

# Palladium salts of heteropolyanions as catalysts in heterogeneous Wacker oxidation of 1-butene

A.W. Stobbe-Kreemers, M. van der Zon, M. Makkee \*, J.J.F. Scholten

*Delft University of Technology, Faculty of Chemical Technology and Materials Science, Department of Chemical Process Technology, Section Industrial Catalysis, Julianalaan 136, 2628 BL Delft, The Netherlands*

## Abstract

Palladium salts of heteropolyanions, of the Keggin-series  $H_{3+n}PV_nMo_{12-n}O_{40}$ , supported on silica, have been successfully applied as catalysts in the gas-phase Wacker oxidation of 1-butene. In such catalysts the palladium reaction centre ( $Pd^{2+}$ ) and the redox component (HPA) are combined in one complex. At 343 K and atmospheric pressure a high initial yield of more than 0.16 g butanone/g of catalyst/h, in combination with a very high butanone selectivity of more than 98%, can be obtained.

In the steady-state, the activity of the catalysts is more than a factor ten lower than initially, due to slow reoxidation of reduced palladium–heteropolyanion complexes. The rate of reoxidation increases with increasing number of vanadium atoms per Keggin unit.

Under reaction conditions the PdHPAs are reduced by approximately five electrons per Keggin unit. DRIFT spectra of the used catalyst show that the Keggin unit is not affected by this reduction and that no oxygen is removed from the HPA. The DRIFT spectra also show that the reduction and the reoxidation at reaction temperature in the absence of water is fast in comparison with the standard reaction conditions.

*Keywords:* Palladium; Heteropolyanions; Wacker oxidation; Butene

## 1. Introduction

To overcome the disadvantages of the classical homogeneous Wacker oxidation process, such as the corrosivity of the system and the formation of chlorinated side products, various types of alternative Wacker oxidation systems have been developed.

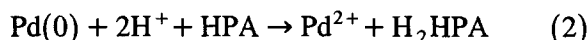
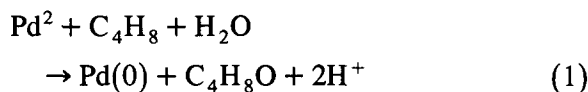
Matveev et al. [1,2] showed the oxidation of ethene to acetaldehyde in the  $PdSO_4$ –HPA system to be approximately 10 times faster than in

the classical chloride-containing ( $PdCl_2/CuCl_2$ ) system. Grate et al. [3] also showed that a factor of 100 can be obtained if the ratio of Pd and HPA is further decreased. 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, the rate-determining step involves the reoxidation of Pd(0) by dioxygen [1–3].

Davison [4] showed HPAs of the Keggin type to be suitable redox components in the liquid-

\* Corresponding author. Tel.: (+31-15) 2781391; fax: (+31-15) 2784452.

phase Wacker oxidation of 1-butene as well. Especially HPAs of the 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. Matveev [1,2], Grate [3], as well as Davison [4] 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 following reactions:



in which  $H_2HPA$  represents the reduced form of the HPA.

In this article the application of HPAs of the series  $H_{3+n}PV_nMo_{12-n}O_{40}$ , with  $n = 0, 2, 3$ , as redox components in heterogeneous Wacker oxidation catalysts is described. The HPAs are deposited on a silica support and impregnated with palladium sulfate. The catalysts have been tested in the oxidation of 1-butene to butanone and the influence of the number of vanadium atoms in the Keggin unit on the activity and selectivity is discussed. To study the existence and persistence of the Keggin unit on the silica support, catalysts have been investigated by means of DRIFT after different reduction and oxidation treatment.

## 2. Experimental

Heteropolyacids (HPAs) of the series  $H_{3+n}PV_nMo_{12-n}O_{40} \cdot xH_2O$ , with  $n$  is 2 or 3, were prepared according to the prescriptions of Brauer [5] and Tsigdinos and Hallada [6].  $H_3PMo_{12}O_{40} \cdot 27H_2O$ , obtained from Merck (reagent grade), was used without any further pretreatment. The palladium salts from the heteropolyacids were prepared according to the procedure described in detail before [7]. Pd:P:V:Mo ratios were determined by ICP analysis. The degree of hydration was determined thermogravimetrically in a Stanton Redcroft TG-750 thermobalance.

The heteropolyacids and the palladium salts were deposited on a silica support, viz. Davisil-300, BET surface area 287 m<sup>2</sup>/g. Two types of catalysts 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 in detail elsewhere [7]. 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 such that a monolayer of Keggin units was arrived at, presuming that the anions are uniformly spread over the

Table 1  
Catalyst codes and composition of heteropolyanions

| Code                                 | Real composition HPA <sup>a</sup>   | HPA loading <sup>b</sup> (wt%) | Palladium loading (wt%) |
|--------------------------------------|---|--------------------------------|-------------------------|
| PMo <sub>12</sub> -Pd                | H <sub>3</sub> PMo <sub>12</sub> O <sub>40</sub> · 27H <sub>2</sub> O                                       | 42.5                           | 0.2 <sup>c</sup>        |
| PV <sub>2</sub> Mo <sub>10</sub> -Pd | H <sub>5</sub> PV <sub>2,2</sub> Mo <sub>9,8</sub> O <sub>40</sub> · 27H <sub>2</sub> O                     | 41.9                           | 0.2 <sup>c</sup>        |
| PV <sub>3</sub> Mo <sub>9</sub> O-Pd | H <sub>6</sub> PV <sub>3,2</sub> Mo <sub>8,8</sub> O <sub>40</sub> · 29H <sub>2</sub> O                     | 41.7                           | 0.2 <sup>c</sup>        |
| PdPMo <sub>12</sub>                  | Pd <sub>1,1</sub> H <sub>0,8</sub> PMo <sub>12</sub> O <sub>40</sub> · 20H <sub>2</sub> O                   | 44.5                           | 2.3                     |
| PdPV <sub>2</sub> Mo <sub>10</sub>   | Pd <sub>1,6</sub> H <sub>1,8</sub> PV <sub>2</sub> Mo <sub>10</sub> O <sub>40</sub> · 21H <sub>2</sub> O    | 42.9                           | 3.4                     |
| PdPV <sub>3</sub> Mo <sub>9</sub>    | Pd <sub>1,3</sub> H <sub>3,4</sub> PV <sub>2,9</sub> Mo <sub>9,1</sub> O <sub>40</sub> · 21H <sub>2</sub> O | 40.4                           | 2.6                     |

<sup>a</sup> Determined by ICP and TGA analysis, P is arbitrarily set to 1.

<sup>b</sup> Defined as (g HPA)/(g silica + HPA).

<sup>c</sup> Palladium sulfate has been applied in a subsequent impregnation step.

surface and that one Keggin unit occupies 1.44 nm<sup>2</sup>. 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 above calcium chloride. Table 1 lists the composition of the HPAs and palladium loadings of the catalysts as deduced from ICP and TGA analysis. In the further discussion, the catalysts will be denoted by the codes given in Table 1.

Catalysts were tested in the oxidation of 1-butene to butanone in a conventional micro-flow apparatus [7]. Approximately 0.7 g of catalyst was mixed together with glass beads and loaded into the stainless-steel reactor. Catalysts were tested under standard reaction conditions (total flow of 50 ml/min, atmospheric pressure and in a temperature range of 313–373 K). The reaction products were analyzed by means of a gas chromatograph equipped with a 25-m capillary FFAP column (internal diameter 320 μm). The butanone yield is expressed in gram butanone produced/g catalyst/h.

DRIFT spectra of the catalysts were recorded on a Nicolet Magna-IR spectrometer 550. Samples were mixed and ground with KBr and loaded into the sample holder.

### 3. Results and discussion

#### 3.1. Performance in 1-butene oxidation

In our previous articles [7,8] we reported that heteropolyanions of the series H<sub>3+n</sub>PV<sub>n</sub>Mo<sub>12-n</sub>O<sub>40</sub> are good reoxidants in heterogeneous Wacker oxidation catalysts. Especially the initial activity of the catalysts is high, resulting in butanone yields of up to 0.16 g butanone/g catalyst/h and butanone selectivities of more than 98%.

Fig. 1 shows the butanone yield and selectivity as a function of time for a catalyst based on the palladium salt of PV<sub>3</sub>Mo<sub>9</sub>. The catalyst shows a high initial activity and it can be concluded that, although palladium is present as the

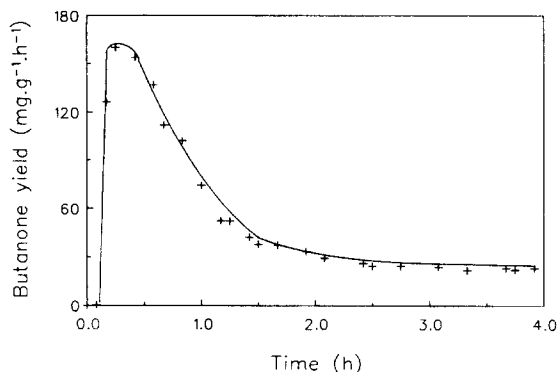


Fig. 1. Butanone yield (+) of catalyst PdPV<sub>3</sub>Mo<sub>9</sub> at 343 K as a function of time. Feed: 1 kPa 1-butene, 7 kPa H<sub>2</sub>O in air.

HPA counter cation, it also acts as the reaction site for Wacker oxidation. The catalyst shows a similar activity profile as the catalysts based on the heteropolyacid, which are afterwards impregnated with palladium sulfate; a high initial activity is observed, which rapidly declines to a lower steady-state activity. Initially the 1-butene in the feed is completely converted with a selectivity of more than 98% to butanone, giving a butanone yield of 0.16 g · g<sup>-1</sup> · h<sup>-1</sup>. After 0.5 h the activity starts to decline and, after 2 h, reaches a value of 0.035 g · g<sup>-1</sup> · h<sup>-1</sup>. In the next 20 h of operation the activity further declines to a yield of approximately 0.016 g · g<sup>-1</sup> · h<sup>-1</sup>. The selectivity to butanone remains constant (> 98%) over the whole period of catalyst screening.

Although the performance of the PdHPA-based catalyst is comparable to that of heteropolyacid-based catalysts, the initial butanone yield is a factor ten higher than that of the acid-based catalysts, to which PdSO<sub>4</sub> was added. The higher activity is probably caused by the higher palladium loading and by the chemical bonding between the palladium cations and the heteropolyanions.

The two types of catalysts are compared in Fig. 2, which shows the initial activity and butanone selectivity as a function of the number of vanadium atoms per Keggin unit (*n*). The initial butanone yield, see Fig. 2A, of the palladium salt-based catalysts (type 2) is a factor 3 to

10 higher than the yield of the catalysts based on the acids to which  $\text{PdSO}_4$  was added (type 1). For both types of catalyst the activity increases with increasing number of vanadium atoms in the Keggin unit. This is due to the fact that the rate of reoxidation of the reduced HPAs increases with increasing  $n$ .

Fig. 2B shows the initial butanone selectivity for the two types of catalysts. The butanone selectivity of the type 1 catalysts increases with increasing number of  $n$ . This is caused by the weakening of the acidity of the protons with increasing number of  $n$ , resulting in the suppression of the acid-catalyzed hydration of 1-butene to 2-butanol. The selectivity of the palladium salt-based catalysts is very high, viz. more than 98%. Since the larger part of the acidic protons are exchanged for palladium cations the formation of 2-butanol is negligible for these

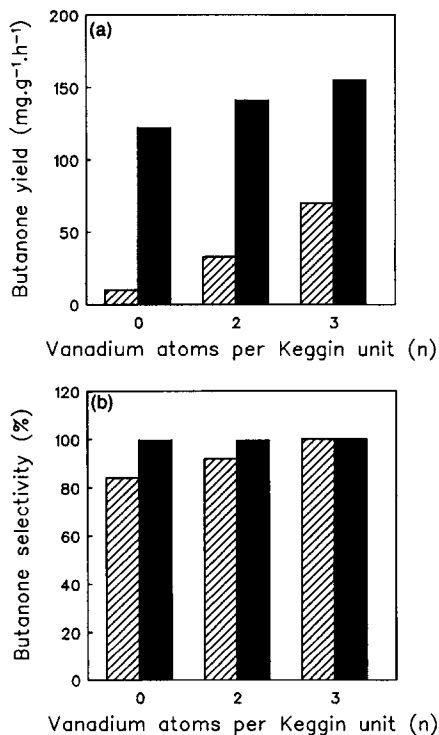


Fig. 2. Difference in initial butanone yield (A) and butanone selectivity (B) between catalyst based on heteropolyacids impregnated with palladium sulfate (dashed) and catalysts based on the palladium salts of these acids (black).

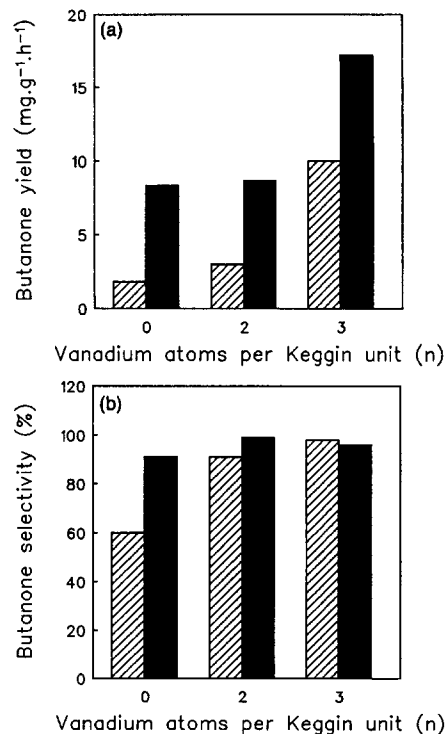


Fig. 3. Difference in butanone yield (A) and selectivity (B) after 6 h, between catalysts based on heteropolyacids impregnated with palladium sulfate (dashed) and catalysts based on the palladium salts of these acids (black).

catalysts. Here the main side product is butanal, which is produced by the anti-Markownikoff addition of water to 1-butene.

Fig. 3A shows the butanone yield of the two types of catalysts after 6 h on stream. For both types of catalysts the yield decreases to a lower steady-state level. The activity of the type 2 catalysts, however, is still a factor two to three higher than that of the type 1 catalysts. The decrease in activity is caused by the slow reoxidation of the reduced HPAs.

The observed decrease in activity is higher for the palladium salt-based catalysts than for the acid-based. This is probably a result of the low HPA over Pd ratio in the PdHPA-based catalysts, e.g. for catalyst  $\text{PdPV}_2\text{Mo}_{10}$  this ratio is 0.6, which means that for every Keggin unit there are almost two palladium atoms which have to be reoxidized. The low HPA/Pd ratio might result into an inefficient reoxidation of

palladium, resulting in the accumulation of Pd(0). Therefore, a HPA/Pd ratio larger than one has to be preferred.

A higher HPA/Pd ratio is also preferred in the case of the homogeneous oxidation of ethene to acetaldehyde. Mateev [1,2] and Grate [3] claimed that the accumulation of Pd(0) can only be prevented by using a high HPA/Pd ratios. Table 2 shows the characteristics of several different Wacker oxidation system. From this table it is very clear that high turn-over frequencies for palladium can only be obtained in the presence of a large excess of redox component, preferably  $\text{redox/Pd} > 1000$ . In this case the reoxidation of the reduced HPA is no longer rate determining due to the high concentration of the redox component. Moreover, in the homogeneous system the reoxidation of HPA is enhanced by the presence of  $\text{VO}_2^+$  species in the aqueous solution as reported by Davison [4]. The  $\text{VO}_2^+$  species are formed by the decomposition of  $\text{H}_{3+n}\text{PV}_n\text{Mo}_{12-n}$  under reaction conditions.

In homogeneous systems the  $\text{redox/Pd}$  ratio can easily be altered, but in the heterogeneous catalysts this is much more complicated. Therefore, other means to improve the activity of the heterogeneous catalysts have to be found, such as in adjusting HPA composition, addition of promoter to the catalyst, optimizing reaction conditions, etc.

### 3.2. Characterization of catalysts used

Since the rate of reoxidation of the reduced PdHPA complex is rate limiting under reaction conditions, the PdHPAs are reduced during the reaction. In our previous paper [7] we showed that HPAs are multi-electron acceptors. The degree of reduction of the PdHPAs can be estimated from the total amount of butanone produced in the absence of dioxygen in the feed. For  $\text{PdPV}_3\text{Mo}_9$  a degree of reduction of approximately 5 electrons per Keggin unit was found [7], which roughly corresponds to the reduction of the vanadium atoms in the Keggin structure from  $\text{V}^{5+}$  to  $\text{V}^{4+}$  and/or  $\text{Pd}^{2+} \rightarrow \text{Pd}(0)$ .

In order to investigate whether the reduction of the PdHPAs under reaction conditions leads to the destruction of the Keggin unit or to the breaking of metal–oxygen bonds, DRIFT spectra of the fresh and used catalyst  $\text{PdPV}_3\text{Mo}_9$  were recorded. Fig. 4A shows the DRIFT spectrum of pure  $\text{PdPV}_3\text{Mo}_9$ . The spectrum shows the absorption bands characteristic of the Keggin structure, viz. absorptions at 790 and 880  $\text{cm}^{-1}$ , at 957  $\text{cm}^{-1}$  and at 1050  $\text{cm}^{-1}$ , respectively due to vibrations of the M–O–M, M=O and P–O bonds (M represents Mo or V). Fig. 4B shows the DRIFT spectrum of the fresh silica-supported catalyst  $\text{PdPV}_3\text{Mo}_9$ . The characteristic absorptions are still present at the same positions showing that the Keggin struc-

Table 2  
Comparison of different Wacker oxidation systems

|                  | Catalitica [3]   | Matveev [3]   | TU Delft   | Industrial [3]                                  |
|------------------|--|---|--|---|
| Catalytic system | HPA, $\text{PdCl}_2$ , NaCl<br>homogeneous, two stages             | HPA, $\text{H}_2\text{SO}_4$ , $\text{PdSO}_4$<br>homogeneous, two stages | HPA, $\text{H}_2\text{SO}_4$ , $\text{PdSO}_4$<br>heterogeneous, one stage | $\text{PdCl}$ , CuCl<br>homogeneous, two stages |
| Reactant         | ethene   | ethene  | butene   | ethene  |
| TOF Pd(1/s)      | 100  | < 0.5   | initial: ca. 0.01<br>steady-state: ca. 0.001                               | 0.1–1   |
| Pd:HPA or Pd:Cu  | 1:3000   | 1:100   | 1:10   | 1:100   |
| Rate limiting    | red.: $\text{Pd}^{2+}/\text{Pd}^0$ ox.: $\text{O}_2$ mass transfer | red.: $\text{Pd}^0/\text{Pd}^{2+}$ ox.: $\text{O}_2$ mass transfer        | $\text{H}_2$ HPA/HPA   |   |
| Conditions       | 10 bar/393 K   | 313 K   | 1 bar/343 K  | 10 bar/393 K                                    |

ture is not affected by the silica support. The P–O vibration is masked by the strong adsorption of the silica support between 1020 and 1300  $\text{cm}^{-1}$ .

Fig. 4C shows the DRIFT spectrum of the catalyst after it has been used for 16 h in the oxidation of 1-butene. This spectrum appears to be identical to the spectrum of the fresh catalyst showing that the Keggin structure has largely remained intact. The only difference is that the adsorption bands in the spectrum of the used catalysts are slightly broader, showing a diversity in bond lengths in the used catalyst, and the evolution of a minor shoulder at 1000  $\text{cm}^{-1}$ , which can be ascribed to the formation of  $\text{MoO}_4^{2-}$ . Since both the M=O and the M–O–M vibrations still have the same intensity as in the spectrum of the fresh catalyst these bonds appear not to be broken during the reduction of the PdHPA. These results indicate that the reduction leads to the incorporation of hydrogen atoms in the overlayer of PdHPA on the silica surface without the removal of oxygen from the Keggin unit, forming a bronze-like structure.

To study the effects of reduction and reoxidation of the HPA structure,  $\text{PV}_2\text{Mo}_{10}\text{-Pd}$  was subjected to cycles of reduction and reoxidation in the DRIFT-cell at 348 K in the absence of water vapour. Fig. 5A shows the change in the DRIFT spectrum during the reduction with di-

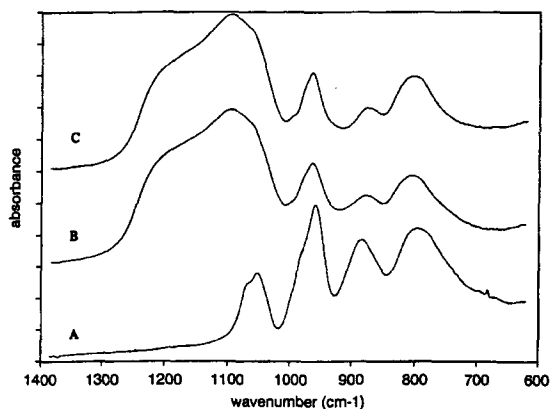


Fig. 4. DRIFT spectra of (A) pure  $\text{PdPV}_3\text{Mo}_9$ , (B) fresh catalyst  $\text{PdPV}_3\text{Mo}_9$ , and (C) catalyst  $\text{PdPV}_3\text{Mo}_9$  after it has been used 16 h in the oxidation of 1-butene.

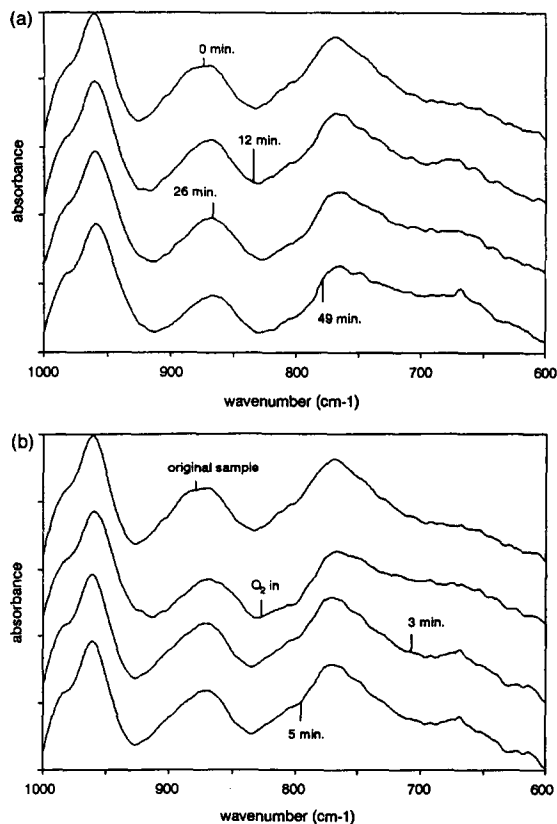


Fig. 5. DRIFT spectra of (A) the reduction of  $\text{PV}_2\text{Mo}_{10}\text{-Pd}$  in the presence of dihydrogen and (B) the reoxidation of reduced  $\text{PV}_2\text{Mo}_{10}\text{-Pd}$  in the presence of dioxygen (both at 348 K).

hydrogen. This figure clearly shows that reduction in dihydrogen proceeds much further than the reduction under Wacker oxidation conditions (see Fig. 4C). During the reduction in dihydrogen, the characteristic absorption bands of the Keggin structure strongly diminish and a new peak is observed at 660  $\text{cm}^{-1}$ , which is assigned to reduced  $\text{V}_2\text{O}_5$  species. The deep reduction clearly results in the disintegration of the Keggin structure. Fig. 5B, however, shows that the treatment in a mixture of 10 vol.% dioxygen in dinitrogen rapidly restores the original DRIFT pattern of the fresh catalyst. Complete reoxidation of the catalyst can be accomplished within 5 min. At a temperature of 423 K the reduction and reoxidation are an order of magnitude faster. At both temperatures the reduction–reoxidation cycles can be repeated at

least five times without loss of intensities in the absorption bands in comparison with the original catalyst.

When 1-butene is used instead of dihydrogen to reduce the catalyst, the degree of reduction of  $PV_2Mo_{10}-Pd$  is comparable with the level of reduction found in the spent catalyst. Moreover, the reoxidation of this reduced HPA is very strongly inhibited. A treatment for at least 4 h at 373 K in 20 vol.% dioxygen in dinitrogen is required to reoxidize the catalyst. The slow reoxidation of the catalyst is probably caused by in the presence of adsorbed butanal on the catalyst. Davison [4] reported that the reoxidation of the reduced HPA is strongly inhibited the presence of butanal.

This inhibiting effect may very well be the cause for the low steady-state activity of the heterogeneous catalyst under our reaction conditions. However, further research is still required to elucidate these phenomena. The presence of water in considerable amounts under reaction conditions may also affect the reduction and reoxidation of the catalysts.

#### 4. Conclusion

Palladium salts of heteropolyanions of the series  $H_{3+n}PV_nMo_{12-n}O_{40}$  have been successfully applied as active components in catalysts for the gas-phase oxidation of 1-butene. 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 three to ten higher than the activity of catalyst based on the separate components, i.e. palladium sulfate deposited on a monolayer of heteropolyacids. An initial butanone yield of more than 0.16 g butanone/g catalyst/h is obtained with catalysts  $PdPV_2Mo_{10}$  and  $PdPV_3Mo_9$ . Due to the fact that the strongly acidic protons of the HPA have been exchanged for palladium cations the butanone selectivity is more than 98% and the main side product isobutanal.

The experiments show that under steady-state conditions the activity of the catalyst is limited by the rate of reoxidation of the reduced  $PdH-PA$ s. This rate of reoxidation increases with increasing number of vanadium atoms per Keggin unit.

DRIFT analyses indicate that the reduction with 1-butene does not lead to removal of oxygen from the Keggin structure. Therefore, the reduction of the catalysts probably comprises the incorporation of hydrogen atoms in the  $PdHPA$  monolayer of the catalyst, giving a bronze-like structure. Reduction of the catalyst with dihydrogen proceeds faster and also further than the reduction under reaction conditions. Reoxidation of the dihydrogen reduced catalyst proceeds fast as well. Both the reduction and reoxidation are enhanced at higher temperatures. Reduction of the catalyst with 1-butene leads to a degree comparable with that found under reaction conditions. Reoxidation after the reduction with 1-butene is very slow, probably due to the strong adsorption of butanal on the catalyst.

#### Acknowledgements

The work described in this paper was supported by the Netherlands Foundation for Chemical Research (SON), with financial aid of the Netherlands Organization for Scientific Research (NWO).

#### References

- [1] K.I. Matveev, *Kinet. Katal.*, 18 (1977) 716.
- [2] K.I. Matveev, E.G. Zhizhina, N.B. Shitova and L.I. Kuznetsova, *Kinet. Katal.*, 18 (1977) 320.
- [3] J.H. Grate and D.R. Hamm, in J.R. Kosak and T.A. Johnson (Eds.), *Catalysis in Organic Reactions*, Dekker, New York, 1994, p. 213, and references cited therein.
- [4] S.F. Davison, PhD Thesis, University of Sheffield, 1982.
- [5] G. Brauer, *Handbuch der Präparativen Anorganische Chemie*, 3rd Ed., Enke Verlag, Stuttgart, 1981, p. 1781.
- [6] G.A. Tsigdinos and C.J. Hallada, *Inorg. Chem.*, 7 (1968) 37.
- [7] A.W. Stobbe-Kreemers, R. Dielis, M. Makkee and J.J.F. Scholten, *J. Catal.*, 154 (1995) 175.
- [8] A.W. Stobbe-Kreemers, G. van der Lans, M. Makkee and J.J.F. Scholten, *J. Catal.*, 154 (1995) 187.