

Fe³⁺ as a reoxidant for Nafion immobilised palladium(II) catalysts

Andrew J. Seen*, Jane C. Bellis

School of Applied Science, University of Tasmania, Launceston, Tasmania 7250, Australia

Received 15 November 1999; accepted 14 June 2000

Abstract

The addition of 1,4-benzoquinone and Fe³⁺ to [Pd(1,10-phen)₂]²⁺ catalyst systems has been undertaken to assess the ability of these oxidants to increase the ethene dimerisation turnover of Nafion immobilised Pd(II) catalysts. Although 1,4-benzoquinone increases the turnover of the Pd(II) catalyst in methanol, it deactivates the catalyst in water. Fe³⁺ ions have, however, been found to extend the life of the Pd(II) catalyst in water. Fe³⁺ is effective both in homogeneous solution and when incorporated into Nafion with [Pd(1,10-phen)₂]²⁺. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Nafion; Palladium; Supported catalysts; Ethene; Oligomerisation

1. Introduction

The application of cationic Pd(II) complexes as catalysts for the oligomerisation and carbonylation of unsaturated hydrocarbons has received much attention in recent years due to their ability to produce industrially important products, such as polyketones and methyl methacrylate, under relatively mild reaction conditions. The impetus for much of this research has come about from work in the early 1980s by Sen. Sen and co-workers showed that the oligomerisation of ethene, polymerisation of styrene and co-polymerisation of CO with a range of olefins could be catalysed under unusually mild conditions using [Pd(CH₃CN)₄](BF₄)₂ and its tertiary phosphine derivatives [1,2]. By the early 1990s, these cationic Pd(II) systems had become of interest to industry and Drent of Shell reported on a variety of reactions, including the hydroformylation and dimerisation of olefins using Pd(II) species with weakly coordinating P and N donor ligands [3]. Fur-

ther work by Drent et al. has shown that perfectly alternating polyketones and carbonylation of alkynes can result by altering the ligands around the Pd(II) centre [4–6].

Drent's work also showed that a weakly coordinating anion (such as *p*-tolyl-SO₃⁻) resulted in higher catalytic activity compared with a more strongly coordinating anion (such as Cl⁻) [3,4]. The simplicity of these cationic Pd(II) catalysts, and their need for a weakly coordinating anion prompted our investigation of the use of the ion exchange polymer Nafion as a support for these complexes [7–9]. Nafion is a perfluorinated polymer with pendant sulfonic acid groups which are believed to form ionic clusters within the hydrophobic fluorocarbon matrix [10]. The coordinating ability of the sulfonate groups in Nafion is between PF₆⁻ or BF₄⁻ and ClO₄⁻ [11], and this property makes Nafion an ideal support for the cationic Pd(II) catalysts. The immobilisation of an otherwise homogeneous catalyst in a solid support combines the advantages of homogeneous catalysts, i.e. selectivity, efficiency and controllability, with the all important benefit of heterogeneous catalysts, ease of separation. Immobilisation of homogeneous catalysts on solid

* Corresponding author. Tel.: +61-3-63243829;
fax: +61-3-63243839.
E-mail address: A.J.Seen@utas.edu.au (A.J. Seen).

supports may also provide an additional benefit in prolonging catalyst lifetime through protection of the catalyst from poisons in solution, or by preventing dimerisation or agglomeration of the active species.

Our initial work showed that a Nafion supported Pd(II) catalyst with ethene dimerisation activity comparable to its homogeneous analogue was possible [7]. This work also found that the catalytic activity and stability of a series of Pd(II) complexes was dependent on the basicity of the N donor ligand coordinated to the palladium and the counter-ion (H^+ or Na^+) in Nafion. For example, whilst the activity of $[Pd(1,10\text{-phen})_2]^{2+}$ was enhanced using Nafion- H^+ , $[Pd(1,10\text{-phen})(py)_2]^{2+}$ appeared to decompose within 15 min. when supported in Nafion- H^+ . This variation in activity suggested that the basicity of the ligands combined with the acid in Nafion- H^+ resulted in increased ligand lability and lower complex stability. In fact UV–VIS characterisation of $[Pd(1,10\text{-phen})py_2]^{2+}$ immobilised in Nafion- H^+ indicated that some of the $[Pd(1,10\text{-phen})(py)_2]^{2+}$ decomposed in the acidic environment to give free pyridine and 1,10-phenanthroline.

Drent found that Pd(II) copolymerisation catalysts generally showed higher activity in the presence of oxidants such as quinones and concluded that these rate enhancements were most likely due to the oxidants, oxidising reduced Pd back to Pd(II) which could then reenter the catalytic cycle [6]. Drent has suggested several ways that the catalytically active species may ‘drop out’ of the catalytic cycle resulting in the formation of Pd(0), precipitation of Pd metal, or formation of Pd_2^{2+} species. Unlike Drent, no oxidant has previously been used with our supported catalyst systems. Accordingly we now report on the development of a Nafion supported Pd(II) catalyst system which incorporates an oxidant.

2. Experimental

$PdCl_2$ (Johnson Matthey Loan Scheme), 1,10-phenanthroline, $Fe_2(SO_4)_3 \cdot 5H_2O$ (Aldrich), and ethene (Matheson Gases CP Grade) were used as received. All other chemicals were of reagent grade and used without further purification unless otherwise stated. Nafion NR50 7–9 mesh beads (Du Pont) were washed in HNO_3 and then water before drying

at $100^\circ C$ under vacuum (0.1 mmHg) for 24 h before use. The syntheses of $[Pd(1,10\text{-phen})_2](NO_3)_2$ and $[Pd(1,10\text{-phen})_2](CF_3SO_3)_2$ have been described previously, as has the immobilisation of $[Pd(1,10\text{-phen})_2]^{2+}$ in Nafion [7,9].

2.1. Preparation of

Nafion- H^+ /Fe $^{3+}$ /Pd(1,10-phen) $_2^{2+}$

2.41 g of dry Nafion- H^+ was added to a 100 ml aqueous solution of $Fe_2(SO_4)_3 \cdot 5H_2O$ (0.119 g, 242 μmol) and stirred for 30 h. After removal of the Nafion from the spent Fe^{3+} solution, the Nafion was added to a 100 ml aqueous solution of $[Pd(1,10\text{-phen})_2](NO_3)_2$ (3.34 mg, 5.66 μmol) and stirred for 30 h. The Nafion was then dried under vacuum at room temperature before being split into two equal portions. UV–VIS analysis of the spent ion exchange solutions confirmed that more than 98% of the Fe^{3+} and $[Pd(1,10\text{-phen})_2]^{2+}$ were exchanged into the Nafion.

2.2. Catalytic testing

Catalytic testing of supported and homogeneous Pd(II) species was carried out in a Büchi BEP 280 laboratory autoclave capable of operation at up to 60 bar. The autoclave consisted of a 250 ml jacketed stainless steel reaction vessel, a baffle, a thermometer sleeve for a thermocouple and an impeller with three blades 15 mm long. The impeller was rotated at 400 rpm for all tests. Heating fluid was circulated from a Lauda KS 20 thermostat through the jacketed vessel to maintain an internal temperature of $80 \pm 0.1^\circ C$. Ethene dimerisation catalytic testing typically consisted of adding ca. 1 g of Nafion beads containing the $[Pd(1,10\text{-phen})_2]^{2+}$ complex (or 10 μmol of $[Pd(1,10\text{-phen})_2](CF_3SO_3)_2$ for homogeneous tests) to the Büchi reactor, followed by 200 ml of solvent, water or methanol. The reactor was then cooled to ca. $5^\circ C$ with an ice bath to aid in the addition of butane standard. Heating to reaction temperature was carried out over a period of 0.5 h, after which time the reactor was charged with ethene to a pressure of 40 bar.

Progress of the catalytic reaction was monitored over a 3–20 h period by expanding ca. 1 ml of solution from the reactor into a 150 ml stainless steel sample bottle, and analysing the sample bottle headspace

Table 1
Effects of oxidants on ethene dimerisation^a

	Catalyst (μmol)	Solvent	Oxidant (μmol)	Maximum activity ($\text{molC}_2\text{H}_4/\text{molPdh}$)	Turnover at 3 h ($\text{molC}_2\text{H}_4/\text{molPd}$)
1	$\text{Pd}(1,10\text{-phen})_2(\text{CF}_3\text{SO}_3)_2$ (10)	methanol	–	18000	21000
2	$\text{Pd}(1,10\text{-phen})_2(\text{CF}_3\text{SO}_3)_2$ (10)	methanol	1,4-benzoquinone (1000)	19000	50000
3	Nafion- H^+ / $\text{Pd}(1,10\text{-phen})_2^{2+}$ (10)	methanol	–	10500	23000
4	Nafion- H^+ / $\text{Pd}(1,10\text{-phen})_2^{2+}$ (10)	methanol	1,4-benzoquinone (1000)	11000	28000
5	$\text{Pd}(1,10\text{-phen})_2(\text{CF}_3\text{SO}_3)_2$ (10)	water	–	30000	17000 ^b
6	$\text{Pd}(1,10\text{-phen})_2(\text{CF}_3\text{SO}_3)_2$ (10)	water	1,4-benzoquinone (200)	1800	1200 ^b
7	$\text{Pd}(1,10\text{-phen})_2(\text{CF}_3\text{SO}_3)_2$ (10)	water	Fe^{3+} (1000)	60000	32000 ^b
8	Nafion- H^+ / $\text{Pd}(1,10\text{-phen})_2^{2+}$ (2.5)	water	–	120000	110000
9	Nafion- H^+ / Fe^{3+} / $\text{Pd}(1,10\text{-phen})_2^{2+}$ (2.5)	water	Fe^{3+} (210)	150000	171000

^a 1.0 g of Nafion- H^+ used in all supported catalyst tests: catalyst loading in tests 3 and 4 is 0.1 wt.% Pd, catalyst loading in tests 8 and 9 is 0.025 wt.% Pd.

^b Turnover at 60 min.

vapour using gas chromatography (GC). A HP 5890 GC fitted with a SGE 25 QC3/BP1-4.0 column was used for separation of butane and butenes (isothermal analyses at 35°C with N_2 carrier gas velocity of 11–13 cm s^{-1}). Activities were followed by the addition of butane (ca. 2–3 g), as an internal standard, to the solvent at the beginning of the run. Subsequent comparison of the GC butane peak area with the area of C_4 alkene products gave a measure of catalytic activity after correction for the differing distributions of butenes and butane in the reactor and sample bottle headspace vapour.¹

3. Results and discussion

The classical reoxidant for palladium is CuCl_2 , as used in the Wacker process, with Pd(0) oxidised to Pd(II) by Cu^{2+} , whilst the resultant CuCl is readily reoxidised back to Cu^{2+} by oxygen. Pennequin et al. [12] have examined the effect of the nature and amount of copper salt on palladium catalysed oxidative carbonylation of alkenes and found that

- The presence of a halide anion is necessary to obtain good activities, with the chloride anion being better than bromide and iodide;

- The reactivity of the system is directly related to the amount of CuCl , at least for a Cu/Pd ratio lower than 100.

Pennequin et al. also tested other reoxidants such as Fe(III) salts, $\text{K}_2\text{S}_2\text{O}_8$ and quinones. As mentioned above, Drent has found that Pd(II) copolymerisation catalysts generally show higher activity in the presence of oxidants such as quinones, and Milani et al. have used 1,4-benzoquinone as an oxidant for Pd(II) catalysed CO-olefin *co*- and *ter*-polymerisation [13]. For an oxidant to oxidise Nafion supported palladium species, it must be able to diffuse into the ionic clusters within Nafion, thus it must be neutral or cationic. This criterion eliminates the use of $\text{K}_2\text{S}_2\text{O}_8$, and also eliminates the use of copper salts as suitable anions, such as chloride, are required to increase the reduction potential of Cu^{2+} .

The addition of 1,4-benzoquinone to a Nafion supported $[\text{Pd}(1,10\text{-phen})_2]^{2+}$ system in methanol resulted in only a moderate increase in the ethene dimerisation turnover, whilst for the analogous homogeneous catalyst, $[\text{Pd}(1,10\text{-phen})_2](\text{CF}_3\text{SO}_3)_2$, the addition of 1,4-benzoquinone resulted in the turnover being more than double after 3 h (Table 1). Sampling of the reactor throughout each catalytic test enabled the turnover number to be followed with time, as is shown in Fig. 1, and as a consequence ‘instantaneous’ catalytic activities have been calculated. The results in Table 1 show that the maximum activities in the homogeneous and supported systems were independent of the presence of 1,4-benzoquinone. This is consistent with Drent’s proposal that the addition of

¹ Determination of the distribution of butenes between the reactor and sample bottle headspace vapour was undertaken by addition of known amounts of butenes to the reactor and then undertaking analyses as per the catalytic tests. Distribution coefficients were then calculated relative to butane.

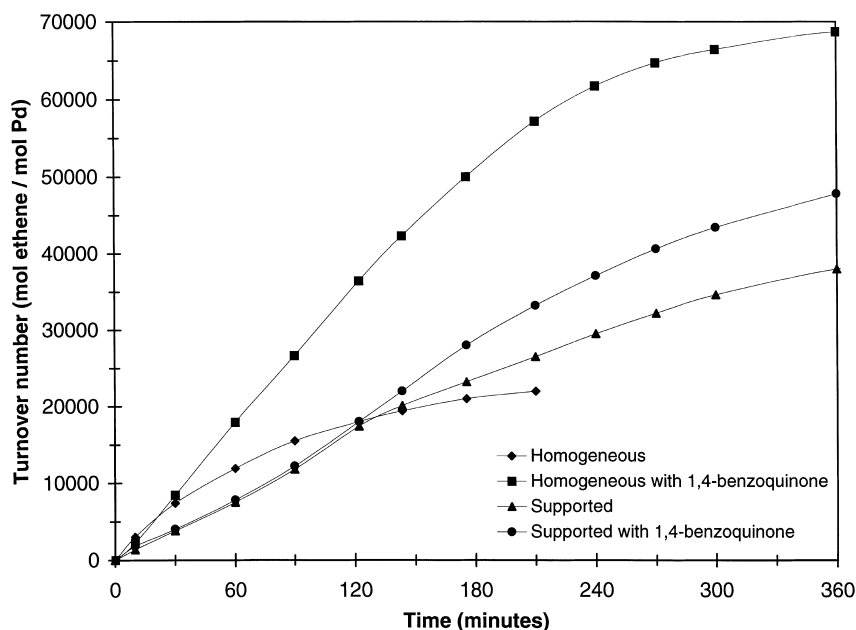


Fig. 1. The effect of oxidants on ethene dimerisation in methanol.

an oxidant does not alter the maximum activity but reoxidises reduced palladium species so that they may re-enter the catalytic cycle [6]. It is evident from the plot of turnover number versus time (Fig. 1) that significant catalyst deactivation occurs in both the homogeneous and supported tests without the addition of 1,4-benzoquinone.

Our previous work has shown that dramatic increases in ethene dimerisation activity result when water is used as the solvent [8,9]. The addition of 1,4-benzoquinone had a detrimental effect on the ethene dimerisation activity of the homogeneous system in water, as can be seen in Table 1 and Fig. 2. A possible explanation for this may be the low solubility of 1,4-benzoquinone in water and the potential for the homogeneous Pd(II) complex to be removed from solution by adsorption on to the surface of undissolved 1,4-benzoquinone.

Having established that 1,4-benzoquinone was unsuitable for use in water, another oxidant needed to be selected that was both water soluble and suitable for use in Nafion. Pennequin et al. have previously used Fe(III) salts for reoxidation of the palladium catalyst used to catalyse oxidative carbonylation of alkenes

[12]. The reduction potential for $\text{Fe}^{3+}/\text{Fe}^{2+}$ is slightly higher than that of 1,4-benzoquinone, 0.771 V compared with 0.699 V, and being positively charged the Fe^{3+} ions can be ion-exchanged into the Nafion ionic clusters.

Homogeneous and supported catalytic tests were undertaken in water with and without Fe^{3+} , with the results shown in Table 1 and Fig. 2. The results in Table 1 show that increases in catalytic turnover of 88 and 55% were observed for the homogeneous and supported systems, respectively, on addition of Fe^{3+} as a reoxidant. Fig. 2 clearly shows that the addition of Fe^{3+} to the supported catalyst system results in a significant increase in the life of the catalyst. Without Fe^{3+} the catalyst activity dramatically decreases at 60 min, whereas addition of Fe^{3+} prolongs catalyst activity for a further 30–50 min. These results demonstrate that Fe^{3+} is a suitable oxidant for reactivating the deactivated $[\text{Pd}(1,10\text{-phen})_2]^{2+}$ catalyst in Nafion- H^+ .

Increases in maximum activity were also observed, from 32,000 to 60,000 turnovers h^{-1} for the homogeneous system and from 120,000 to 150,000 turnovers h^{-1} for the supported system (Table 1). This

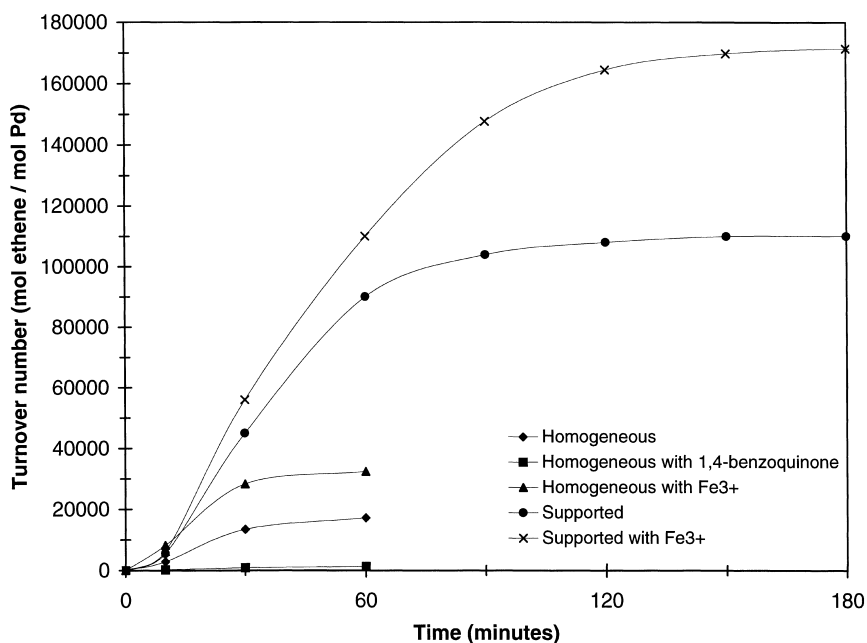


Fig. 2. The effect of oxidants on ethene dimerisation in water.

is in contrast to the behaviour of the homogeneous and supported systems in methanol on addition of 1,4-benzoquinone, and suggests that Fe^{3+} may also be functioning as a catalyst activator, particularly in the case of the homogeneous system. This is conceivable, considering that our previous studies have indicated that the acid in Nafion- H^+ increases catalytic activity by labilising the N donor ligands [7,9], in a similar way the formation of complexes between Fe^{3+} and 1,10-phenanthroline would increase the lability of the ligand in the $[\text{Pd}(1,10\text{-phen})_2]^{2+}$ complex.

The dramatic decrease in catalytic activity after 30 min for the homogeneous system in water suggests that significant decomposition of the catalyst occurs during the first 30 min of testing. Reactivation of reduced palladium species by Fe^{3+} during the initial stages of testing would also contribute to the observed increases in catalyst activity.

It is worth noting that whilst significant increases in activity are observed when water is used as the solvent, the stability of the catalyst is dramatically reduced. Comparison of the Turnover number vs time plots shown in Figs. 1 and 2 indicates that decomposition of the catalyst occurs more readily in water than

methanol. Whilst a mechanism has not been proposed for the deactivation of these Pd(II) catalysts, decomposition via a Wacker-type reduction to palladium metal is a likely route. In fact, we have observed a blackening of Nafion beads at the end of catalytic testing of higher loading supported catalyst systems, suggesting the presence of metallic palladium. The increased lability of the 1,10-phenanthroline ligands in water, as indicated by the increased activity, the lower ethene solubility in water and the highly polar nature of water all potentially contribute to the reduced stability of the Pd(II) catalyst in water.

It is also notable from the plot of turnover number versus time (Fig. 2) that the Nafion supported complex is superior to the homogeneous analogue, regardless of whether or not Fe^{3+} is present. We have previously proposed that the higher activity of the Nafion- H^+ supported system is most likely due to the very polar, strongly acidic environment in Nafion which ensures effective anion–cation separation and promotes labilisation of the N donor ligands [9]. The turnover number versus time plot (Fig. 2) illustrates that Nafion- H^+ not only acts as a catalyst activator and support, but also provides protection from decomposition/deactivation

for the Pd(II) species. Several factors may be giving rise to this effect, including:

- Exclusion of anions (such as Cl^- impurities in the solvent) from the ionic clusters and thus preventing coordination of anions to the Pd(II) centre.
- Restricting any dissociated nitrogen-donor ligands to the vicinity of the complex and thus ensuring that they are available to re-coordinate to the complex at the completion of a catalytic cycle.
- Isolating one Pd species per ionic cluster and minimising potential deactivation through dimerisation of Pd species.

4. Conclusions

Whilst the addition of 1,4-benzoquinone to the homogeneous $[\text{Pd}(1,10\text{-phen})_2](\text{CF}_3\text{SO}_3)_2$ system in methanol resulted in the turnover being more than double after 3 h, the addition of 1,4-benzoquinone to a Nafion supported $[\text{Pd}(1,10\text{-phen})_2]^{2+}$ system in methanol resulted in only a moderate increase in the ethene dimerisation. The addition of 1,4-benzoquinone to an aqueous homogeneous $[\text{Pd}(1,10\text{-phen})_2]^{2+}$ catalyst system had a detrimental effect on the ethene dimerisation. Having established that 1,4-benzoquinone was unsuitable for use in aqueous systems, Fe^{3+} was selected due to its ability to ion

exchange into the ionic clusters in Nafion. Increases in catalytic turnover of 88 and 55% were observed for the homogeneous and Nafion supported systems, respectively, on addition of Fe^{3+} , thus showing that an oxidant can be incorporated into Nafion to extend the life of Nafion supported Pd(II) catalysts.

References

- [1] A. Sen, T.-W. Lai, *J. Am. Chem. Soc.* 103 (1981) 4627–4629.
- [2] A. Sen, T.-W. Lai, *J. Am. Chem. Soc.* 104 (1982) 3520–3522.
- [3] E. Drent, *Pure Appl. Chem.* (1990) 661–669.
- [4] E. Drent, J.A.M. van Broekhoven, M.J. Doyle, *J. Organomet. Chem.* 417 (1991) 235–251.
- [5] E. Drent, P. Arnoldy, P.H.M. Budzelaar, *J. Organomet. Chem.* 475 (1994) 57–63.
- [6] E. Drent, P.H.M. Budzelaar, *Chem. Rev.* 96 (1996) 663–681.
- [7] A.J. Seen, K.J. Cavell, A.W.-H. Mau, A.M. Hodges, *J. Membr. Sci.* 87 (1994) 149–157.
- [8] A.J. Seen, K.J. Cavell, A.W.-H. Mau, A.M. Hodges, *J. Mol. Catal.* 94 (1994) 163–172.
- [9] A.J. Seen, A.T. Townsend, J.C. Bellis, K.J. Cavell, *J. Mol. Catal. A: Chemical* 149 (1999) 233–242.
- [10] S.J. Sondheimer, N.J. Bunce, C.A. Fyfe, *JMS-Rev. Macromol. Chem. Phys.* C26 (3) (1986) 353–413.
- [11] F.J. Waller, *Br. Polymer J.* 16 (1984) 239–242.
- [12] P. Pennequin, M. Fontaine, Y. Castanet, A. Mortreux, F. Petit, *Appl. Catal. A: General* 135 (1996) 329–339.
- [13] B. Milani, L. Vicentini, A. Sommazzi, F. Garbassi, E. Chiarparin, E. Zangrando, G. Mestroni, *J. Chem. Soc., Dalton Trans.* (1996) 3139–3144.