

## Evaluation of Hydrogen Spillover in Diffusion Processes\*

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### Abstract

The contribution of the spillover of hydrogen adsorbed on a silica gel supported platinum catalyst to gas phase mass transport has been studied under atmospheric pressure at 30~300°C. The amount of spillover hydrogen was evaluated by the hydrogenation of ethylene, and the spillover hydrogen was characterised by the temperature programmed desorption spectrum. The spillover of hydrogen from platinum to the SiO<sub>2</sub> surface enhanced gas phase diffusion more than 60% at 90°C. The higher percentage of platinum supported on SiO<sub>2</sub> increased the temperature dependency of the diffusion coefficient.

### 1. Introduction

The spillover has been designated as the transport of a species adsorbed on one surface to another, for example, hydrogen adsorbed on platinum moves onto an oxide or carbon support. As has been demonstrated by a large number of investigators,<sup>1-7)</sup> hydrogen spillover is a well-documented phenomenon which occurs with a variety of metals and supports. In addition, the activity and reactivity of hydrogen atoms formed is strongly influenced by the kind of metals and the situation of metals such as the percentage exposed, particle diameter, and the stereo structure of metals standing on supports.

In the spillover process, one may consider the following steps as (1) dissociative adsorption of hydrogen on metals, (2) surface diffusion of hydrogen atoms from a specified area to others on metals, (3) transfer of hydrogen atoms from the specified surface of metals to the area of support such as localized surface hydroxyl groups, (4) surface diffusion of hydrogen on supports, and (5) recombination of hydrogen atoms forming gaseous hydrogen molecules (desorption of H<sub>2</sub>). Most prior calculations of the diffusion coefficient for spillover hydrogen were done by indirectly volumetric adsorption studies.<sup>8-12)</sup> Moreover, the authors concluded that the migration on the surface was the rate-determining step (step (2)) in contrast with other results, in which the spillover process was rate-controlling (step (3)). As a result, the estimated values varied from 10<sup>-3</sup> to 10<sup>-14</sup> cm<sup>2</sup>/s, indicating wide spread.

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In the present study, our interest is focused on the contribution of the spillover of hydrogen to gas phase diffusion. The objectives are: (1) to develop an experimental procedure for measuring the diffusion and the spillover, and (2) to examine the contribution of spillover to gas phase diffusion, (3) the effect of the particle size of metals on the spillover and (4) the reactivity of the spillover hydrogen. For the experimental procedure, the transient response method (TRM),<sup>13-15)</sup> temperature programmed desorption (TPD),<sup>16)</sup> and temperature programmed reaction (TPR)<sup>16)</sup>, are applied.

## 2. Experimental Procedure

### (1) Materials

The granular silica gel support was Davison Grade 62 which had a BET surface area of 285 m<sup>2</sup>/g, pore volume of 1.2 cm<sup>3</sup>/g and average pore diameter of 140 Å. The resulting solid mass was crushed and sieved and the 0.13 to 0.15 mm diameter fraction was chosen for the support. The detailed procedure to prepare the catalyst was almost the same as our previous work<sup>17-19)</sup> and the work of Professor Burwell's school.<sup>20-22)</sup> An incipient wetness method was used to prepare the samples as shown in Table 1. The support for each sample was slowly rotated in a flask at a temperature of 80°C. Aqueous H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O of desired concentration was dropped onto the support. The samples obtained thus were evaporated and dried in air at 100°C. Each sample was calcined in air at 290~350°C for 3.5~4 hr and then in H<sub>2</sub> at 80~205°C for 2~3 hr. The Pt content of each sample was presumed to be equal to the dropped amount without conducting a separate chemical analysis. The amount of Pt loaded was in the range 0.8~2.0 wt%. The population of metal atoms exposed to the surface was evaluated by the chemisorption of hydrogen (designate D<sub>h</sub>) or the inverse titration due to oxygen (designate D<sub>o</sub>). It was characterised as D<sub>o</sub>=0.59, 1.6, 2.0, 2.1, 2.2, 9.5 and 9.9% and D<sub>h</sub>=7%.

Table 1. Characterization of Pt/SiO<sub>2</sub>

D <sub>o</sub> (%)	Pt/SiO <sub>2</sub> (wt %)	Calcination		Reduction	
		Temp. (°C)	Time (hr)	Temp. (°C)	Time (hr)
0.59	1.43	300	4	205	2
1.6	1.6	300	4	205	2
2.0	2.0	300	4	205	2
2.1	1.43	350	3.5	205	2
2.2	0.8	300	4	205	2
9.5	2.0	290	4	200	2.5
9.9	2.0	340	4	200	2
D <sub>h</sub> =7%	1.5	293	4	80°C (1 hr)+205°C (2 hr)	

### (2) Temperature-Programmed Desorption (TPD) Spectra

The TPD measurements were carried out in a flow system similar to ones reported in our previous papers.<sup>23-26</sup> The temperature of the sample was programmed to rise at a constant rate of 2, 4, 5°C/min, and the amount of the H<sub>2</sub> uptake during the reduction was measured by a gas chromatograph.

### (3) Diffusion Cell

The diffusion cell was made of Pyrex glass as shown in Fig. 1, which was the same as in our previous work.<sup>24,27</sup> A stainless steel mesh (400 mesh) was set at each end of the catalyst bed and about 0.6 g of the catalyst was mounted between the two meshes as a diffusion diaphragm. The top mesh was pressed down by a stainless steel spring so as to keep constant void fraction of the catalyst diaphragm. The length of catalyst bed was 1.8~2.6 cm.

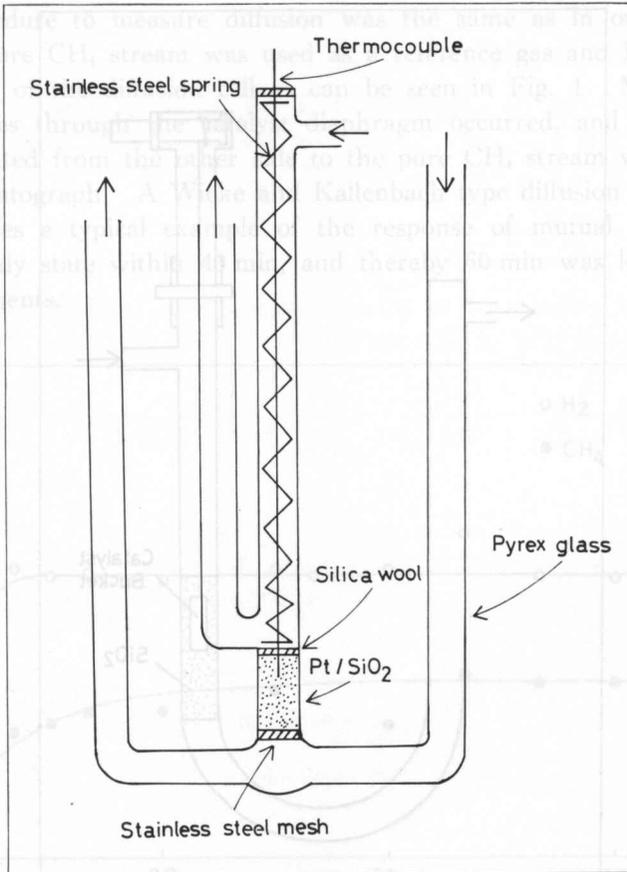
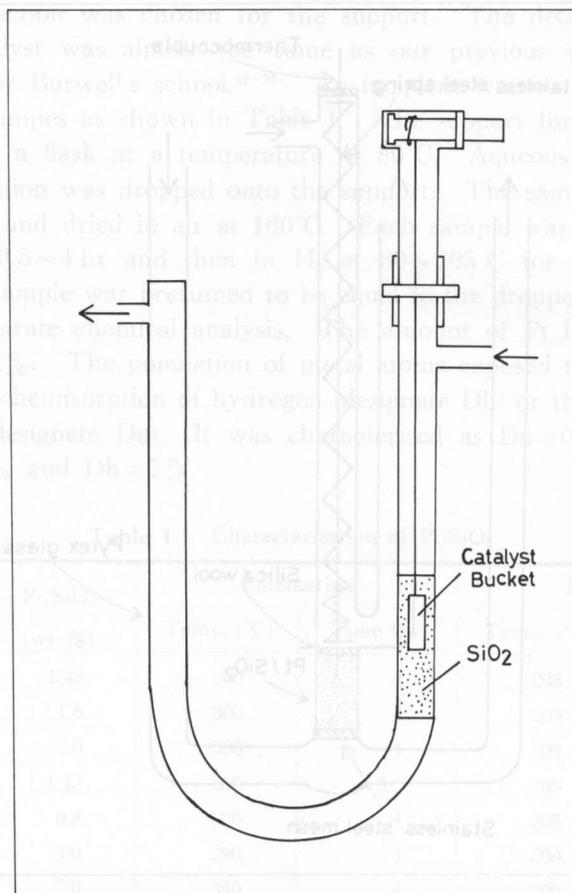


Fig. 1. Depiction of the diffusion cell used to evaluate the mutual diffusion of gases.

#### (4) Apparatus to Evaluate the Amount of Hydrogen Spillover

The experimental system is shown schematically in Fig. 2, and it is similar to the reactor used by Lenz and Conner.<sup>1,2)</sup> A stainless steel mesh bucket, which is filled with the supported platinum catalyst, can be lowered by a winch mechanism from the upper compartment (whose volume is approximately 20 cm<sup>3</sup>) into the lower compartment (whose volume is approximately 80 cm<sup>3</sup>). The silica support which is the spillover acceptor is packed into the lower compartment. After hydrogen atoms transferred from the platinum catalyst are spread onto the silica support in the given conditions, the bucket is lifted and the stopcock closed; the activated silicagel is effectively isolated from the supported platinum by using a stopcock to cut off the path which is located between upper compartment and lower one. The reactor and the inlet and outlet arms are surrounded by an insulated furnace capable of achieving temperatures up to 300°C. The gas



**Fig. 2.** Depiction of the reactor used to activate the silica (in contact with the lowered Pt containing bucket), and then to remove and isolate the bucket from the reaction system (by raising the bucket and closing the upper stopcock).

chromatograph used was a Hitachi 164, and the column for separation of ethylene/ethane was Porapak S of 80/100 mesh and 1 m in length at 32°C.

The activation procedure for the silica gel containing the bucket consisted of two steps: (1) elevating temperature up to the desired temperature (100~300°C) in a pure He stream (40 cm<sup>3</sup>/min) and (2) the pure He stream was switched into a H<sub>2</sub> stream (40 cm<sup>3</sup>/min) at the given temperature and kept in the same stream for the given time. After the procedure, the bucket was lifted into the upper compartment in the H<sub>2</sub> stream and isolated from the lower compartment by the cock. The H<sub>2</sub> stream was changed into an ethylene stream in a stepwise fashion. The ethane formed was analysed by two gas chromatographs as continuously as possible, and many syringes (1 cm<sup>3</sup>) were prepared to store the sampling gases at various elapsed times to follow the response of ethane as continuously as possible.

### (5) Diffusion Measurement

The procedure to measure diffusion was the same as in our previous papers.<sup>26,27</sup> A pure CH<sub>4</sub> stream was used as a reference gas and H<sub>2</sub> was fed into the upper side of the diffusion cell as can be seen in Fig. 1. Mutual diffusion from both sides through the catalyst diaphragm occurred, and the amount of H<sub>2</sub> gas permeated from the other side to the pure CH<sub>4</sub> stream was analysed by the gas chromatograph. A Wicke and Kallenbach type diffusion cell<sup>28</sup> was used. Fig. 3 illustrates a typical example of the response of mutual diffusion which reached a steady state within 40 min, and thereby 60 min was long enough for all the experiments.

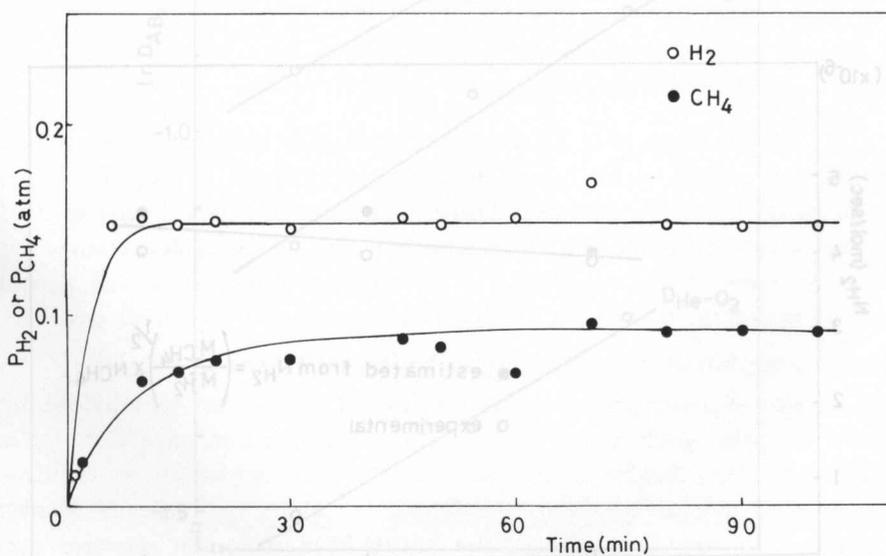


Fig. 3. Variation of the concentration of H<sub>2</sub> and CH<sub>4</sub> on both sides of the sample diaphragm in time on stream.

### 3. Experimental Results and Discussion

#### 3-1. Diffusivity from the Wicke-Kallenbach Type Measurements

The effective binary diffusion fluxes measured with the Wicke-Kallenbach technique at temperatures from 30 to 90°C are presented in Fig. 4, and compared to the theoretical values which were calculated from Eq. (1).

$$N_{A \text{ in } B} = N_{B \text{ in } A} (M_B/M_A)^{1/2} \quad (1)$$

where  $N_{A \text{ in } B}$ ,  $N_{B \text{ in } A}$  and  $M_A$ ,  $M_B$  are the flux of moles of diffusion components  $A$  and  $B$  and the molecular weights of  $A$  and  $B$ , respectively. The deviation of experimental data from theoretical ones is less than 20%. This is very important; the following equation (2) can be adopted to evaluate the diffusivities, based on Fick's first law, because the diffusivities calculated from the flux measurements based on Fick's law have been obtained<sup>29</sup>. Eq. (2) is used to evaluate the effective diffusivity.

$$N_{A \text{ in } B} = -D_{eA}(S/L)(C_{AV_2} - C_{AV_1}) \quad (2)$$

where  $D_{eA}$  is the effective diffusivity of  $A$  gas,  $S$  is the diffusion area,  $L$  is the diffusion length and  $C_{AV_1}$  and  $C_{AV_2}$  are the concentration of  $A$  gas on both sides. Using  $C_{AV_1} = (P/RT) y_{AV_1}$  and  $C_{AV_2} = (P/RT) y_{AV_2}$ , Eq. (2) is rewritten as

$$D_{eA} = \frac{LRN_{A \text{ in } B} T}{SP(y_{AV_1} - y_{AV_2})} \quad (3)$$

where  $R$  is gas constant,  $P$  is total pressure,  $T$  is temperature and  $y_{AV_1}$  and  $y_{AV_2}$  are mole fraction of  $A$  in both sides.

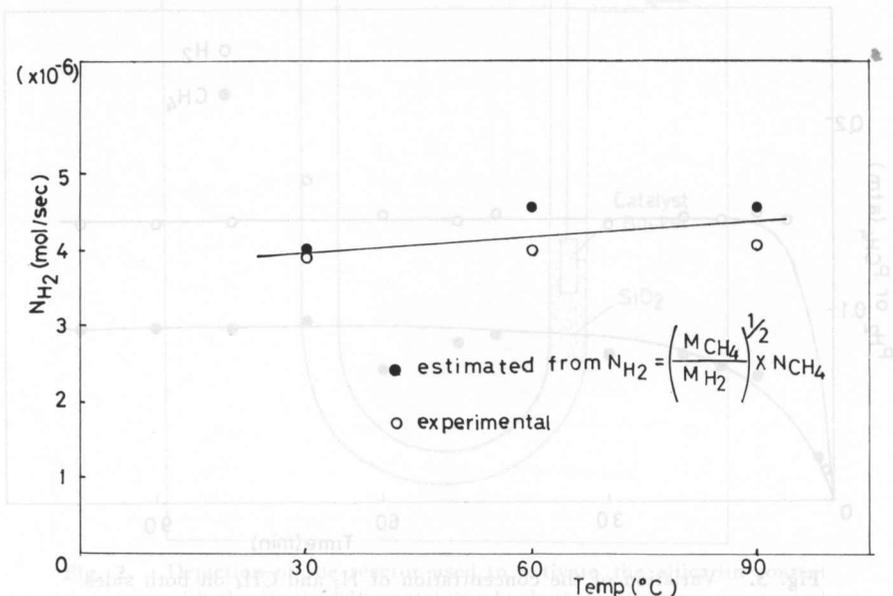


Fig. 4. Comparison of the diffusion rates of  $H_2$  in  $CH_4$  between experimental and theoretical, using Eq. (1).

The temperature dependence of the macropore diffusion is nearly  $T^{3/2}$  based on the Lennard-Jones potential and ideal gas law as follows<sup>30</sup>.

$$D_{AB} = \frac{0.001858 T^{3/2} [(M_A + M_B) / M_A M_B]^{1/2}}{\pi \sigma_{AB}^2 \Omega_D} \quad (4)$$

where  $D_{AB}$  is diffusion coefficient of  $A$  into  $B$  gas ( $\text{cm}^2/\text{sec}$ ),  $M_A$  and  $M_B$  are the molecular weights of  $A$  and  $B$ -gases ( $\text{g}/\text{mole}$ ),  $T$  is temperature ( $^\circ\text{K}$ ),  $\pi$  is total pressure ( $\text{atm}$ ),  $\sigma_{AB}$  is the force constant ( $\text{\AA}$ ), and  $\Omega_D$  is the collision integral which is a function of  $kT/\epsilon_{AB}(-)$ , and  $\epsilon_{AB}$  is the Lennard-Jones potential ( $J$ ). Eq. (4) can be rewritten as follows.

$$\ln D_{AB} = 3/2 \ln T + \ln \left[ \frac{0.001858 [(M_A + M_B) / M_A M_B]^{1/2}}{\pi \sigma_{AB}^2 \Omega_D} \right] \quad (5)$$

The diffusion coefficients for  $\text{H}_2\text{-CH}_4$  ( $D_{\text{H}_2\text{-CH}_4}$ ),  $\text{He-N}_2$  ( $D_{\text{He-N}_2}$ ) and  $\text{He-O}_2$  ( $D_{\text{He-O}_2}$ ) systems on silica gel are measured as a function of temperature, and the results obtained are shown in Fig. 5. The slope of the straight lines gives 1.4

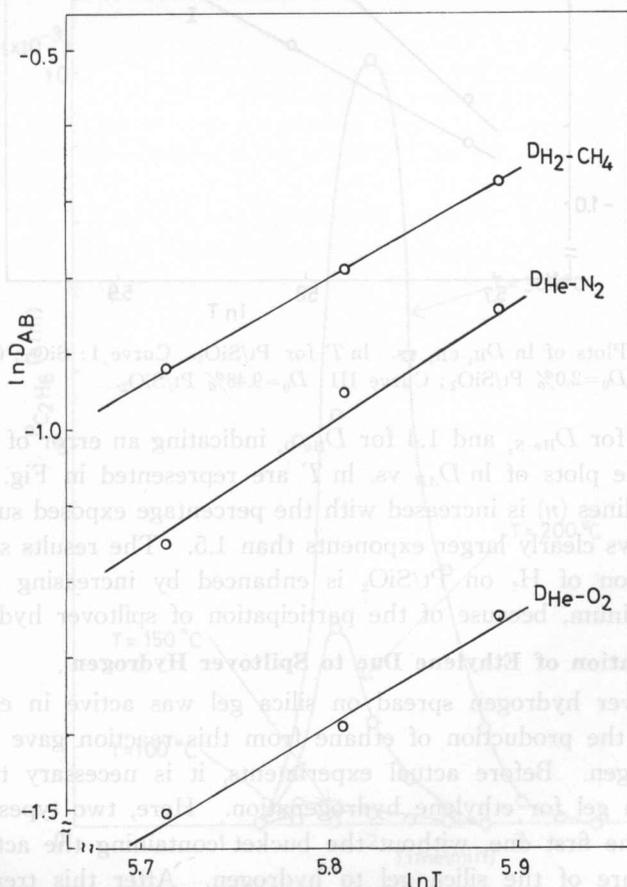


Fig. 5. Plots of  $D_{AB}$  vs.  $\ln T$  for  $\text{SiO}_2$ .  $D_{AB}$  is the diffusion coefficient of  $A$  in  $B$ -gas, and  $T$  is diffusion temperature ( $^\circ\text{K}$ ).

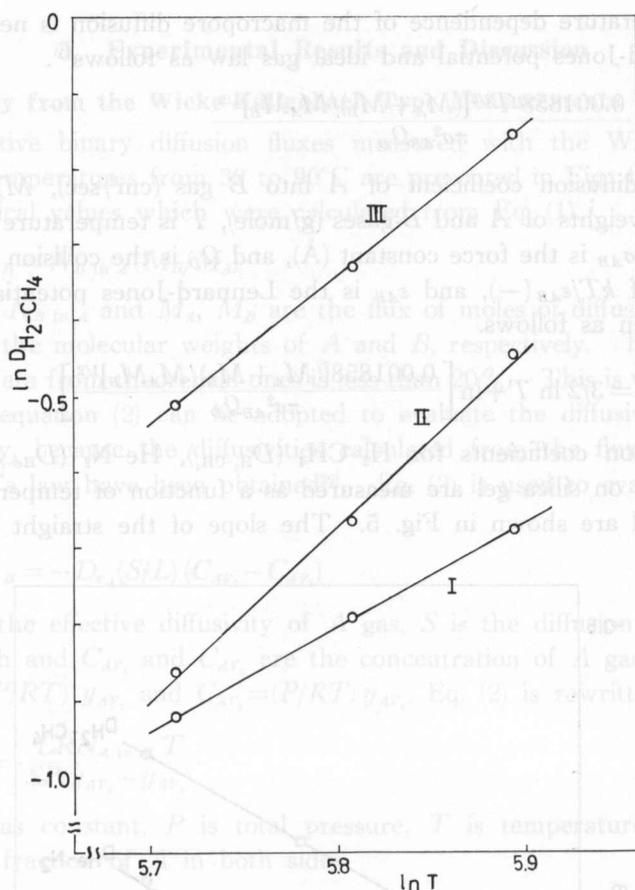


Fig. 6. Plots of  $\ln D_{\text{H}_2\text{-CH}_4}$  vs.  $\ln T$  for Pt/SiO<sub>2</sub>. Curve I: SiO<sub>2</sub>; Curve II:  $D_0=2.0\%$  Pt/SiO<sub>2</sub>; Curve III:  $D_0=9.48\%$  Pt/SiO<sub>2</sub>.

for  $D_{\text{H}_2\text{-CH}_4}$ , 1.6 for  $D_{\text{He-N}_2}$  and 1.4 for  $D_{\text{He-O}_2}$  indicating an error of less than 20%. For Pt/SiO<sub>2</sub>, the plots of  $\ln D_{AB}$  vs.  $\ln T$  are represented in Fig. 6. The slope of the straight lines ( $n$ ) is increased with the percentage exposed such as  $n=1.9-2.3$ , which shows clearly larger exponents than 1.5. The results strongly suggest that the diffusion of H<sub>2</sub> on Pt/SiO<sub>2</sub> is enhanced by increasing the percentage exposed of platinum, because of the participation of spillover hydrogen.

### 3-2. Hydrogenation of Ethylene Due to Spillover Hydrogen

The spillover hydrogen spread on silica gel was active in ethylene hydrogenation,<sup>2)</sup> and the production of ethane from this reaction gave the amount of spillover hydrogen. Before actual experiments, it is necessary to evaluate the activity of silica gel for ethylene hydrogenation. Here, two types of blank runs were done. The first one, without the bucket containing the activator present, involved exposure of the silica gel to hydrogen. After this treatment no hydrogenation of ethylene was evident indicating no reactivity of the silica gel. For the second type of blank run, the stainless steel bucket without the activator

was immersed in the silica gel bed and was exposed to the  $H_2$  stream for 2 hr at  $200^\circ C$ . The bucket was lifted and put in the upper compartment, and then ethylene was introduced into the lower compartment. No hydrogenation of ethylene was evident either. Finally, one may conclude that the silica gel and the stainless steel bucket are not active in the hydrogenation of ethylene without the participation of an activator (platinum metal).

Fig. 7 illustrates typical examples of the spectra of ethane production due to spillover hydrogen on silica gel at various temperatures. The graphical integration of the spectra gives the amount of spillover hydrogen. The amount of spillover hydrogen ( $q_{H_2}$ ) is dependent on the contact time with  $H_2$  as shown in Fig. 8. One may recognize  $q_{H_2}$  reaches a steady state within 90 min. All the values of spillover were, therefore, measured at 120 min.  $q_{H_2}$  is strongly influenced by the spillover temperature as shown in Fig. 9, indicating strong activation of hydrogen spillover onto the silica gel.

The extrapolation of the linear plots of  $\ln q_{H_2}$  vs.  $\ln 1/T$  using the data

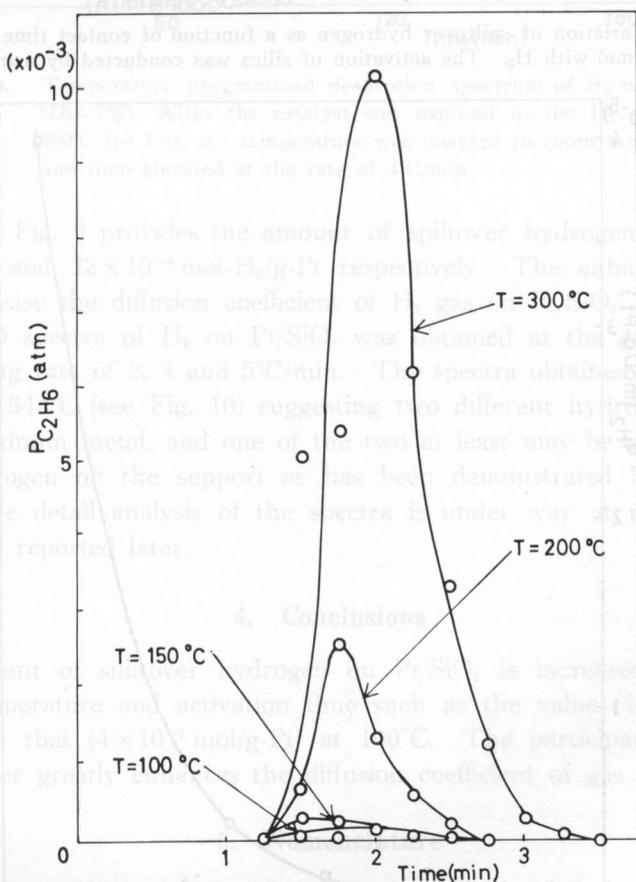


Fig. 7. Ethane production spectra due to the reaction between ethylene and spillover hydrogen on silica. The activation of silica was done by using Pt-plate.

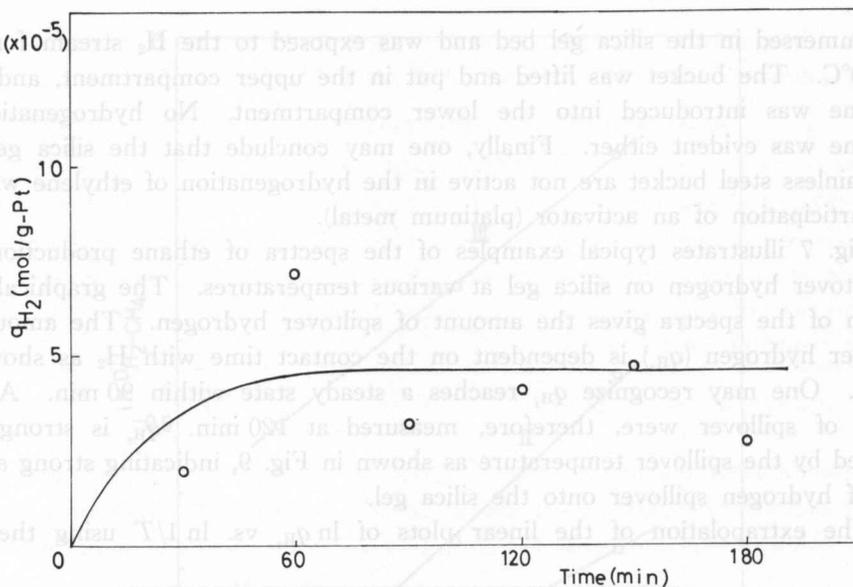


Fig. 8. Variation of spillover hydrogen as a function of contact time (activation time) with  $H_2$ . The activation of silica was conducted by using Pt-plate.

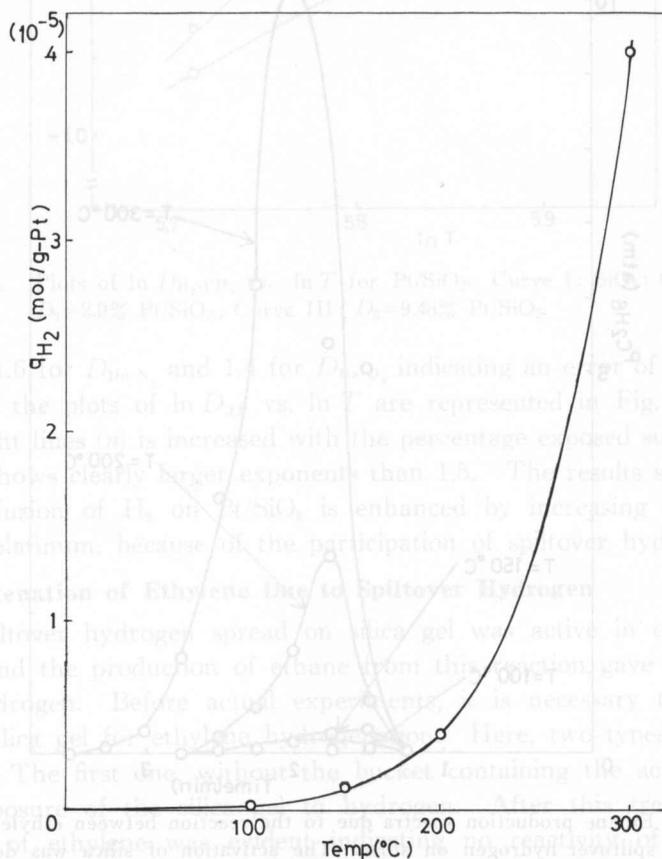


Fig. 9. The amount of spillover hydrogen as a function of temperature. The activation of silica was conducted by using a Pt-plate.

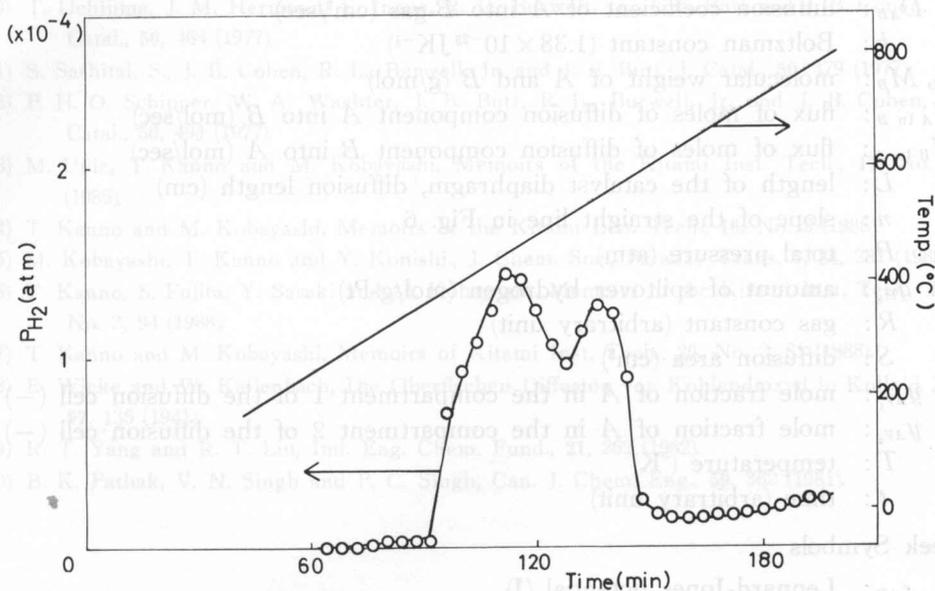


Fig. 10. Temperature programmed desorption spectrum of  $H_2$  on  $Pt/SiO_2$  ( $D_h=7\%$ ). After the catalyst was exposed to the  $H_2$  stream at  $200^\circ C$  for 1 hr, the temperature was lowered to room temperature and then elevated at the rate of  $4^\circ C/min$ .

represented in Fig. 9 provides the amount of spillover hydrogen at 30, 60 and  $90^\circ C$  as 2, 9 and  $32 \times 10^{-8}$  mol- $H_2/g$ -Pt respectively. The enhancement of  $q_{H_2}$  works to increase the diffusion coefficient of  $H_2$  gas on  $Pt/SiO_2$ .

The TPD spectra of  $H_2$  on  $Pt/SiO_2$  was obtained at the range  $50 \sim 800^\circ C$  and the heating rate of 2, 4 and  $5^\circ C/min$ . The spectra obtained gave two peaks at  $447^\circ C$  and  $544^\circ C$  (see Fig. 10) suggesting two different hydrogen species adsorbed on platinum metal, and one of the two at least may be attributed to the spillover hydrogen on the support as has been demonstrated by Kræmer and Andre<sup>8</sup>. More detail analysis of the spectra is under way at present and the results will be reported later.

#### 4. Conclusions

The amount of spillover hydrogen on  $Pt/SiO_2$  is increased ten times by activation temperature and activation time such as the value ( $4 \times 10^{-6}$  mol/g-Pt) at  $200^\circ C$  than that ( $4 \times 10^{-7}$  mol/g-Pt) at  $100^\circ C$ . The participation of the hydrogen spillover greatly enhances the diffusion coefficient of gas.

#### 5. Nomenclature

- $C_{AF_1}$ : concentration of A in compartment 1 of the diffusion cell (mol/cm<sup>3</sup>)
- $C_{AF_2}$ : concentration of A in compartment 2 of the diffusion cell (mol/cm<sup>3</sup>)
- $De_A$ : effective diffusivity of A (cm<sup>2</sup>/sec)

- $D_{AB}$ : diffusion coefficient of  $A$  into  $B$ -gas ( $\text{cm}^2/\text{sec}$ )  
 $k$ : Boltzman constant ( $1.38 \times 10^{-23} \text{JK}^{-1}$ )  
 $M_A, M_B$ : molecular weight of  $A$  and  $B$  ( $\text{g/mol}$ )  
 $N_{A \text{ in } B}$ : flux of moles of diffusion component  $A$  into  $B$  ( $\text{mol/sec}$ )  
 $N_{B \text{ in } A}$ : flux of moles of diffusion component  $B$  into  $A$  ( $\text{mol/sec}$ )  
 $L$ : length of the catalyst diaphragm, diffusion length ( $\text{cm}$ )  
 $n$ : slope of the straight line in Fig. 6  
 $P$ : total pressure ( $\text{atm}$ )  
 $q_{\text{H}_2}$ : amount of spillover hydrogen ( $\text{mol/g-Pt}$ )  
 $R$ : gas constant (arbitrary unit)  
 $S$ : diffusion area ( $\text{cm}^2$ )  
 $y_{AV_1}$ : mole fraction of  $A$  in the compartment 1 of the diffusion cell ( $-$ )  
 $y_{AV_2}$ : mole fraction of  $A$  in the compartment 2 of the diffusion cell ( $-$ )  
 $T$ : temperature ( $^\circ\text{K}$ )  
 $t$ : time (arbitrary unit)

#### Greek Symbols

- $\varepsilon_{AB}$ : Lennard-Jones potential ( $\text{J}$ )  
 $\pi$ : total pressure ( $\text{atm}$ )  
 $\sigma_{AB}$ : force constant ( $\text{\AA}$ )  
 $\Omega_D$ : the "collision integral", a function of  $kT/\varepsilon_{AB}$  ( $-$ )

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## Introduction

In the immobilized enzyme or microbial reactor system, a large number of reactor types has been used such as a backmix reactor, fixed bed, fluidized bed, trickle bed and suspension bubble tower reactor<sup>1-6</sup>. For these reactors, the operating conditions should be chosen to maximize the amount of product while minimizing the undesired products and without bacteria infection. In the heterogeneous catalytic reaction using solid catalysis and immobilized biocatalysts, the reactor has operated under steady state conditions with a constant flow rate, temperature, pressure, and reactant composition, because of ease of operating the reactor system and analyzing the reaction data. In the heterogeneously catalysed reaction system, the unsteady state operating system has increasingly been employed, such as the forced cyclic operation of feed reactants, reactor temperature or feed flow rate in a flow reactor<sup>7-10</sup>. Because those cyclic operations sometimes enhance the product yields through averaged operating time more than the fixed operating conditions. Huanz and Chen<sup>11</sup> have reported the enhancement of ethanol production under the temperature cycling system compared with the fixed temperature system. Very recently, Wu and Weng<sup>12</sup> have applied the transient response method to elucidate the mechanism of reaction

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