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Perfluorinated membranes as catalyst supports

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The perfluorinated polymer Nafion and porous PTFE/Nafion composite membranes have been employed as supports for nickel complexes or for platinum and palladium metal particles. The resultant materials have been employed as catalysts in various olefin conversion processes. Supported platinum and palladium metal systems were evaluated as catalysts for the hydrogenation of cyclohexene. Rates of reaction are better than those of commercially available catalysts; turnover numbers in excess of 6000 have been obtained with no poisoning apparent. Catalysts may be regenerated many times. The reduction rate approaches a limit at high pressures of hydrogen and has an activation energy of 13 kJ mol^{-1} in neat cyclohexene. Nafion was employed as a strong acid co-catalyst to activate and then support a nickel complex catalyst. The resultant catalyst was active for double-bond-shift isomerization.

Keywords: Perfluorinated membrane, catalyst support, metal particle catalysts, metal complex catalysts, hydrogenation, isomerization

INTRODUCTION

As part of an ongoing research programme looking at novel materials as catalysts and catalyst supports we have investigated the perfluorinated polymer Nafion (Du Pont). The catalyst systems reported here may be broadly classified into two types:

(1) supported 'metal particle catalysts' (dispersed metal particles, supported on perfluorinated membranes);
(2) supported 'molecular catalyst systems' (metal complex species immobilized on a perfluorinated membrane).

Conceptually, catalysts on membrane supports offer several possible advantages over traditional powder-type systems. The catalyst is immobilized in the membrane so that it cannot agglomerate, filtration is unnecessary to separate the catalyst from the reaction mixture, and complete catalyst recovery is facilitated. Membranes with catalytic activity also make it possible to combine catalytic and separation processes in one operation as well as being suited to continuous-flow reactors.

Using a perfluorinated ion-exchange polymer such as Nafion (Du Pont) as the support material has a number of specific advantages. It is highly chemically resistant and can be used to relatively high temperatures. Metal ions can be incorporated via ion-exchange into its small (~40 Å; ~4 nm) hydrophilic domains which are connected by ~10 Å channels,[1] thus encouraging the growth of small metal particles. Ionic metal complexes and polarizable species may also be entrapped within these domains. Pure Nafion, however, is relatively expensive and has a low permeability to gases and liquids compared with more open-pore types of support. To address these disadvantages we have fabricated composite membranes consisting of a thin layer of Nafion on a porous PTFE ('Goretex', W. R. Gore & Assoc.) support.

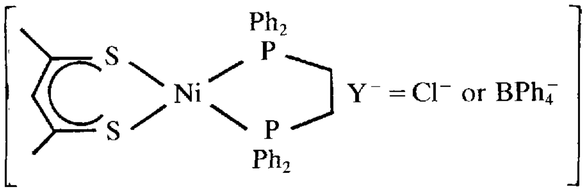
A number of reports have appeared on Nafion-supported metal particle catalysts and are discussed in recent reviews.[2–4]

Mau *et al.*[5] incorporated metallic particles of platinum into Nafion membranes using $Pt(NH_3)_2I_2$ by ion-exchanging $Pt(NH_3)_2^{2+}$ into the polymer and subsequently reducing the complex with borohydride. Using X-ray line broadening they observed ~100 Å-diameter platinum particles. Later, Mattera *et al.*[6] studied the oxidation of CO using Nafion powder supported rhodium, ruthenium and platinum. They incorporated the platinum using $Pt(NH_3)_4Cl_2$ and obtained the metal by reduction with hydrogen, giving 34 Å platinum particles.

In this work we have incorporated metallic palladium or platinum into Nafion sheets and composite membranes via chemical reduction of the appropriate ionic metal complexes and evaluated their performance as hydrogenation catalysts, using cyclohexene reduction as a model reaction. Nafion films and membranes containing Ni(II) complexes have also been prepared and characterized spectroscopically. The catalytic behaviour of these supported complexes for olefin isomerization has been studied.

Few reports of Nafion-supported molecular catalyst systems have appeared in the literature. Very recently Chang[7] has reported the carbomethoxylation of propylene catalysed by Pd(0) and Pd(II) complexes supported on Nafion-bound metal-complex catalysts.

Two approaches were adopted for the formation of supported molecular catalyst systems. In one case a cationic Ni(II) complex (I) was preformed, then ion-exchanged onto the sodium form of Nafion (i.e. Nafion–Na). Complex (**I**) was selected as it gives rise to a highly active olefin oligomerization and double-bond-shift isomerization catalyst in homogeneous solution when activated with an alkylaluminium co-catalyst.[8]



$Y^- = Cl^-$ or BPh_4^-

I $[Ni(sacsac)(dppe)]^+Y^-$

The second approach involved the interaction of a zero-valent nickel complex, tetrakis(triethylphosphite)nickel(0) ($Ni[P(OEt)_3]_4$) with the acid form of Nafion (i.e. Nafion–H) to give supported Ni(II) species. The interaction of $Ni[P(OEt)_3]_4$ with methanolic sulphuric acid yields a well-characterized homogeneous olefin isomerization catalyst.[9]

EXPERIMENTAL

General

Solid-state nuclear magnetic resonance (NMR) spectra were recorded at ambient temperature in a Bruker AM-300 NMR spectrophotometer. ^{31}P HP (high-power decoupling)/Magic Angle Spin (MAS) NMR spectra were recorded at 120.5 MHz. The external standard for ^{31}P HP/MAS NMR spectra was triphenylphosphine. Chemical shifts were expressed in ppm from the external standard. Spinning rates were chosen between 3 kHz and 4 kHz.

Infrared (IR) spectra were recorded on a Digilab FTS 20E FTIR spectrophotometer using the absorbance mode. For Nafion and Nafion-supported complexes, attenuated total reflectance (ATR) spectra of the film were obtained in the mid-IR range (4000–500 cm^{-1}) and transmission spectra were obtained in the far-IR range (500–140 cm^{-1}).

UV–visible spectra were recorded on a Shimadzu UV-160 spectrophotometer, set at a scanning speed of 2400 nm min^{-1}, with sampling intervals of 1 nm and a slit width of 3 nm. Quartz cells were used.

The chromatograms of samples taken during catalytic testing were recorded on an HP 5890 gas chromatograph (GC) using an SGE 50 QC3/BP1 2.0P column or using a 0.2% Carbowax 1500 on 60/80 Carbopak C (Supelco Inc.) packed column. The GC was connected to an ASI personal computer equipped with a DAPA softwear system, which allows for manipulations such as integration, peak selection, peak labelling and GC paremeter control. A WW–CPA80 printer was asttached to the computer for hard-copy print-out.

Gas chromatography–mass spectroscopy (GC MS) work was performed on an HP 5890 GC coupled to a 5970 Mass Selective Detector. The column was an HP5 25m column.

The composite Nafion membranes were prepared by spreading 1 ml of Nafion solution [20% (w/w) 1100 EW in butanol; Du Pont] onto an ethanol-wetted Goretex membrane (40 mm × 40 mm, 0.45 μm pore size; W. R. Gore & Assoc.) and the solvent evaporated to form a skin of ion-exchange polymer. Nafion could be deposited on one or both sides of the Goretex, so single- or dual-sided catalytic membranes could be manufactured to suit particular applications.

The acid form of Nafion (Nafion–H) was converted to the sodium form (Nafion–Na), by stirring in 5M sodium hydroxide solution overnight. This was then washed with distilled water and the above process repeated. After a final thorough washing in distilled water it was dried under vacuum ($\sim 10^{-2}$ mm Hg) at 60–80 °C overnight.

The acid form of Nafion was regenerated from Nafion on which a metal ion or metal complex was supported by refluxing in concentrated HNO_3 for 1 h on three separate occasions or until the Nafion had become clear. It was then thoroughly washed with distilled water and dried under vacuum (~10^{-2} mm Hg) at 60–80 °C overnight.

Preparation of complexes

Solutions of $Pd(NH_3)_4Cl_2$ were prepared by dissolving palladium(II) chloride (Merck) in the minimum amount of 25% aqueous ammonia, then diluting to the appropriate concentration with water. $Pt(NH_3)_4Cl_2$ was prepared according to Ref. 10.

Complex **I** was prepared by the method of Vinal and Reynolds.[11]

Preparation of supported species

Platinum or palladium was ion-exchanged into the Nafion of the composite membrane, or Nafion sheet (117; Aldrich Chemicals) as the tetrammine complex. Reduction to the metal was accomplished by soaking overnight in an aqueous solution of sodium borohydride (BDH; AnalR grade), either in slight stoichiometric excess or in large (200-fold molar) excess. Soaking the membrane in water under hydrogen (20 atm, 80 °C for 3 h) was also used. Upon reduction the ion-exchange sites of the Nafion were freed, so to increase the catalyst loading more complex could be exchanged into the membrane and reduced. The amount of complex adsorbed by the Nafion was determined by measuring the UV absorbance of the fresh and depleted tetrammine solutions at 200 nm. 5% platinum on Triton Kaowool was supplied by BDH; 4% platinum on carbon was prepared according to Ref. 12.

An estimate of the platinum particle size for the catalyst membranes was made using UV spectroscopy (after Furlong *et al.*[9]) and with X-ray diffraction. Particles were generally within the range of 20–60 Å.

Initially, and after each experiment, the Nafion-supported platinum catalysts were cleaned by boiling them in concentrated nitric acid, then water, and drying them under vacuum (~10^{-2} mm Hg) at room temperature.

Nafion–Na- and Nafion–H-supported Ni[(sacac)(dppe)]Cl and Ni[(sacsac)(dppe)]BPh_4 complexes were prepared by the following general method. The complex was dissolved in dry oxygen-free acetone and aliquots were withdrawn and stirred with Nafion in dry, oxygen-free acetone and aliquots were withdrawn and stirred with Nafion in dry, oxygen-free nitrogen. The Nafion, which was originally colourless, took on the colour of the solution, while the solution faded in colour. The spend solution was then withdrawn and a further aliquot added. The Nafion was washed in acetone and dried under vacuum (~10^{-2} mm Hg) at 80–100 °C.

From UV–visible spectra of the solutions before and after treatment the amount of complex loaded onto the Nafion may be calculated by a difference method. Loadings of up to 10 % by weight of complex could be achieved.

Catalytic testing

Cyclohexene hydrogenation

Cyclohexene (Fluka AG; puriss p.a.) was hydrogenated neat or at 3.5 mol kg^{-1} methanol (BDH; AnalR grade) solutions, in a glass-lined stainless-steel autoclave, magnetically stirred and thermostated to ±0.5 °C.

Nafion–[Ni($CH_3C(S)CHC(S)CH_3$)dppe]Y/Et_2AlCl isomerization of 1-octene

1-Octene was purified by refluxing with sodium and freshly distilled before use. Chlorobenzene was dried over phosphorus pentoxide and freshly distilled when required.

A strip of Nafion–Na (80–100 mg) with a 10% loading by weight of Ni[(sacsac)(dppe)]Cl was dried under vacuum (~10^{-2} mm Hg) at 100 °C overnight in a 100 ml round-bottom schlenk vessel. The schlenk vessel was allowed to cool and then filled with nitrogen. Dry, deoxygenated chlorobenzene (50 ml) was added, and stirring commenced. 1-Octene (5 ml) was added and the solution heated to approximately 80 °C. After 2 h a sample was taken for analysis. When Et_2AlCl (0.15–0.2 ml) was added to the solution to activate the catalyst, no noticeable colour change occurred on the Nafion and the solution remained colourless. Aliquots were taken, deactivated with dilute aqueous hydrochloric acid and then analysed by GC to determine the degree of isomerization of 1-octene. After 2 h the solution was separated from the Nafion and the Nafion carefully washed with dry chlorobenzene. The solution was stirred and aliquots were taken and analysed as before. Fresh chlorobenzene (50 ml) and 1-octene (5 ml) were added to the Nafion strip and heated with stirring to 80 °C. After 2 h a sample was taken for analysis. Et_2AlCl (0.15–0.2 ml) was then added to the solution. Aliquots were taken and analysed as before.

The catalytic activity of the homogeneous system Ni[(sacsac)(dppe)]Cl/Et_2AlCl was investigated for comparison with the equivalent Nafion-supported system.

Ni[P(OEt)$_3$]$_4$/Nafion isomerisation of 1-octene
Ni[P(OEt)$_3$]$_4$ (0.05–0.1 g) was added to a 100 ml round-bottom schlenk vessel under nitrogen. Methanol (5 ml) which had been deoxygenated was added with stirring to dissolve the Ni[P(OEt)$_3$]$_4$. 1-Octene (5 ml) was added to the solution. This solution was then added to the acid form of Nafion (0.15–0.20 g) which had been dried at 60–80 °C under vacuum ($\sim 10^{-2}$ mm Hg) for 2 h. The Nafion strip quickly changed from being colourless to a light yellow colour. After $\frac{1}{2}$ h the Nafion strips had become an orange colour and remained this colour after 2 h. The solution initially remained colourless, after $\frac{1}{2}$ h it had become a light yellow colour and after 2 h the solution was a light orange colour. Aliquots were taken from the reaction mixture, and analysed by GC.

The catalytic activity of the homogeneous system Ni[P(OEt)$_3$]$_4$/H_2SO_4 was investigated for comparison with the Nafion-supported system.

RESULTS AND DISCUSSION

Supported metal-particle catalysts

Cyclohexene hydrogenation rates, expressed as turnover frequencies (TOFs; moles of substrate converted per mole of catalyst per second) are given in Table 1. Since these results are based on the total amount of metal present and not the number of active sites, they probably underestimate the true TOFs. At hydrogen pressures above ~1.0 MPa there is a linear drop in hydrogen pressure over the course of the experiments (up to 100 h), thus indicating a constant hydrogenation rate and implying that there was no catalyst poisoning. The membrane catalyst rates compare very favourably with those of the more traditional catalysts. As this was a comparative

Table 1 Rates of hydrogenation of cyclohexene (~20 °C, 1.0 MPa hydrogen)

	Turnover frequency[b] (s^{-1})	
Catalyst[a]	Neat	3.5 mol kg^{-1} in methanol
5% Pt on Triton Kaowool	0.0024	0.011
4% Pt on carbon	0	0.10
1% Pt on composite[c]	0.045	0.14
0.9% Pt on Nafion 117[c]	0.0048	0.073
0.8% Pt on Nafion 117[d]	—	0.077
0.4% Pt on Nafion 117[e]	—	0.15
0.9% Pt on Nafion 117[c]	—	0.17
1.3% Pt on Nafion 117[c]	—	0.071
1.8% Pt on Nafion 117[e]	—	0.069
0.6% Pd on composite[c]	0.051	0.13

[a]Catalyst concentration is % wt/wt. [b]Based on 100% catalyst dispersion. [c]Reduced with a slight excess of borohydride. [d]Reduced with hydrogen. [e]Reduced with a large excess of borohydride.

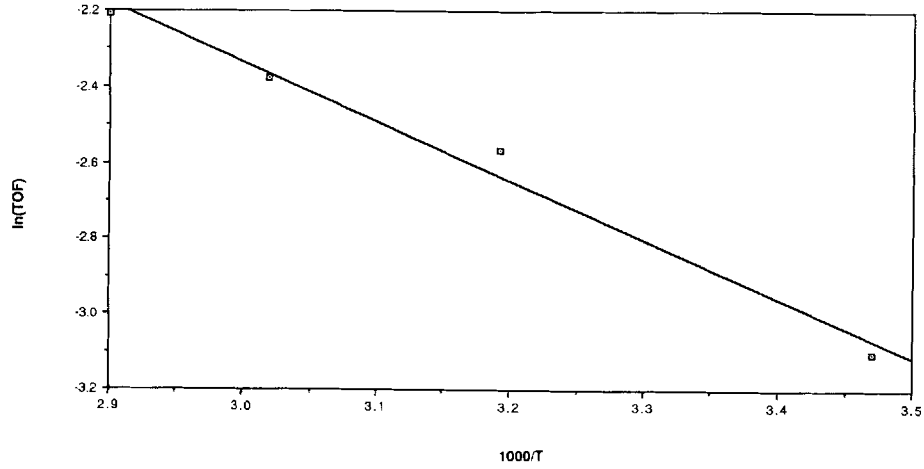


Figure 1 Variation of hydrogenation rate of neat cyclohexene with temperature (1% Pt on composite, 1 MPa H_2).

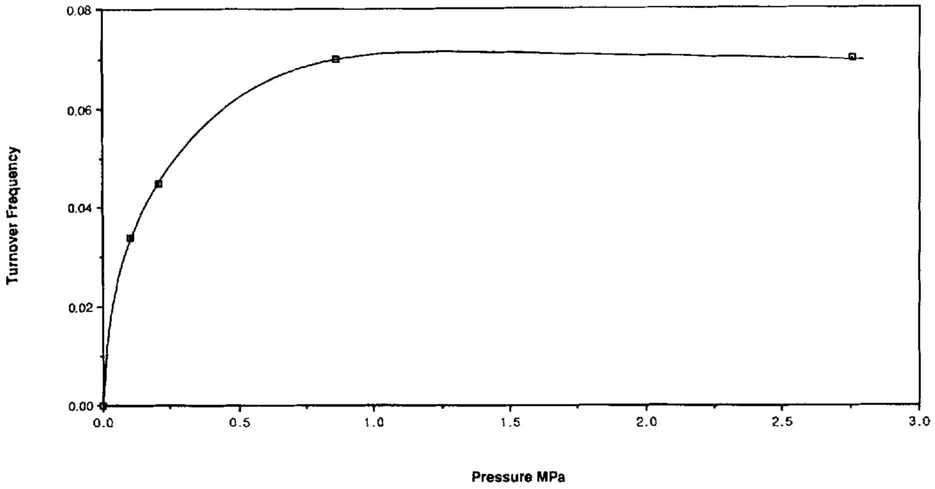


Figure 2 Variation of hydrogenation rate of 3.5 mol kg^{-1} cyclohexene in methanol with hydrogen pressure (1.8% Pt on Nafion 117 at 20 °C).

study, little attempt was made to optimize the reaction conditions.

Hydrogenations were carried out which demonstrated turnover numbers (mol cyclohexene reduced/mol platinum or palladium) in excess of 6000, and total conversions of cyclohexene to cyclohexane were achieved.

The higher rates observed for the composite membranes compared with the neat Nafion prepared under similar conditions support the contention that the thinner Nafion layer allows greater access to the catalytic surface.

Poisoning occurred if the used, wet catalysts were exposed to air. However, platinum catalysts were easily regenerated by using the cleaning method outlined in the Experimental section. Hydrogenation rates quoted here refer to catalysts which had been regenerated on several occasions. No loss in activity was observed after regeneration.

For the Nafion 117, the method of metal-ion reduction used gave membranes with different activities and appearances. Those reduced with near-stoichiometric amounts of borohydride or hydrogen were brown and gave similar hydrogenation rates. The metal formed by a large excess of borohydride, which corresponded to a more rapid reduction, gave a membrane which had a metallic sheen, displayed surface electrical conductivity and produced a higher hydrogenation rate. With the metal-ion reduction occurring more quickly we woud expect less penetration of the reductant into the Nafion, giving more catalytic particles near the surface of the membrane. These particles would be more accessible for reaction. By varying the method of reduction it appears the platinum particle diameter may be controlled. However, further studies are required to verify this aspect.

The temperature dependence of the rate of hydrogenation of neat cyclohexene using a 1 % platinum composite membrane is given in Fig. 1. Arrhenius behaviour is displayed with an activation energy of 13 kJ mol^{-1}; this can be compared with 23.8 kJ mol^{-1} for the hydrogenation of cyclohexene in cyclohexane on Pt/Al_2O_3 from Hussey *et al.*[13] and 27.9 kJ mol^{-1} for the hydrogenation of neat cyclohexene on Pt/SiO_2 from Boudart and co-workers.[14]

Figure 2 gives the pressure dependence for 1.8 % platinum on Nafion 117 at 20 °C. The rate becomes pressure-independent about ~0.8 MPa; presumably diffusion of one or more of the reactants and products within the Nafion, or the surface reaction of the catalyst, is rate-limiting in this region.

Supported metal-complex catalysts

The Ni(sacsac)(dppe)–Nafion was readily prepared as described and was conveniently characterized by UV–visible and solid-state ^{31}P NMR. Spectra are shown in Figs 3 and 4. By comparison with spectra of the known [Ni(sacsac)(dppe)]Y complexes, the supported species were confirmed, with the exception of the species produced from the interaction of Nafion–H with

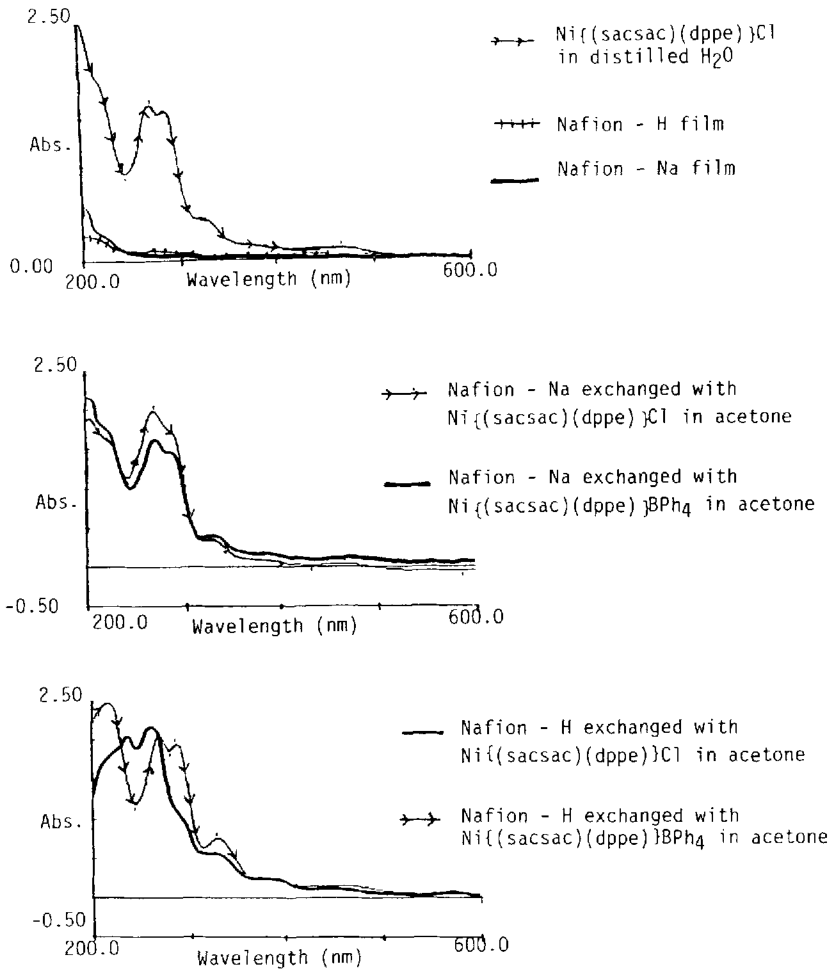


Figure 3 UV–visible spectra.

[Ni(sacsac)(dppe)]Cl. The UV–visible spectrum of this product shows distinct differences when compared with the spectra of all other species. There is an apparent change from the normal square-planar structure displayed by the other compounds. The reason for this is unclear. It may be that the Cl^- produced as a by-product from this process is able to approach the nickel centre leading to structure distortion. However, further study is required to understand the observed spectra. FTIR was less valuable in characterizing structures of the complexes. Although the main peaks assigned to the complex were present, spurious peaks due to solvent and small amounts of decomposition products were also present.

The marked, characteristic colour changes observed on formation of the Ni(sacsac)(dppe)–Nafion and HNi[P(OEt)]$_x$–Nafion species provide further evidence of their formation. Due to the instability of the HNi[P(OEt)$_3$]$_x$ species, spectroscopic evidence for its formation in Nafion has not been obtained. However, studies are continuing.

Catalytic activity of the supported metal-complex catalysts was low under the conditions described. This could well be a diffusion problem, as discussed for the metal-particle catalysts, which may be overcome by using composite on Goretex or some other support. Results for catalytic testing of the Ni[P(OEt)$_3$]$_x$–Nafion system are shown in Fig. 5. The equivalent homogeneous system is shown for comparison. What little activity was evident for the [Ni(sacsac)(dppe)]–Nafion may well have been due to material leached from the Nafion support.

Initial activity for the Ni[P(OEt)$_3$]$_x$–Nafion system was quite high and comparable with that

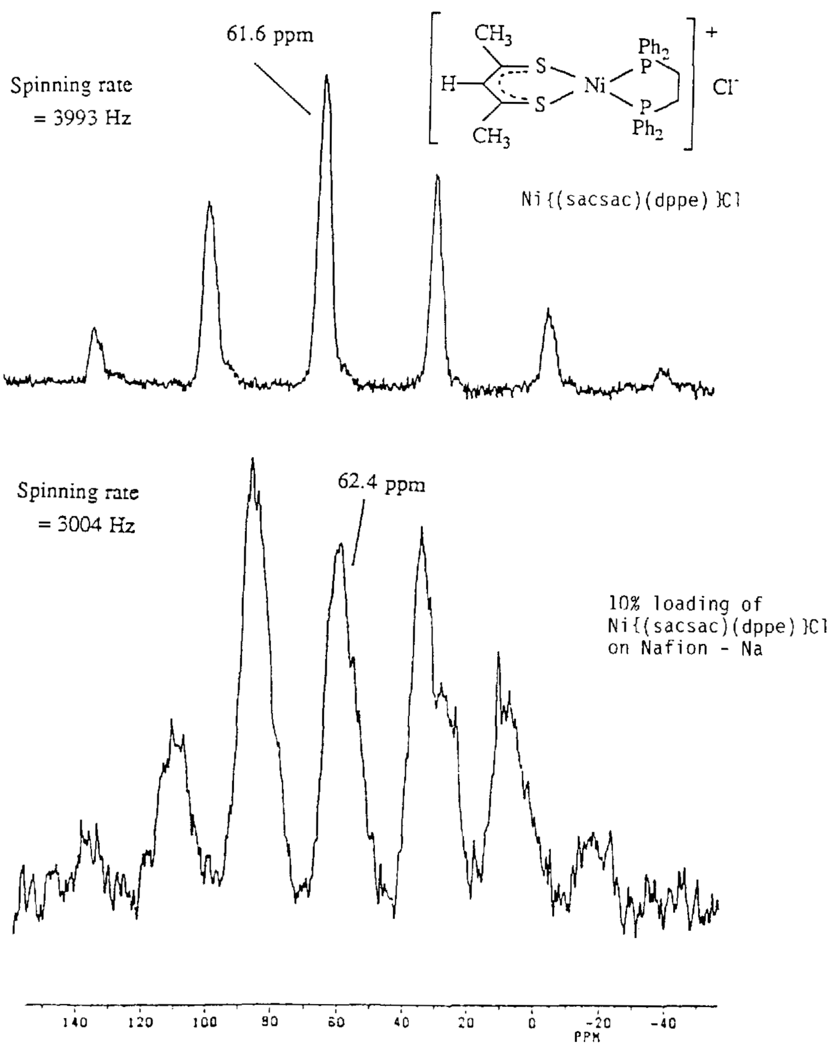


Figure 4 ^{31}P solid-state NMR spectra.

of the homogeneous system. However, activity decreased rapidly and had ceased altogether after about 30 min. Concomitant with cessation in activity there were marked colour changes in the Nafion strip (which turned orange and then green) and the solution (which went from colourless to pale yellow).

Based on the observed colour changes and on the catalytic behaviour of the $HNi[P(OEt)_3]$–Nafion, circumstantial evidence is provided for the proposed reaction sequence[9] for catalyst formation and deactivation given in Scheme 1.

$H^+ + Ni[P(OEt)_3]_4 \rightleftharpoons HNi[P(OEt)_3]_4^+$ [1]

$HNi[P(OEt)_3]_4^+ \rightleftharpoons HNi[P(OEt)_3]_3^+ + P(OEt)_3$ [2]

$H^+ + HNi[P(OEt)_3]_3^+ \rightarrow H_2 + Ni(II) + 3P(OEt)_3$ [3]

$P(OEt)_3 \xrightarrow{H^+} HPO(OEt)_2$ [4]

Scheme 1

It appears likely that the Nafion–H has activated the $Ni[P(OEt)_3]_4$ to give a cationic species which is in turn held within the Nafion structure

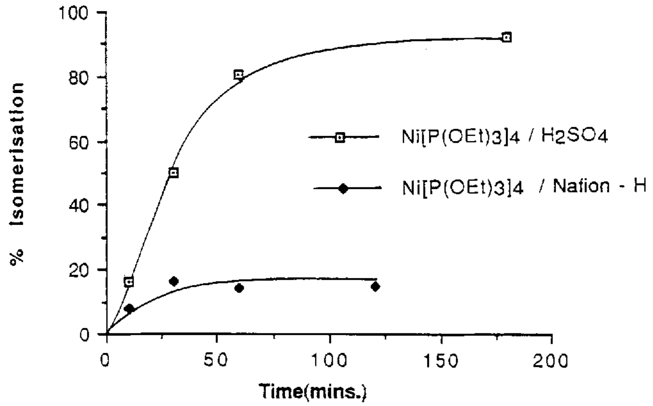


Figure 5 Percentage isomerization of 1-octene at ambient temperature.

according to Eqn [5].

$$\begin{array}{ll} \mathrm{Ni[P(OEt)_3]_4 + Nafion{-}H} & \\ \quad \rightarrow \mathrm{HNi[P(OEt_3]_4^+\ Nafion^-} & [5] \\ \qquad \upharpoonleft\downharpoonright & \\ \quad \mathrm{HNi[P(OE\ \ t)_3]_3^+ Nafion^- + P(OEt)_3} & \end{array}$$

Active species

Decomposition of the active species by excess acid as described in Eqns [3] and [4] would explain the rapid decomposition observed for the entrapped complex. Mobile H^+ within the inverse micelles of Nafion would readily interact with entrapped catalyst.

CONCLUSIONS

Platinum and palladium have been incorporated into Nafion 117 sheet and porous PTFE/Nafion composite membranes giving metallic particles as small as a few nanometres in diameter.

In the hydrogenation of cyclohexene the catalytic membranes give rates comparable to commercially available catalysts, having demonstrated turnover numbers in excess of 6000. No poisoning is apparent during operation, and catalysts may be successfully regenerated.

The reduction rate approaches a limit at high pressures of hydrogen and has an activation energy of 13 kJ mol^{-1} in neat cyclohexene.

These types of supported metal-particle catalysts show great potential in applications where a well-dispersed, totally immobilised and durable catalyst is needed, such as in flow reactors, and where the separation properties of the membranes can be utilized.

To date the Nafion-supported metal-complex catalysts have been less successfully applied. However, this work and that of Chang[7] have demonstrated that active systems may be developed by interacting Nafion with cationic complexes, or more interestingly, by using the strong acid character of Nafion–H to generate the catalyst, which if cationic may be supported by the Nafion. The opportunity to isolate or stabilize charged intermediates in catalytic processses for spectroscopic investigation is also presented.

Diffusion limitations may be overcome by operating at increased pressure if gaseous feeds are employed or by employing solvents which will swell the Nafion where possible.

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REFERENCES

1. Gierke, T D and Hsu W Y The cluster-network model of ion clustering in perfluorosulfonated membranes. In: *Perfluorinated Ionomer Membranes*, Eisenberg, A and Yeager, H L (eds). American Chemical Society, ACS Symp. Ser. No 180, Washington DC, 1982, pp 283–307
2. Waller, F J *Catal. Rev.–Sci. Eng.*, 1986, 28: 1
3. Waller, F J and Scoyoc, R W *Chemtech*, July 1987, 438
4. Olah, G A, Pradeep, S I and Prakash, G K S *Synthesis*, July 1986, 513

5. Mau, A W-H, Huang, C-B, Kakuta N, Bard, A J, Campion, A, Fox, M A, White, J M and Weber, S E *J. Am. Chem. Soc.*, 1984, 106: 6537
6. Mattera, V D, Barnes, D M, Choudhuric, S N, Risen, W M and Gonzalez, R D *J. Phys. Chem.*, 1986, 90: 4819
7. Chang, B-H *Inorg. Chim. Acta*, 1988, 150: 245
8. Cavell, K J and Masters, A F *Aust. J. Chem.*, 1986 39: 1129
9. Furlong, D N, Launikonis, A and Sasse, W H F *J. Chem. Soc., Faraday Trans. 1*, 1984, 80: 571
10. Keller, R N Tetrammineplatinum(II) Chloride. In: *Inorganic Synthesis*, vol 2, Fernelius, W C (ed), McGraw Hill, New York, 1946, p 250
11. Vinal, R S and Reynolds, L T *Inorg. Chem.*, 1964, 3: 1062
12. Augustine, R L *Catalytic Hydrogenation: Techniques and Applications in Organic Synthesis*, Marcel Dekker Inc, New York, 1965, p 151
13. Hussey, A S, Keulks, G W, Nowack, G P and Baker, R H *J Org. Chem.*, 1968, 33: 610
14. Madon, R J, O'Connell, J P and Boudart, M J *AIChE J.*, 1978, 24: 904