

Dynamic Behavior of Heterogeneously Catalyzed Reaction on a Modified Solid Polymer Electrolyte Membrane.* —Hydrogenation of CO over Nafion Membrane Supported Rhodium Catalysts—

Masafumi OKAMOTO**, Tohru KANNO***,
and Masayoshi KOBAYASHI***

(Received April 30, 1992)

Abstract

The hydrogenation of CO forming methane has been studied on Nafion membrane supported rhodium catalyst, and the performance of the membrane reactor is compared between three different procedures: (1) mixed gas operation(MGO), (2) single gas operation(SGO), and (3) cyclic operation(CYO) is compared. The performances for methane formation in the three operations are ordered as CYO > SGO > MGO.

1. INTRODUCTION

In recent years, membrane reactions have emerged as one of the most viable unit operation in both separation and selective reaction processes^{1),2)}. The high technological relevance become obvious from increased application of membrane based separation for the fields of chemical processing, biotechnology & biomedical applications, environmental techniques and natural gas & oil exploitation. The potential application of membranes in reaction engineering is being recognized. The technology of organic membrane, accelerated by the needs of desalination in the 1970s, has advanced from liquid separation to gas separation applications and become an acceptable and, in many cases, economically viable unit operation.

As is well known, transition-metal-containing complexes which are either active catalysts or potential catalytic precursors are bound to the support by covalent attachment. Recently, there have been reports of catalytic reaction involving transition-metal complexes incorporated into polyelectrolyte resins^{3),4)}. Nafion is well known commercially as a typical functioning organic polymer, which was developed by du Pont and Company. This polymer consists of a perfluorinated polyethylene backbone with pendant side-chains terminating with $-SO_3^-M^+$ groups, where M^+ is an exchangeable cation, as is shown schematically in Fig.1.

The equivalent weights(EW) of Nafion membranes used in electrochemical applications

* This paper was presented at the Hokkaido regional meeting of the Chemical Society of Japan in 1991 (Sapporo).

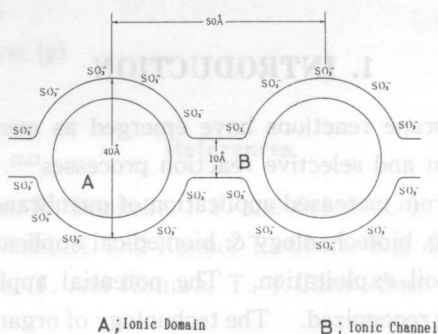
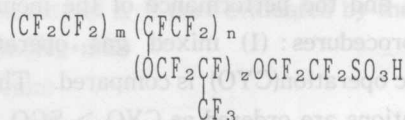
** Chemical Environmental Engineering.

*** Department of Industrial Chemistry.

are evaluated to be 1100~1500 per $-\text{SO}_3^-\text{M}^+$ group. M^+ is easily ionexchanged by a metal ion⁵⁻⁹).

A large number of investigations have reported interesting and important reactions that are catalyzed by conventional heterogeneous catalysts at temperatures below 500K whose kinetics and mechanisms could be investigated by using Nafion-supported transition metals and other catalytically active metals such as Pt, Ni, Rh, Pd, Ru, and Ir¹⁰). These metal ions can readily be accessed into the ionic domains present in Nafion by ionexchange, and small gaseous molecules, C_2H_4 , H_2 , CO , CO_2 , N_2 , NO , and O_2 , which are possible to diffuse the ionic

Solid Polymer Electrolyte membrane (SPE)



	EW	thickness
	(g)	(inches)
Nafion-417	1100	0.017

Fig. 1 Structure of membrane in this study

channel of Nafion membrane body can form known intermediates of heterogeneous catalytic reactions.

In this work, a reactor containing a rhodium-ionexchanged Nafion membrane has been designed and operated in a such way to have a catalytic reaction in the membrane itself⁴).

The catalytic activity of Rh/Nafion has been examined under atmospheric pressure at temperature range of 120-140°C by using CO-hydrogenation. The efficiency of membrane reactor is compared to a conventional reactor and the advantage of it is reconfirmed.

2. EXPERIMENTAL

2-1. Catalyst Membrane Preparation

The Nafion materials used in the present study are commercially supplied as Nafion-417. The brown membrane of Nafion-417 had thick in 0.2mm and an equivalent weight of 1250⁴⁾.

The rhodium catalyst supported in the Nafion membrane (4.5×11.5cm) was prepared by ion-exchange in 0.07M aqueous solution of Rh(NO₃)₃ (Wako Products), stirring the solution for 7days at room temperature. The catalyst membrane was washed by redistilled water up to becoming pH=7.0 and after that it was dried for 24hrs at 60°C. Dehydrated Rh/Nafion membranes were chemically analyzed by the tinchloride method and found to contain 0.33wt % Rh. The catalyst membrane was attached into the reactor and reduced by hydrogen at 120°C for 2hrs. According to these procedures, rhodium ion inserted into the ionic domains can easily be reduced to metallic rhodium.

2-2. Experimental Setup

Fig.2 illustrates a schematic drawing of the membrane reactor. The reactor consisted of two flat plates (stainless steel, 12×5×0.5=30cm³) in each of which a groove was prepared for the gas flow (0.76cm³), and the catalyst membrane (7.6cm²) was sandwiched between the two plates. The groove of the two plates was divided by the membrane. The reaction gases in both grooves partly permeated between the two plates through the membrane, with a counter current. The permeation through the membrane from one side to the other side was visualized in the figure. The reaction was conducted under atmospheric pressure at 30ml/min and the temperature range of 120-140°C. The membrane reactor was put into an air both the temperature of which was well controlled at the accuracy of ±0.5°C.

Fig.3 illustrates the flow diagram of the experimental system. Three flow controlling systems each of which could prepare a different gas mixture were used to feed an inert gas and adsorptive gas into the reactor with no change in the gas flow rate. A water manometer was connected to the three systems and a needle valve was attached to the outlet of the cell to ensure the pressure in the two grooves of the diffusion cell was equalized. A four-port valve (7) was connected to an inert gas stream (He or N₂) to measure the absolute flow rate of the groove, before starting the reaction experiment. The reaction gases and product gases were sampled at the sampling holes (4) by a syringe of 1cm³. The total gas flow rate was measured by a film soap meter (10). For the standard experiments, we have two different gas flows which pass simultaneously the two grooves of membrane reactor. Our designation for the two flows is as follows: (1) R-side (reference gas) which is containing hydrogen and (2) S-side (sense gas) which is containing other mixed gas. The designation of R- and S-sides is fixed through all the experiments when even the two flows are switched by the four way valve during reaction.

2-3. Gas Analysis

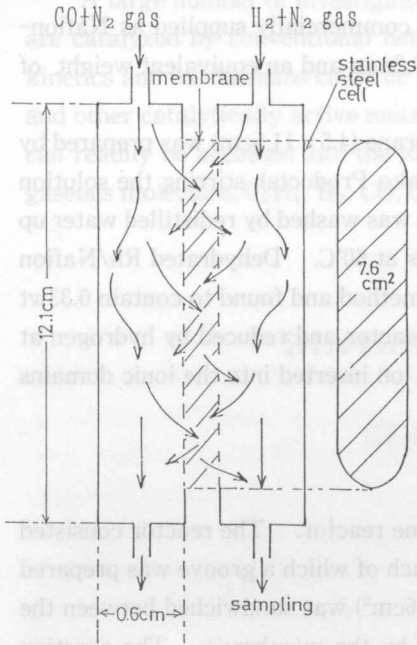


Fig. 2 The diffusion cell used in this study.

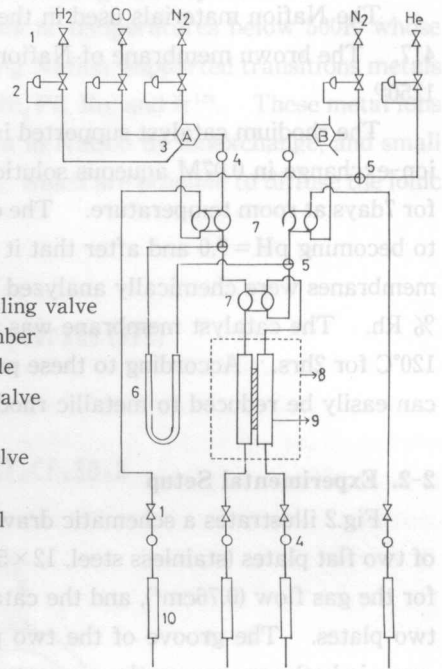


Fig. 3 Schematic diagram of apparatus for this study.

All the gases produced or effused out of the reactor was analyzed by two gas chromatographs. One attached to a thermal conductivity detector (TCD:HITACHI-164T) was used to analyze N_2 , H_2 and O_2 by using Molecular Sieve 5A and CO_2 and CO by a Porapak Q column. The other attached to the hydrogen flame ionization detector (FID : SHIMADZU GC-3BF) was used to analyze CH_4 , C_2H_4 , C_3H_6 , C_2H_2 , and C_3H_8 by using a Porapak Q ($\Phi = 3\text{mm}$, 2m in length).

Carbon monoxide 99.95 %, hydrogen 99.99 %, helium 99.99 %, ethylene 98.5 % and propylene 95.5 % were all supplied by Nittetsu Kagaku Co.

2-4. Experimental Procedure

Fig.4 illustrates a schematic diagram of typical experimental procedures. Fig.4s (1) and (2) indicate a steady state operation and a cyclic operation respectively. In the steady state operation, for example, a $CO-N_2$ mixture and a H_2-N_2 mixture are introduced into S - and R-sides respectively, with a stepwise fashion. The outlet gas stream at each side is analyzed and the mode of the response curves of products is visualized. CO and H_2 can react

in the membrane by Knudsen diffusion through the ionchannel and the ion domain, with a counter current flow. The response of products at the outlet of two sides exhibits different mode because of the separation factor of the membrane. The steady state operation can be categorized into two different types : One in which CO and H₂ gases are introduced into S- and R-sides respectively (single gas operation = SGO), and one in which a CO-H₂ mixture and N₂ gas introduced into respectively (mixed gas operation = MGO).

In the cyclic operation, the two mixtures are switched periodically at the inlet of S- and R-sides, and the response of products is followed separately for the two sides.

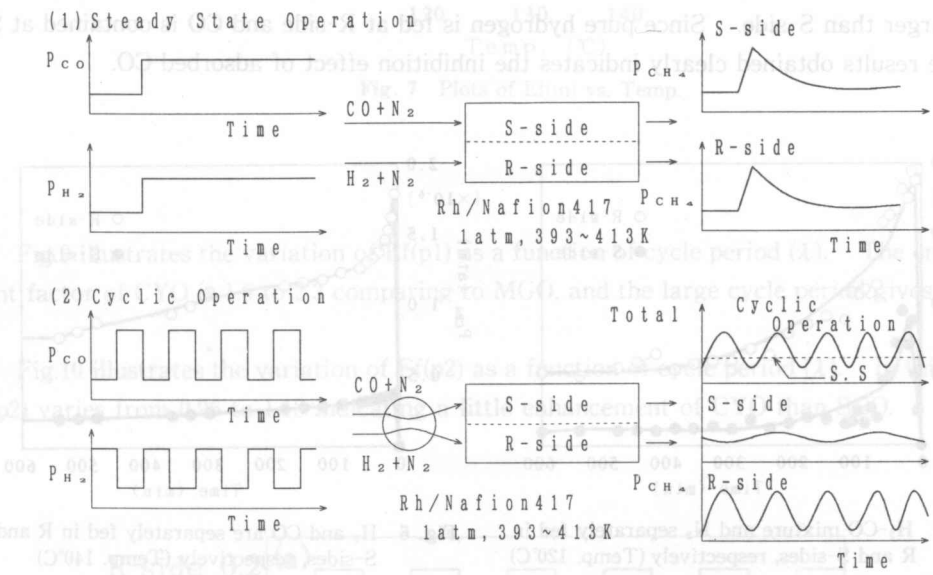


Fig. 4 Schematic explanation for the experiment

3. EXPERIMENTAL RESULTS AND DISCUSSION

3-1. Definition of Enhancement Factor

A rate enhancement factor, Ef, is defined to compare with the given procedure as follows¹¹⁾.

$$Ef(m) = \frac{\text{time averaged production rate } (r_{av}) \text{ at the single gas operation}}{\text{time averaged production rate } (r_{av}) \text{ at the mixed gas operation}} \dots\dots\dots(1)$$

$$Ef(p1) = \frac{r_{av} \text{ at the cyclic operation}}{r_{av} \text{ at the mixed gas operation}} \dots\dots\dots(2)$$

$$Ef(p2) = \frac{r_{av} \text{ at the cyclic operation}}{r_{av} \text{ at the single gas operation}} \dots\dots\dots(3)$$

When Ef is larger than 1, the numerator of equations (1)~(3) is advantage than the denominator. Here, r_{av} is evaluated as the sum of two rate at S- and R-sides.

3-2. Characterization of Ef(m)

Figs.5 and 6 illustrate the transient behavior of methane production at the mixed gas operation (MGO) and the single gas operation (SGO) respectively, comparing between R- and S-sides. In the both operations, the rate of methane formation at R-side is about three times larger than S-side. Since pure hydrogen is fed at R-side and CO is contained at S-side, the results obtained clearly indicates the inhibition effect of adsorbed CO.

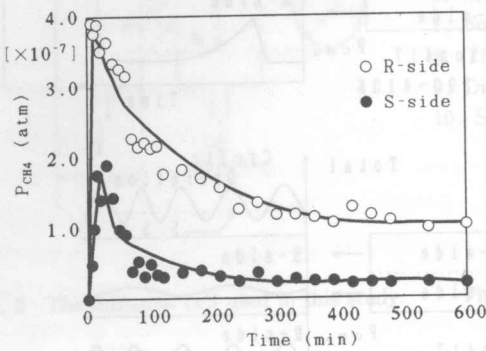


Fig. 5 H₂-CO mixture and N₂ separately fed in R and S-sides, respectively (Temp. 120°C)

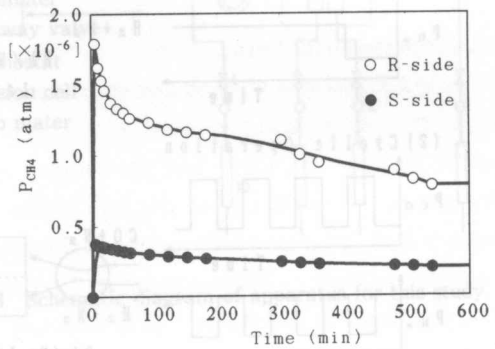


Fig. 6 H₂ and CO are separately fed in R and S-sides, respectively (Temp. 140°C)

One may easily compare the efficiency of MGO to SGO by using Ef(m). The results obtained at 120-140°C is presented in Fig.7, indicating the methane production of SGO to be 1.6~2.4 times larger than MGO.

3-3. Characterization of the Cyclic Operation.

Fig.8(a) shows the input signal of R- and S-sides during the cyclic operation. Fig.8(b) illustrates the typical response curves during CYO. The broken line indicates the methane formation at the steady state procedure and the flow decay of the line is due to the gradual accumulation of adsorbed CO. Comparing the mode of the two response curves, one in R-side shows an ordinal oscillation the period of which is synchronized with the period of the input signal, whereas one in S-side shows a steady state with no oscillation. The time averaged value of methane at R-side is about 4.4 times larger than one at S-side. This extraordinary difference will be resulted from the long pretreatment of the membrane by the CO stream at S-side before starting the cyclic operation.

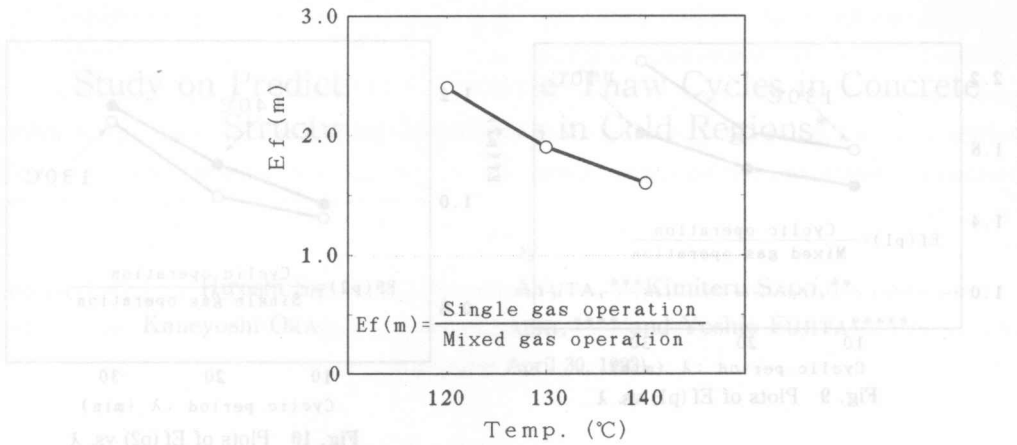


Fig. 7 Plots of Ef(m) vs. Temp.

Fig.9 illustrates the variation of Ef(p1) as a function of cycle period (λ). The enhancement factor of CYO is 1.6 to 2.3 comparing to MGO, and the large cycle period gives larger Ef.

Fig.10 illustrates the variation of Ef(p2) as a function of cycle period (λ). In this case, Ef(p2) varies from 0.96 to 1.18 indicating a little enhancement of CYO than SGO.

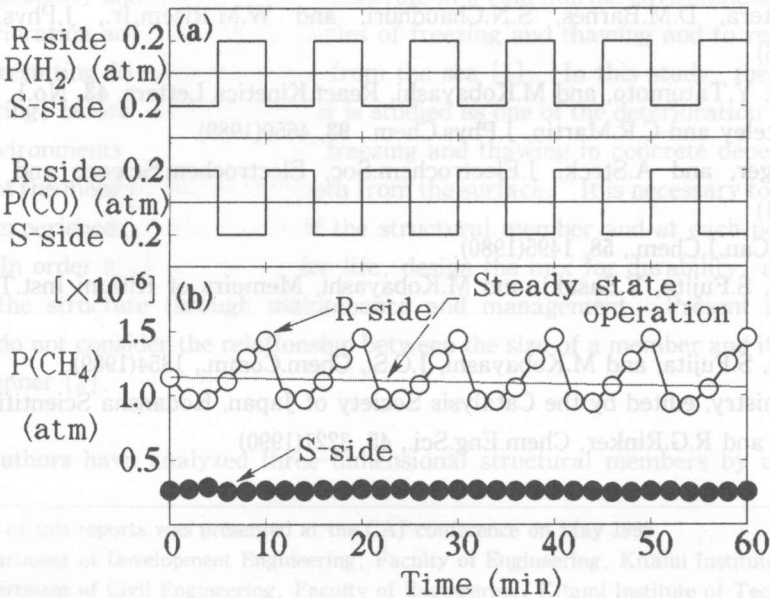


Fig. 8 Cyclic operation [140°C, $\lambda = 10(\text{min})$]

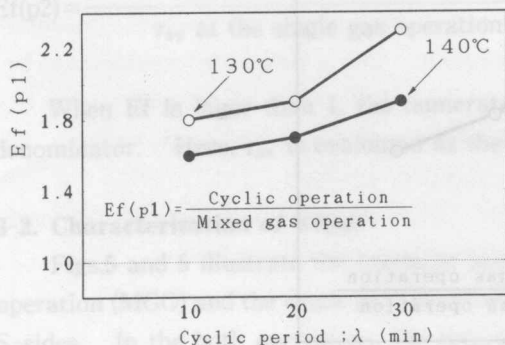


Fig. 9 Plots of Ef(p1) vs. λ

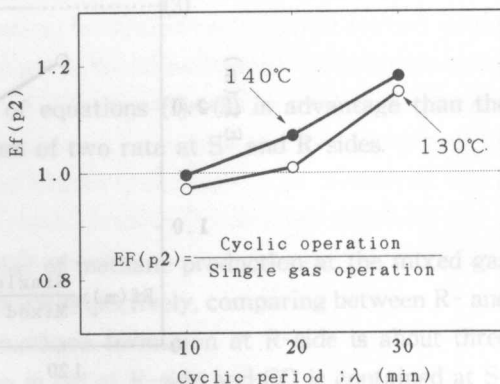


Fig. 10 Plots of Ef(p2) vs. λ

4. CONCLUSIONS

An advantage of membrane reactor is evaluated by using CO-hydrogenation on a Rh/Nafion catalyst as a model reaction, combining the cyclic operation and the single gas operation. The yield of the two operations is 1.2~2.4 times larger than conventional steady state operation.

5. REFERENCES

1. Y.M.Sun and S.J.Khang, IEC.Res., **29**, 232(1990)
2. Y.M.Sun and S.J.Khang, IEC.Res., **27**,1136(1988)
3. V.D.Mattera, D.M.Barnes, S.N.Chaudhuri, and W.M.Risem,Jr., J.Phys.Chem., **90**, 4819(1986)
4. T.Kanno, Y.Tatumoto, and M.Kobayashi, React.Kinetics Letters, **43**, No.1, 237(1991)
5. L.D.Whiteley and C.R.Martin, J.Phys.Chem., **93**, 4650(1989)
6. H.L.Yeager, and A.Steck, J.Electrochem.Soc, Electrochem.Science and Tech., **128**, 1880(1981)
7. M.Falk, Can.J.Chem., **58**, 1495(1980)
8. T.Kanno, S.Fujita, Y.Sasaki, and M.Kobayashi, Memoirs of Kitami Inst.Tech., **20**, 93 (1988)
9. T.Kanno, S.Fujita, and M.Kobayashi, J.C.S., Chem.Comm., 1854(1989)
10. C1-Chemistry, edited by the Catalysis Society of Japan, Kodansha Scientific (1985)
11. R.Yadav, and R.G.Rinker, Chem.Eng.Sci., **45**, 3221(1990)