A Unique Application of Acid-Nafion as a Co-catalyst and Support

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The perfluorinated ion-exchange polymer, Nafion-H^+, has been used as a Brönsted acid to activate $[Ni\{P(OEt)_3\}_4]$ and as a support for the resulting cationic species. Spectroscopic evidence has confirmed that the species present within the Nafion-H^+ film are the same as those found in a homogeneous solution using H_2SO_4 as the Brönsted acid. Activity for oct-1-ene isomerization in the first 30 min was approximately one third of the activity obtained in homogeneous solution using H_2SO_4 as co-catalyst with a similar $[Ni\{P(OEt)_3\}_4]$: H^+ ratio, and the activity varied linearly with the amount of Nafion-H^+ present. Comparative tests with but-1-ene employing homogeneous and supported catalyst systems have demonstrated a significant increase in isomerization rate on changing from oct-1-ene to but-1-ene when using the supported catalyst. This indicates that diffusion of oct-1-ene into, and/or products out of, Nafion-H^+ are controlling factors. Diffusion coefficients of oct-1-ene and but-1-ene in Nafion have been determined and support this conclusion. It has also been demonstrated that very little, if any, of the catalyst species is leached from the Nafion support during catalysis.

In the past the most frequently used materials for supporting metal-complex catalysts have generally been hydroxylated inorganic materials and various polystyrenes.[1] More recently the perfluorinated ion-exchange polymer, Nafion, has been considered as a support.[2]

Nafion is an ionomer with a chemically resistant polymeric backbone similar to Teflon. It phase separates into hydrophobic and hydrophilic regions.[3] These latter ionic domains or clusters are inverted micelles surrounded by a fluorocarbon matrix, they are typically 40 Å in diameter, and are interconnected by hydrophilic channels of about 10 Å in diameter.[4]

The use of Nafion-H^+ (Nafion polymer with H^+ as counter ion) as a solid acid catalyst has been extensively covered.[5] However, more recently it has been realized that the exchange, or partial exchange, of acidic protons for transition-metal ions or complexes might offer even greater opportunities in catalysis. To date only a few examples of cation-exchanged perfluorinated ion-exchange polymer catalysts have been reported;[2] only three of these reports have involved a metal–organic complex.[6–8]

The H_2SO_4–$[Ni\{P(OEt)_3\}_4]$ catalyst system for olefin double-bond shift isomerization was first reported by Cramer and Lindsey.[9] Tolman[10] later undertook comprehensive studies of the olefin isomerization mechanism and kinetics and postulated steps (1)–(4) for the formation and decomposition

$$H^+ + [Ni\{P(OEt)_3\}_4] \overset{K_1}{\rightleftharpoons} [HNi\{P(OEt)_3\}_4]^+ \quad \text{rapid, reversible} \quad (1)$$

$$[HNi\{P(OEt)_3\}_4]^+ \overset{K}{\rightleftharpoons} [HNi\{P(OEt)_3\}_3]^+ + P(OEt)_3 \quad (2)$$

$$H^+ + [HNi\{P(OEt)_3\}_3]^+ \longrightarrow H_2 + Ni^{II} + 3P(OEt)_3 \quad \text{irreversible} \quad (3)$$

$$P(OEt)_3 \longrightarrow HPO(OEt)_2 \quad \text{irreversible} \quad (4)$$

of the proposed active species, $[HNi\{P(OEt)_3\}_3]^+$. The mechanism consists of rapid protonation of $[Ni\{P(OEt)_3\}_4]$ to form $[HNi\{P(OEt)_3\}_4]^+$ followed by slow ligand dissociation to give the active species $[HNi\{P(OEt)_3\}_3]^+$. Decomposition of the active species is thought to occur in the presence of excess acid resulting in the formation of nickel(II) salts and hydrogen. The studies were based on UV/VIS spectroscopy, which showed an initial peak at 238 nm, assigned to $[Ni\{P(OEt)_3\}_4]$, and the formation of a shoulder at 325 nm on addition of acid which was assigned to $[HNi\{P(OEt)_3\}_4]^+$. By undertaking UV/VIS studies at various concentrations of acid, $[Ni\{P(OEt_3\}_4]$ and $P(OEt)_3$ Tolman arrived at the mechanism shown above.

The purpose of the present work was to demonstrate the concomitant use of Nafion-H^+ membrane as an acid co-catalyst and also as a support for the activated cationic catalyst species. The formation of the active species in Nafion-H^+ can be described by equations (5) and (6). Preliminary work[8] showed

$$\text{Nafion-}H^+ + [Ni\{P(OEt)_3\}_4] \overset{K_1'}{\rightleftharpoons} \text{Nafion-}[HNi\{P(OEt)_3\}_4]^+ \quad (5)$$

$$\text{Nafion-}[HNi\{P(OEt)_3\}_4]^+ \rightleftharpoons \text{Nafion-}[HNi\{P(OEt)_3\}_3]^+ + P(OEt)_3 \quad (6)$$

that it was possible to activate the $[Ni\{P(OEt)_3\}_4]$ complex with Nafion-H^+ and isomerize oct-1-ene. In this paper we have demonstrated the nature of this catalyst system and extended our studies to include the isomerization of the smallest isomerizable terminal olefin but-1-ene. Spectroscopic studies have successfully identified the supported species.

Experimental

The complex $[Ni\{P(OEt)_3\}_4]$ was prepared according to the method of Vinal and Reynolds.[11] Oct-1-ene was purchased from Aldrich Chemicals and but-1-ene was obtained from Matheson Gases. Nafion 117, of equivalent weight 1100 and thickness 180 μm, was obtained from Du Pont and Nemours in the acid form and was cleaned prior to use in 5 mol dm^{-3} HNO_3, washed in boiling deionized water and dried *in vacuo* (0.1 mmHg, ≈ 13.3 Pa) at room temperature. All other solvents and chemicals used were of reagent grade and were not purified

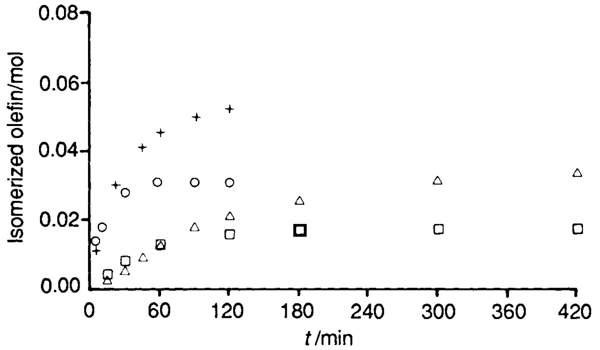

Fig. 1 Isomerization of oct-1-ene using the homogeneous and supported systems, $[Ni\{P(OEt)_3\}_4]:H^+ = 1:2$; homogeneous (○) 0.032, (+) 0.064 mol of oct-1-ene; supported (□) 0.032, (△) 0.064 mol of oct-1-ene

further. Manipulations involving $[Ni\{P(OEt)_3\}_4]$ were carried out under nitrogen using standard Schlenk techniques.

Determination of Equivalent Weight and Partial Neutralization of Nafion-H^+.—Determination of the equivalent weight of Nafion-H^+ was undertaken by titrating the acid ion-exchanged from 0.3 g of Nafion-H^+ against 0.01 mol dm^{-3} NaOH. The acid was ion-exchanged with Na^+ using a concentrated NaCl solution.

Partially neutralized Nafion-H^+ was obtained by selectively ion-exchanging about 50% of the acid from 0.9 g of Nafion-H^+ with Na^+ using cation-exchange selectivity data previously reported by Steck and Yeager.[12] The Nafion-H^+ was placed in a 0.01 mol dm^{-3} ionic strength solution containing 68 mmol of NaCl for 24 h. The liberated acid was titrated against 0.01 mol dm^{-3} NaOH and the degree of neutralization calculated from the equivalent weight.

*Diffusion Rates of Oct-*1*-ene and But-*1*-ene in* Nafion-H^+.—The diffusion coefficients of oct-1-ene and but-1-ene in Nafion-H^+ were measured using a cell consisting of two magnetically stirred compartments, separated by a Nafion 117 membrane. A mixture of but-1-ene or oct-1-ene, an internal standard, and methanol was placed in one compartment and methanol plus the internal standard in the other compartment. Acetone was the internal standard in the case of but-1-ene and cyclohexane in the oct-1-ene experiment. Both compartments were sealed with rubber septa to prevent vapour escaping. The pure methanol compartment was sampled at intervals by a syringe inserted through the septum and the samples analysed by gas chromatography (GC), isothermally at 225 °C using a 2 m Tenex column.

*Oct-*1*-ene Isomerization.*—In both the homogeneous and supported catalyst cases solutions [0.032 (5 cm^3) or 0.064 mol (10 cm^3)] of oct-1-ene in methanol (5 cm^3) were used. About 0.05 g (7×10^{-5} mol) of $[Ni\{P(OEt)_3\}_4]$ was added and activated with either 0.013 g (13×10^{-5} mol) of H_2SO_4 or 0.038–0.15 g ($3.2–12.5 \times 10^{-5}$ mol) of Nafion-H^+. Isomerization was carried out at room temperature and samples were analysed using GC.

*But-*1*-ene Isomerization.*—Isomerization of but-1-ene was undertaken at 22 °C in a Fisher–Porter tube fitted with a GC septum to allow sampling. Solutions of but-1-ene (5 g, 0.090 mol) in methanol (5 cm^3) containing *ca.* 0.05 g (7×10^{-5} mol) of $[Ni\{P(OEt)_3\}_4]$ were used. Activation was undertaken with either 0.013 g (13×10^{-5} mol) of H_2SO_4 or 0.15 g (12.5×10^{-5} mol) of Nafion-H^+ for the homogeneous and supported reactions respectively. Samples were periodically taken from the solution for GC analysis to follow the isomerization, and were immediately diluted with cold methanol to avoid loss of butenes.

Gas Chromatographic Analysis of Isomerization Solutions.—Gas chromatographic analyses were undertaken using a HP 5890 instrument fitted with a SGE 50 QC3/BP1-2.0 column and using N_2 as carrier gas. Separation of C_8 isomers was achieved by temperature programming between 35 and 140 °C. The Kovats retention indices for the C_8 isomers were determined at 110 °C and peaks assigned according to the assignments by Rang *et al.*[13] Analysis of C_4 isomers was carried out isothermally at 35 °C and isomer peaks assigned by injecting the individual C_4 isomers.

Characterization of Species supported in Nafion-H^+.—The UV/VIS spectra were obtained using a Varian DMS 100 spectrometer with 1 mm pathlength silica cells for solutions and a specially made cell with Supracil windows for analysing the Nafion-H^+ supported complex.

Results and Discussion

Equivalent Weight and Partial Neutralization of Nafion-H^+.—The equivalent weight determined for the Nafion-H^+ analysed was approximately 1100 and the subsequent partial neutralization yielded Nafion-H^+/Na^+ with about 50% H^+ and 50% Na^+ counter ions.

*Diffusion Coefficients of Oct-*1*-ene and But-*1*-ene in* Nafion-H^+.—Measurement of the diffusing olefin concentration with time enabled the determination of diffusion coefficients by applying an integrated form of Fick's first law.[14] Diffusion coefficients of 5.8×10^{-7} and 6.9×10^{-6} cm^2 s^{-1} for oct-1-ene and but-1-ene respectively through Nafion-H^+ were obtained.

*Oct-*1*-ene Isomerization.*—Homogeneous isomerization of oct-1-ene using $[Ni\{P(OEt)_3\}_4]$–H_2SO_4 in a 1:2 molar ratio was undertaken as a control experiment. The $[Ni\{P(OEt)_3\}_4]$ complex in the presence of oct-1-ene and H_2SO_4 immediately formed a yellow-orange solution but over a period of several hours the solution changed to green. Activation of $[Ni\{P(OEt)_3\}_4]$ was also achieved using Nafion-H^+ in the molar ratios $[Ni\{P(OEt)_3\}_4]:H^+$ of 2:1, 1:1 and 1:2, and also using 50% neutralized Nafion-H^+ with a $[Ni\{P(OEt)_3\}_4]:H^+$ ratio of 1:1. On addition of $[Ni\{P(OEt)_3\}_4]$ to a solution containing pieces of Nafion-H^+, methanol and oct-1-ene, the Nafion-H^+ changed colour over a period of several minutes from clear to yellow-orange. Over several hours the Nafion changed colour to emerald green whilst the supernatant solution remained colourless during the entire experiment.

The rate of oct-1-ene isomerization is shown in Fig. 1 for homogeneous and supported isomerization tests using 0.032 and 0.064 mol of oct-1-ene. The homogeneous systems displayed high activity for about 30 min after which the rate decreased to approximately zero as the octene isomer equilibrium was approached. By increasing the amount of oct-1-ene present to 0.064 mol the isomerization activity was maintained for a longer period of time. The supported systems displayed constant activity for about 120 min and then the rate decreased significantly. The initial activity was approximately one third that for the homogeneous systems. For the supported systems the percentage of oct-1-ene that had isomerized after 120 min was only half that in the homogeneous cases.

The isomerization of solutions containing 0.032 mol of oct-1-ene with various amounts of Nafion-H^+ and Nafion-H^+/Na^+ is shown in Fig. 2. The supported systems displayed varying periods of near linear activity with the actual activities over these periods directly proportional to the amount of Nafion-H^+ present. The system using partially neutralized Nafion-H^+/Na^+ as co-catalyst and support displayed higher isomerization activity than the system using Nafion-H^+ with the same $[Ni\{P(OEt)_3\}_4]:H^+$ ratio, possibly indicating that the catalytic species were more accessible or that there was a lower excess acid concentration within the Nafion.

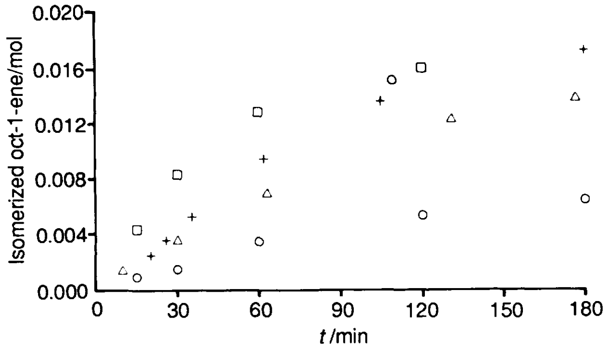

Fig. 2 Isomerization of oct-1-ene using the supported system, 0.032 mol of oct-1-ene; $[Ni\{P(OEt)_3\}_4]:H^+$ = (□) 1:2, (△) 1:1, (○) 2:1; $[Ni\{P(OEt)_3\}_4]$:50% neutralized Nafion-H^+/Na^+ = (+) 1:1

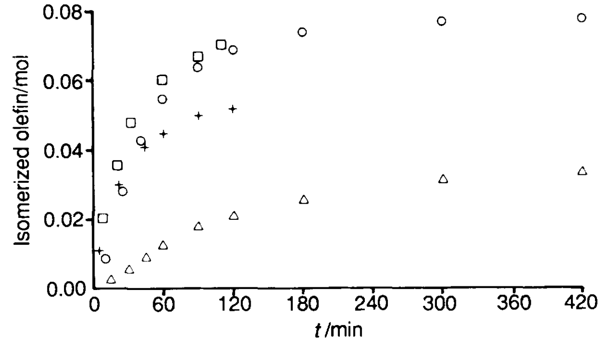

Fig. 3 Isomerization of but-1-ene and oct-1-ene using the homogeneous and supported systems, $[Ni\{P(OEt)_3\}_4]:H^+$ = 1:2; homogeneous (□) 0.09 mol of but-1-ene, (+) 0.064 mol of oct-1-ene; supported (○) 0.09 mol of but-1-ene, (△) 0.064 mol of oct-1-ene

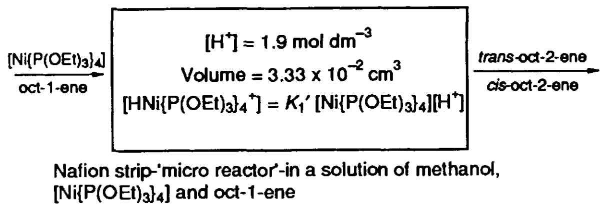

Fig. 4 Model of the Nafion supported catalyst system

The C_8 isomers produced were predominantly *trans*-oct-2-ene and *cis*-oct-2-ene in the ratio of 4:1 and 3.2:1 in the homogeneous and supported cases respectively. This can be compared with the *trans*-oct-2-ene to *cis*-oct-2-ene ratio of approximately 5.5:1 for an equilibrium distribution.[15]

But-1-ene Isomerization.—Homogeneous isomerization of but-1-ene using $[Ni\{P(OEt)_3\}_4]$–H_2SO_4 was again undertaken as a control experiment. Addition of $[Ni\{P(OEt)_3\}_4]$ to a solution of H_2SO_4 and but-1-ene resulted in the immediate formation of a yellow-green solution and a decrease in butene vapour pressure due to the lower vapour pressures of the but-2-enes compared to but-1-ene. Under the reaction conditions of 22 °C and but-1-ene vapour pressure of 170 kPa approximately 88% of the but-1-ene was in the liquid phase at the beginning of the reaction.* This proportion would have slowly increased as but-1-ene was isomerized. Thus the total isomerization rate was approximated to the rate of isomerization of but-1-ene in the liquid phase. But-1-ene isomerization was also achieved using Nafion-H^+ as co-catalyst and support with a $[Ni\{P(OEt)_3\}_4]:H^+$ ratio of 1:2. The Nafion took on a yellow-green colour over a period of 5–10 min and the vapour pressure decreased gradually.

Fig. 3 shows a comparison of the homogeneous and supported isomerization rates for solutions containing 0.09 mol of but-1-ene and 0.064 mol of oct-1-ene. The Figure shows that the supported system had a rate equal to that of the homogeneous system for isomerization of but-1-ene. The improvement in isomerization rate for the supported system on changing from oct-1-ene to but-1-ene indicates that diffusion of octenes through the Nafion-H^+ polymer may be a limiting step. This is also supported by the fact that a catalytic test carried out over 20 h using a supported system resulted in 95% isomerization of 0.032 mol of oct-1-ene. Determination of the diffusion coefficients of oct-1-ene and but-1-ene in Nafion-H^+ has shown that but-1-ene diffuses through Nafion-H^+ more readily than oct-1-ene, and it could reasonably be expected that C_4 products would diffuse out more readily than C_8 products.

The C_4 product distribution was the same for both the homogeneous and supported systems with the ratio of *trans*-but-2-ene to *cis*-but-2-ene being 2.3:1. This can be compared with an equilibrium distribution of *trans*-but-2-ene to *cis*-but-2-ene of approximately 3:1.[15]

Tolman[10b] has reported that 'complete mathematical analysis is quite complex, particularly so because of the acid-catalysed ligand decomposition reaction'. The supported systems considered here involve additional complications in that the local environment in the Nafion-H^+ contained an acid concentration about one hundred times† that of the homogeneous solution, and diffusion of $[Ni\{P(OEt)_3\}_4]$ and oct-1-ene into, and octene isomers out of, the Nafion-H^+ may have affected the isomerization rates. Whereas in the homogeneous system all the $[Ni\{P(OEt)_3\}_4]$ in solution had the potential to be protonated, in the supported system only those molecules within the Nafion-H^+ could be protonated. However, a model for the supported system can be proposed whereby the Nafion strip is considered as a micro-reactor, Fig. 4.

It would be expected that the Nafion-H^+ contained high, localized concentrations of $[HNi\{P(OEt)_3\}_4]^+$, which would be dependent on the concentrations of $[Ni\{P(OEt)_3\}_4]$ and H^+ in the Nafion, and on the equilibrium constant K_1' in Nafion-H^+. However, it is likely that the homogeneous solution contained a greater number of activated species at any one time. In the supported system the isomerization rate is dependent on the diffusion of $[Ni\{P(OEt)_3\}_4]$ and oct-1-ene into the Nafion-H^+, and the diffusion of octenes out of the Nafion-H^+, as well as the number of active species, and hence the lower isomerization rate.

The lifetime of the active species in the Nafion-H^+ would depend on the effect of the acid concentration on the decomposition reactions shown in equations (3) and (4), and it is most likely that the total number of catalyst turn-overs would be less than in the homogeneous system due to the high, localized acid concentration.

Spectroscopic Characterization of the Species present in Nafion.—Evidence to confirm that the catalytic species was in fact supported in the Nafion-H^+ was obtained by undertaking a UV/VIS spectroscopic study of Nafion-H^+ which had been treated with a solution of $[Ni\{P(OEt)_3\}_4]$ and oct-1-ene in methanol. Fig. 5 shows the spectra of $[Ni\{P(OEt)_3\}_4]$ in acidified methanol and in Nafion-H^+. Fig. 5(*a*) is consistent with the homogeneous solution spectra obtained by Tolman and shows a strong absorption below 300 nm and a peak at 323 nm. According to Tolman[10a] these absorptions are due to

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* At 22 °C and 170 kPa the densities of the but-1-ene liquid and vapour are 0.595 and 0.0066 g dm^{-3} respectively.[16] Thus for 5 g of but-1-ene in a total volume of 100 cm^3 there is 4.385 g (88%) in the liquid phase and 0.615 g (12%) in the vapour phase.

† The acid concentration in Nafion-H^+ was calculated by dividing the amount of acid in the Nafion by the volume of the strip of Nafion.

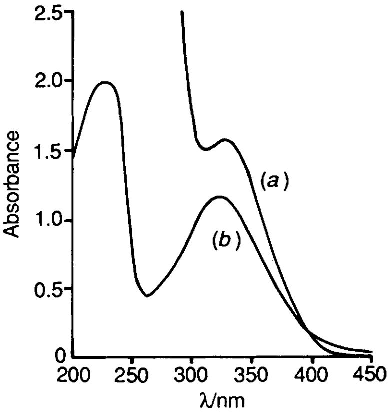

Fig. 5 UV/VIS spectra of $[Ni\{P(OEt)_3\}_4]$ and $[HNi\{P(OEt)_3\}_4]^+$ in: (*a*) methanol and H_2SO_4 and (*b*) supported in Nafion-H^+, *i.e.* no solution present

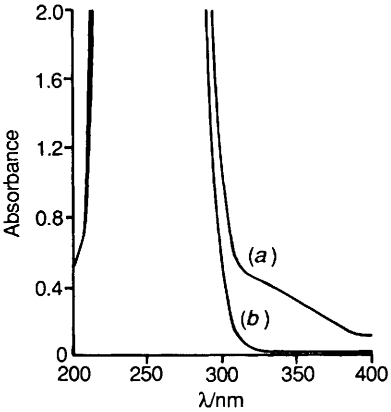

Fig. 6 The UV/VIS spectra of solutions during catalytic testing: (*a*) homogeneous system and (*b*) Nafion supported system

$[Ni\{P(OEt)_3\}_4]$ and $[HNi\{P(OEt)_3\}_4]^+$ with absorption coefficients of 2.5×10^4 and 2.0×10^3 dm^3 mol^{-1} cm^{-1} respectively. The spectrum in Fig. 5(*b*) was obtained by forming the Nafion-$[HNi\{P(OEt)_3\}_4]^+$ complex *in situ* in a cell under nitrogen followed by washing the strip of Nafion with methanol. Washing the Nafion with methanol removed most of the excess $[Ni\{P(OEt)_3\}_4]$ whilst leaving the ion-exchanged $[HNi\{P(OEt)_3\}_4]^+$. As the absorption coefficient of the neutral complex is 12.5 times greater than that of the cationic species it is apparent that very little neutral complex was present in the Nafion.

Testing for Complex Leaching.—Two approaches were used to assess the leaching of catalyst species from the Nafion-H^+. (*i*) Analysing the octene–methanol supernatant solution by UV/VIS spectroscopy during a catalytic run to confirm that the protonated $[HNi\{P(OEt)_3\}_4]^+$ species was not present in solution. Results can be seen in Fig. 6. (*ii*) Undertaking a catalytic run whereby the original octene–methanol solution was exchanged with fresh solution after 75 min. After a further 3 h both solutions were analysed by GC. Negligible change to the original solution was observed but significant isomerization of the fresh solution had occurred.

Conclusion

This work has demonstrated the concomitant use of Nafion-H^+ as a co-catalyst and as a support. The H^+ in the Nafion-H^+ activated $[Ni\{P(OEt)_3\}_4]$ to give the cationic species $[HNi\{P(OEt)_3\}_4]^+$ which was then supported within the Nafion-H^+ at anionic sites. This approach opens up the possibility of using Nafion and related polymers in this unique manner. In the early stages of this work some difficulties in obtaining reproducibility were experienced and it was apparent that when using Nafion-H^+ the washing and drying steps are particularly important. This has been previously noted by Grot.[17] In earlier work using pent-1-ene, Bingham *et al.*[18] have also noted poor reproducibility in homogeneous isomerization rates and they suggested that the reason was the presence of traces of oxygen. These results have shown that reaction rates and the period over which rates are linear are dependent on the amount of Nafion-H^+ used, *i.e.* dependent on the acid sites present. This can be explained if the Nafion-H^+ strips are considered as micro-reactors as shown in Fig. 4. By doubling the amount of Nafion-H^+ the $H^+:[Ni\{P(OEt)_3\}_4]$ ratio was doubled and the initial amount of Nafion–$[HNi\{P(OEt)_3\}_4]^+$ formed doubled, hence doubling the isomerization rate. However, the overall lifetime of the catalyst system halved since the amount of $[Ni\{P(OEt)_3\}_4]$ available remained constant.

Comparison of isomerization rates of oct-1-ene and but-1-ene using both the homogeneous and supported systems has shown that the supported system is limited by the diffusion of oct-1-ene into and/or products out of the Nafion-H^+. Diffusion measurements are consistent with this proposal. Determination of diffusion coefficients has revealed a factor of ten difference in diffusion rates for oct-1-ene and but-1-ene in Nafion-H^+. The slow diffusion of octenes can also be used to explain the lower percentage of oct-1-ene isomerized by the supported systems at the time at which the activity flattened out.

The use of partially neutralized Nafion-H^+/Na^+ to activate and support the catalytic species showed an increase in isomerization rate when compared to the supported system with a similar $[Ni\{P(OEt)_3\}_4]:H^+$ ratio, thus indicating that accessibility to the catalytic species and/or H^+ concentration were important in determining the isomerization rate. The catalytic behaviour of the system formed from the partially neutralized Nafion also provides evidence in favour of the proposal that the catalyst is deactivated by excess acid.[10]

Based on the UV/VIS assignments of Tolman[10] for the $[HNi\{P(OEt)_3\}_4]^+$ species, spectroscopic studies have confirmed the presence of the $[HNi\{P(OEt)_3\}_4]^+$ catalyst precursor in Nafion. The current studies provide strong evidence in support of the mechanistic proposals of Tolman; *i.e.* acid attack on the neutral nickel phosphite complex to give the cationic nickel hydride catalyst precursor.[10] The proposal that the active species is cationic is also supported by the observation that very little, if any, catalyst is leached from the Nafion during catalyst operation.

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