

Increased catalytic activity of cationic palladium(II) complexes on immobilisation in Nafion-H⁺

Andrew J. Seen^{a,*}, Ashley T. Townsend^b, Jane C. Bellis^c, Kingsley J. Cavell^c

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

^b Central Science Laboratory, University of Tasmania, Hobart, Tasmania 7005, Australia

^c School of Chemistry, University of Tasmania, Hobart, Tasmania 7005, Australia

Received 30 November 1998; received in revised form 12 December 1998; accepted 8 March 1999

Abstract

Catalytic dimerisation of ethene by $[\text{Pd}(1,10\text{-phen})_2]^{2+}$ supported in three forms of Nafion has confirmed that diffusion of reactants and/or products through Nafion is rate-limiting. However, a combination of low catalyst loading and high dispersion of Nafion has resulted in extraordinary increases in ethene dimerisation activities when compared with the homogeneous analogue. Initial activities as high as 760,000 turnovers h^{-1} have been obtained for the supported complex compared with a homogeneous activity of 32,000 turnovers h^{-1} . These increases in activity most likely result from the very polar, strongly acidic environment in Nafion which ensures effective anion–cation separation and promotes labilisation of the nitrogen donor ligands. Enhancements in activities for co-polymerisation of ethene and carbon monoxide, and carbomethoxylation of ethene have also been observed using Nafion supported Pd(II) catalysts in methanol. © 1999 Elsevier Science B.V. All rights reserved.

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

1. Introduction

‘Clean chemical processing technology’ is a growing area of community and hence, industrial interest. In this context, the application of well-defined, homogeneous catalysts in chemical processing offers advantages of enhanced activity and selectivity by providing a single active site for reaction, hence, minimising by-product formation and maximising efficient resource utilisation. However, practical difficul-

ties in separating homogeneous catalysts from products has mitigated against their widespread industrial use. The hybridisation of homogeneous and heterogeneous catalysts with the catalyst supported on an inorganic or polymeric support has thus been an attractive option for combining the advantages of homogeneous catalysts, i.e., specificity, efficiency and controllability, with the ease of separation of heterogeneous catalysts.

In the past, a number of materials have been used as supports, the most frequent being silica and polystyrene [1]. The development of the highly chemically resistant and thermally stable

* Corresponding author. Tel.: +61-3-63243829; Fax: +61-3-63243839; E-mail: a.j.seen@utas.edu.au

perfluorinated ion-exchange polymer, Nafion, in the 1960s provided another suitable organic support material [2]. Nafion is a perfluorinated polyethylene with pendant sulfonic acid groups that provide superacid ion-exchange properties [3]. The structure of the polymer is that of an 'inverted micelle' with the sulfonate groups forming internal, hydrophilic cells of approximately 40 Å diameter and the perfluorinated backbone forming hydrophobic channels of 10 Å diameter [4]. These sizes are dramatically influenced by the presence of polar molecules such as water.

While the use of Nafion as a solid acid catalyst in organic synthesis has been extensively covered [5], the use of Nafion as a support for metal-complex catalysts has been limited to only a handful of studies. The first successful use of Nafion as a catalyst support was reported in 1978 when Olah and Meidar [6] catalysed the hydration of alkynes using partially exchanged mercuric Nafion. In 1984, Kanemoto et al. [7] reported the oxidation of alcohols into the corresponding carbonyl compounds using *t*-butylhydroperoxide and Cr(III) or Ce(IV) exchanged Nafion. Waller [8] used Nafion supported palladium (Pd) catalysts to catalyse the methoxycarbonylation of alkenes in 1984, and methoxycarbonylation of alkenes using Nafion supported Pd complexes has since been reported by Chang [9] and more recently by Crocker and Herold [10]. Apart from our own work, the most recently reported studies of Nafion as a metal-complex catalyst support have been by Hanson et al. [11,12] who have immobilised rhodium complexes containing cationic phosphine ligands in Nafion and catalysed the hydrogenation of dehydroaminoacids.

Over the past decade, we have undertaken extensive studies on the ability of Nafion to act both as a metal-complex support and catalyst activator [13–17]. The main focus of our work in recent years has been the use of Nafion as a support for cationic Pd(II) catalysts for the oligomerisation and carbonylation of unsaturated hydrocarbons. Interest in cationic Pd(II)

complexes as catalysts has rapidly increased in the past decade as a result of studies showing the usefulness of such species to activate unsaturated hydrocarbons. In the early 1980s, Sen et al. reported the oligomerisation of ethene, polymerisation of styrene and co-polymerisation of CO with a range of olefins using $\text{Pd}(\text{CH}_3\text{CN})_4$ [18,19]. By the 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 [20]. Further 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 [21–23].

Our interest in these Pd(II) complexes stems from the fact that they require a strong Brønsted acid and weakly coordinating anions to achieve maximum reactivity [20], a chemical environment that Nafion can provide.

Our initial work showed that a Nafion supported Pd(II) catalyst with ethene dimerisation activity comparable to its homogeneous analogue was possible [15]. A distinct trend in activities was observed depending on the nitrogen donor ligand and counter-ion in Nafion, either H^+ or Na^+ [15]. This variation in activity suggested that the basicity of the ligands combined with the acid in Nafion- H^+ resulted in increased ligand lability which is consistent with the assumption that dissociation of a ligand needs to occur to produce a vacant coordination site on the Pd metal centre [18,21,24].

In addition, $[\text{Pd}(1,10\text{-phen})_2]^{2+}$ immobilised in the acid form of Nafion was found to be active in water, thus allowing the synthesis of organic chemicals in an inexpensive, non-toxic solvent [17]. Jiang and Sen [25] have also reported the use of water as a solvent using water-soluble Pd(II) compounds as catalysts for co-polymerisation of alkenes with CO. One of the complexes used by Jiang and Sen was, in fact, $[\text{Pd}(1,10\text{-phen-SO}_3\text{Na})(\text{H}_2\text{O})_2][\text{BF}_4]_2$, similar to the complexes we have immobilised in

Nafion. Although they found these compounds to be effective catalysts in water, they did report that their activities were much lower than that usually observed in non-aqueous solvents. Our results were in contrast to Sen's findings as we found increased ethene dimerisation activity for Nafion supported $[\text{Pd}(1,10\text{-phen})_2]^{2+}$ in water compared with methanol as solvent [17].

Our initial studies also showed that the activity of a supported Pd(II) catalyst was dependent upon the loading in Nafion and activities two to three times the homogeneous analogue could be obtained if the loading was reduced to 0.065 wt.% Pd [17]. Previously, Pd loadings in Nafion were commonly of the order of 1 wt.% [8–10]. Waller has suggested that diffusional effects may play a role in the activity of the Nafion immobilised species [8], but no studies looking at the dependence of activity on catalyst loading in Nafion or dispersion of Nafion had been undertaken prior to our work. In this paper, we report on studies to determine if ethene diffusion through Nafion is the rate-limiting process. A range of catalyst loadings and several forms of Nafion of various particle sizes have been used to assess the trend in activity as the dispersion of Nafion is increased.

2. Experimental

PdCl_2 (Johnson Matthey Loan Scheme), 1,10-phen, $\text{Ag}(\text{CF}_3\text{SO}_3)$, 1,5-cyclooctadiene (COD), 2-bromopyridine (Aldrich), carbon monoxide and ethene (Matheson Gases CP Grade) were used as received. Chlorodiphenylphosphine (Aldrich) was freshly vacuum distilled before use. All other chemicals were of reagent grade and used without further purification unless otherwise stated. Three types of Nafion were used in this work, namely Nafion NR50 granules (equiv. wt. 1250), Nafion 117 film (equiv. wt. 1100), and Nafion 60–100 mesh powder (equiv. wt. 1100), all of which were generously donated by Du Pont and were regenerated by washing in HNO_3 and then water for

approximately 24 h. Nafion was dried at 100°C under vacuum (0.1 mm Hg) for 24 h before use. Nafion was used in the acid form for all catalytic tests. The synthesis of $[\text{Pd}(1,10\text{-phen})_2][\text{NO}_3]_2$ has been described previously, as has the immobilisation of $[\text{Pd}(1,10\text{-phen})_2]^{2+}$ in Nafion [15]. $[\text{Pd}(1,10\text{-phen})_2][\text{CF}_3\text{SO}_3]_2$ was prepared in a similar manner to $[\text{Pd}(1,10\text{-phen})_2][\text{NO}_3]_2$ using $\text{Ag}(\text{CF}_3\text{SO}_3)$ instead of AgNO_3 to remove the chloride anions from the $\text{Pd}(1,10\text{-phen})_2\text{Cl}_2$ intermediate.

2.1. Preparation of $[\text{Pd}(\text{Ph}_2\text{Ppy})_2][\text{BF}_4]_2$

The preparation of $[\text{Pd}(\text{Ph}_2\text{Ppy})_2][\text{BF}_4]_2$ was carried out using $\text{PdCl}_2(\text{COD})$, which was prepared from PdCl_2 using the method of Drew and Doyle [26], and Ph_2Ppy , which was made from chlorodiphenylphosphine and 2-bromopyridine using an adaptation of a literature method by Maisonnnet et al. [27].

Two equivalents of Ph_2Ppy (0.83 g; 3.16 mmol) was added to a solution of $\text{PdCl}_2(\text{COD})$ (0.45 g; 1.58 mmol) in CH_2Cl_2 (20 ml). There was a colour change from yellow to orange while the reaction mixture was allowed to stir for half an hour. The mixture was evaporated to dryness, washed twice with hexane to remove COD, filtered, and then dried. The resultant product was a yellow-orange solid $\text{Pd}(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$.

The $\text{Pd}(\text{Ph}_2\text{Ppy})_2\text{Cl}_2$ was redissolved in CH_2Cl_2 . Two equivalents of AgBF_4 (0.62 g; 3.16 mmol) was added and AgCl precipitated. To ensure that all of the complex was in solution and not filtered off with the AgCl , methanol (10 ml) was added. The complex changed colour immediately from orange to red. The solution was then filtered through Celite, the solvent was evaporated off, washed with hexane, and dried in vacuo.

Analysis calculated for $\text{PdC}_{34}\text{H}_{28}\text{P}_2\text{N}_2\text{B}_2\text{F}_8 \cdot 1/2\text{CH}_2\text{Cl}_2$: C, 48.80; H, 3.44; N, 3.30. Found: C, 48.63; H, 3.95; N, 3.26. MS(LSIMS) of the cationic part: m/z 632 $[M + e^-]^+$ (17), 651 $[M + F]^+$ (7), 554 $[M\text{-py}]^+$ (30), 447 $[M\text{-}$

Ph_2P^+ (100), 369 [$M\text{-Ph}_2\text{Ppy}^+$] (50). ^1H NMR (300 MHz, CD_2Cl_2): δ 8.0–7.0 (vb). ^{13}C NMR (75 MHz, CD_2Cl_2): δ , 134.8–132.6, 130.8–129.5, (vb, phenyl and pyridyl carbons). ^{31}P NMR (120 MHz, CD_3OD): δ 37.42 (s), 33.15, 27.33, -1.85 , -5.48 .

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 reactor vessel, a baffle, a thermometer sleeve for a thermocouple and an impellor with three blades 15 mm long. The impellor 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 $80 \pm 0.1^\circ\text{C}$ for ethene dimerisation and ethene and carbon monoxide co-polymerisation, and $44 \pm 0.1^\circ\text{C}$ for methoxycarbonylation of ethene.

Ethene dimerisation catalytic testing typically consisted of adding ca. 1 g of Nafion- H^+ containing the $[\text{Pd}(1,10\text{-phen})_2]^{2+}$ complex (or 10 μmol of $[\text{Pd}(1,10\text{-phen})_2][\text{CF}_3\text{SO}_3]_2$ for homogeneous tests) to the Büchi reactor followed by 200 ml of water. The reactor was then cooled to ca. 5°C with an ice bath to aid in the addition of butane standard. Heating to reaction temperature was carried out over a period of half an hour, after which time the reactor was charged with ethene to a pressure of 40 bar. Timing of the reaction commenced when the ethene pressure reached 30 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 vapour using gas chromatography (GC). 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

Co-polymerization of ethene and carbon monoxide was undertaken using both $[\text{Pd}(1,10\text{-phen})_2][\text{CF}_3\text{SO}_3]_2$ and Nafion supported $[\text{Pd}(1,10\text{-phen})_2]^{2+}$. For homogeneous tests, ca. 50 μmol of $[\text{Pd}(1,10\text{-phen})_2][\text{CF}_3\text{SO}_3]_2$ and 80 equivalents of *p*-toluenesulfonic acid were added with 100 ml of methanol to the reactor. For supported tests, ca. 1 g of Nafion NR50 granules, containing 10 μmol of $[\text{Pd}(1,10\text{-phen})_2]^{2+}$, was added to the reactor with 100 ml of methanol. The reaction temperature of ca. 80°C was achieved over a period of 30 min, after which time the reactor was charged with CO to 20 bar, followed by a further 20 bar of ethene. Timing of the reaction commenced on addition of ethene and was monitored for 20 h. Analysis of samples collected revealed no liquid products were produced, however, solid product was produced during catalysis.

Product analysis for homogeneous tests: Khaki solid: analysis calculated for $\text{C}_3\text{H}_4\text{O}$: C, 64.27; H, 7.19. Found: C, 63.28; H, 6.95; N, 0.22; S, 1.86. IR (KBr disc): ν (C=O) 1688 cm^{-1} . ^{13}C NMR (75 MHz, $\text{CF}_3\text{COOH}/\text{C}_6\text{D}_6$): δ 215.4 (C=O), 36.3 (CH_2).

Product analysis for Nafion supported tests: Off-white solid: analysis calculated for $\text{C}_3\text{H}_4\text{O}$: C, 64.27; H, 7.19. Found: C, 52.40; H, 5.34; S, 0.49. IR (KBr disc): ν (C=O) 1692 cm^{-1} . ^{13}C NMR (75 MHz, $\text{CF}_3\text{COOH}/\text{C}_6\text{D}_6$): δ 215.3 (C=O), 36.2 (CH_2).

Methoxycarbonylation of ethene was conducted under strictly oxygen-free conditions with the Büchi autoclave purged with N_2 before each catalytic test. For supported tests, ca. 1 g

¹ Determination of the distribution of butenes between the reactor and sample bottle headspace vapour was undertaken by the 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.

of Nafion NR50 beads, containing 10 μmol of $[\text{Pd}(\text{Ph}_2\text{Ppy})_2]^{2+}$, were added to the reactor, which was sealed immediately, evacuated, and then purged with N_2 . The addition of 100 ml of dry oxygen-free methanol via syringe followed. For homogeneous tests, ca. 50 μmol of $[\text{Pd}(\text{Ph}_2\text{Ppy})_2][\text{BF}_4]_2$ and 80 equivalents of *p*-toluenesulfonic acid in 10 ml of methanol were added to the reactor via syringe, followed by the addition of 90 ml of dry oxygen-free methanol. These additions were made after the reactor was sealed and purged with N_2 . Heating to the reaction temperature of ca. 44°C was carried out over a period of 10 min, after which time the reactor was charged first with carbon monoxide to 20 bar and then with ethene to 40 bar. Timing of the reaction commenced on addition of ethene. Progress of the catalytic reaction was monitored over a 20 h period by expanding ca. 1 ml of catalytic solution into a 150 ml stainless steel sample bottle and analysing the liquid using GC. An external standard, ethyl hexanoate, was used. Sample preparation before analysis involved weighing one to two drops of the standard, followed by the addition of a known weight of sample into a sample vial.

2.3. Gas chromatographic analysis

Products from catalytic testing were analysed by GC using a HP 5890 GC fitted with a SGE 25 QC3/BP1-4.0 or SGE 25 QC3/BP1-0.5 column, with N_2 as the carrier gas.

For ethene dimerisation, butane and butenes separation was achieved using a SGE 25 QC3/BP1-4.0 by undertaking isothermal analyses at 35°C (N_2 carrier gas velocity of 11–13 cm^{-1}) while analysis for C_6s and C_8s was carried out by temperature programming from 35°C to 200°C at 5°C min^{-1} with a N_2 pressure of 17 kPa. Peak assignment was made after injecting individual isomers. The reaction turnover number (TON) was defined as the moles of ethene consumed per mole of Pd catalyst, while the activity was defined as the TON per hour.

For methoxycarbonylation of ethene GC analyses were carried out using a SGE 50 QC3/BP1-0.5 column and a heating rate of 10°C min^{-1} from 35°C to 250°C (N_2 pressure of 100 kPa). Samples were analysed immediately after addition of the external standard to avoid formation of the methyl ester of the external standard. Since the main product for analysis was methyl propionate, it was necessary to use a correction factor, which was established to be 1.9. Therefore, to calculate the number of moles of methyl propionate produced, the calculation based on the GC analysis had to be multiplied by this factor. GC-MS was used for initial identification of products. The reaction TON was defined as the moles of methyl propionate produced per mole of Pd catalyst, while the activity was defined as the TON per hour.

3. Results and discussion

As noted above, our initial studies of Nafion supported Pd(II) catalysts revealed that the catalytic activity of the supported catalyst was dependent on the catalyst loading in Nafion [17]. The increased catalytic activity observed with decreasing catalyst loading in Nafion was considered to potentially arise from a combination of several factors. Firstly, the reaction may be rate-limited at higher loadings by the diffusion of ethene to the catalytic centres with only those centres close to the outer surface able to attain maximum activity. Catalytic sites towards the centre of the support would be severely rate-limited by low ethene diffusion. Secondly, the water content of clusters in Nafion has been observed to decrease as the protons in Nafion are exchanged with larger cations [4], thus, a decrease in complex loading could be expected to lead to an increase in the amount of solvent incorporated into the Nafion. This would result in an increase in the free volume in Nafion and cause the Nafion to swell. Consequently, an increase in the free volume in Nafion and a decrease in catalyst concentration would reduce

Table 1
Ethene dimerisation activities for Nafion supported catalysts

Type of Nafion used	Loading (wt.% Pd)	Maximum activity (mol C ₂ H ₄ / mol Pd h)	Maximum turnover (mol C ₂ H ₄ / mol Pd)
Granules	0.100	87,000	135,000
	0.050	190,000	195,000
	0.025	300,000	465,000
Ribbon	0.100	155,000	220,000
	0.050	325,000	560,000
	0.025	533,000	450,000
Powder	0.100	270,000	160,000
	0.050	528,000	400,000
	0.025	764,000	590,000
Homogeneous [Pd(1,10-phen) ₂][CF ₃ SO ₃] ₂	10 μ.mol	32,000	17,200

diffusion limitations as well as reduce intermolecular interactions. These intermolecular interactions may sterically hinder the catalytic steps or result in deactivation of catalytic intermediates. The possibility of intermolecular interactions being a significant problem is quite valid when we consider the dimensions of the [Pd(1,10-phen)₂]²⁺ complex, ca. 10 × 8 Å [28], and the size of the ionic clusters in Nafion which are approximately 40 Å in diameter [4].

To determine if ethene diffusion through Nafion or intermolecular interactions between catalyst molecules is the predominant factor responsible for the dependence of activity on loading, a range of catalyst loadings and three forms of Nafion have been used to assess the trend in activity as the dispersion of Nafion is increased. The Nafion supports ranged in size from the Nafion NR50 10–35 mesh granules which are ca. 0.5–1.0 mm in thickness, to Nafion 117 film which is 180 μm thick, to the Nafion 60–100 mesh powder which is ca. 150–200 μm in diameter.

Table 1 summarises the ethene dimerisation results found for Nafion-H⁺ supported [Pd(1,10-phen)₂]²⁺ for the three forms of Nafion studied. The maximum activity for each system was determined by sampling the autoclave throughout the testing period and generally occurred within the first 30–60 min of each test. The increased activity with decreasing Pd loading is clearly displayed by each of the Nafion forms and is consistent with our previous observations [17]. A plot of TON vs. time is also shown for the homogeneous system and the 0.025 wt.% Pd supported systems, Fig. 1, and

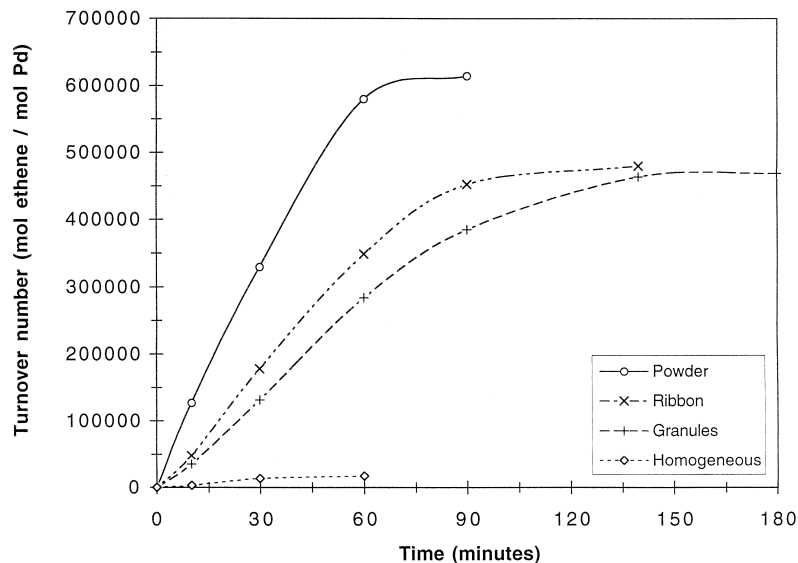


Fig. 1. TON vs. time for ethene dimerisation using homogeneous and 0.025 wt.% Pd Nafion supported catalyst systems.

illustrates how activity decreased with time. The homogeneous catalyst was active for approximately 1 h, while the catalysts in the Nafion granules and ribbon continued to be active for 1.5 h. In all cases, the supported catalysts outperformed the homogeneous catalyst with superior turnovers.

In this study, catalytic activities as high as 760,000 turnovers h^{-1} were observed for the Nafion powder based system with a Pd loading of 0.025 wt.% (300,000 turnovers h^{-1} for Nafion granules), while in our previous study using Nafion granules, activities up to 80,000 were typically found [17]. This increase can be partly attributed to the type of Nafion employed. There was also a difference in experimental design between the two studies. In our previous work, using a 350 ml Parr autoclave, the catalyst was contained in a small basket attached to the stirrer shaft. With the Büchi reactor, the catalyst was not contained in a basket but was allowed to freely disperse in the reaction solvent. This has most likely resulted in an increase in the rate of transfer of reactant and product between the solvent and Nafion support.

The extremely high activities of the Nafion supported Pd(II) complexes using water as the solvent are possibly due to two contributing factors. Protic solvents and weakly coordinating anions have been determined to be important in catalysis using cationic Pd(II) complexes, as it is believed that effective anion–cation separation is required for efficient catalysis [20]. The highly polar environment in the clusters in Nafion combined with the fact that the SO_3^- anion in Nafion is very weakly coordinating, with coordination ability between PF_6^- or BF_4^- and that of ClO_4^- [8], should ensure excellent anion–cation separation. Secondly, the acid concentration in the Nafion clusters is relatively high for catalysis, with 70 SO_3^- groups per 40 Å cluster [4] equating to an acid concentration of ca. 2 M.

The increase in activity as the dispersion of Nafion is increased from granules to ribbon to

the highly dispersed powder confirms that ethene diffusion is, in fact, the major rate limitation. By varying the dispersion of Nafion while maintaining the catalyst loading, we have eliminated effects such as changes in Nafion cluster morphology and steric restrictions on the catalyst molecules in the crowded Nafion cluster environment.

Fig. 1 shows that the lifetimes of the supported catalysts are in the order granules > ribbon > powder, this is also consistent with diffusion limitations and suggests that each catalyst can undergo a certain number of cycles prior to deactivation. Increasing the dispersion of the Nafion, as happens when the form of the Nafion goes from granules to ribbon to powder, will increase the percentage of molecules initially active thus, decreasing the life of the overall catalyst system. In the case of the granules, for example, catalytic sites towards the centre of the granules will never achieve maximum activity due to diffusion limitations and thus, will continue to be active after the majority of the catalytic sites have been deactivated.

Selectivity of the immobilised $[\text{Pd}(\text{1,10-phen})_2]^{2+}$ species for ethene dimerisation has previously been found to be more than 90% for both homogeneous and supported catalytic tests [15], with the distribution of butene isomers relatively constant during the course of a reaction. The product distribution does, however, vary from homogeneous to supported systems in water, typically, the product distribution obtained for the homogeneous system was 22–25% 1-butene with 38–40% each of *cis*-2-butene and *trans*-2-butene. For the supported systems, the product distribution was 12–14% 1-butene with 42–44% each of *cis*-2-butene and *trans*-2-butene. This again supports the suggestion that diffusion limitations exist in Nafion since the increased proportion of 2-butenes from the supported systems would result from increased isomerisation of 1-butene due to its slow diffusion away from the catalytic centres.

Co-polymerisation of ethene and carbon monoxide and methoxycarbonylation of ethene

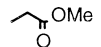
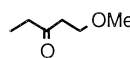
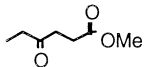
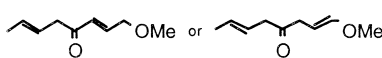
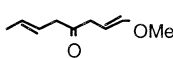
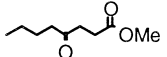
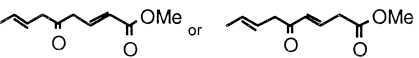
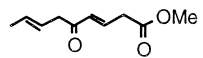
have also been studied using Nafion supported $[\text{Pd}(1,10\text{-phen})_2]^{2+}$ and $[\text{Pd}(\text{PhPpy})_2]^{2+}$, respectively, in methanol. The results again show that in addition to Nafion functioning as a support, it is able to act as a catalyst activator with increased activities resulting for the supported systems when compared with the homogeneous systems.

For co-polymerisation, the TON for the homogeneous system was calculated to be 14 g polymer g^{-1} Pd while the TON for the supported system was 70 g polymer g^{-1} Pd. Spectroscopic analysis of the products from both systems gave results consistent with a strictly alternating structure. The solid product from the supported catalytic tests was off-white in colour, whereas khaki coloured solids were formed in the homogeneous tests. For the homogeneous system, it was evident from the colour of the sample that the polymer was not pure and elemental analysis indicated that the polyketone contained decomposed catalyst. For the Nafion

supported system the crude product was a mixture of polyketone product plus fragmented Nafion beads caused by the growing polymer chain breaking up the Nafion beads during catalysis. Despite the product containing fragments of the support, the results are particularly interesting since the Nafion supported system produced a cleaner product with a higher turnover than the homogeneous system.

Carbomethoxylation of ethene resulted in TON of 160 mol and 750 mol of methyl propionate produced per mol of Pd for the homogeneous and supported systems, respectively, and activities of 10 turnovers h^{-1} and 235 turnovers h^{-1} , respectively. GC-MS analysis was used to identify products formed in both the homogeneous and supported systems. Products ranged from C_4 to C_{10} co-oligomers with the distribution of products shown in Table 2. A significant observation from comparison of product distributions for methoxycarbonylation of ethene for supported and homogeneous systems was that

Table 2
Product distribution for methoxycarbonylation of ethene

Product	Homogeneous System (%)	Nafion- H^+ Supported System (%)
 Methyl propionate	39	78
 1-methoxy-3-pentanone	7	2
 Methyl 4-oxo-hexanoate	22	12
$\text{C}_9\text{H}_{14}\text{O}_2$  or 	10	2
$\text{C}_9\text{H}_{16}\text{O}_3$ 	4	-
$\text{C}_{10}\text{H}_{14}\text{O}_3$  or 	16	6
Unidentified Products	2	-

the supported system had significantly higher selectivity toward methylpropionate than the homogeneous system. This selectivity towards the C₄ product by the supported system is most likely a result of diffusion limitations of ethene or carbon monoxide through Nafion. A low concentration of ethene or carbon monoxide relative to methanol in the vicinity of the catalytic sites in Nafion would result in the termination step via methanol addition predominating over the insertion of a second ethene or carbon monoxide molecule into the co-oligomer. This is consistent with Drent and Budzelaar's proposed mechanisms for alternating co-oligomerisation of ethene and carbon monoxide [23].

4. Conclusions

The use of water for ethene dimerisation using Nafion supported Pd(II) catalysts has resulted in extraordinary increases in product yield (25 times) and activities approaching commercially viable activities (760,000 turnovers h⁻¹). This is most likely due to the very polar, strongly acidic environment in Nafion which ensures effective anion–cation separation and promotes labilisation of the nitrogen donor ligands. Enhancements in activities for co-polymerisation of ethene and carbon monoxide, and carbomethoxylation of ethene have also been observed using Nafion supported Pd(II) catalysts in methanol. Diffusion limitations do, however, exist and a combination of low catalyst loading and high dispersion of Nafion are required to achieve these increased activities.

The use of Nafion provides the opportunity to improve catalyst efficiency, to alter product selectivity, and to use water as the reaction medium for synthesis of organic chemicals. While diffusion limitations through the Nafion are apparent, increased product selectivity for the supported system may more than offset any reductions in activity. The dimerisation of ethene in water shows that the conversion of hydropho-

bic species, such as alkenes, is possible in water avoiding the use of expensive and potentially hazardous organic solvents.

Acknowledgements

The authors gratefully acknowledge the Australian Research Council for funding to carry out this work. The donation of Nafion by Du Pont and the loan of PdCl₂ by Johnson Matthey is also acknowledged. The assistance of staff within the Central Science Laboratory, University of Tasmania, for NMR and GC-MS analyses has been greatly appreciated.

References

- [1] F.R. Hartley, P.N. Vezey, *Adv. Organomet. Chem.* 15 (1977) 189–234.
- [2] S.C. Stinson, *Chem. Eng. News* 60 (11) (1982) 22–25.
- [3] S.J. Sondheimer, N.J. Bunce, M.E. Lemke, C.A. Fyfe, *Macromolecules* 19 (1986) 339–343.
- [4] T.D. Gierke, G.E. Munn, F.C. Wilson, *J. Polym. Sci.: Polym. Phys. Ed.* 19 (1981) 1687–1704.
- [5] G.A. Olah, S.I. Pradeed, G.K.S. Prakash, *Synthesis* (1986), pp. 513–531.
- [6] G.A. Olah, D. Meidar, *Synthesis* (1978), pp. 671–672.
- [7] S. Kanemoto, H. Saimoto, K. Oshima, H. Nozaki, *Tetrahedron Letters* 25 (1984) 3317–3320.
- [8] F.J. Waller, *Br. Polymer J.* 16 (1984) 239–242.
- [9] B.-H. Chang, *Inorg. Chim. Acta* 150 (1988) 245–247.
- [10] M. Crocker, R.H.M. Herold, *J. Mol. Catal.* 70 (1991) 209–216.
- [11] I. Toth, B.E. Hanson, M.E. Davis, *J. Organomet. Chem.* 397 (1990) 109–117.
- [12] I. Toth, B.E. Hanson, *J. Mol. Catal.* 71 (3) (1992) 365–371.
- [13] A.M. Hodges, M. Linton, A.W.-H. Mau, K.J. Cavell, J.A. Hey, A.J. Seen, *J. Appl. Organomet. Chem.* 4 (1990) 465–473.
- [14] A.J. Seen, K.J. Cavell, A.M. Hodges, A.W.-H. Mau, *J. Chem. Soc., Dalton Trans.* (1992), pp. 1381–1385.
- [15] A.J. Seen, K.J. Cavell, A.W.-H. Mau, A.M. Hodges, *J. Membr. Sci.* 87 (1994) 149–157.
- [16] A.J. Seen, K.J. Cavell, A.W.-H. Mau, A.M. Hodges, *J. Mol. Catal.* 90 (1994) 245–256.
- [17] A.J. Seen, K.J. Cavell, A.W.-H. Mau, A.M. Hodges, *J. Mol. Catal.* 94 (1994) 163–172.
- [18] A. Sen, T.-W. Lai, *J. Am. Chem. Soc.* 103 (1981) 4627–4629.
- [19] A. Sen, T.-W. Lai, *J. Am. Chem. Soc.* 104 (1982) 3520–3522.
- [20] E. Drent, *Pure Appl. Chem.* (1990), pp. 661–669.
- [21] E. Drent, J.A.M. van Broekhoven, M.J. Doyle, *J. Organomet. Chem.* 417 (1991) 235–251.

- [22] E. Drent, P. Arnoldy, P.H.M. Budzelaar, *J. Organomet. Chem.* 475 (1994) 57–63.
- [23] E. Drent, P.H.M. Budzelaar, *Chem. Rev.* 96 (1996) 663–681.
- [24] B. Milani, L. Vicentini, A. Sommazzi, F. Garbassi, E. Chiarparin, E. Zangrando, G. Mestroni, *J. Chem. Soc., Dalton Trans.* (1996), pp. 3139–3144.
- [25] Z. Jiang, A. Sen, *Macromolecules* 27 (1994) 7215–7216.
- [26] D. Drew, J.R. Doyle, *Inorg. Synth.* 28 (1990) 348.
- [27] A. Maisonneet, J.P. Farr, M.M. Olmstead, C.T. Hunt, A.L. Balch, *Inorg. Chem.* 21 (1982) 3961–3967.
- [28] P.C. Chieh, *J. Chem. Soc., Dalton Trans.* (1972), pp. 1643–1646.