Nafion: an excellent support for metal-complex catalysts

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Abstract

A number of studies over the past 20 years have demonstrated that the perfluorinated ion-exchange polymer Nafion is an excellent support for metal-complex catalysts. A variety of cationic metal-complex catalysts have been successfully immobilized in Nafion with little if any leaching occurring during catalysis, and in several instances the supported catalyst has been re-used with little loss in activity. Whilst the activity of Nafion-supported catalysts has been shown to be dependent upon catalyst loading, suggesting diffusion limitations, activities comparable with homogeneous activities have been observed by increasing the dispersion of Nafion. The physical structure and chemical properties of Nafion offer the additional benefits of providing protection to the supported catalyst from deactivation and the potential to increase the activity of the supported catalyst compared with its homogeneous analogue. Although diffusion limitations and the high cost of Nafion have potentially limited its application as a metal-complex catalyst support, the recent development of high surface area Nafion–silica nanocomposites provides the opportunity to solve these issues. © 2001 Elsevier Science B.V. All rights reserved.

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1. Chemical and physical properties of Nafion

The perfluorinated ion-exchange polymer Nafion (Fig. 1) was developed by DuPont in the early 1960s during work with General Electric on a fuel cell [1]. The major application of Nafion has been as a separating membrane in electrolytic cells used to produce chlorine and sodium hydroxide [1]. Other applications have included its use as a solid polymer electrolyte in fuel cells [2,3] and batteries [4,5], and as an electrode coating [6,7].

Nafion is unaffected by strong bases, strong oxidizing and reducing acids, chlorine, oxygen, hydrogen, and hydrogen peroxide at temperatures at least up to 125°C [8]. Nafion is thermally stable to about 170°C

in the acid form and stable to higher temperatures, ca. 200–235°C, on replacement of the protons by metal counter-ions [9]. Its resistance to chemical attack and thermal stability, in addition to its high mechanical strength, make it ideal for applications where a strong chemically resistant polymer is required.

The morphology of Nafion has been extensively studied using SAXS, and although it is agreed that ion clusters exist within Nafion there is some doubt as to the shape and size of these clusters [10–12]. Various models have been proposed which explain the structure as a group of hydrophilic ionic clusters of the order of 40–50 Å diameter separated by channels within a hydrophobic perfluorocarbon matrix as is shown in Fig. 2. Although Nafion is mechanically strong, cross-linking does not exist in Nafion and the dimensions of the ionic clusters can vary according to solvent, temperature and counter-ions.

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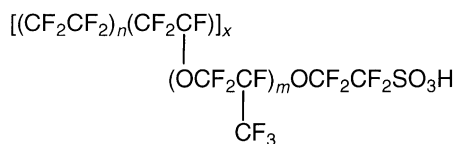*E-mail address:* a.j.seen@utas.edu.au (A.J. Seen).

$[(CF_2CF_2)_n(CF_2CF)]_x$

$(OCF_2CF)_mOCF_2CF_2SO_3H$

CF_3

Fig. 1. Chemical structure of Nafion (acid form), where $m = 1, 2$, or 3; n typically has a value in the range 6–7, and x is about 1000.

2. Examples of Nafion as a metal-complex catalyst support

The fluorocarbon backbone of the Nafion polymer is strongly electron withdrawing, and hence, the sulfonic acid sites within Nafion are quite strong. This has led to the use of Nafion as an acid catalyst which has been extensively covered [13]. Nafion has also
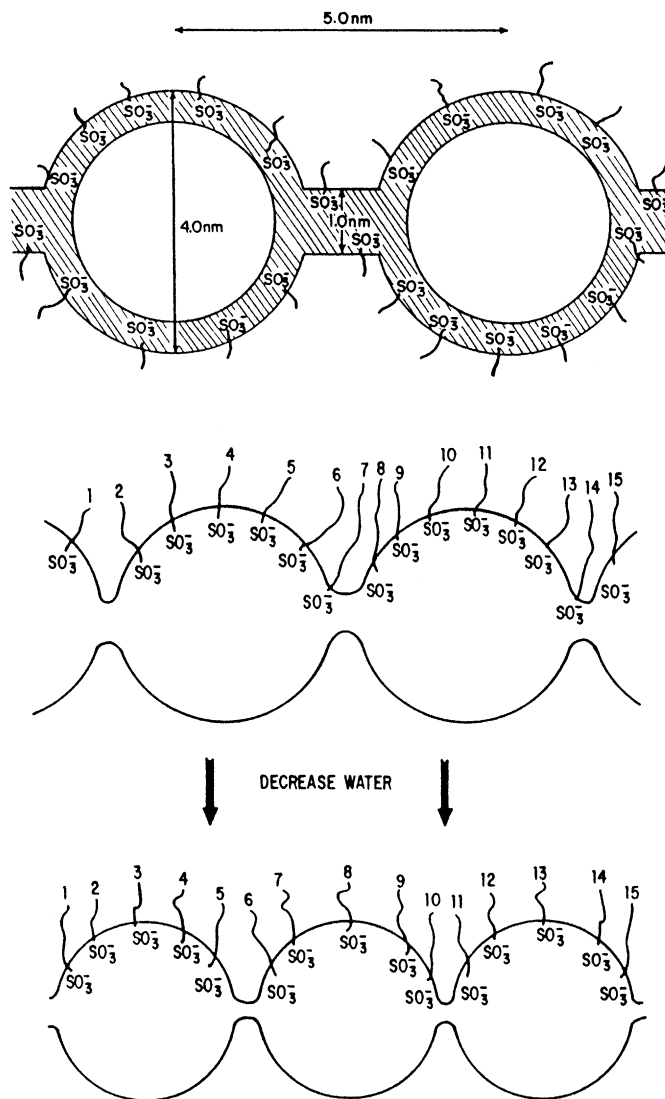

Fig. 2. The cluster-network model for Nafion proposed by Gierke et al. showing the dimensions of the clusters and channels (up), and the re-distribution of ion-exchange sites on dehydration (down) [11].

been considered as a support for metal-complex catalysts and work in this area by Olah and Meidar dates back to 1978 when they used partially exchanged mercuric Nafion as a catalyst for the hydration of alkynes [14]. Oshima and coworkers reported on the catalytic oxidation of alcohols by *t*-butylhydroperoxide using Cr(III) or Ce(VI) exchanged Nafion in 1984 [15]. The catalyst was re-usable after a simple washing.

In 1984, Waller reported that the rate of [Pd(PPh$_3$)$_4$] catalyzed carbomethoxylation of alkenes was increased by immobilization of the complex in Nafion [16]. Waller also reported that the initial turnover rate data suggested that diffusional effects were important in understanding activity which was dependent upon alkene size, with catalytic activity for ethene > propene > 1-hexene, whereas a homogeneous system using CF$_3$SO$_3$H reversed the order of 1-hexene and propene.

A further report of the use of Nafion as a support for a palladium alkene carbomethoxylation catalyst was made in 1988 when Chang reported on the use of [Pd(CH$_3$CN)(PPh$_3$)$_3$]$^{2+}$ as a carbomethoxylation catalyst for propene [17]. Chang compared three sulfonated ion-exchange resins, Nafion, Amberlyst and Dowex, and found that the Nafion-H$^+$-supported complex was more than twice as active as the Amberlyst- or Dowex-supported complex. These results were further supported by Crocker and Herold when they compared the ethene carbomethoxylation activity of [Pd(CH$_3$CN)(PPh$_3$)$_3$]$^{2+}$ intercalated in a number of smectite clays and in Dowex and Nafion [18]. The acid form of Nafion was superior to all other supports and it was notable that the potassium form of Nafion displayed nil activity. Hence, Crocker's claim that the acidic ion-exchange resins have a dual role, acting both as a support and as an acid promoter.

In 1990, Hanson and coworkers reported on the immobilization of Rh complexes containing cationic phosphine ligands in several cation exchange resins and the use of these supported complexes for the catalytic asymmetric hydrogenation of several dehydroaminoacids [19]. The rates and enantioselectivities of these hydrogenations depend not only on the ligand used, but also on the nature of the ion-exchange resin upon which the complex was immobilized. Nafion-H$^+$ exhibited superior activity to the Amberlyst-H$^+$-supported catalyst in terms of allowing the complexes to retain their enantioselectivity. The reaction rate of the

Nafion-H$^+$-supported catalysts was, however, much slower than the homogeneous complex. Hanson and coworkers also showed that no detectable leaching of rhodium into the substrate phase occurred for any of the resin-supported catalysts. This was supported by the observation that the filtered solutions obtained during the recycling experiments showed no catalytic activity when charged with new substrate and pressurized with H$_2$.

Further work by Hanson and Toth in 1992 showed that reaction rates approaching the homogeneous catalyst could be achieved by using the "soluble" form of Nafion [20]. This "soluble" form of Nafion is in fact a suspension of colloidal Nafion particles in a water–alcohol mixture which is obtained by dissolving solid Nafion at 250°C under pressure [21]. Addition of five equivalents of a colloidal Nafion suspension to a methanol solution of [BDPP(NMe$_2$)$_4$RhNBD]$^+$ or [Chiraphos(NMe$_2$)$_4$RhNBD]$^+$ resulted in the immediate precipitation of an orange solid. The solid was collected on a fine porosity glass-frit and used as a catalyst for asymmetric hydrogenation of dehydroaminoacids. Hydrogenation rates with the finely divided precipitated resin were orders of magnitude faster than those obtained with Nafion beads and nearly as fast as the rates obtained with the analogous homogeneous catalysts. However, the activity of the precipitated resin was dependent upon its treatment with best results obtained when the catalysts were not subjected to vacuum drying. Extensive drying of the collected solid in vacuo solid caused an irreversible collapse of the resin resulting in only moderate catalytic activity. It was also of note that the catalysts could be recycled without significant loss in enantioselectivity or activity.

3. Dependence of supported catalyst activity on metal-complex loading in Nafion

Many of the works outlined above have been exploratory with little follow-up work or attempts to optimize the Nafion-supported systems. For example, although Waller suggested that diffusional effects may be important in understanding the activity of Nafion-supported catalysts [16], catalytic testing was undertaken at the extremely high catalyst loading of 3.25 wt.% Pd and no attempt was made to investigate the effect of diffusion on activity. Similarly, testing

by Chang [17] and Crocker and Herold [18] was also undertaken at relatively high catalyst loadings of ca. 1 wt.% Pd.

Over the past decade, we have undertaken extensive studies on the application of Nafion as a metal-complex catalyst support with the main focus of our work being the use of Nafion as a support for cationic Pd(II) catalysts for the dimerization of ethene [22–25]. Our initial attempts to dimerize ethene using $[Pd(1,10\text{-phen})_2]^{2+}$-supported in 10–35 mesh Nafion-H^+ granules met with limited success, with the activity of the supported system approximately 10% of that of the homogeneous system [23]. The catalyst loading in this initial-supported system was about 2 wt.% Pd and an activity of 1500 turnovers/h was obtained at 80°C in methanol compared with a homogeneous activity of 15 000.

The supported catalysts were prepared by stirring the acid form of Nafion in a methanol solution of $[Pd(1,10\text{-phen})_2](NO_3)_2$. The ion-exchange process was allowed to continue overnight in an effort to achieve a uniform distribution of the complex throughout the Nafion, whilst UV analysis of the ion-exchange solutions after removing the Nafion

showed that more than 95% of the $[Pd(1,10\text{-phen})_2]^{2+}$ was ion-exchanged into the Nafion [22]. Thus, the loading of the complex in Nafion was easily modified.

It was found that on decreasing the catalyst loading in Nafion the activity of the supported catalyst markedly increased, as is shown in Fig. 3, becoming comparable with the activity of the homogeneous system for catalyst loadings <0.065 wt.% Pd [23]. An obvious explanation for this increase in catalyst activity with reduction in loading is a substrate diffusion limitation. Since the ion-exchange of $[Pd(1,10\text{-phen})_2]^{2+}$ into Nafion was carried out over an extended period of time, it is reasonable to assume that the catalyst was evenly distributed throughout the cross-section of each Nafion granule, and hence, under the constraint of an ethene diffusion limitation the supply of ethene to any $[Pd(1,10\text{-phen})_2]^{2+}$ complex in a Nafion granule was dependent upon the number of catalytic sites between that complex and the outer surface of the Nafion granule. Thus, at high catalyst loadings only those $[Pd(1,10\text{-phen})_2]^{2+}$ complexes close to the outer surface of a Nafion granule were supplied with sufficient ethene to attain maximum activity, but as the catalyst loading in Nafion was
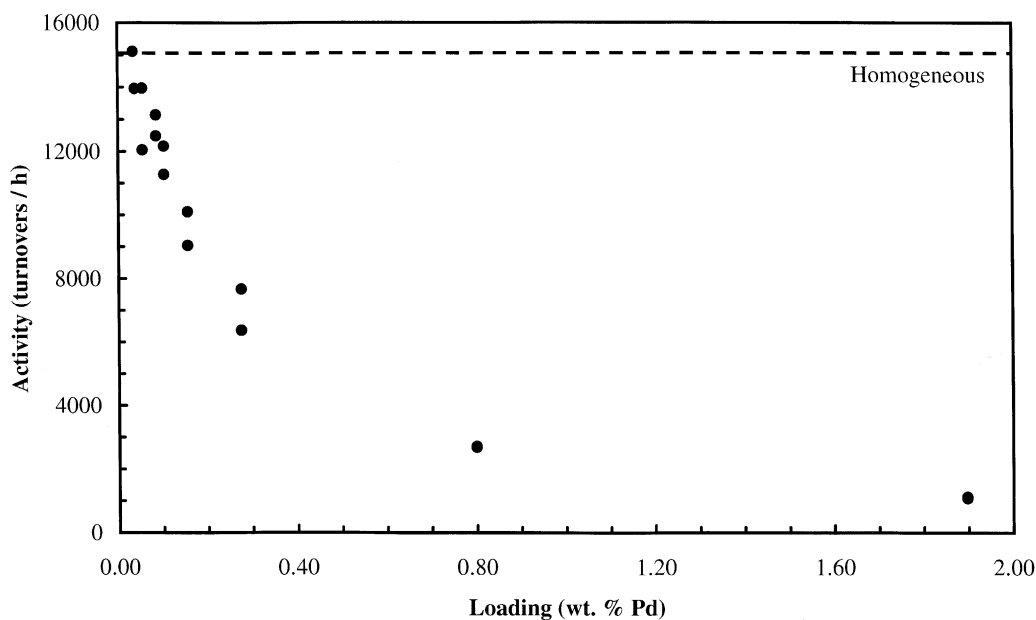

Fig. 3. Ethene dimerization activity vs. catalyst loading for $[Pd(phen)_2]^{2+}$ in Nafion-H^+ (conditions: catalytic tests conducted in methanol at 80°C and 300–400 psi ethene).

decreased a greater proportion of $[Pd(1,10\text{-phen})_2]^{2+}$ complexes were able to attain maximum activity, hence, the observed increase in ethene dimerization activity.

Tests with propene and 1-butene as substrates also suggested that catalytic activity was limited by substrate diffusion with the activity of the supported catalyst being significantly less than the homogeneous catalyst activity, even at a catalyst loading of 0.065 wt.% Pd, the loading at which ethene dimerization was no longer rate limited [23]. In an effort to confirm that ethene diffusion through Nafion was rate limiting the dispersion of Nafion was increased by decreasing the size of the Nafion particles. On changing from 10–35 mesh granules to 60–100 mesh powder ethene dimerization activity more than doubled for a 0.025 wt.% Pd catalyst loading, thus, confirming that ethene diffusion was rate limiting [24].

A further factor that needs to be taken into consideration is the steric constraints that may exist on catalyst molecules in the clusters within Nafion. As was mentioned previously, Nafion is not cross-linked and it is able to swell and shrink as it absorbs or desorbs solvent as is shown in Fig. 2. The cluster-network model proposed by Gierke et al. predicts that as the water content of Nafion increases then the cluster diameter and the number of ionic sites per cluster will also increase [10,11]. This phenomenon is explained by a reorganization of the polymer with a re-distribution of ionic sites from adjacent clusters. The model predicts that Nafion swollen with ca. 20 wt.% water will have a cluster diameter of 40–50 Å with approximately 70 sulfonate groups present in each cluster. It has been observed that the water content of Nafion decreases as the protons in Nafion are exchanged with larger cations [10,11], thus, an increase in complex loading could be expected to lead to a decrease in the amount of solvent incorporated into Nafion, and hence, a decrease in cluster diameter.

In addition, whilst the bulk swelling of Nafion with methanol is known to be greater than with water [26], the manner in which this swelling occurs is not known. It is possible that the relationship between cluster size and the number of ionic sites per cluster may be different for Nafion swollen with methanol, as the methanol may partition into different regions of the polymer than does water. Infrared OH stretching studies of hydrated Nafion by Falk have shown that the ionic clusters have

a high surface to volume ratio, possibly due to the ionic clusters being of irregular shape with frequent local intrusions of the fluorocarbon phase [27]. In fact, a comparison of ESR spectra of VO^{2+} in Nafion swollen by water, methanol and ethanol with spectra of VO^{2+} in the neat solvents has suggested that smaller solvent clusters are formed, where the motion of the cation is highly hindered with less polar solvents [28]. These results were explained by assuming that the alcohols penetrate further into the perfluorinated regions than water, and form small solvent pools compared with the larger clusters formed by water in Nafion.

The possibility of steric constraints causing intermolecular interactions between catalyst molecules, and thus, hindering catalytic steps is a valid consideration in view of the morphology of the clusters within Nafion and the fact that the $[Pd(1,10\text{-phen})_2]^{2+}$ complex is approximately 10 Å × 8 Å in size with a slight twist to square planar [29].

4. Suitable solvents for Nafion

Nafion is non-porous and relies on the solvation of the ionic groups by an appropriate solvent to form solvent channels and clusters. The use of solvents that do not swell Nafion has resulted in low catalytic activities, most probably due to the failure of the substrate to be able to access the catalyst. For example, our attempts to use chlorobenzene as a solvent for an arylnickel(II) complex immobilized in Nafion resulted in low activities [30]. The Nafion was not swollen in chlorobenzene, and in fact appeared to shrink and become opaque compared with its appearance when soaked in methanol or water. Hanson and coworkers have had similar experience when testing Rh complexes containing cationic phosphine ligands for the catalytic asymmetric hydrogenation of several dehydroaminoacids [19]. Attempts to use THF as a solvent were unsuccessful with the Nafion-supported catalysts showing no activity due to the failure of THF to swell the Nafion.

Water was tried as a solvent for Nafion-supported Pd(II) catalysts and was found to be an extremely effective solvent for ethene dimerization [23–25]. Extraordinary increases in product yield (25 times) and activities approaching commercially viable activities (760 000 turnovers/h) were observed [24,25].

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 [31]. The highly polar environment in the clusters in Nafion combined with the fact that the SO_3^- anion is weakly coordinating should ensure excellent anion–cation separation.

5. Nafion as a catalyst activator and acid co-catalyst

Our interest in Pd(II) complexes with weakly coordinating nitrogen donor ligands as dimerization catalysts stemmed from work by Drent which showed that a non-coordinating anion was required for optimum activity [31]. The sulfonate anion in Nafion is a very weakly coordinating anion, with coordination ability between PF_6^- or BF_4^- and that of ClO_4^- [16], and is thus, ideal as a counter-ion for the cationic Pd(II) com-

plexes. During our studies, we supported three cationic Pd(II) complexes in Nafion, $[Pd(1,10\text{-phen})_2]^{2+}$, $[Pd(2,2'\text{-bipy})_2]^{2+}$ and $[Pd(1,10\text{-phen})(py)_2]^{2+}$ [22]. Catalytic testing of ethene dimerization showed that the catalyst activity was dependent upon the basicity of the N donor ligand and the counter-ion in Nafion (H^+ or Na^+) as is shown in Fig. 4. The much lower activity of the $[Pd(1,10\text{-phen})(py)_2]^{2+}$ complex in Nafion-H^+ compared with immobilization in Nafion-Na^+ was attributed to the low stability of the complex in the acid form of Nafion. In fact, a UV–VIS spectrum of $[Pd(1,10\text{-phen})(py)_2]^{2+}$ immobilized in Nafion suggested that partial decomposition of the complex to free pyridine and 1,10-phenanthroline occurred in Nafion-H^+, but not in Nafion-Na^+. These observations indicated that the basicity of the nitrogen ligands combined with the highly acidic environment in Nafion-H^+ resulted in increased ligand liability. Thus, in the cases of the $[Pd(1,10\text{-phen})_2]^{2+}$ and $[Pd(2,2'\text{-bipy})_2]^{2+}$ complexes, Nafion-H^+ not only acted as a catalyst support, but also promoted the activity of the resultant catalyst.

The ability of Nafion to act as a catalyst activator has in fact been extended to the use of Nafion as a Brönsted
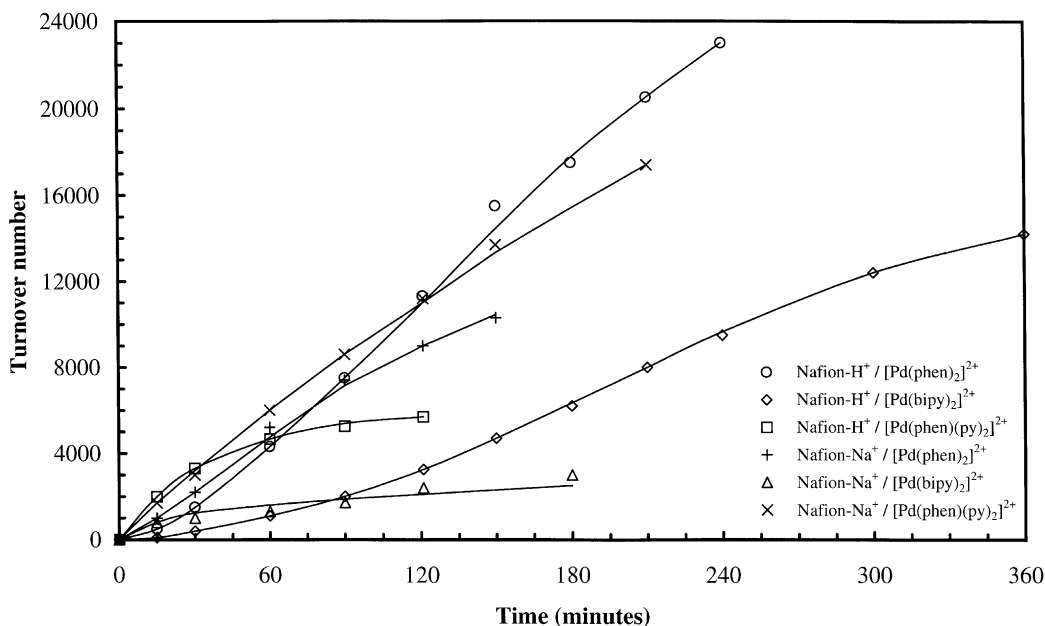

Fig. 4. Turnover number vs. time for various palladium complexes supported in Nafion (conditions: catalytic tests conducted in methanol at 70°C, 300–400 psi ethene and at catalyst loadings of 0.06 wt.% Pd).

acid co-catalyst to activate [Ni{P(OEt$_3$)}$_4$] [32]. The resultant cationic hydride species, [HNi{P(OEt$_3$)}$_4$]$^+$, was immobilized within the Nafion and shown to be active for alkene isomerization. Although the supported catalyst activity for oct-1-ene isomerization was found to be approximately one third of the activity of the homogeneous catalyst using H$_2$SO$_4$ as co-catalyst, the isomerization rate of but-1-ene by the supported catalyst was comparable with that of the homogeneous catalyst. It was also demonstrated that very little, if any, of the catalyst leached from the Nafion support during use.

6. Protection of supported catalysts from deactivation

The immobilization of complex catalysts in Nafion offers a further advantage, namely the ability to provide some protection to the catalyst from deactivation/decomposition. This ability of supported catalyst systems has long been known, for example, in the early 1970s Grubbs and coworkers found that immobilization of a titanocene species on a polymer prevented dimerization of the titanocene species and allowed it to act as a hydrogenation catalyst, whereas the same species in homogeneous solution was inactive due to dimerization [33]. Yagi et al. have clearly demonstrated the ability of Nafion to provide some protection to an immobilized catalyst from deactivation/decomposition [34]. In aqueous solution, the catalytic activity of [Ru(en)$_3$]$^{3+}$ for oxidation of water was found to decrease with concentration due to bimolecular decomposition of the complex. Immobilization of the complex in Nafion provided the opportunity to reduce the bimolecular decomposition, and hence, reduce deactivation of the catalyst.

We have also found that immobilization of an aryl-nickel(II) complex in Nafion appeared to reduce deactivation of the catalyst [30], and similarly our ethene dimerization studies with [Pd(1,10′-phen)$_2$]$^{2+}$ have shown that the Nafion-supported complex not only has higher activity than the homogeneous complex, but is active for longer [25]. Several factors may give rise to these effects and include the ability of Nafion to protect the catalyst from poisons (e.g. oxygen or anions such as Cl$^-$), the ability to restrict dissociated ligands to the vicinity of the catalyst thereby ensuring that free ligand is available to re-coordinate to the catalyst at the completion of the catalytic cycle, and the ability to isolate one catalyst center per ionic cluster minimizing the potential for deactivation through dimerization of catalytic species.

7. Increasing the dispersion of Nafion

A major problem with Nafion has been the fact that diffusion limitations exist and acceptable activities can only be achieved at low catalyst loadings. As was mentioned previously, we have shown this to be the case by varying Pd loadings in Nafion and also by varying the form, and hence, physical dispersion of Nafion. For example, on changing from 10–35 mesh granules to 60–100 mesh powder ethene dimerization activity more than doubled for a 0.025 wt.% Pd catalyst loading [24].

Hanson and Toth have increased the dispersion of Nafion by using the "soluble" form of Nafion [20]. A finely divided form of Nafion containing either of two Rh complexes was prepared by addition of a colloidal suspension of Nafion to solutions of the Rh complexes. Rates for the hydrogenation of dehydroaminoacids with the catalysts prepared from the soluble form of Nafion were much faster than previously obtained with identical complexes immobilized on large Nafion beads.

Another approach to increasing the dispersion of Nafion is the formation of Nafion–silica nanocomposites by sol–gel processing. Harmer et al. have produced a nanocomposite with 20–60 nm diameter Nafion particles dispersed within a porous silica network [35]. The use of this nanocomposite form of Nafion to isomerize 1-butene resulted in a near thermodynamic equilibrium being achieved, whereas <1% isomerization was observed under the same reaction conditions using Nafion NR50 beads [36]. Harmer and coworkers have also used this Nafion–silica nanocomposite as a support for several bis(oxazoline)–copper complexes [37]. These immobilized complexes were successfully used to catalyze the cyclopropanation reaction of styrene with ethyl diazoacetate in 1,2-dichloroethane, and could be recovered and re-used with almost the same catalytic performance. This new highly dispersed form of Nafion offers the potential to overcome diffusion limitations whilst maintaining

the superior physical and chemical properties of Nafion.

8. Conclusions

Although it is 40 years since Nafion was developed, there have been limited studies into its use as a metal-complex catalyst support. The studies that have been undertaken do, however, demonstrate that Nafion has great potential as a metal-complex catalyst support. Its superior chemical and thermal stability, combined with its high acidity, place it in a unique position as a catalyst support. Nafion appears to not only offer the potential to act as a catalyst support, but also the ability to increase activities and protect catalysts from deactivation/decomposition.

However, the drawbacks with Nafion are its cost and diffusion limitations. These can no doubt be overcome by increasing the dispersion of Nafion using techniques such as coating Nafion onto inert supports or forming nanocomposites as has recently been done by Harmer et al. Nafion is marketed by DuPont as a strong acid catalyst and at least one commercial operation exists of Nafion as a metal-complex catalyst support [38], it is most likely that we will see more applications in the future.

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