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Transition metal salts of heteropoly acids as palladium co-catalysts for Wacker oxidation of butene-1 to MEK

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The transition metal salts of heteropoly acids have been applied as palladium re-oxidants in heterogeneous solid Wacker catalysts for the oxidation of butene-1 to MEK. Silica, γ-alumina and titania were used as supports for the Pd/MeHPMoV$_x$ system. The influence of cations bonded to heteropoly anions and also the effect of the catalysts acidity on the butene-1 to MEK oxidation have been elucidated.

Keywords: Wacker process, butene-1 oxidation, methyl ethyl ketone, heteropoly compounds

1. Introduction

The Wacker process of olefins oxidation to carbonyl compounds has been developed with homogeneous catalysis [1] comprising palladium chloride as a catalyst and copper chloride as co-catalyst. The process occurs according to the following equations:

$$\mathrm{CH_2{=}CH_2 + H_2O + PdCl_2 \rightarrow CH_3CHO + Pd(0) + 2HCl} \qquad (1)$$

$$\mathrm{Pd(0) + 2CuCl_2 \rightarrow PdCl_2 + 2CuCl} \qquad (2)$$

$$\mathrm{2CuCl + \tfrac{1}{2}O_2 + 2HCl \rightarrow 2CuCl_2 + H_2O} \qquad (3)$$

The Wacker process is efficient for the ethene to acetaldehyde oxidation, however, the oxidation of higher olefins is less selective towards the carbonyl compounds and also leads to various chlorine derivatives. Attempts have been made to apply chloride-free catalytic systems for oxidation of butene-1 [2,3] and of higher olefins (C_8–C_{16}) [4–6] under homogeneous conditions. Heteropoly acids containing combinations of molybdenum and tungsten ($\mathrm{PMo_{12-x}W_x}$) or molybdenum and vanadium ($\mathrm{PMo_{12-x}V_x}$) as the terminal atoms have been found to be efficient re-oxidants of palladium(0) in liquid phase [2,3,5–8]. Stobbe-Kreemers et al. [9–11] reported that heteropoly acids could also be used as palladium co-catalysts in the solid catalytic system for butene-1 to MEK oxidation. However, the solid catalysts lost their activity very fast and this seems to be a main restriction in the application of solid catalysts. Jacobs et al. reported [12] that the Y zeolite modified with palladium and copper showed high ethene conversion for 50 h, but they did not test this catalytic system for higher olefins oxidation. Our earlier results [13–15] have also indicated that catalysts containing transition metal salts of heteropoly acids as a palladium co-catalyst were capable of oxidising ethene with high acetaldehyde yield for at least 50 h. Such a promising result prompted us to examine these catalysts for the oxidation reaction of butene-1 to MEK.

In this paper we present the effect of different cations attached to $\mathrm{PMo_{12-x}V_x}$ heteropoly anions on the activity for the oxidation of butene-1 to MEK. The influence of different supports and the effect of acidic centres on the activity and lifetime of solid Wacker catalysts for butene-1 oxidation have been studied, as well.

2. Experimental

Catalysts. Mixed heteropoly acids (HPA) containing molybdenum and vanadium as polyatoms were synthesised according to the literature recipe [16]. Heteropoly acid salts were prepared in aqueous solution using different HPA's and stoichiometric amounts of carbonates, sulphates, nitrates or acetates of the appropriate metals. Heteropoly acid salts were supported on silica (Si), γ-alumina (Al), titania (Ti), and potassium salt of HPMo (KPMo). The incipient wetness method was applied. The catalysts were dried at 70°C to obtain MePMoV$_x$/S systems (S = support). Pd (0.2 wt%) was introduced on MePMoV$_x$/S systems as PdCl$_2$ in aqueous solution of hydrochloric acid and then dried at 70°C.

Catalytic test. The oxidation of butene-1 to MEK was conducted in a continuous flow reactor. 0.5 g of catalyst was used at WHSV = 3.0 g/(g h). The feed contained: air : water vapour : butene-1 (in molar proportion = 66 : 11 : 1).

The acidity of the catalysts was preliminary estimated regarding their activity in the acid catalysed reactions. The activity for *i*-propanol dehydration and cumene cracking was measured at 130 and 250°C, respectively, in a pulse microreactor connected to GC as described earlier [17].

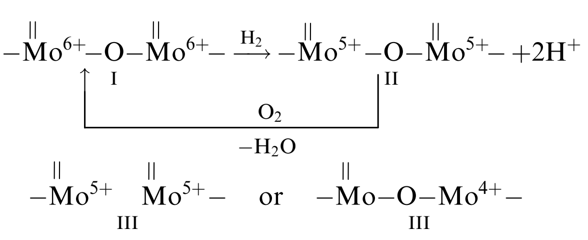
Butene-1 isomerisation was carried out in a pulse microreactor at 70°C.

3. Results and discussion

3.1. The cations effect on the activity for butene-1 oxidation

In our earlier reports [13–15] we found very high and stable activity of solid Wacker catalysts containing heteropoly acid salts with transition metal cations for oxidation of ethene to acetaldehyde. It seems reasonable that the catalysts can also be effective for the oxidation of butene-1 to MEK in the solid/gas phase system. Stobbe-Kreemers et al. [9,10] have reported that some of the transition metal cations (Cu^{2+}, Ni^{2+}) bonded to heteropoly anions stabilised the activity of the solid Wacker catalysts used for butene-1 to MEK oxidation. However, the steady state activity of these catalysts (measured after 20 h on stream) was very low.

In our experiments, the silica supported catalysts containing heteropoly acids ($H_{3+x}PMo_{12-x}V_xO_{40}$ – HPMoV$_x$; $0 \leqslant x \leqslant 3$) as palladium reoxidants lost their activity very fast, which was also observed by Stobbe-Kreemers et al. [9,10]. The following study showed that the transition metal salts (Zn^{2+}, Na^{+}, Fe^{2+}, Bi^{3+}, Cr^{3+}, Co^{2+}, Mn^{2+}) of heteropoly acids ($H_{3+x}PMo_{12-x}V_x$) ($0 \leqslant x \leqslant 3$) as palladium co-catalysts influenced both the catalysts activity and their lifetime. The initial activity of the catalysts supported on silica varied depending on the cations, in the following way: Co > Zn > Fe > Mn ⩾ Bi (figure 1, curve 1). Butene-1 conversion decreased with time. The Zn salt containing catalyst appeared most stable (figures 2 and 3) whereas the other catalysts lost their activity already after 10 h. The question arises what the reason for such a significant deactivation of the catalysts is. We noticed [14,15] that the heteropoly compounds (HPC) of very low ability to remove the oxygen from the Keggin unit during the reduction process were especially suitable for palladium reoxidation in the ethene to acetaldehyde oxidation. Stobbe-Kreemers et al. [11] also mentioned that the active catalysts used for Wacker oxidation did not loose the oxygen from HPA structure during the butene-1 oxidation. As was shown by Akimoto et al. [18] and also in our reports [14,15], the cations present in the heteropoly acids salts modify the reducibility and the reoxidation ability of heteropoly anions. The oxidation activity of the catalysts containing heteropoly compounds could, however, be modified by cations. According to Misono [19] the reduction and reoxidation of the solid heteropoly compounds proceeds in two steps:



$$-\overset{\|}{Mo}{}^{6+}-O-\overset{\|}{Mo}{}^{6+}- \xrightarrow{H_2} -\overset{\|}{Mo}{}^{5+}-O-\overset{\|}{Mo}{}^{5+}- +2H^+ \xrightarrow[-H_2O]{}$$

$$\text{I} \xleftarrow[-H_2O]{O_2} \text{II}$$

$$-\overset{\|}{Mo}{}^{5+} \quad \overset{\|}{Mo}{}^{5+}- \quad \text{or} \quad -\overset{\|}{Mo}-O-Mo^{4+}- \qquad \text{III} \qquad (4)$$

The first step of the reduction (I → II) occurs rapidly and is reversible. The second step involves oxygen removal from the Keggin unit (I → III) and is only partly reversible. The application of the heteropoly compounds of very low oxygen removal ability during the reduction process (MnPMoV$_x$ and ZnPMoV$_x$) resulted in solid Wacker catalysts of high steady state activity for acetaldehyde formation, measured after 50 h on stream. One could expect that the same catalysts should also be efficient for the butene-1 to MEK oxidation. It should be considered, of course, that the rate of butene-1 oxidation is significantly lower than the rate of ethene oxidation [20]. The rate of oxidation of olefins changes in the following order: ethene > propene ≫ butene-1 [21]. The catalyst containing ZnPMoV$_x$ as palladium reoxidant appeared as the only one in a studied series to show a high activity for butene-1 to MEK oxidation after 10 h on stream (figures 2 and 3). The others, including those of low reducibility (expressed as the ability of oxygen removal from the Keggin structure, e.g. MnPMoV$_x$ containing catalyst [14,15]), lost their activity for butene-1 oxidation very quickly (figure 2).

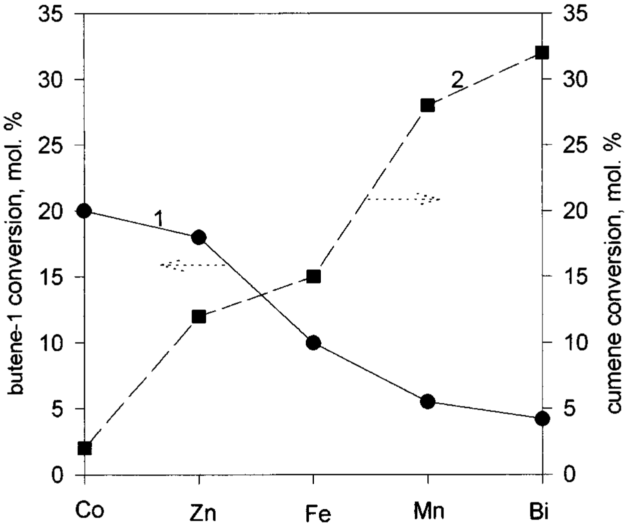


Figure 1. A correlation of the initial conversion of butene-1 to MEK over the Pd/MeHPMoV$_x$/Si catalysts with their activity for cumene cracking (Me = Co^{2+}, Zn^{2+}, Mn^{2+}, Bi^{3+}, Fe^{2+}). (1) Initial activity for butene-1 oxidation; (2) cumene cracking conversion.

It is commonly known that the feasibility of the catalysts for reduction and reoxidation is the important factor affecting their red-ox activity and stability. Nevertheless, these parameters are not the only features influencing the red-ox activity. The acidity of the catalysts surface affects the reagents and products adsorp-

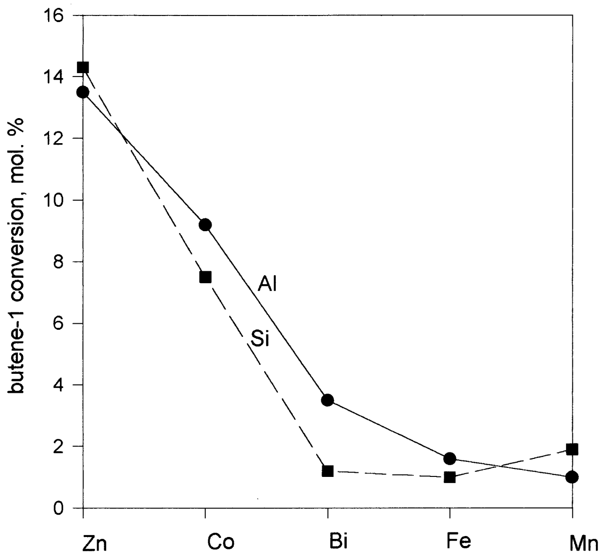


Figure 2. The conversion of butene-1 to MEK over Pd/MPMoV$_2$/Si and Pd/MPMoV$_2$/Al after 10 h on stream.

tion. Strongly adsorbed compounds may undergo a total oxidation or may be transformed to undesired by-products.

3.2. *Acidity of the samples*

All the catalysts studied show some acidity (measured as an activity for *i*-propanol dehydration (figure 4) and cumene cracking (figure 1 curve 2 and figure 5 curve 2).

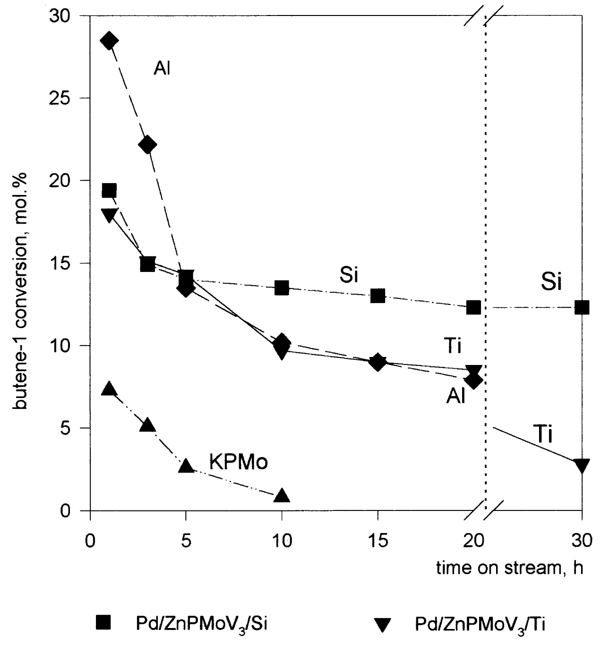


Figure 3. The influence of different supports applied for solid Wacker catalysts containing ZnPMoV$_3$ as a palladium reoxidant on the catalysts lifetime.

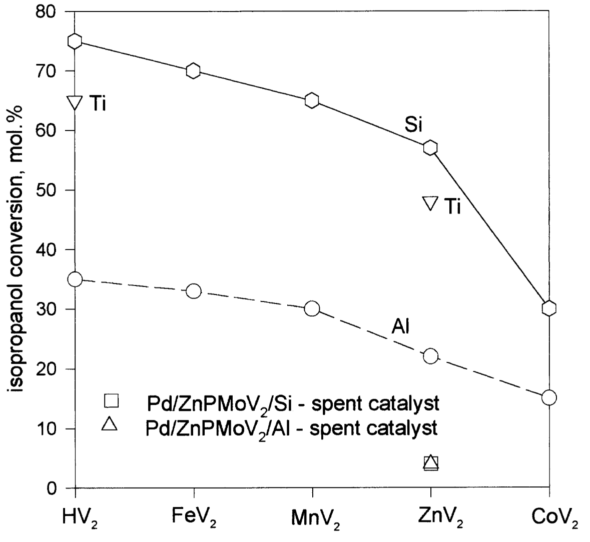


Figure 4. The acidity of the Pd/MPMoV$_2$/Si and Pd/MPMoV$_2$/Al catalysts measured as the activity for *i*-propanol dehydration.

According to refs. [22,23], the *i*-propanol dehydration correlates with the total acidity of the sample comprising even very weak acid centres. The cumene cracking reaction is catalysed by strong protonic sites. The acidic centres can initiate the butene-1 isomerisation and also oligomerisation or polymerisation of olefins. Each of these reactions may compete with butene-1 oxidation. Butanone-2 may be formed by means of oxidation of either butene-1 or cis- and trans-butene-2. Since the rate of olefins oxidation changes in the following order: butene-1 $\approx$ cis-butene-2 $>$ trans-butene-2 [21], the isomerisation of butene-1 to trans-butene-2 decreases in the MEK formation. The studied catalysts showed high activity for butene-1 isomerisation already at 70°C (figure 6A) (from about 30 mol% on Pd/MnPMoV$_2$/Al

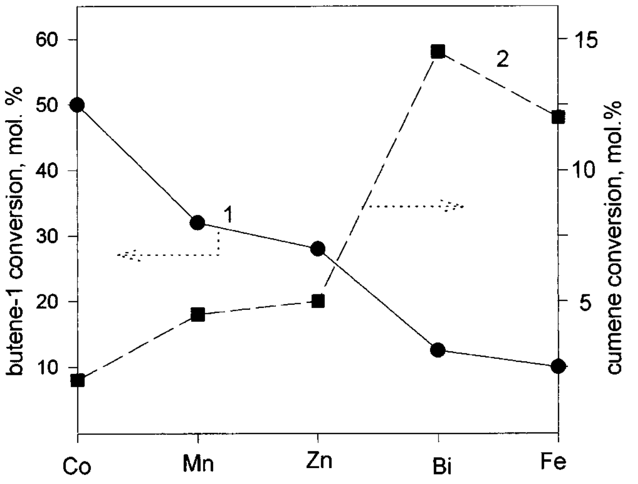


Figure 5. A correlation of the initial conversion of butene-1 to MEK over the Pd/MeHPMoV$_x$/Al catalysts with their activity for cumene cracking (Me = Co^{2+}, Zn^{2+}, Mn^{2+}, Bi^{3+}, Fe^{2+}). (1) Initial activity for butene-1 oxidation; (2) cumene cracking conversion.

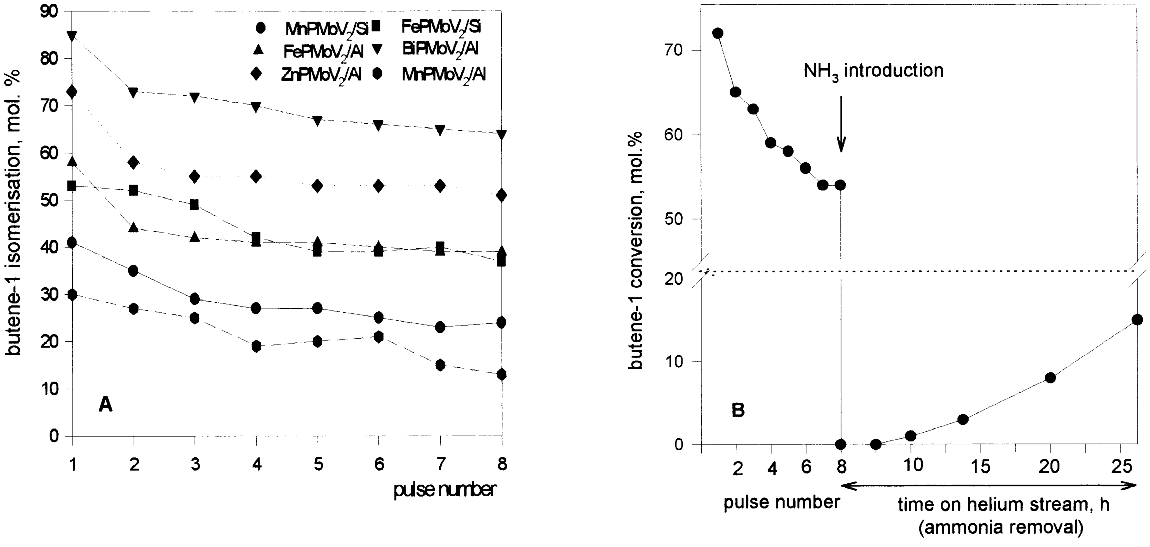


Figure 6. The activity of the Pd/MeHPMoV$_x$/Si(Al) catalysts for butene-1 isomerisation. (A) Fresh catalysts; (B) the Pd/ZnHPMoV$_x$/Al catalyst treated with ammonia, which was continuously removed with a helium stream.

up to 85 mol% over Pd/BiMoV$_2$/Al catalysts). The ratio of trans/cis isomers was always higher than 1 (1.4–1.9) and it was practically stable for a long time. The introduction of water into the catalyst bed did not affect the catalyst's activity for butene-1 isomerisation. It shows that butene-1 isomerisation may occur during the oxidation reaction (butene-1 oxidation was carried out in the presence of steam). Ammonia injected into a catalyst bed suppressed the isomerisation activity almost completely. However, after subsequent 10 h purging of helium (at 70°C), the activity for butene-1 isomerisation appeared again (4 mol%) and rose up to 10% after the next 10 h (figure 6B). We have also used ammonia to suppress the acidity of the catalyst applied for butene-1 oxidation. The catalyst Pd/ZnPMoV$_x$/Al(Si), treated with ammonia, showed higher activity for oxidation of butene-1 to MEK than the untreated one (both for initial and steady state periods) (figure 7). The decrease in the oxidation activity of the ammonia treated catalysts was observed after about 30 h on stream (figure 7) when the acidic centres responsible for butene-1 isomerisation were recovered (figure 6B). The influence of adsorbed ammonia is quite different for the oxidation and isomerisation of butene-1. The low acidity (adsorbed ammonia) results in high MEK formation, whereas the yield of MEK decreases as acidic sites have been recovered (figures 7 and 6B).

The presence of strong acidic sites (high activity for cumene cracking, figures 1 and 5 curves 2) may also result in the oligomerisation of butene-1 with formation of "white cokes" covering the surface of the catalyst and isolating the reagents from the surface active centres. Vaughan et al. [24] have recently reported the activity of free and supported heteropoly acids and their salts for propene oligomerization. The oligomerization of isobutene over MgF$_2$ supported heteropoly acids was reported to occur at 70°C in pentadecane solution [25]. Adsorption of butene-1 over heteropoly acids supported on silica was carefully investigated by means of the IR spectra by Gao and Moffat [26]. They showed the formation of the branched polymerised butene on the surface of catalysts which could be concluded from the intensities of IR bands of methylene groups when compared to methyl ones. These results suggest that the higher olefins undergo some other reactions on the catalyst surface, which could compete with the oxidation process. Advantageous influence of adsorbed ammonia confirms the assumption that the side-reactions catalysed by the acidic centres may be responsible for fast deactivation of the catalysts studied.

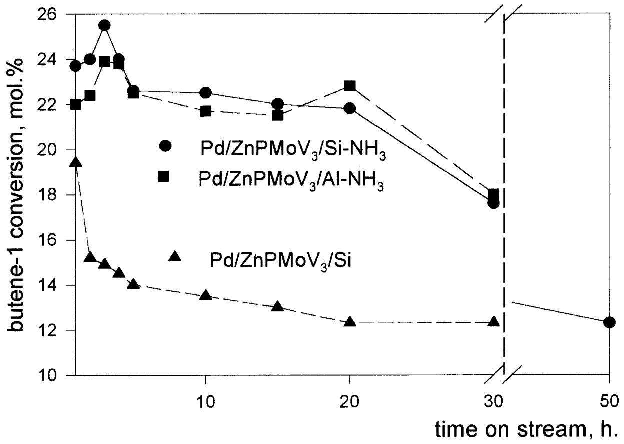


Figure 7. The influence of ammonia introduced into the catalyst bed on the activity of the Pd/ZnPMoV$_3$ catalyst supported on silica and γ-alumina.

3.3. *Influence of the support*

The activity and also the acidity of the catalysts containing heteropoly compounds may be modified by the use of different supports. These are mainly weakly acidic silanol OH groups on the surface of the silica support. However, the interaction of the silica OH groups with the heteropoly acids protons leads to a decrease in HPA acidity, especially, at a low HPA coverage [27]. The γ-alumina, titania, magnesia and zinc oxide surfaces contain mostly basic centres of different strengths. HPA supported on magnesia and zinc oxide showed no activity for butene-1 oxidation. It resulted probably from the HPA structure degradation in contact with strong base centres which was concluded from IR spectra [17]. γ-alumina support reduces HPA acidity. Nevertheless, the presence of quite strong acidic centres was reported on the samples containing 30–60 wt% of HPA on the γ-alumina surface [17]. The acidity of the samples supported on γ-alumina is considerably lower than that of the catalysts supported on silica (figures 1, 4 and 5). The lower acidity of γ-alumina supported catalysts may be an explanation of the higher initial activity of the Pd/ZnPMoV$_3$/Al catalyst than that of Pd/ZnPMoV$_3$/Si (figure 3). The acidity of the spent catalysts, both silica and γ-alumina supported, was practically the same (figure 4) and this is probably the reason that the activities of these samples for butene-1 oxidation to MEK were very close to each other after the first 5 h on stream (figure 3). KPMo support, successfully applied as a support of heteropoly acid used for oxidation of acrolein to acrylic acid [27], gave catalysts with rather low activity for butene-1 oxidation and it made them deactivate relatively fast with time on stream (figure 3). The low activity of the KPMo supported catalyst can be due to a partial exchange of potassium and zinc cations. This kind of interaction between HPMo supported on KPMo was described by Black et al. [27]. The alkali metal salts of HPMoV$_x$ used as a palladium co-catalyst resulted in rather poor activity for butene-1 oxidation. Our experiments have shown that the use of the sodium salt of HPMoV$_2$ as a palladium reoxidant leads to very poor butene-1 conversion, as was similarly observed for caesium salt by Stobbe-Kreemers et al. [10]. Therefore, the low butene-1 conversion on the KPMo supported catalysts can result from the negative effect of potassium cations present in the surface layer.

3.4. *Effect of the vanadium amount introduced into the Keggin structure*

The introduction of vanadium atoms into the Keggin structure significantly increased the reoxidative activity of the heteropoly compounds. Taking into account that the zinc salt of HPMoV$_x$ appeared to be the best palladium reoxidant, we present mainly those experiments carried out on the catalysts containing ZnPMoV$_x$ ($x = 0$–3). The vanadium-free Pd/ZnPMo/SiO$_2$ system showed rather poor butene-1 oxidation (figure 8). The introduction of only one vanadium atom into the Keggin unit noticeably improved the activity of the catalyst. The catalysts containing two or three vanadium atoms in the Keggin unit showed the highest activity for butene-1 oxidation. They were able to catalyse butene-1 oxidation for 20 h. The influence of the number of vanadium atoms present in the Keggin structure was also observed for the catalysts applied for oxidation of ethene to acetaldehyde [13–15]. Moreover, Stobbe-Kreemers et al. [9–11] reported that the activity for butene-1 oxidation on the catalysts containing heteropoly acids as palladium co-catalysts increased with the number of vanadium atoms in the Keggin unit ($H_{3+x}PMo_{12-x}V_x$; $x = 0$–6) and achieved the maximum for $x = 3$.

4. Conclusions

(1) The steady state activity of Pd^{2+}/HPMoV$_x$/SiO$_2$ catalysts for butene-1 to MEK oxidation can be improved by the replacement of HPA protons with transition metal cations (Zn $\gg$ Co $>$ Bi $\geqslant$ Fe $\geqslant$ Mn).

(2) The presence of strong acidic centres on the surface of the catalyst is unfavourable for the reaction under investigation and their poisoning with ammonia prolongs the catalysts lifetime up to 50 h.

(3) Both the initial and steady state activities of the heteropoly compounds containing solid Wacker catalysts for oxidation of butene-1 to MEK increase with the increasing number of vanadium atoms introduced into the Keggin structure.

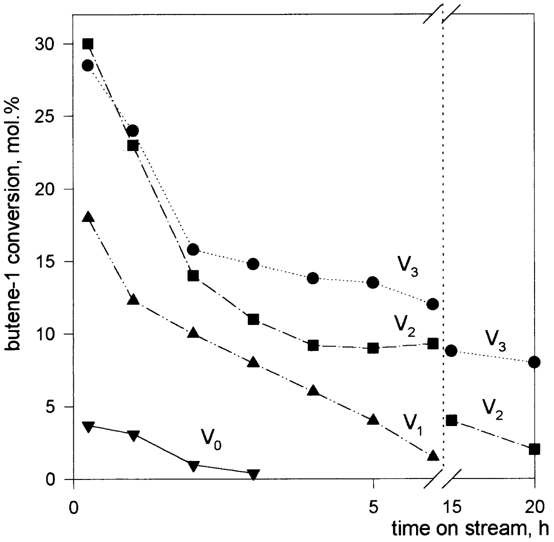


Figure 8. Butene-1 conversion over Pd/ZnPMoV$_x$/Si catalysts containing a different number of vanadium atoms (x) in the Keggin unit as a function of time on stream.

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