Kinetics of Gas-Phase Hydration of Propene Heterogeneously Catalysed on a Solid Polymer Electrolyte*

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Abstract

The kinetics of the hydration of propene on a Solid Polymer Electrolyte (SPE) and a silver-supported one have been studied by using the steady state and unsteady state methods at a temperature range of 100~160°C, using an ordinary flow reactor under atmospheric pressure. The reaction gave two products in parallel reaction, iso-propylalcohol and hexene, and the reaction rates are represented as follows
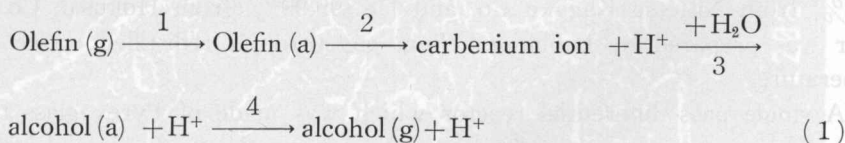
$$r_{PrOH} = k P_{C_3H_6} P_{H_2O}{}^m \text{ and } r_{hex} = k P_{C_3H_6} P_{H_2O}{}^n$$

with activation energies 46 and 90 kJ/mol, respectively.

All the transient response curves caused by the concentration jump of propene gave a monotonic mode suggesting a Langmuir-Hinshelwood mechanism with the rate controlling step of carbenium ion formation.

1. Introduction

The gas-phase catalysed hydration of olefin has been studied mainly on solid phosphoric acids (SPA), metallic salts (MS), ion exchange resins (IER) and metal oxides (MO)[1]. A large number of reports have proposed general classification for reaction mechanism: (1) rate equations involving acidity functions on the SPA[2~4] similar to homogeneous reactions, and (2) Langmuir-Hinshelwood mechanism on the MS[5,6] and the MO[7,8]. The catalytic activity is strongly related to the electron negativity of metals and surface acidity, for example, $-8.2 < H_0 < -3.0$ for ethylene hydration and $-3.0 < H_0 < 1.5$ for propene hydration[9] are optimum acidity. On the MS and MO, generally speaking, the following mechanism has been accepted.

$$\text{Olefin (g)} \xrightarrow{\ 1\ } \text{Olefin (a)} \xrightarrow{\ 2\ } \text{carbenium ion } + H^+ \xrightarrow[\ 3\ ]{+H_2O}$$

$$\text{alcohol (a) } + H^+ \xrightarrow{\ 4\ } \text{alcohol (g)} + H^+ \tag{1}$$

The rate of Step 2 is the slowest and the other steps rapidly reach an equilibrium. Taking into account this information, one may be interested in the use of functionating organic polymers which have increasingly been used as supports for heterogenized homogeneous catalytic processes[10].

In the present study, ion-exchange (polyelectrolyte) resins have been taken as a catalyst or a support for metals. Nafion is well-known commercially as a typical functioning organic polymer. Nafion is a perfluorosulfonic acid and the detailed analysis of it using a variety of diffraction, spectroscopic and other techniques has revealed that Nafion is one of the useful materials from the view of microscopic morphology. The sulfo groups have ionic domains that are embedded randomly in a fluorocarbon matrix. The size of the ionic domains is sensitively controlled by the degree of hydration and the concentration of the ionic sites. The average diameter of the ionic domains is about $30 \sim 40$ Å and the domains are connected by hydrophilic channels of 10 Å in diameter. The sulfo groups should show strong acidity which should bring about the enhancement of propene hydration at lower temperatures.

In this paper, the catalytic activity of NR–50 (Nafion, from du Pont) has been examined under atmospheric pressure at a temperature range of $100 \sim 160°C$, and the reaction mechanism is revealed by using the steady state rate analysis and the transient response method[11~13]. In addition, a silver ion exchanged Nafion was also used to reveal the effects of silver ion on the catalytic activity and the selectivity to alcohols.

2. Experimental Section

The Nafion materials used in the present study are commercially supplied as NR–50. The white cylindrical granules of NR–50 had average diameter of ca. 1 mm and length in 1 mm, and an equivalent weight of 1250. Fig. 1 shows electron micrographs of NR–50.

The silver supported catalyst was prepared by ion-exchange in 0.1 M aqueous solution of $AgNO_3$ (Wako products), stirring the solution for 7 days. The amount of the loading was 10.7 wt% of Ag, which was taken from the sample dried in air for 24 hrs under room temperature and whose weight was obtained by a chemical analysis technique.

The gases used in the present study were supplied commercially: C_3H_6 (99.5%) from Nittetsu Kagaku Co. and He (99.99%) from Hokusan Co. Water vapor was prepared by bubbling helium gas through redistilled water at room temperature.

A single pass differential reactor which was made of Pyrex glass tube was used. The reactor 10 mm in diameter was put into the fluidized sand bath whose temperature was controlled within the accuracy of $\pm1.0°C$ through all experimental conditions. The sheathed thermocouple of 1.0 mm in diameter was inserted directly in the middle of catalyst bed to detect the catalyst temperature more sensitively. The Hitachi Model 164 gas-chromatograph (G. C.) was used

(a)

400 µm

(b)
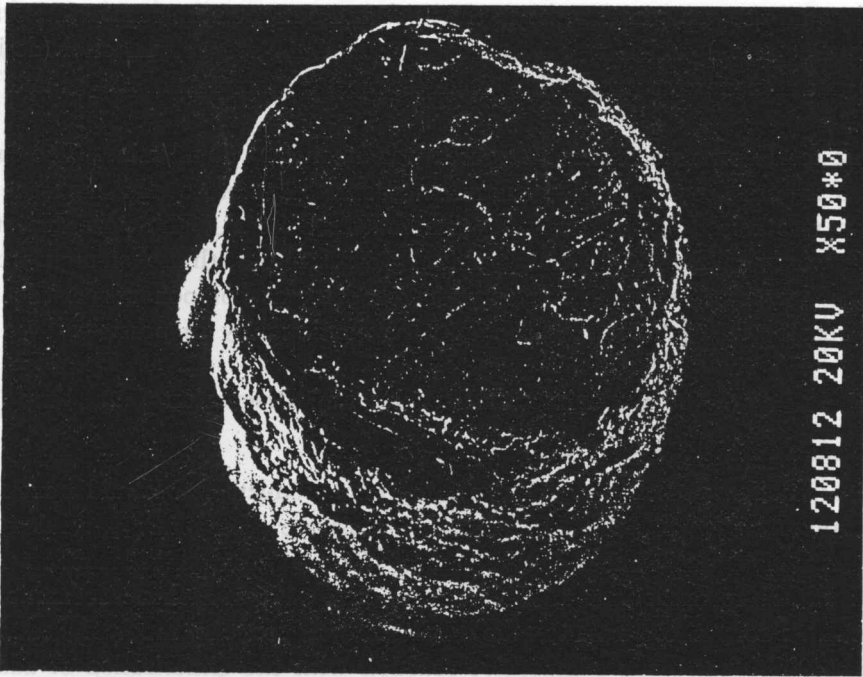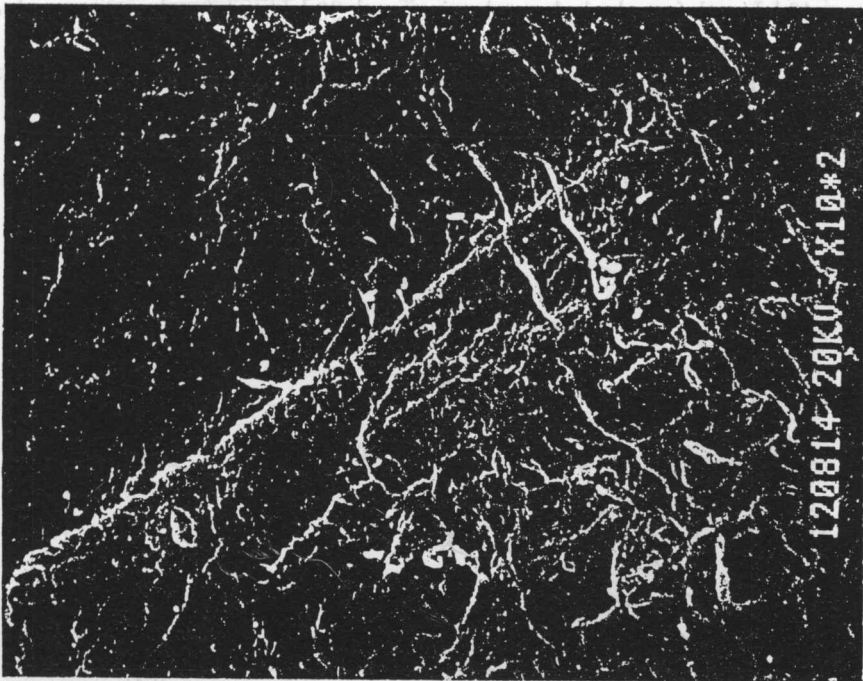
20 µm

Fig. 1. SEM photographs of NR-50.

to analyse all the gas components at the inlet and outlet of the reactor. Porapack Q (100~200 mesh) which was used to separate C_3H_6, isopropylalcohol (designate PrOH) and hexene was packed in a stainless steel column 1 m in length and 4 mm in o. d..

The total flow rate of reactant gases was a constant 80 ml/min. The catalyst bed was exposed to a pure He stream at room temperature and then the temperature was raised to the desired value in this stream. The pure He stream was stepwise changed into the reaction gas mixture with no changing of the total gas flow rate, and the response of reaction gas components at the outlet of the reactor was followed by the G. C. as continuously as possible.

3. Experimental Results and Discussion

3-1. Steady State Rate Analysis on NR-50

The reaction proceeds steadily forming two products PrOH and hexene at a temperatures below 160°C. Figs. 2 and 3 illustrate plots of r_{PrOH} and r_{hex} vs. $P_{C_3H_6}$, respectively at various temperatures. There was a big reduction in the rate of PrOH formation at 160°C, whereas the rate of hexene formation was enhanced. From these results, the hydration of propene may be reduced at around 140°C, due to the competitive reaction with the dimerization of adsorbed propene which may be steeply accelerated at higher temperatures. This idea can be accepted due to the difference of the apparent activation energies of the two reactions, 46 kJ/mol for alcohol production and 90 kJ/mol for hexene production. The results are presented in Fig. 4.

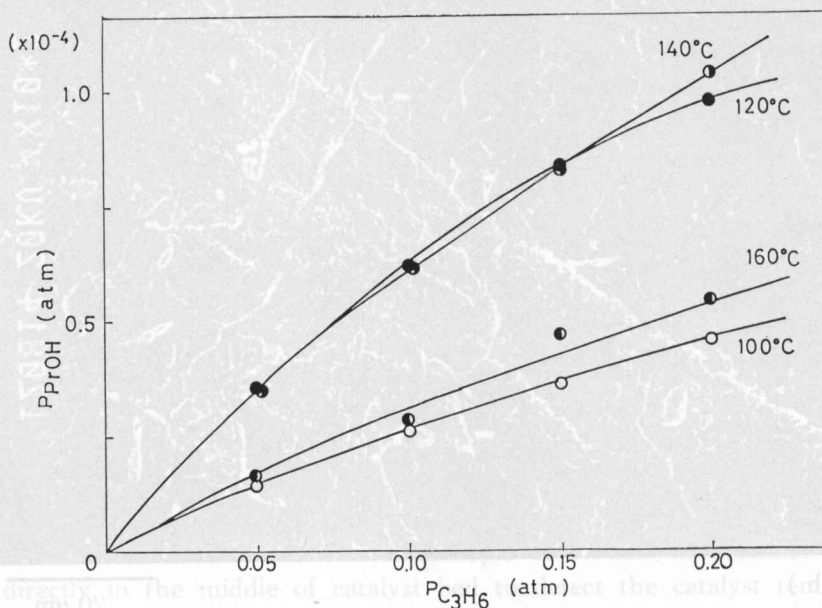At temperatures higher than 160°C, acrolein is formed as shown in Fig. 5

Fig. 2.   Plots of $P_{C_3H_6}$ vs. P_{PrOH} on NR-50.

and this reaction becomes more predominant with increasing temperature, suggesting the advantage of oxyhydration rather than hydration.

The apparent rate equations are expressed as follows.

$$r_{PrOH} = k P_{C_3H_6}^{0.8} P_{H_2O}^{m} \tag{2}$$
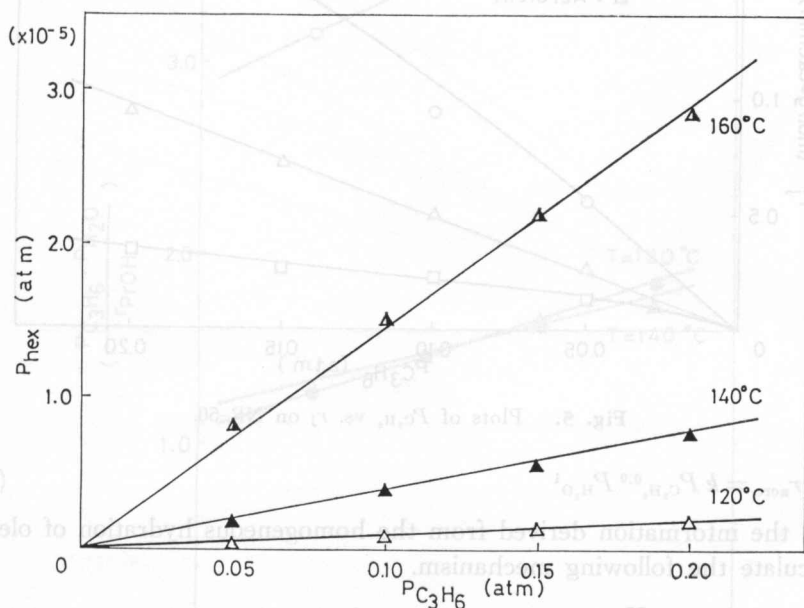
$$r_{hex} = k P_{C_3H_6} P_{H_2O}^{n} \tag{3}$$

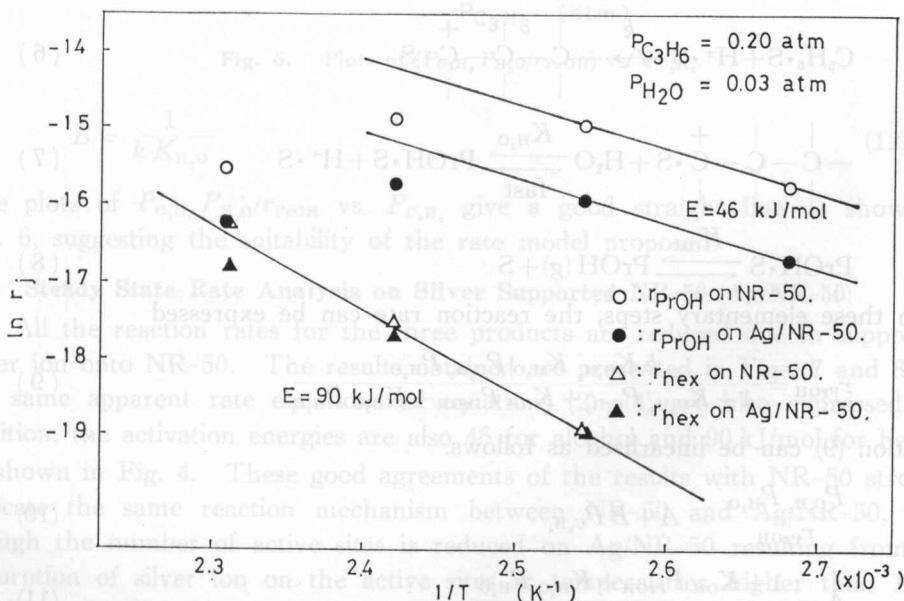**Fig. 3.**   Plots of $P_{C_3H_6}$ vs. P_{hex} on NR-50.

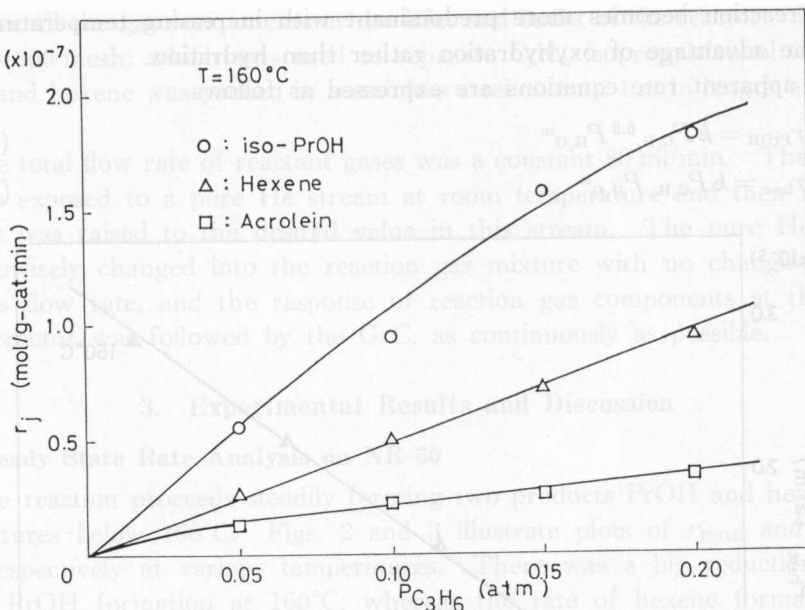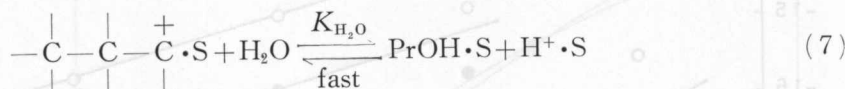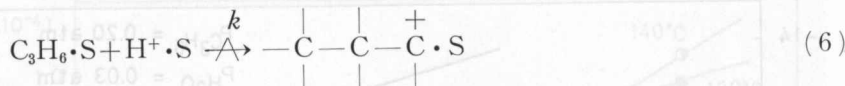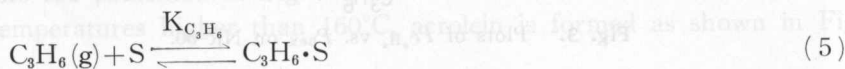**Fig. 4.**   Arrhenius plots of formation of PrOH and Hexene on NR-50.

Fig. 5.   Plots of $P_{C_3H_6}$ vs. r_j on NR-50.

$$r_{acro} = k \, P_{C_3H_6}^{0.9} \, P_{H_2O}^1 \qquad (4)$$

Based on the information derived from the homogeneous hydration of olefin, one may speculate the following mechanism.

$$C_3H_6(g) + S \underset{\longleftarrow}{\overset{K_{C_3H_6}}{\rightleftharpoons}} C_3H_6 \cdot S \qquad (5)$$

$$C_3H_6 \cdot S + H^+ \cdot S \overset{k}{\longrightarrow} \underset{|}{-}\overset{|}{C}-\overset{|}{C}-\overset{+}{C} \cdot S \qquad (6)$$

$$\underset{|}{-}\overset{|}{C}-\overset{|}{C}-\overset{+}{C} \cdot S + H_2O \underset{\text{fast}}{\overset{K_{H_2O}}{\rightleftharpoons}} PrOH \cdot S + H^+ \cdot S \qquad (7)$$

$$PrOH \cdot S \overset{K_{OH}}{\rightleftharpoons} PrOH(g) + S \qquad (8)$$

From these elementary steps, the reaction rate can be expressed

$$r_{PrOH} = \frac{k \, K_{C_3H_6} \, K_{H_2O} \, P_{C_3H_6} \, P_{H_2O}}{1 + K_{C_3H_6} \, P_{C_3H_6} + K_{OH} \, P_{PrOH} + K_{H_2O} \, P_{H_2O}} \qquad (9)$$

Equation (9) can be linearized as follows.

$$\frac{P_{C_3H_6} \, P_{H_2O}}{r_{PrOH}} = A + B \, P_{C_3H_6} \qquad (10)$$

$$A = \frac{1 + K_{OH} \, P_{PrOH} + K_{H_2O} \, P_{H_2O}}{k \, K_{C_3H_6} \, K_{H_2O}} \qquad (11)$$
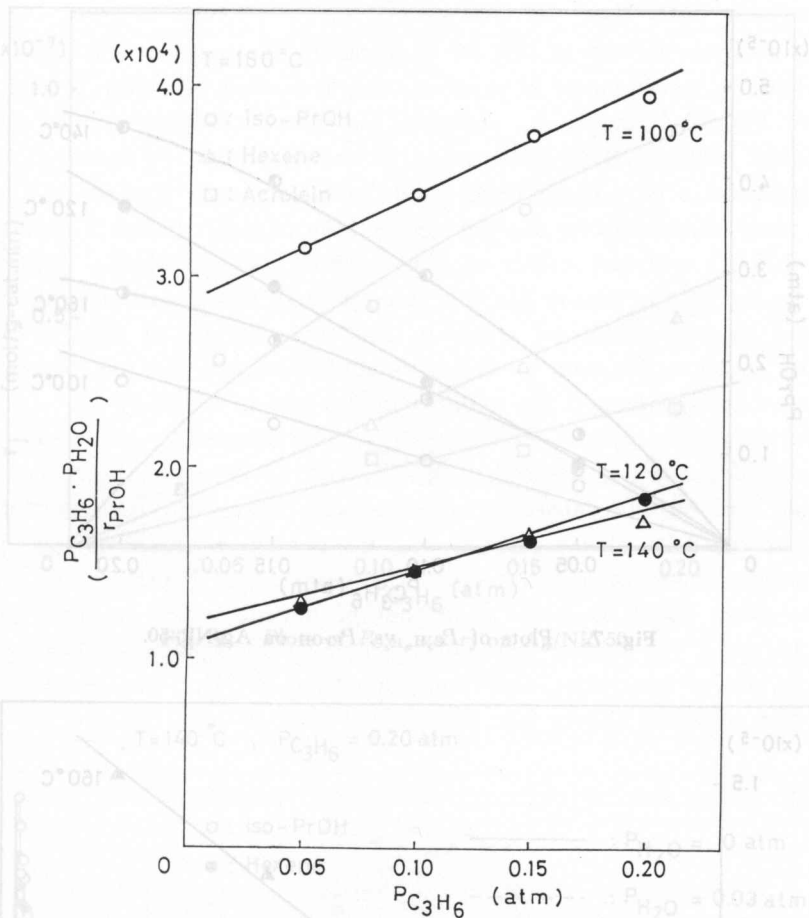
Fig. 6.   Plots of $(P_{C_3H_6} P_{H_2O}/r_{PrOH})$ vs. $P_{C_3H_6}$.

$$B = \frac{1}{k K_{H_2O}} \tag{12}$$

The plots of $P_{C_3H_6} P_{H_2O}/r_{PrOH}$ vs. $P_{C_3H_6}$ give a good straight line as shown in Fig. 6, suggesting the suitability of the rate model proposed.

3-2. Steady State Rate Analysis on Silver Supported NR-50 (Ag/NR-50)

All the reaction rates for the three products are reduced due to supporting sliver ion onto NR-50. The results obtained are presented in Figs. 7 and 8 and the same apparent rate equations as equations (2)～(4) are also expressed. In addition, the activation energies are also 46 for alcohol and 90 kJ/mol for hexene as shown in Fig. 4. These good agreements of the results with NR-50 strongly indicate the same reaction mechanism between NR-50 and Ag/NR-50, even though the number of active sites is reduced on Ag/NR-50 resulting from the adsorption of silver ion on the active sites at temperatures higher than 160°C as shown in Fig. 9.
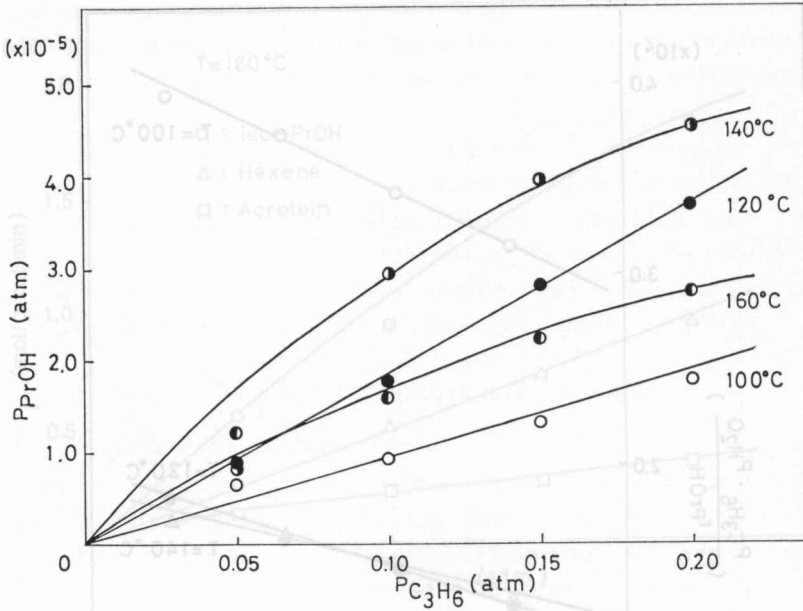
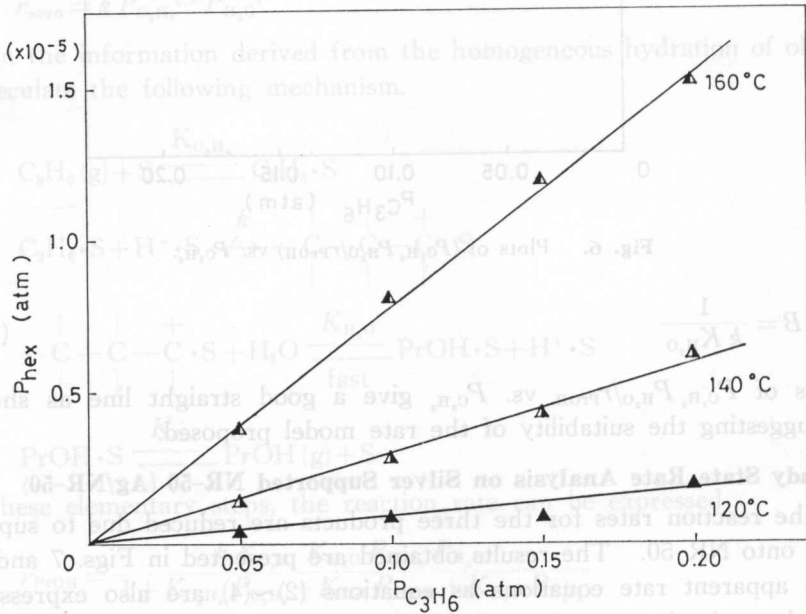**Fig. 7.** Plots of $P_{C_3H_6}$ vs. P_{PrOH} on Ag/NR-50.

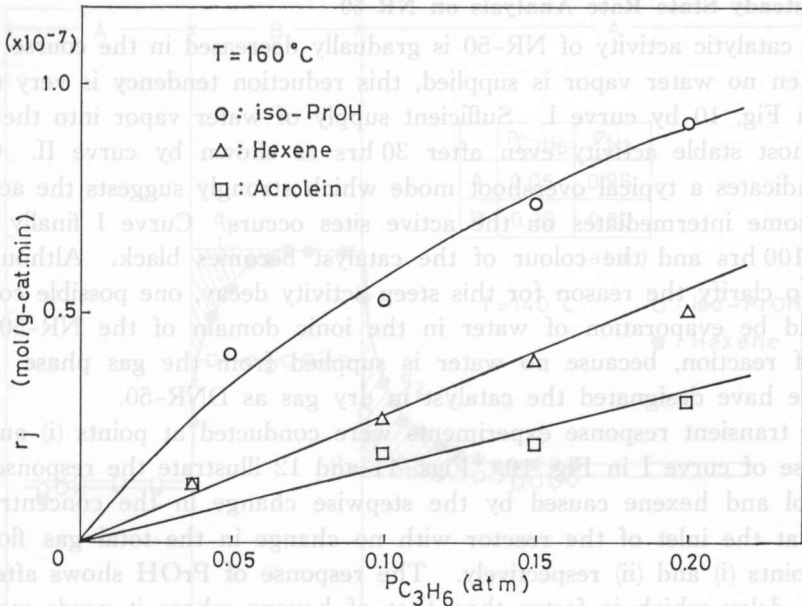**Fig. 8.** Plots of $P_{C_3H_6}$ vs. P_{hex} on Ag/NR-50.

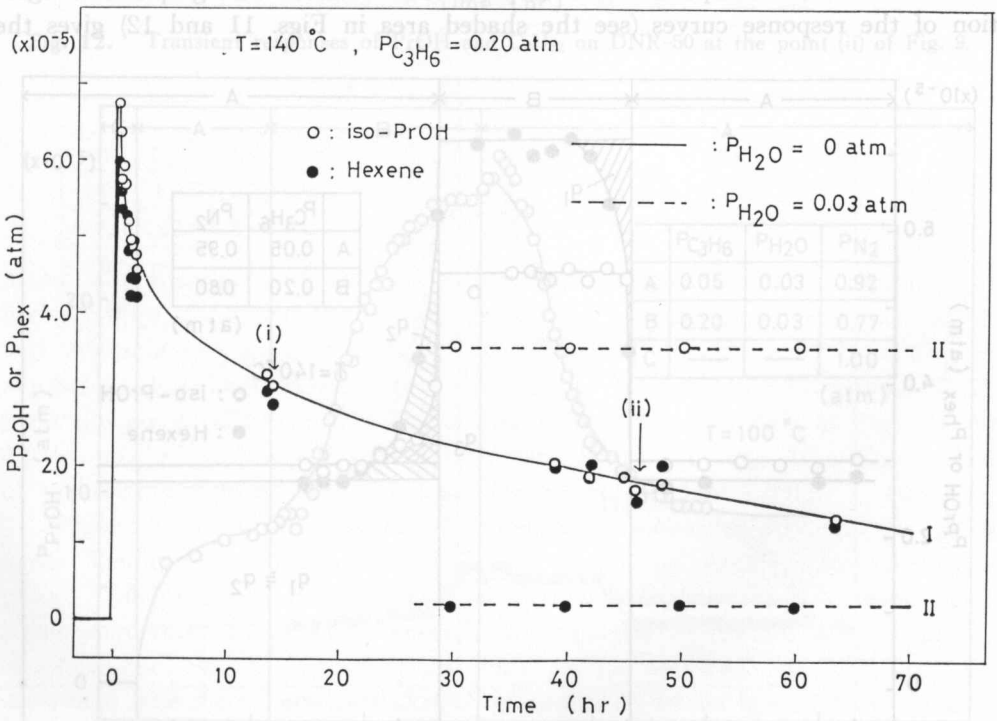**Fig. 9.** Plots of $P_{C_3H_6}$ vs. r_j on Ag/NR-50.

Fig. 10. Activity decay on NR-50.

3-3. Unsteady State Rate Analysis on NR-50

The catalytic activity of NR-50 is gradually decreased in the course of reaction; when no water vapor is supplied, this reduction tendency is very steep as shown in Fig. 10 by curve I. Sufficient supply of water vapor into the reactor gives almost stable activity even after 30 hrs as shown by curve II. Curve I clearly indicates a typical overshoot mode which strongly suggests the accumulation of some intermediates on the active sites occurs. Curve I finally reaches zero in 100 hrs and the colour of the catalyst becomes black. Although it is difficult to clarify the reason for this steep activity decay, one possible consideration could be evaporation of water in the ionic domain of the NR-50 in the course of reaction, because no water is supplied from the gas phase. In this paper, we have designated the catalyst in dry gas as DNR-50.

The transient response experiments were conducted at points (i) and (ii) in the course of curve I in Fig. 10. Figs. 11 and 12 illustrate the response curves of alcohol and hexene caused by the stepwise change in the concentration of propene at the inlet of the reactor with no change in the total gas flow rate, at the points (i) and (ii) respectively. The response of PrOH shows after about a 15 min delay which is faster than that of hexene where it needs more than 40 min to reach the steady state level. The slow response of hexene may be due to its slower adsorption and desorption than PrOH. The graphical integration of the response curves (see the shaded area in Figs. 11 and 12) gives the

Fig. 11.   Transient responses of PrOH and C_6H_{12} on DNR-50 at the point (i) of Fig. 9.

	$P_{C_3H_6}$	P_{N_2}
A	0.05	0.95
B	0.20	0.80

(atm)

$T = 140\,°C$ O : iso-PrOH   ● : Hexene
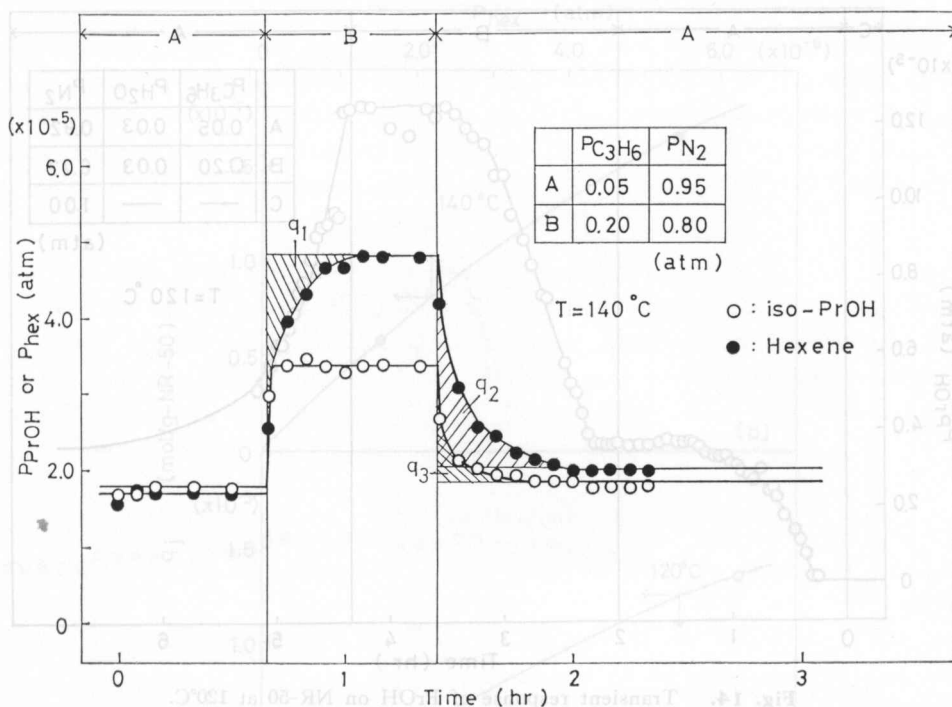
Fig. 12. Transient responses of PrOH and C_6H_{12} on DNR–50 at the point (ii) of Fig. 9.

	$P_{C_3H_6}$	P_{H_2O}	P_{N_2}
A	0.05	0.03	0.92
B	0.20	0.03	0.77
C	—	—	1.00

(atm)
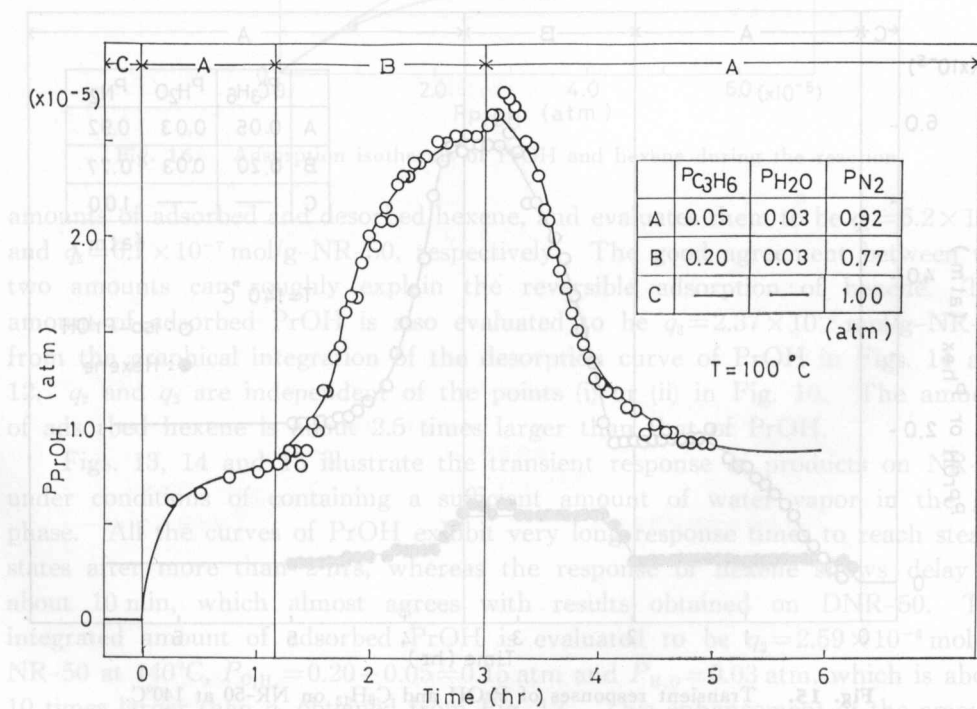
$T = 100\,°C$

Fig. 13. Transient response of PrOH on NR–50 at 100°C.

3-3. Unsteady State Rate Analysis on NR-50

The catalytic activity of NR-50 is gradually decreased in the course of reaction; when no water vapor is supplied, this reduction is ... as shown in Fig. 10 by curve 1. Sufficient supply of water vapor gives almost stable activity even after 50 hrs as shown ... curve 1 clearly indicates a typical overshoot mode which ... the accumulation of some intermediate ... active sites occur. Curve 1 ... approaches zero in 100 hrs and the colour of the catalyst ... black. Although it is difficult to clarify the reason for the steep activity decay, one of the consideration could be evaporation of water in the ionic domain of the NR-50 in the course of reaction, because no water is ... in the gas phase. In this paper, we have designated the catalyst in dry gas as DNR-50.

The transient response experiments were conducted at points (i) and (ii) in the course of ... Figs. 11, 12 and 15 illustrate the response curves of alcohol and hexene caused by the stepwise change in the concentration of propene at the inlet of the reactor with no change in the total gas flow rate, at the point (i) and (ii) respectively. The response of PrOH shows after about a 15 min delay which is faster than that of hexene where it needs more than 40 min to reach the steady state level. The slow response of hexene may be due to its slower adsorption and desorption ... of PrOH. The graphical integration of the response curves (see the shaded area in Figs. 11 and 12) gives the ...
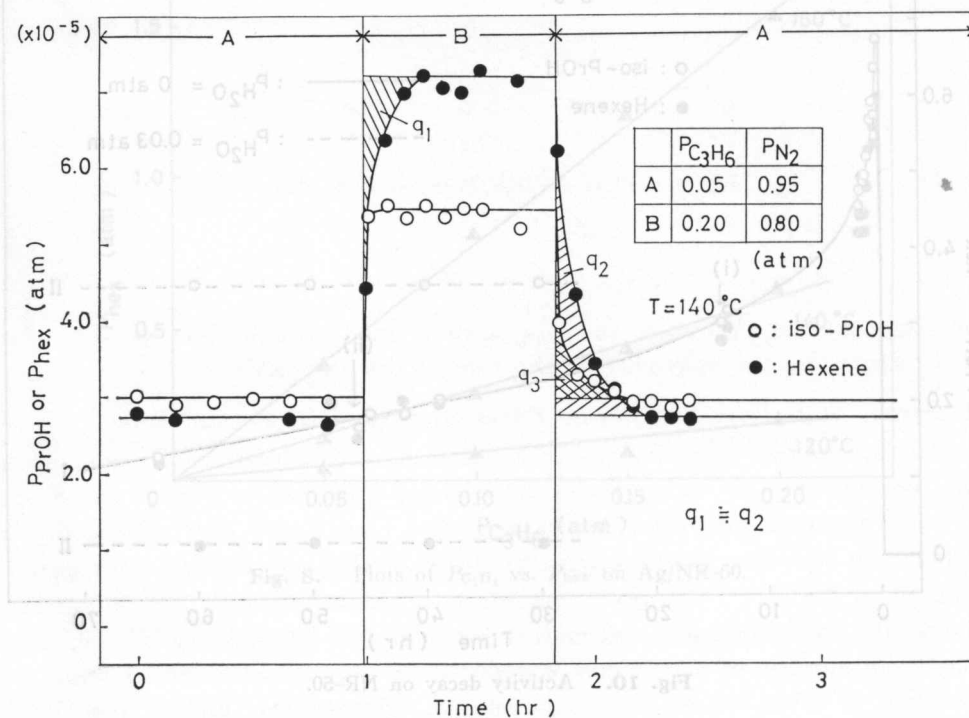

Fig. 14. Transient response of PrOH on NR-50 at 120°C.

	$P_{C_3H_6}$	P_{H_2O}	P_{N_2}
A	0.05	0.03	0.92
B	0.20	0.03	0.77
C	—	—	1.00

(atm)

T = 120 °C
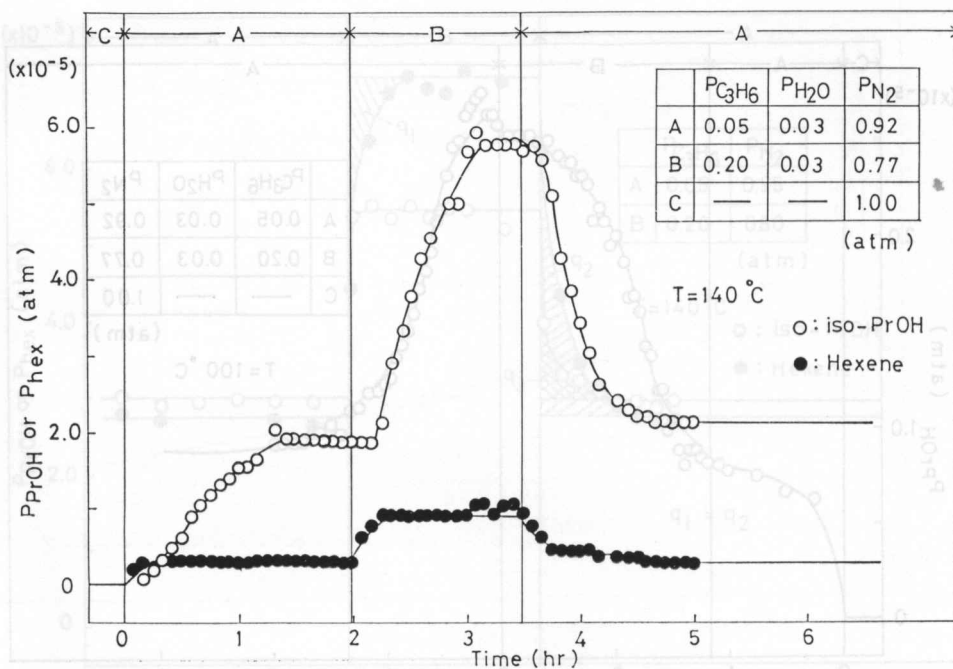
Fig. 15. Transient responses of PrOH and C_6H_{12} on NR-50 at 140°C.

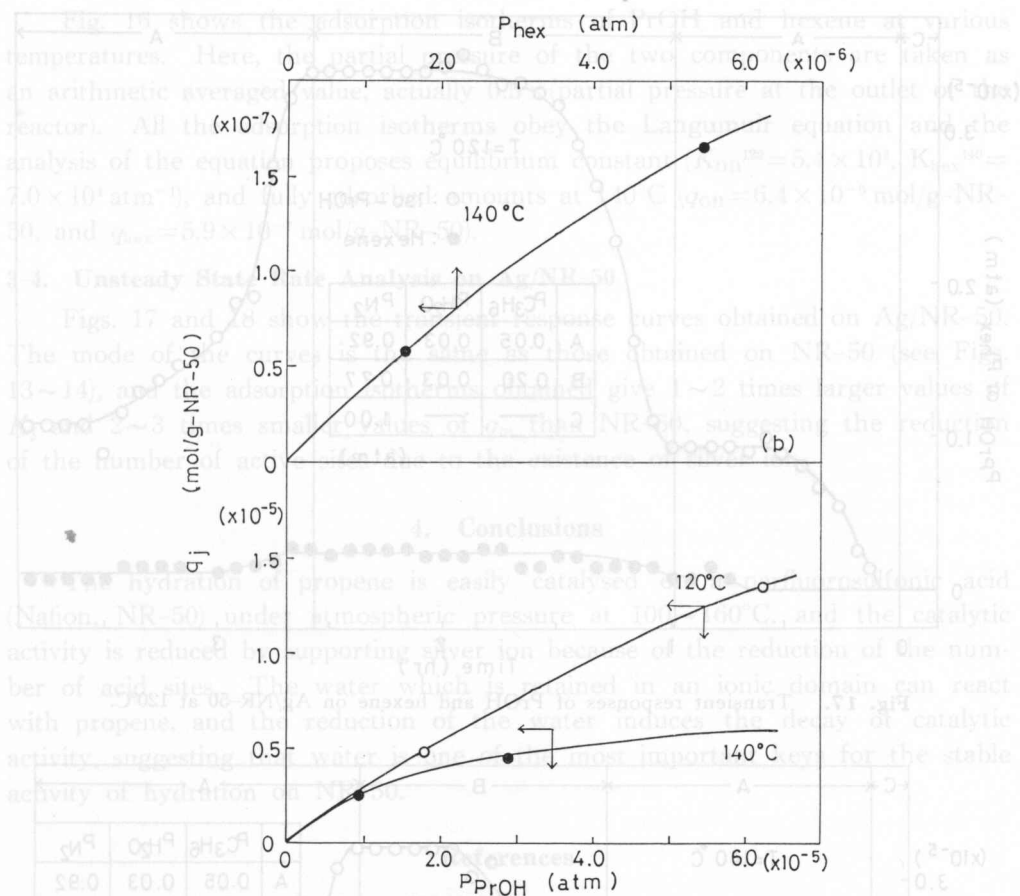|	$P_{C_3H_6}$	P_{H_2O}	P_{N_2}
A	0.05	0.03	0.92
B	0.20	0.03	0.77
C	—	—	1.00

(atm)

T = 140 °C

○ : iso-PrOH
● : Hexene

Fig. 16. Adsorption isotherms of PrOH and hexene during the reaction.

amounts of adsorbed and desorbed hexene, and evaluates them to be $q_1=6.2\times10^{-7}$ and $q_2=6.7\times10^{-7}$ mol/g–NR-50, respectively. The good agreement between the two amounts can roughly explain the reversible adsorption of hexene. The amount of adsorbed PrOH is also evaluated to be $q_3=2.37\times10^{-7}$ mol/g–NR-50 from the graphical integration of the desorption curve of PrOH in Figs. 11 and 12. q_2 and q_3 are independent of the points (i) or (ii) in Fig. 10. The amount of adsorbed hexene is about 2.5 times larger than that of PrOH.

Figs. 13, 14 and 15 illustrate the transient response of products on NR-50 under conditions of containing a sufficient amount of water vapor in the gas phase. All the curves of PrOH exhibit very long response times to reach steady states after more than 2 hrs, whereas the response of hexene shows delay in about 10 min, which almost agrees with results obtained on DNR-50. The integrated amount of adsorbed PrOH is evaluated to be $q_3=2.59\times10^{-6}$ mol/g–NR-50 at 140°C, $P_{C_3H_6}=0.20-0.05=0.15$ atm and $P_{H_2O}=0.03$ atm, which is about 10 times larger than q_3 obtained from Fig. 12. This enhancement of the amount adsorbed may result from PrOH dissolved into water in NR-50.
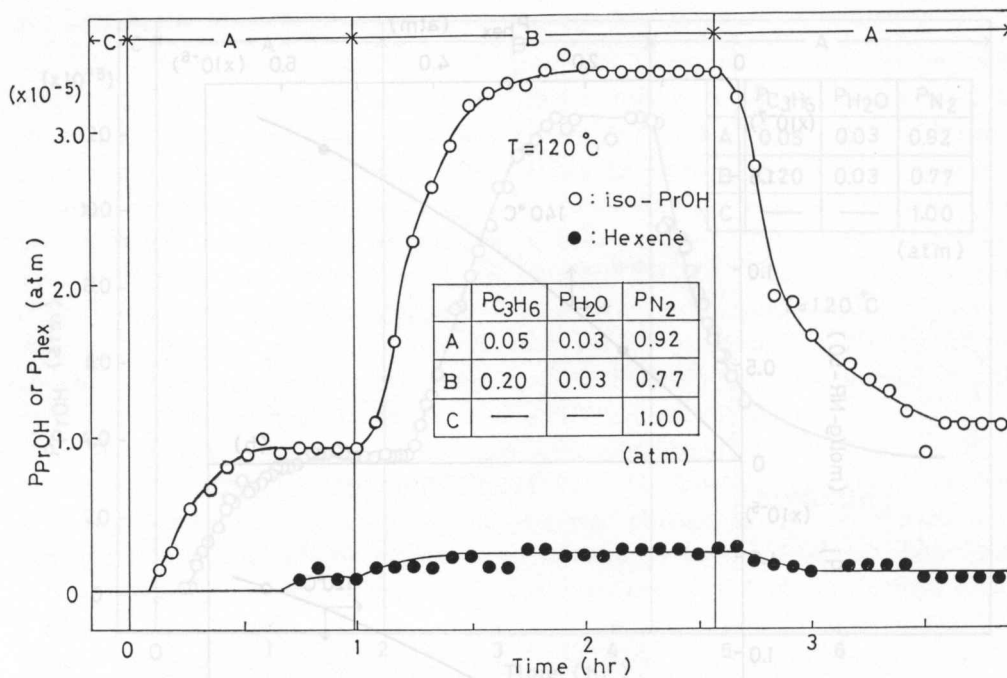
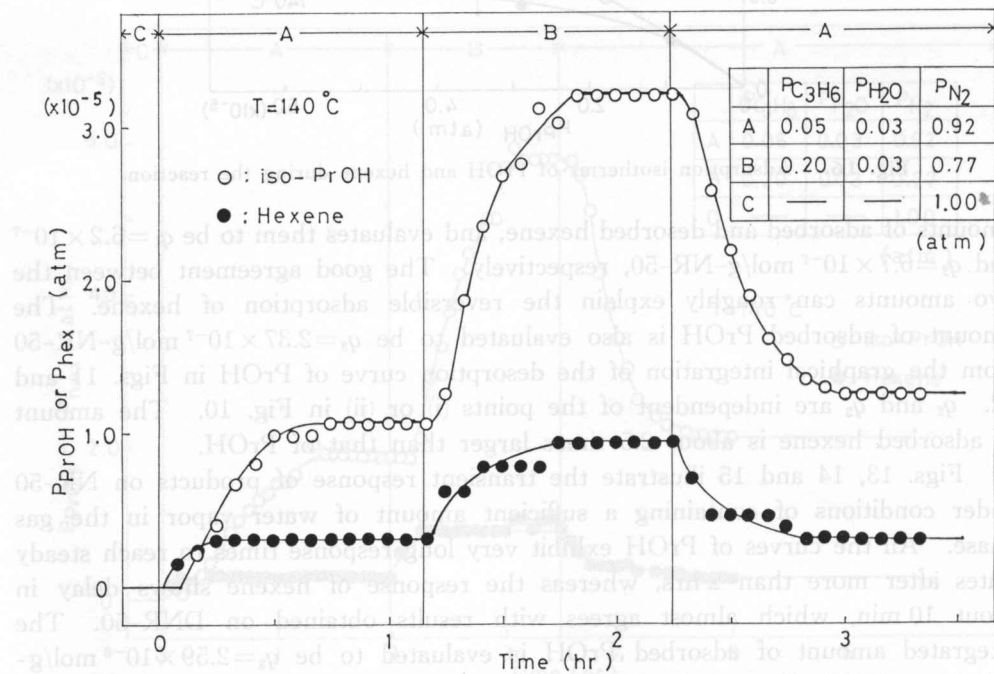**Fig. 17.** Transient responses of PrOH and hexene on Ag/NR-50 at 120°C.

Table (Fig. 17):

	$P_{C_3H_6}$	P_{H_2O}	P_{N_2}
A	0.05	0.03	0.92
B	0.20	0.03	0.77
C	—	—	1.00

(atm)

Fig. 18. Transient responses of PrOH and hexene on Ag/NR-50 at 140°C.

Table (Fig. 18):

	$P_{C_3H_6}$	P_{H_2O}	P_{N_2}
A	0.05	0.03	0.92
B	0.20	0.03	0.77
C	—	—	1.00

(atm)

Fig. 16 shows the adsorption isotherms of PrOH and hexene at various temperatures. Here, the partial pressure of the two components are taken as an arithmetic averaged value, actually $0.5 \times$(partial pressure at the outlet of the reactor). All the adsorption isotherms obey the Langumuir equation and the analysis of the equation proposes equilibrium constant ($K_{OH}^{120}=5.4 \times 10^3$, $K_{hex}^{140}=7.0 \times 10^4$ atm^{-1}), and fully adsorbed amounts at 140°C ($q_{OH}=6.4 \times 10^{-6}$ mol/g-NR-50, and $q_{hex}=5.9 \times 10^{-7}$ mol/g-NR-50).

3-4. Unsteady State Rate Analysis on Ag/NR-50

Figs. 17 and 18 show the transient response curves obtained on Ag/NR-50. The mode of the curves is the same as those obtained on NR-50 (see Figs. $13 \sim 14$), and the adsorption isotherms obtained give $1 \sim 2$ times larger values of K_j and $2 \sim 3$ times smaller values of q_m than NR-50, suggesting the reduction of the number of active sites due to the existence of silver ion.

4. Conclusions

The hydration of propene is easily catalysed on a perfluorosulfonic acid (Nafion, NR-50) under atmospheric pressure at $100 \sim 160$°C, and the catalytic activity is reduced by supporting silver ion because of the reduction of the number of acid sites. The water which is retained in an ionic domain can react with propene, and the reduction of the water induces the decay of catalytic activity, suggesting that water is one of the most important keys for the stable activity of hydration on NR-50.

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