

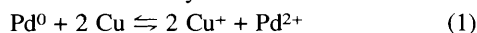
Pd²⁺Mn²⁺HPA: a heterogeneous Wacker system catalyst

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High efficiency for selective ethene oxidation of catalysts containing PdCl₂ and Mn²⁺ salts of heteropoly acids [H_{3+x}PMo_{12-x}V_xO₄₀ (0 ≤ x ≤ 3)] supported on silica suggests a synergetic interaction between Pd²⁺ and Mn²⁺HPMoV_x.

The Wacker process for the direct oxidation of ethene to acetaldehyde has been developed on the grounds of homogeneous catalysis, with PdCl₂ and CuCl₂ employed as catalyst and co-catalyst, respectively.¹ The process was found to be very effective for oxidation of ethene, whereas the oxidation of higher olefins yields a variety of products (mainly chlorohydrocarbons). The corrosive conditions (presence of hydrochloric acid) have been an additional significant drawback. To minimise the chloride content, some non-volatile inorganic acids (sulfuric or heteropoly acids) have been used instead of hydrochloric acid.²⁻⁴ Heteropoly acids containing molybdenum and vanadium as terminal atoms have been found to reoxidise the reduced Pd, therefore, they could be used instead of the (CuCl₂ + HCl) system in the homogeneous Wacker process.²⁻⁸ An attempt was made to prepare a heterogeneous catalyst that would allow avoidance of the problems imposed by homogeneous catalytic systems. The Pd²⁺/V₂O₅/Al₂O₃ catalyst was active for oxidation of ethene to acetaldehyde and of but-1-ene to butan-2-one (MEK) in the temperature range 90–140 °C.^{9,10} The oxidation of but-1-ene to MEK over Pd/HPMoV_x/SiO₂ under heterogeneous conditions has also been recently reported.^{11,12} The main problem with these heterogeneous catalysts is a decrease in their activity because the process of reoxidation of palladium is not fast enough in the solid catalyst. The palladium–copper exchanged zeolite Y, reported by Jacobs and coworkers,¹³ was considered by the authors to be ‘a true heterogeneous Wacker catalyst’ and its activity was stable for 50 h. The proposed mechanism was very similar to that suggested for the homogeneous PdCl₂–CuCl₂ system. The crucial factor for both very active and stable catalysts is a synergism between Pd and Cu in the oxidation of ethene.¹³ This synergism consists of the equilibrium of eqn. (1), and it makes Wacker catalysts so extraordinarily effective.



In this paper we demonstrate a special influence of Mn²⁺ bonded to heteropoly anions on the activity and stability of the palladium(II) catalyst for oxidation of ethene to acetaldehyde under heterogeneous conditions. In our study we used HPMoV_x acids such as H_{3+x}PMo_{12-x}V_xO₄₀ (0 ≤ x < 4) and their Mn²⁺ salts as co-catalysts with palladium (as PdCl₂). The mixed Mn²⁺–Pd²⁺ salt of HPMoV₂ was also applied for ethene oxidation. The H_{3+x}PMo_{12-x}V_xO₄₀ system is very complicated. It has been reported that the stability of these systems in solution depends on concentration and pH of the solution.^{14,15} Tsigdinos and Halada¹⁶ claimed that their preparation procedure enabled the production of very pure solid acids containing up to three vanadium atoms per Keggin unit (KU). These solid acids (x = 1–3) were characterised by XRD,^{17,18} IR,¹⁹ and DTA–TG studies.²⁰ Heteropoly acids with x = 1–8 have been used as catalysts both for homo- and hetero-geneous processes.^{2,8,11,12}

The catalytic systems were supported on silica (230 m² g⁻¹) with 30 mass% of heteropoly anion and 0.2 mass% of Pd.

Vanadium containing heteropolyacids were synthesised according to literature procedures¹⁶ and manganese salts of HPAs were prepared in aqueous solution using HPA and Mn(NO₃)₂ or Mn(CO₃)₂.

The activity of the Pd/HPMoV_x/SiO₂ system for ethene oxidation shows some similarity to homogeneous catalytic systems containing HPA.²⁻⁴ The activity of the catalysts correlates with the number of vanadium atoms (x) introduced into HPA and it increases with x. HPMo as a co-catalyst results in a rather low activity and ethene conversion over this catalyst decreases very rapidly with time on stream. Introduction of 3 vanadium atoms into the Keggin unit results in high initial ethene conversion (≈ 80%) but the activity decreased gradually and after 6 h it was < 20%.

Application of Mn²⁺HPA salts to the Pd^{II} co-catalyst increased ethene conversion significantly and catalysts containing both MnHPMoV₁ and MnHPMoV₂ transformed ethene to acetaldehyde in 50% conversion even after 10 h on stream. The presence of vanadium atoms in heteropoly anions was also important for Mn^{II} salt activity; the highest ethene conversion was achieved for x = 1 (initial activity) or for x = 2 (steady activity) (Fig. 1) and not for x = 3 in contrast to HPMoV_x catalysts.

The catalytic activity is also affected by the procedure of catalyst preparation. The catalysts were prepared by means of incipient wetness method using two different sequences:

(i) heteropoly compounds (30 mass% of heteropoly anion) were supported on silica from aqueous solution and dried at 70 °C. Then the sample was impregnated with PdCl₂ (0.2 mass%) dissolved in aqueous 0.1 mol dm⁻³ HCl; these catalysts are designated Pd/(MnHPMoV_x/SiO₂).

(ii) A solution of PdCl₂ in 0.1 mol dm⁻³ aqueous HCl was first supported on silica and dried at 70 °C. Then the sample was impregnated with heteropoly compounds from aqueous solution; these catalysts are designated MnHPMoV_x/(Pd/SiO₂).

The catalysts prepared according to procedure (ii) showed higher activity and much longer lifetimes than those prepared according to method (i). Catalysts prepared by method (ii) showed 80% ethene conversion (Fig. 1) with very high

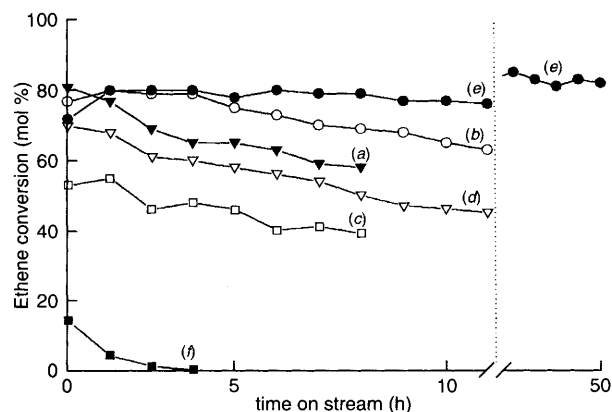


Fig. 1 Ethene conversion over Pd/MnPMoV_x/SiO₂ catalysts vs. time on stream: (a) Pd/(MnPMoV₁/SiO₂), (b) Pd/(MnPMoV₂/SiO₂), (c) Pd/(MnPMoV₃/SiO₂), (d) PdMnPMoV₂/SiO₂ (mixed salt), (e) MnPMoV₂/(Pd/SiO₂), (f) Pd/MnPMo/SiO₂

selectivity ($\approx 98\%$) to acetaldehyde even after 50 h on stream. Considering the results reported by Stobbe-Kreemers *et al.*^{11,12} concerning high activity of palladium salts of heteropoly acids for but-1-ene oxidation, we assumed that formation of a palladium salt may be responsible for such a high catalytic activity. Therefore we prepared a mixed salt containing the same number of Pd^{2+} and Mn^{2+} cations as those in the $\text{MnHPMoV}_2/(\text{Pd}/\text{SiO}_2)$ catalyst. However, while the mixed salt showed high initial ethene conversion, its activity decreased to 50% conversion after 10 h (Fig. 1).

Comparing the catalytic activity of HPMoV_x and MnPMoV_x containing catalysts we can conclude that the presence of Mn^{2+} cations is favourable for ethene oxidation and for stability of $\text{Pd}^{2+}/\text{MnHPMoV}_x/\text{SiO}_2$ catalytic systems. The question arises as to the role of Mn^{2+} cations in heterogeneous ethene oxidation. According to earlier reports, reoxidation of $\text{Pd}^0 \rightarrow \text{Pd}^{2+}$ in such catalysts occurs with simultaneous reduction of the heteropoly anion.^{2-4,11,12} Therefore, the ease of reduction and reoxidation of the heteropoly anion should be a crucial factor for catalyst working stability. The affect of transition-metal cations on the reducibility and reoxidizability of molybdenum atoms in 12-molybdophosphoric acid has been studied by Akimoto *et al.*^{21,22} and some correlation with standard electrode potentials (SEP) of cations has been found.

According to these results, the reduction and reoxidation of molybdenum atoms in heteropoly anions, is not facilitated by Mn^{2+} (SEP for Mn^{2+} is lower than for H^+).²² On the other hand, we noted a change in colour of the catalysts from orange-red for fresh samples to greenish after use which indicated some reduction of the heteropoly anion. Eguchi *et al.* have studied the reduction of heteropoly compounds by IR spectroscopy²³ and showed that some IR bands characteristic of the KU structure were sensitive to KU reduction (1065, 870 and 800 cm^{-1}) while the band at 960 cm^{-1} ascribed to $\nu(\text{Mo}=\text{O})$ was not. The catalysts applied for ethene oxidation were supported on silica and therefore we could observe only two bands (at 960 and 870 cm^{-1}), which did not overlap silica IR bands. IR spectra of the working $\text{Pd}^{2+}/\text{HPMoV}_x/\text{SiO}_2$ catalysts, showed a lower intensity of the band at 870 cm^{-1} compared to fresh catalysts (Table 1). This suggested that some reduction of heteropoly anion, including oxygen removal, took place.²³⁻²⁵ On the other hand, the IR spectra for the fresh and working $\text{Pd}^{2+}/\text{Mn}^{2+}\text{PMoV}_x/\text{SiO}_2$ catalysts did not show any visible change in intensity of the 870 cm^{-1} band despite evidence of some reduction. It is thus assumed that in the presence of Mn^{2+} , only the first reduction stage of heteropoly anion (according to mechanism proposed by Misono²⁴), without oxygen removal takes place. The first step of heteropoly anion reduction leads to a reduction of heteroatoms ($\text{Mo}^{6+} \rightarrow \text{Mo}^{5+}$ or $\text{V}^{5+} \rightarrow \text{V}^{4+}$) with simultaneous appearance of additional protons (Scheme 1).

The assumption that only the first reduction stage of heteropoly anions in the presence of Mn^{2+} occurs to a

Table 1 Integrated intensities of IR bands at 960 and 870 cm^{-1} of fresh and working $\text{Pd}/\text{HPMoV}_2/\text{Si}$ and $\text{Pd}/\text{MnPMoV}_2/\text{Si}$ catalysts

Catalyst	Integrated intensities (a.u.)	
	960 cm^{-1}	870 cm^{-1}
$\text{Pd}/\text{HPMoV}_2/\text{Si}$		
Fresh	300	96
After ethene oxidation	300	56
$\text{Pd}/\text{MnPMoV}_2/\text{Si}$ (ii)		
Fresh	297	98
After ethene oxidation	297	99



Scheme 1

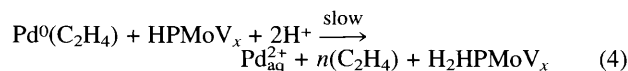
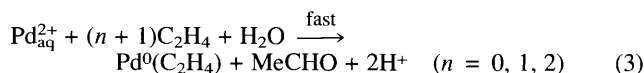
significant extent is supported by the results of $\text{CO} \rightarrow \text{CO}_2$ oxidation. CO oxidation was performed by the pulse method over samples dried at 150 $^\circ\text{C}$ (temperature for water removal without structural damage of the KU unit was chosen on the basis of TGA measurements) in a dry helium stream. CO oxidation in the absence of oxygen in the gas phase, can occur only at the expense of the (bridging) oxygen from HPA structure. The manganese-modified catalyst (ii) was able to release only 4×10^{21} oxygen atoms per mol KU (in the reaction $\text{CO} + 1/2 \text{O}_2 \rightarrow \text{CO}_2$ performed at 70 $^\circ\text{C}$) while 4 times more oxygen atoms were removed from the $\text{HPMoV}_2/\text{Pd}^{2+}/\text{SiO}_2$ catalyst, under the same conditions. These results are consistent with our IR spectra (Table 1) showing a noticeable decrease in the band intensity at 870 cm^{-1} for the HPMoV_x containing catalysts and practically no change in intensity of this band for the $\text{Pd}^{2+}/\text{Mn}^{2+}\text{PMoV}_x/\text{SiO}_2$ (ii) catalyst.

Reoxidation of the reduced samples occurs easily with dioxygen according to equation (2).



An additional argument for the non-involvement of the bridging oxygen of the heteropoly anion in ethene oxidation, is the insensitivity of the catalyst activity upon introduction of ammonia into the catalyst bed; upon ammonia injection ethene conversion did not decrease at all. According to suggestion by Bielański *et al.*¹⁹ ammonia introduced into HPMoV_x is located as NH_4^+ ion either in the vicinity of the bridging oxygen (characterised by a band at 870 cm^{-1}) or close to the terminal oxygen. If the bridging oxygens of HPA structure were involved in the ethene oxidation over the $\text{Pd}^{2+}/\text{MnHPMoV}_x$ catalyst, then ammonia adsorption should result in changes in ethene conversion.

A mechanism involving only the first reduction stage of HPA was proposed for ethene oxidation over a $\text{Pd}^{2+}/\text{HPMoV}_x$ system in the liquid phase by Matveev *et al.*^{3,4} and also Davison *et al.*² [eqns. (3) and (4)].



It is very likely, that this mechanism also prevails here with $\text{Mn}^{2+}\text{HPMoV}_x$. Reoxidation of MnHPMoV_x can proceed fast and reversibly [according to eqn. (1)] which results in a steady and efficient response of the catalyst.

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