# 특별강연 Ⅳ

## The Application of Perfluorinated Cation-exchange Membrane in the Catalytic process

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## 촉매공정에서 양이온 교환 분리막의 응용

### 변흥식

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## 1. INTRODUCTION

Functionalized organic polymers have been used as supports for heterogenized homogeneous catalytic process[1]. Sprcific advantages of using these resins as support reagents have been reviewed[2-4]. These include:

- -ease of by-product separation from the main reaction product usually by simple filtration.
- -prevention of intermolecular reaction of reactive species or functional groups by simulating high dilution conditions[5].
- -utility of the "fish-hook" principle in which a minor component in fished out of a large excess substrate by the insoluble polymer[6].
- -the possibility of reusing recovered reagents as well as eliminating the use of volatile or noxious substances[7].

Catalysis by ion-exchange membranes is perhaps one of the latest examples of the use of a polymer-supported species. Conceptually, catalysts on membrane supports offer several possible advantages over traditional powder type systems. They are: (1) Membranes immobilize the catalyst, preventing agglomeration. (2) Filtration is unnecessary for the catalyst separation and so complete catalyst recovery is facilitated. (3) Catalytyic and separation processes can be combined, allowing membrane supported catalysts for the continous flow reactors.

The best known of the perfluorinated cation-exchange membranes is the "Nafion", a product of DuPont. A potential advantage to using Nafion material for catalytic application involving transition metals is that the fluorocarbon backbone imparts a thermal stability to the Nafion materials which far exceeds that of widely studied functionalized polystyrene-supported catalysts or homogeneous bimetallic systems. There

is another conceptual advantage to using Nafion as a catalytic support. Since metal ions can be incorporated via ion-exchange into its small hydrophilic domains (about 4nm) which are connected by about 1nm channels[8], a narrow distribution of metal particle size may result. Ionic metal complexes and polarizable species may also be entrapped within these domains. The physical structure of the ionic domains might contribute to their potential to function as chemical reactors by enabling them to confine a reactant molecule in the proximity of an active site and other reactants. Any reactant molecule that diffuses into the domains could be confined for a residence time that would permit the sites and reactants to interact in the domain much as they would if they were surface sites and gaseous reactants from a gas at much higher pressures. Thus, the possibility exists that reactions can be catalysed in Nafion ionomers under milder conditions than would be required otherwise.

The catalyst systems with Nafion may be broadly classified into two types:

(1)  Supported "metal paricle catalyst", i.e. dispersed metal particles supported on perfluorinated membranes.

(2)  Supported "metal catalyst systems", i.e. metal complex or alkyl-containing species immobilized on a perfluorinated membrane.

Metallic particles of platinum dispersed onto Nafion were prepared by Mau et, al.[9]. The homogeneous deposition of Pt into polymer was obtained using a dilute solution of $Pt(NH_3)_2I_2$ (0.1-0.5 mM) by ion-exchanging $Pt(NH_3)_2^{2+}$ into the polymer and subsequently reducing the complex with borohydride. Using X-ray powder diffraction line broading methods, about 10nm diameter of incorporated Pt particles were observed. They also employed semiconductor (CdS) crystallites embedded in a Nafion matrix containing Pt. It was found that hydrogen-production efficiencies from water containing sacrificial electron donor (sulfide ion) were greater than thoes commonly obtained with unsupported colloidal or powdered semi-conductors under similar conditions.

Mattera and co-workers[10] investigated the oxidation of CO using Nafion powder supported rhodium, ruthenium and platinum. They incorporated Rh, Ru, and Pt into Nafion using $Rh(NO_3)_3 2H_2O$ ($1 \times 10^{-2}$ M), $RuCl_3 3H_2O$ ($1 \times 10^{-2}$ M) and $Pt(NH_3)_4Cl_2H_2O$ ($1 \times 10^{-2}$ M), respectively. Obtained particle sizes were 2.8 nm for Nafion-Rh, 3.3 nm for Nafion-Ru, and 3.4 nm for Nafion-Pt, which were ditermined by transmission electron microscopy. Narrow particle size distributions were also obtained. They reported that the activity sequence Ru>Rh>Pt did not depend on the support material, indicating the potential utility of Nafion as an ionomer-based catalyst. However, it was found that some diffusion limitations over Nafion-Ru and Nafion-Rh system, but not over Nafion-Pt. The formation of a rhodium oxide species occurred in the Nafion-Rh system after flowing of $CO/O_2$ over the catalyst.

In the case of Nafion supported molecular catalyst systems not many reports have appeared in the literature. Murata and Noyori[11] prepared Nafion-Trialkylsilyltriflates (Nafion-TMS) by heating resin with chlorotrimethylsilane followed by washing with petroleum ether and dichloromethane. The catalysts obtained showed considerable moisture-stability and reasonable chemical reactivity. Another alkyl-containing species immobilised over Nafion has been prepared using perfluoroalkylphenyliodonium trifluoromethanesulfonate (FITS) reagents, which are known to be remarkable sources of electrophilic perfluoroalkyl group in perfluoroalkylation and oxyperfluoroalkylation reactions[12]. But FITS showed several difficulties in the isolation of FITS from the reaction mixture, and separation of products and recovery of expensive triffic acid after use. These limitations of FITS can be solved by immobilizing FITS over Nafion. In addition, FITS-Nafion systems were found to have sufficient stability and high reactivity.

Molecular catalyst systems using metal complexes have been investigated very recently. The cationic palladium complex, $[Pd(CH_3CN)(PPH_3)_3](BF_4)_2$ suppported on Nafion was prepared by Chang[13]. In the carbomethoxylation of propylene, the supported cationic $Pd^{2+}$ complex precursors showed higher catalytic activity than the supported $Pd(NO_3)_2$ and $Pd(PPH_3)_4$ catalyst precursors. It was found that $Pd^{2+}$ complex supported Nafion gave higher catalytic activity than the same complex supported onto the other sulfonated resins such as macroreticular sulfonated polystyrene ion-exchange resin (Amberyst) and sulfonated polystyrene ion-exchange resin (Dowex). However, much investigation in the Nafion-bound metal-complex catalyst would be necessary to verify the catalytic behaviour.

The catalytic system used in this work is metallic platinum dispersed into Nafion. Since platinum has been known as a reforming catalyst with high activity and unique selectivity characteristics, Nafion supported Pt is used to hydrogenate cyclohexene.

## 2. EXPERIMENTAL

### 2.1. Material preparation

[Pt(NH$_3$)$_4$]Cl$_2$ was prepared according to the method described by Ferneluis[14]. A standard solution of [Pt(NH$_3$)$_4$]Cl$_2$ was prepared for ion-exchanging with Nafion by dissolving 10.31 mg of [Pt(NH$_3$)$_4$]Cl$_2$ in the minimum amount of 25% aqueous ammonia, and then dilution with water to give a final concentration of 6% Pt/100ml [Pt(NH$_3$)$_4$]Cl$_2$ solution. Using this solution. a concentration range of $1.0 \times 10^{-7}$ moles of Pt to $9.6 \times 10^{-6}$ moles of Pt was produced.

### 2.2. Preparation of Pt supported on perfluorinated ion-exchange membranes

Nafion (117. Du Pont). perfluorinated cation-exchange membrane was used as a support material. All Nafion films were cleaned by boiling in concentrated nitric acid, and then washing with the boiling water and drying them in vacuo at room temperature.

The homogeneous platinization started with soaking of fully dried membranes, which were carefully weighed. in the diluted complex solutions for one day. Membranes incorporating Pt complexes were then immersed in a large excess of borohidride solution to reduce the metal Pt. Soaking the membranes in water under hydrogen was also used for reduction to the metal.

### 2.3. U.V. Visible Spectroscopy

The amount of complex absorbed by the perflluorinated ion-exchange membranes is determined by measuring the U.V. absorbance of the fresh and depleted complex solutions at 200 nm.

### 2.4. Hydrogenation of cyclohexene

3.5 molal cyclohexene in methanol and net cyclohexene were hydrogenated in a glass lined stainless steel high pressure bomb with magnetic stirring and thermostatting to $^+$ 0.5 ºC. The schematic diagram of the high pressure reactor is illustrated in Figure 2-1. The compositions of the samples taken during the catalyst testing were measured by a HP 5890 GC using a 0.2% carbowax 1500 on 60/80 Carbopak C packed column. The GC was connected to an ASI personal computer which allows for manipulations such as integration, peak selection, peak labelling and GC parameter control.

## 3. RESULTS AND DISCUSSIONS

### 3.1.  Nafion supported Pt particles

The U.V. visible spectra of complex solutions are summarized in Table 1.  It indicates that about 70 to 80% of the complexes are ion-exchanged into the membranes.

The reduction to metal by sodium borogydride in large excess was successfully achieved and an even distribution of metal on the membrane surface was obtained.  In the case of reduction using the hydrogen bomb at 80 °C and 3.05 MPa, partial reduction to the metal was obtained. This may be due to improper stirring in the system.  As the percentage of Pt loading on the membranes increased, the black colour became more pronounced, indicating that more Pt particles have been incorporated with the strong acidic ion-exchange membranes.

### 3.2.  Catalytic testing

The rate of hydrogenation of cyclohexene (expressed as Turnover Frequencies, TOF's) is plotted in Figure 1.  TOF's are calculated by equation (1).

$$TOF's = \frac{\dfrac{WT_{c-h}}{MW_{c-h}} \times C}{M_{Pt} \times S} \tag{1}$$

where $WT_{c-h}$ = weight of cyclohexene, $MW_{c-h}$ = molecular weight of cyclohexene, $M_{Pt}$ = moles of Pt on the membrane, C = percentage conversion from cyclohexene to cyclohexane and S = number of seconds for hydrogenation.

Catalytic activity of Nafion supported Pt increased with increase of percentage platinum loading on Nafion.  However, after 0.5% Pt loading on Nafion was reached, the TOF's of the reaction rapidly decreased. This indicates that when the %Pt loading on the membrane reaches 0.5, the system should be the optimum to produce the highest catalytic activity of Nafion-Pt in the hydrogenation of cyclohexene in methanol. If more than 0.5% Pt exists on the membrane, Pt particles will possibly block the membrane pores and obscure the Pt loaded previously on the membrane.  This may affect the diffusion of cyclohexene through membrane, and limit the contact surface of Pt to the reactant.

Hydrogenation rates at various pressures are plotted in Figure 2.  It showes that the rate becomes pressure independent at about 0.78 MPa, indicating that the diffusion of reactants in the membrane or the reaction on the catalyst is rate limiting in this region.

The temperature dependence of the rate of hydrogenation of neat cyclohexene (Arrehenius behaviour) at 1.0 MPa on the membrane is plotted in Figure 3. Activation energy for the Nafion-Pt catalyst was 13.1 KJ/mole, which is showing high catalytic efficiency with low activation energy compared to the others: 23.8 KJ/mole for the hydrogenation of cyclohexene in cyclohexane on $Pt/Al_2O_3$ [15] and 27.9 KJ/mole for the hydrogenation of neat cyclohexene on $Pt/SiO_2$ [16].

## 4. CONCLUSIONS

Although it is difficult to identify the most suitable polymer for chemical reactions with polymer supported catalyst, the present work shows the great potential of perfluorinated cation-exchange membranes, Nafion, as insoluble polymer support for the hydrogenation of cyclohexene.

Nafion supported Pt shows relatively high catalytic activity in the hydrogenation of neat cyclohexene compared to the other types of Pt catalyst.

Pt loading on the membrane is a major factor influencing the optimum reaction conditions. It was found that 0.5% Pt loading offer the highest rate of hydrogenation of cyclohexene in methanol for Nafion supported Pt catalyst.

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Table 1. UV visible spectra of complex solution and percentage of Pt loading on the membrane.

| Sample code | Pt in complex solution(mg) | UV before ion-exchange | UV after ion-exchange | Pt on Nafion (% wt/wt) |
|---|---|---|---|---|
| PN 1 | 0.217 | 0.253323 | 0.222924 | 0.012 |
| PN 2 | 0.490 | 0.524970 | 0.211776 | 0.24 |
| PN 3 | 1.061 | 0.954345 | 0.379010 | 0.49 |
| PN 4 | 1.061 | 0.953998 | 0.347152 | 0.51 |
| PN 5 | 1.080 | 0.917861 | 0.285369 | 0.55 |
| PN 6 | 1.488 | 1.227340 | 0.375396 | 0.91 |
| PN 7 | 1.463 | 1.223890 | 0.249038 | 1.04 |
| PN 8 | 2.371 | 1.308600 | 0.234817 | 1.64 |

Figure 2-1. The schematic diagram of the high pressure reactor.



Thermocouple

Pressure gauge

H2

Stainless steel

3.5 molar c-hexene in MeOH

Pyrex glass

Heating block

Membrane supported metal catalyst
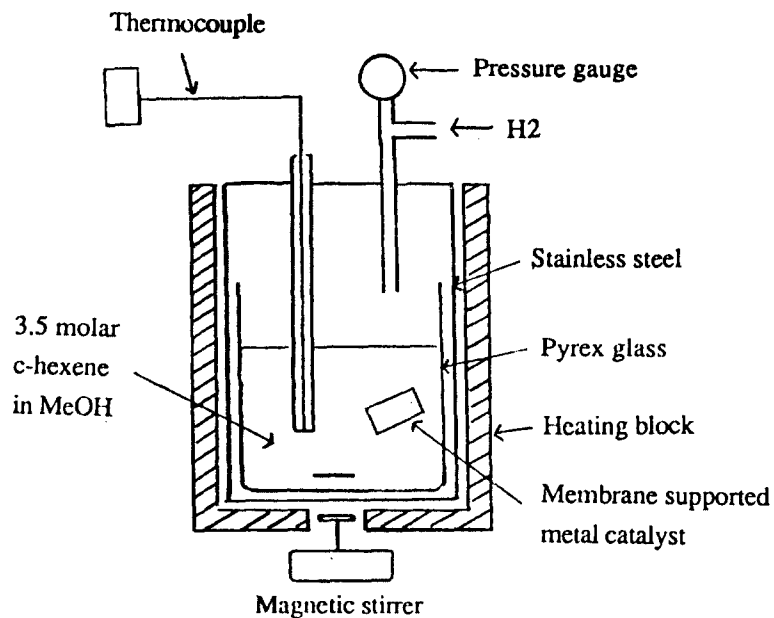
Magnetic stirrer

Figure 1. The rate of hydrogenation of 3.5 molal cyclohexene in methanol with Nafion supported Pt.
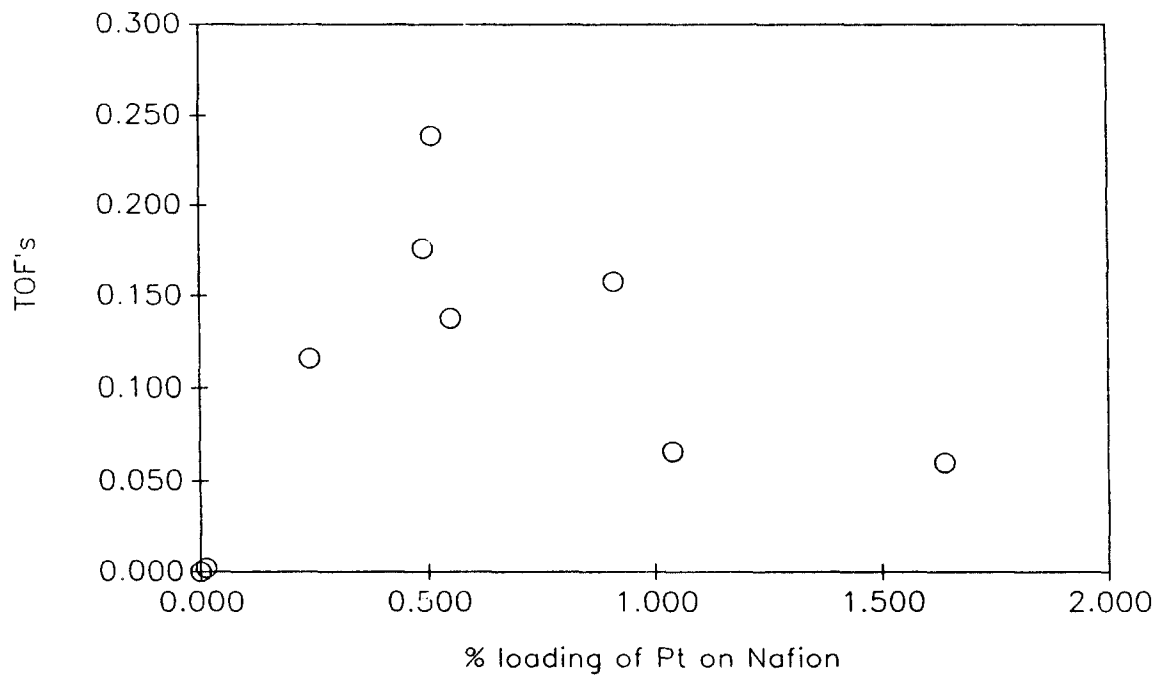
Figure 2. Hydrogenation rate of 3.5 molar cyclohexene in methanol at various pressure using 1.8% Pt on Nafion at 20 C.
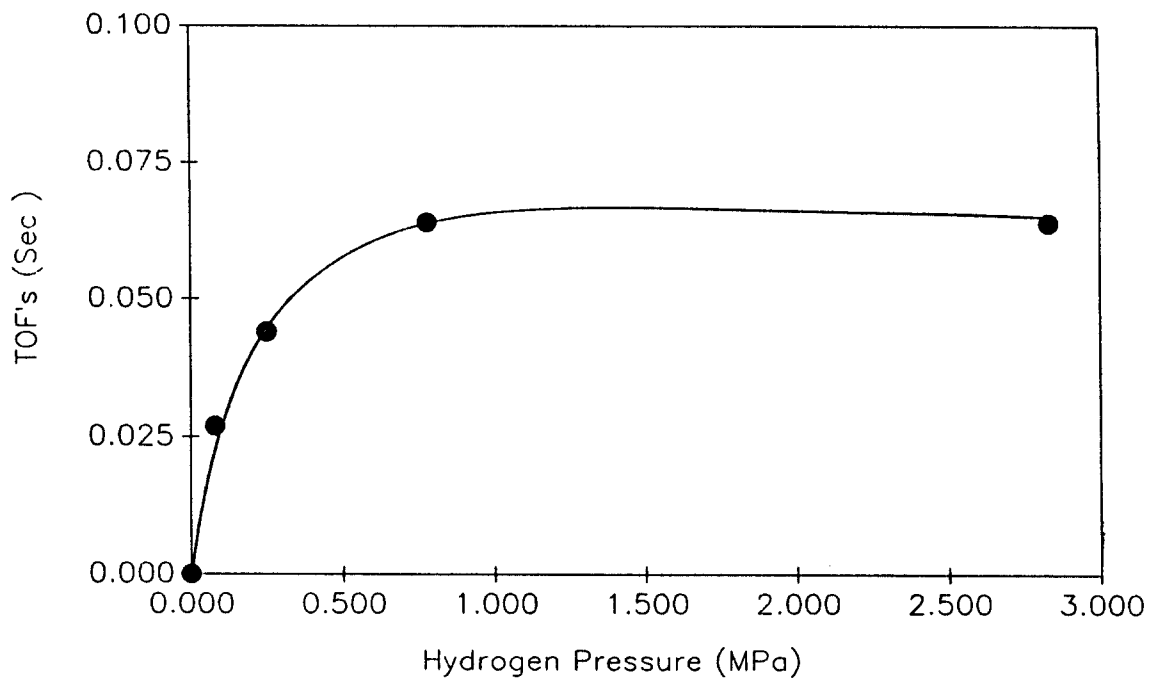
Figure 3. Temperature dependence of the rate of hydrogenation (Arrhenius plot) of neat cyclohexene using Nafion–Pt (1% Pt on membrane, 1MPa)