate in the reduction and reoxidation cycle of the Keggin unit. Akimoto *et al.* (27–29) showed that upon reduction of $CuPMo_{12}$–Pd at 478 K almost all the copper cations are reduced. The reoxidation of salts of the HPA appeared to be enhanced by a higher standard reduction potential of the counterion. Application of palladium salts is very attractive, as stated in the Introduction.

Alkali metals, like caesium, do not participate in the redox cycle and their influence on the redox properties of the HPA is explained by their effecting a change in the Mo–O bond strength. The rate of reoxidation of reduced alkali metal salts of PMo_{12} is enhanced by the lower electronegativity of the alkali metal. Akimoto *et al.* (28) showed reduced $CsPMo_{12}$ to be readily oxidized by dioxygen below 370 K.

The TPR profiles of PV_2Mo_{10}–Pd, $CuPV_2Mo_{10}$–Pd, and $CsPV_2Mo_{10}$–Pd in Fig. 10 show that the reducibility of the HPA is indeed influenced by the nature of the counterion. When the protons of the heteropolyacid are replaced by Cu^{2+} the reduction peak at 430 K becomes broader and a shoulder is observed at 480 K. This shoulder probably stems from the reduction of the Cu^{2+} cations. The exchange of the protons for Cu^{2+} appears to increase the electron accepting ability of the HPA. However, the reduction starts at a higher temperature, which makes it uncertain whether this reduction also proceeds under 1-butene oxidation conditions.

Exchange of the protons for Cs^{+} strongly decreases the electron accepting abilities of the HPA (see Fig. 10, curve C); the reduction peak at 430 K is much smaller for the caesium salt than for the acid. Since the caesium salt is insoluble in water it was not supported on silica but was used nonsupported.

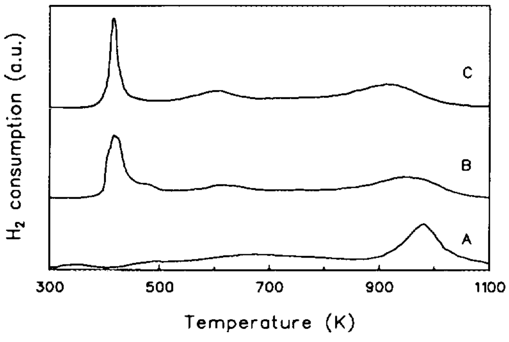

FIG. 10. TPR profiles of catalysts of the series XPV_2Mo_{10}–Pd, where X is (A) Cs^{+}, (B) Cu^{2+}, and (C) H^{+}. The heating rate is 0.17 K/s.

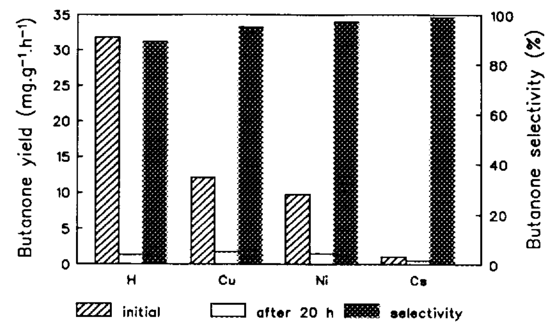

FIG. 11. Performance of catalysts of the series XPV_2Mo_{10}–Pd, where $X = H^{+}$, Cu^{2+}, Ni^{2+}, and Cs^{+}, in the oxidation of 1-butene at 343 K.

Unfortunately it was not possible to determine the onset temperatures of reoxidation of the reduced samples, due to the strong physisorption of dioxygen.

Figure 11 shows the initial and steady-state activity and the butanone selectivity of HPA salts in the oxidation of 1-butene. The steady-state activity of the copper and nickel salts is slightly higher than the activity of the acid. The steady-state activity of the caesium salt is a factor of 3 lower than that of the acid. The low activity of the caesium salt might be related to the fact that it is used as a nonsupported catalyst and has a lower specific surface area than the silica-supported catalysts. For the salts the difference between initial and steady-state activity is smaller than for the acid, indicating that their reducibility is lower (lower initial activity) and their reoxidizability is higher (higher steady-state activity). The butanone selectivity of the salts is also higher, viz. >95%. This is due to the fact that the strong acidic protons of the acid have been replaced by metal cations.

Although the steady-state activity of the catalysts is not much increased by the exchange of protons for copper or nickel, the stability of these HPA salt-based catalysts appears to be better than that of the acid-based one. After steady-state activity is reached the activity of PV_2Mo_{10}–Pd still slowly decreases with time, while the activity of $CuPV_2Mo_{10}$–Pd remains virtually constant for at least 50 h. The deactivation of acid-based catalysts might be caused by a slow degradation of the Keggin units under reaction conditions.

The application of palladium as a countercation leads to enhanced activity of the catalyst; see Fig. 12. The catalysts show a high initial activity and it can be concluded that although palladium is present as the HPA countercation it can act as a reaction site for Wacker oxidation. The performance of the PdHPA-based catalyst is comparable to that of heteropolyacid-based catalysts, but the initial butanone yield is a factor of 10 higher than that of the acid-based catalysts, to which $PdSO_4$ is added (see Fig. 8A). The higher activity is probably caused by the higher palladium loading and by the chemical bonding

FIG. 12. Performance of catalyst of the series $PdPV_nMo_{12-n}$, where n = 0, 2, and 3, in the oxidation of 1-butene at 343 K.

between the palladium cations and the heteropolyanions. Figure 12 shows that for Pd salt-based catalysts the activity also increases with increasing number of vanadium atoms in the Keggin unit, just as for the acid-based catalysts.

The palladium salts do show a higher steady-state activity, but their stability is lower than for the other salts and also lower than for the acid-based catalysts. This is probably a result of the high Pd/HPA ratio in the PdHPA-based catalysts. For catalysts $PdPV_2Mo_{10}$ this ratio is 1.6, which means that for every Keggin unit there are almost two palladium atoms which have to be reoxidized. The high Pd/HPA ratio might result in an inefficient reoxidation of palladium, resulting in an accumulation of Pd(0). Therefore, a Pd/HPA ratio smaller than one has to be preferred.

Characterization of Used Catalysts

The activity of the HPA-based catalyst can only be maintained when the Keggin structure of the HPA is not affected by the multiple reduction–oxidation cycles. For heteropolyacid and palladium salt based catalysts a slow deactivation with time is observed, which might be caused by the degradation of the HPA. Therefore, the stability of the HPA under reaction conditions is investigated by means of several characterization techniques, i.e., by ESR, TPR, IR, and solid state ^{51}V and ^{31}P NMR.

Figure 2 shows the DRIFT spectra of catalyst PV_3Mo_9–Pd, fresh (curve B) and after use for 20 h in the oxidation of 1-butene under standard reaction conditions (curve C). Both samples show the vibrations characteristic of the Keggin structure and the broad features of the silica support. The absorption bands of the Keggin unit appear not to be changed as a result of the reduction under reaction conditions. No indications of the formation of degradation products could be found, either with DRIFT or with ^{31}P and ^{51}V NMR spectroscopy.

Figure 3 shows the ESR spectra of catalyst PV_2Mo_{10}–Pd, fresh and after several different treatments. Curve A shows the spectrum of the fresh catalyst, which was discussed above. Curve B shows the spectrum of the used catalyst, which shows a broad isotropic signal with g = 1.9904. This isotropic signal is caused by the overlap of orbitals of V^{4+} atoms in each other's vicinity and shows that both of the vanadium atoms in the Keggin unit are in the reduced V^{4+} state. Superposed on the broad isotropic signal the signal of isolated V^{4+} ions is still observed characterized by the hyperfine splitting of curve A. This shows that at least some of the Keggin units are still intact. Curve C shows the ESR spectrum of the catalyst after reduction at 475 K under hydrogen and reoxidation at 525 K in air. TPR showed that reduction at 475 K leads to the reduction of the HPA with about 20 electrons per Keggin unit (see Fig. 4). This deep reduction almost certainly leads to the destruction of the Keggin structure. The spectrum of the reoxidized sample is, however, identical to the spectrum of the fresh catalyst, indicating that the Keggin units are not destroyed. It is, however, difficult to distinguish whether the Keggin units remain intact during the reduction–reoxidation cycle or whether they are reconstructed after reoxidation. Serwicka and Grey (22) showed that thermally destroyed HPAs are spontaneously reconstructed from the degradation products when they are exposed to humid air. Reconstruction of the Keggin units upon exposure to the air in the sample for curve C (Fig. 3) is very well possible.

The presence of intact HPA in the sample for curve C is confirmed by the fact that the sample shows the same activity in 1-butene oxidation as the fresh catalyst. A quick reconstruction of the Keggin units upon exposure to humid air after the reduction–oxidation cycle might explain the presence of the intact HPA. The reconstruction of the Keggin unit under reaction conditions also follows from the performance of the catalyst in 1-butene oxidation after reduction at 475 K. Initially the catalyst shows no activity, but after approximately 20 min the activity starts to increase and, after several hours, reaches a steady-state level comparable to the activity of a fresh catalyst. This shows that the extensively reduced HPAs are spontaneously regenerated under reaction conditions within a period of several hours.

A problem with palladium salt-based catalysts might be the segregation of metallic palladium from the salts. We have not so far found any evidence for this, but segregation of palladium might be the cause of deactivation of the palladium salt-based catalysts. Further research is required to elucidate this.

DRIFT results indicate that the Keggin unit is not affected by the reduction–oxidation cycles and that reduction of the Keggin unit does not involve the breaking of metal–oxygen bonds. This means that reduction results in the incorporation of hydrogen in the layer of HPAs. Figure 1C shows the TGA profile of the used catalyst $PdPV_3Mo_9$. This profile resembles the profile of the fresh catalyst but an additional weight reduction is observed at approximately 500 K. It is likely that this high temperature step is due to the destruction of the reduced Keggin structure, during which incorporated hydrogen reacts with the oxygen atoms in the Keggin structure to give water. The additional weight reduction corresponds to the desorption of approximately two water molecules per Keggin unit, which is in good agreement with the observed degree of reduction of five hydrogen atoms per Keggin unit.

CONCLUSIONS

Heteropolyacids of the Keggin type can be applied as redox components in heterogeneous Wacker oxidation catalysts. The performance of catalysts based on HPAs of the series PV_nMo_{12-n} in the oxidation of 1-butene is determined by the redox properties of the HPA. The regeneration of Pd(0) by the HPA proceeds very quickly, resulting in a high initial activity level for the catalyst, with butanone yields up to 0.07 g butanone per gram of catalyst per hour. However, the activity strongly decreases after 1 h on stream due to the slow reoxidation of the reduced HPA. Under steady-state conditions the activity of the catalyst is determined by the rate of reoxidation of the reduced HPA and the butanone yield is about $0.01\ g \cdot g^{-1} \cdot h^{-1}$.

The steady-state activity can be increased by enhancing the rate of reoxidation of the reduced HPA. This can be achieved either by increasing the number of vanadium atoms per Keggin unit or by exchanging the protons of the heteropolyacids for copper or nickel cations. Exchange of the protons for caesium cations gives a lower activity in the oxidation of 1-butene. A strong increase in the initial activity is observed with palladium salts. The palladium salt combines the Wacker reaction centre (Pd^{2+}) and a redox component (the HPA). The activity of catalysts based on palladium salts is a factor of 3 to 10 higher than the activity of catalysts based on the separate components, i.e., palladium sulfate deposited on a monolayer of heteropolyacids. An initial butanone yield of more than 0.2 grams of butanone per gram of catalyst per hour is obtained with catalysts $PdPV_2Mo_{10}$ and $PdPV_3Mo_9$.

The selectivity to butanone depends on the acidity of the protons of the HPA in the catalyst but is higher than 95% for catalysts based on vanadium-containing HPA. The major side product is 2-butanol, which is the product of the acid-catalyzed hydration of 1-butene. The selectivity increases when the number of vanadium atoms per Keggin unit increases and when the protons are exchanged for metal cations. If the acidic protons are exchanged for Cu^{2+} or Pd^{2+} the selectivity becomes more than 98% and the main side product is butanal.

The stability of the HPAs in the catalysts appears to be high, especially in the case of heteropolysalts. Heteropolyacid-based catalysts show, however, some deactivation upon application for longer periods of time in the oxidation of 1-butene. TPR experiments show that the HPAs are partly reduced under reaction conditions and that the degree of reduction roughly corresponds with the reduction of the vanadium atoms to the tetravalent state. The presence of high concentrations of V^{4+} in the used catalysts is confirmed by ESR experiments. The Keggin structure appears not be affected by this reduction. IR, ESR, ^{51}V NMR, and ^{31}P NMR showed no indications for the presence of degradation products of the Keggin structure in the used catalysts. Moreover, it was found that the Keggin structure is spontaneously restored when the catalysts are exposed to humid air. Even extensively reduced HPAs (more than 20 electrons per Keggin unit) are spontaneously regenerated under 1-butene oxidation conditions within several hours. Palladium salt-based catalysts also show continuing deactivation, which is probably a result of the high concentration of palladium in these catalysts. Deactivation might be caused by segregation of part of the palladium.

The steady-state activity of the HPA-based catalysts is comparable to the activity of the catalysts with vanadium oxide as a redox component (5, 6). The selectivity to butanone is, however, much higher for the HPA-based catalysts, e.g., 98% for PV_3Mo_9–Pd versus ~85% for V_2O_5-based catalysts. Also, the initial activity of especially the PdHPA-based catalysts is more than one order of magnitude higher. Therefore, HPA- and PdHPA-based catalysts appear to be very promising for the gas-phase Wacker oxidation of alkenes. Further research is required, however, mainly to optimize the reaction conditions and to improve the stability of this type of catalyst in long-term operations. The high initial activity can possibly be retained for longer periods of time by optimizing reaction conditions and catalyst composition. The results of variations in the reaction conditions and of regeneration experiments with spent catalysts will be reported in a following article.

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