北見工業大学研究報告
第20巻 第2号 (昭和63年)

Memoirs of the Kitami Institute of Technology
Vol. 20 No. 2 (1988)

Gas Diffusion Process in a Silver Catalyst Used for Ethylene Oxidation*

by Tohru KANNO** and Masayoshi KOBAYASHI**

(Received October 13, 1988)

Abstract

The diffusion processes of N_2, He, CO_2, C_2H_4 and C_3H_6 in a silver catalyst for ethylene partial oxidation have been studied with a steady state diaphragm cell method using an atomospheric flow system at 30~180°C, relating to ethylene oxidation. Three different catalyst surfaces were prepared as oxidized (S_{ox}), reduced (S_{red}) and treated with ethylene (S_{In}) on which the stable intermediates (In) were accumulated, compared among the effective diffusivities of the gases (*De*). The molecular diffusion process was achieved with N_2 and He for all the surfaces and at all the gases except O_2 on S_{red}. The *De*'s of CO_2, C_2H_4 and C_3H_6 on S_{In} were higher than those on S_{red}, suggesting the contribution of surface diffusion on S_{In}.

(In) works to increase the amount of isolated surface oxygen species which is available for the adsorption sites of CO_2, C_2H_4 and C_3H_6. This phenomena causes localization of the gases on the surface and change in their surface diffusion rate.

1. Introduction

As has been demonstrated by a large number of investigators, surface diffusion is one of the important surface processes in heterogeneous catalysis[1~7], especially when the effectiveness factor of a catalyst deviates from 1. The surface diffusion has a sensitive effect on the apparent reaction order and activation energy, the total reaction rate, and selectivity of desired products. Miller and Kirk[1] presumed the effect of the surface diffusion of primary alcohols on their dehydration on silica-alumina catalyst was significant, and Krasuk and Smith[8] calculated the degree of its effect to be ordered as butanol>propanol>ethanol.

H. H. Kung and M. C. Kung[9] have analyzed the effect of surface diffusion on the selectivity of the specific reaction by using a consecutive model reaction A→B→C. They presumed there were two different regions on the surface as cycles of α distributed uniformly on a surface β, and the adsorbed species migrates between the two species. Their conclusions were that the surface diffusion of adsorbed species strongly affects the reaction selectivity which is influenced by the flow rate of reactants, crystal sizes, and conditions of the loading of catalyst metal.

R. B. Grant and R. M. Lambert[10~11] examined oxygen species on silver by

* The paper was presented at the Hokkaido regional meeting of the Chemical Society of Japan in the winter period of 1983.

** Department of Industrial Chemistry, Kitami Institute of Technology Kitami, Hokkaido 090, Japan.

a Temperature Programmed Reaction (TPR) technique and concluded that adsorbed atomic oxygen played a major role in producing ethylene oxide. In our previous papers[12~16], it has been demonstrated that an appreciable portion of a silver surface is occupied by the adsorption of some stable intermediates (In) formed during the oxidation of ethylene in the temperature range 70~150°C under atomospheric pressure. (In) strongly influences the total reaction conversion, and selectivity of ethylene oxide. There are two different active oxygen species on the surface: One is active in the formation of ethylene oxide (EO) and the decomposition of (In) to CO_2 (designate O_α), and the other in the formation of (In) (designate O_β). When one ethylene molecule reacts with three or more O_β's aggregated, (In) is formed and then decomposed consecutively into CO_2 and H_2O by the reaction with adjacent O_α. When C_2H_4 is adsorbed on isolated O_α on the other hand, EO is produced immediately, whereas C_2H_4 adsorbed on O_β produces no products. O_β, therefore, works as an adsorption site for C_2H_4 and CO_2. The accumulation of (In) on the surface strongly influences the amount of the aggregated O_α on the surface, thereby the amount of the aggregated C_2H_4 may be increased. When the rate of surface migration of the adsorbed C_2H_4 is faster than its desorption rate into the gas phase, it can easily react with O_α to form EO rather than gaseous C_2H_4. Accordingly, the surface diffusion of C_2H_4 may be able to work to enhance the selectivity of EO.

In the present study, the contribution of the surface diffusion of CO_2, C_2H_4 and C_3H_6 to the mass transport of gases through the powdered catalyst diaphragm is studied in detail on three different surfaces: oxidized (S_{ox}), reduced (S_{red}) and that treated with C_2H_4 (S_{In}). Our special interest is focused on the role of surface diffusion of C_2H_4 on S_{In}. To analyze the adsorption and desorption behavior of the gases, the transient response method is applied.[17 and 18]

2. Experimental

(1) Catalyst

248 g of silver nitrate was dissolved in 2.2 liters of redistilled water and put in a dark room for 1 day. Potassium hydroxide solution (10 wt %) was slowly added into the silver nitrate solution until it reaches an amount 5% below equilibrium point. The dark brown precipitated sample thus obtained was filtrated by a suction filter and washed in redistilled water until there was no detection of silver ion using a chlorine solution as an indicator. The brown precipitate obtained was dried at 105°C in a dark room for one day and then the temperature was decreased slowly to that of room level. The black powder sample was supplied as a silver oxide for the coating catalyst.

175 ml of potassium sulfate aqueous solution (3 mg/ml) was added to 105 g of Ag_2O, and the black paste sample was dried slowly in a water bath. an amount of ethanol was then added to the sample to make a black paste and α-alumina (20~40 mesh) was added for the coating. The coating procedure was conducted for convenience in a 300 ml- glass beaker and it was shaken up to

become 12~20 mesh of grounds with evaporating ethanol. α-alumina was supplied from Norton Co. and washed carefully in redistilled boiling water.

The coated silver oxide (12~20 mesh) sample was packed into a tubular reactor made of Pyrex glass and reduced by hydrogen at 50°C for 12 hrs and then at 100°C for 12 hrs. The sample was cooled down slowly to room temperature in the H_2 stream. The composition of the catalyst obtained thus was 60.2 g-Ag, 0.361 g-K_2SO_4/119.9 g-α-Al_2O_3 and the density of the catalyst bed was 1.56 g/cm^3. Some of the experiments were done with the catalysts; 4.65 g-Ag, 0.0027 g-K_2SO_4/1.01 g-α-Al_2O_3 and 206.0 g-Ag, 1.33 g-K_2SO_4/53.5 g-α-Al_2O_3.

For the diffusion experiments, the catalyst which had been exposed to various conditions was taken out of the reactor and α-Al_2O_3 in the catalyst was removed carefully to make fine silver powder smaller than 400 mesh by using an agate motor.

(2) Reactor and Diffusion Cell

Figs. 1 and 2 respectively illustrate the schematic diagrams of the reactor and diffusion systems and other equipment used in this study. The reactor for ethylene oxidation was made of Pyrex glass tube of 8.0 mm ID and 163 cm length. The diffusion cell was also made of Pyrex glass as shown in Fig. 3. A stainless steel mesh (400 mesh) was set at each end of the catalyst bed and 5.2 g of catalyst was mounted between the two meshes as a diffusion diaphragm. The mesh at the top side was pressed by a stainless steel spring so as to keep constant void fraction of the catalyst diaphragm.

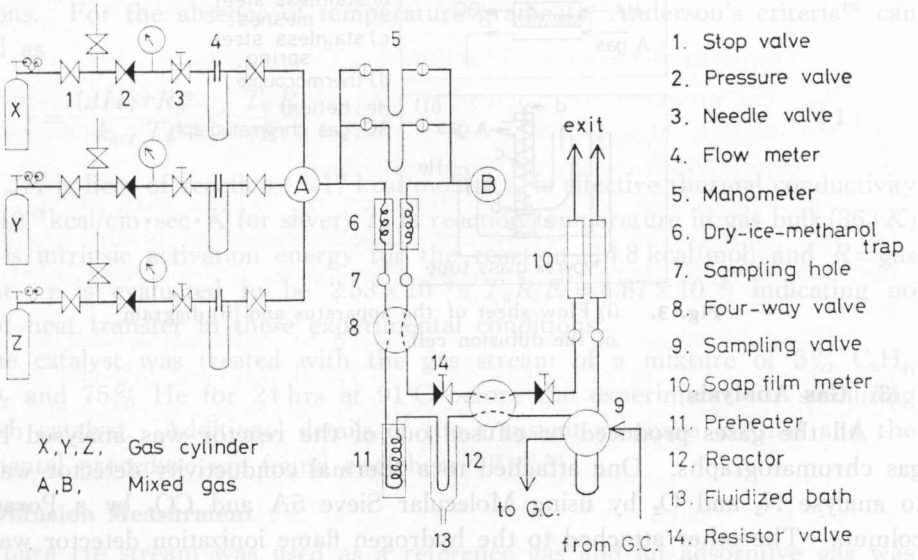

Fig. 1. Schematic diagram of the apparatus for transient response method.

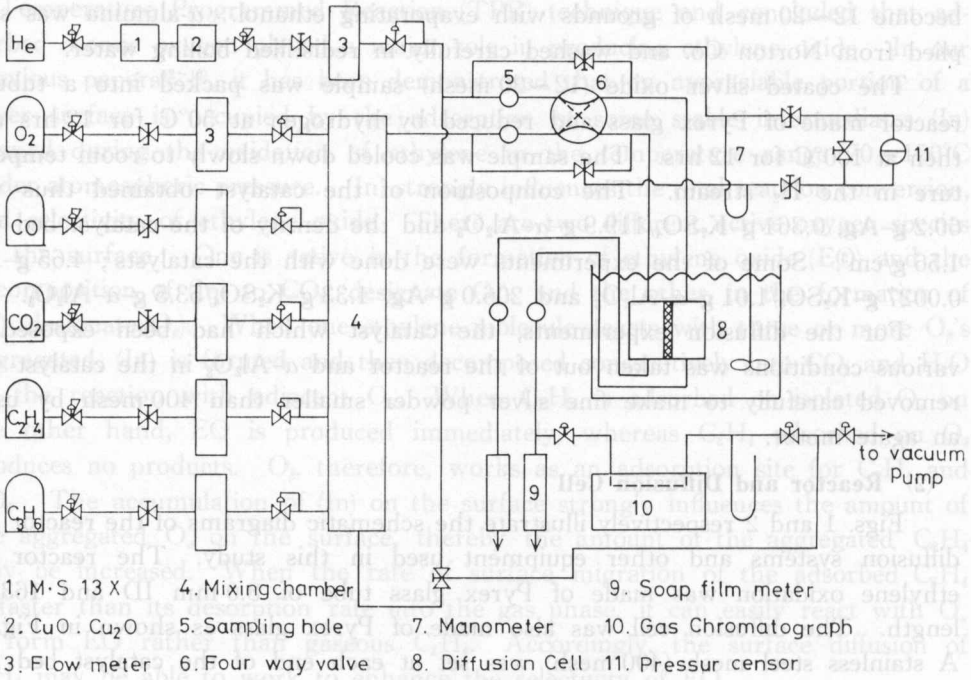

Fig. 2. Schematic diagram of the apparatus for measurement of gas diffusion.

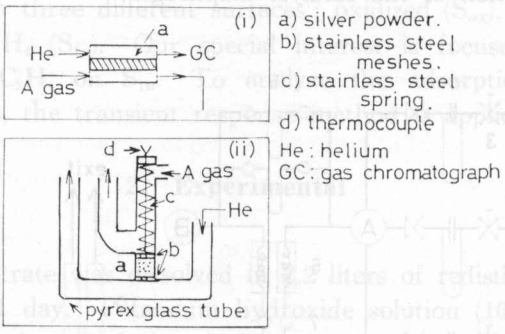

Fig. 3. (i) Flow sheet of the apparatus and (ii) diagram of the diffusion cell.

(3) Gas Analysis

All the gases produced or effused out of the reactor was analysed by two gas chromatographs. One attached to a thermal conductivity detector was used to analyse N_2 and O_2 by using Molecular Sieve 5A and CO_2 by a Porapak Q colmun. The other attached to the hydrogen flame ionization detector was used to analyse C_2H_4 and C_3H_6 by using a Porapak Q column.

(4) Transient Reaction Experiment

The reactor was immersed into a fluidized sand bath, the temperature of which was strictly controlled within $\pm 1°C$. The temperature controller (Ohkura

EC-7) was used for heating the bath, and the thermo-couple of chromel-alumel (1 mm in diameter) was inserted directly into the catalyst bed to monitor the fluctuation of the temperature during the transient response experiments. The temperature difference of the catalyst bed between the top and the bottom sides was measured and confirmed to be less than 1°C at most, even in the transient state of the step changes in gas composition, indicating no serious effect on the rate data at the given temperature.

The gas composition at the inlet of the reactor was changed in stepwise fashion by using the two flow controlling systems. The systems worked conveniently to make the rectangular function of gas composition without any change in the flow rate by using a four way valve. The change in the flow rate at the step change was reconfirmed to be less than 5% of the total flow rate. The residence time was about 17 sec at 160 ml/min of the total flow rate and the gas mixing between two flow systems was completed within 6~7 sec, suggesting no serious error of the flow rate fluctuation at the step change in the gas composition.

The criteria of intraparticle transport in isothermal spherical particles is suggested by Weisz and Prater[19] as $\phi = rR_p^2/C_0\,\mathrm{Deff} < 1$ which indicates no contribution to the reaction rate. In our experiments at 90°C, since the reaction rate (r) is 8.76×10^{-10} mol-C_2H_4O/cm^3-cat. sec, the mean radius of catalyst particle (R_p) is 0.079 cm, the bulk concentration of ethylene (C_0) is 8.93×10^{-6} mol-C_2H_4/cm^3 and effective diffusivity of ethylene (Deff) is 0.27 cm^2/sec, ϕ may be evaluated to be $2.27\times10^{-6} \ll 1$ indicating no mass transfer effect in the present reaction conditions. For the absence of temperature gradients, Anderson's criteria[19] can be used as

$$\gamma = \frac{(\Delta H)\, rR_p^2}{k_{\mathrm{eff}}\, T_0} < \frac{T_0 R}{E} \qquad (1)$$

Where ΔH is heat of reaction (=17 kcal/mol), k_{eff} is effective thermal conductivity (1.19×10^{-3} kcal/cm·sec·K for silver) T_0 is reaction temperature in gas bulk (363 K) and E is intrinsic activation energy for the reaction (14.8 kcal/mol) and R=gas constant. γ is evaluated to be $2.53\times10^{-9} \ll T_0R/E(=4.87\times10^{-2})$ indicating no effect of heat transfer in these experimental conditions.

The catalyst was treated with the gas stream of a mixture of 5% C_2H_4, 20% O_2 and 75% He for 24 hrs at 91°C before the experiments for stabilizing the fresh catalyst. Additional details of the transient response method and the experimental procedure are found elsewhere.[17,18 and 20]

(5) Diffusion Measurment

A pure He stream was used as a reference gas and an adsorptive gas was fed into the upper side of the diffusion cell as can be seen from Fig. 3. The mutual diffusion from both sides through the catalyst diaphragm occurs and the amount of adsorptive gas permeated from the other side to the pure He stream is analysed by the gas chromatograph (Wicke and Kallenbach type diffusion

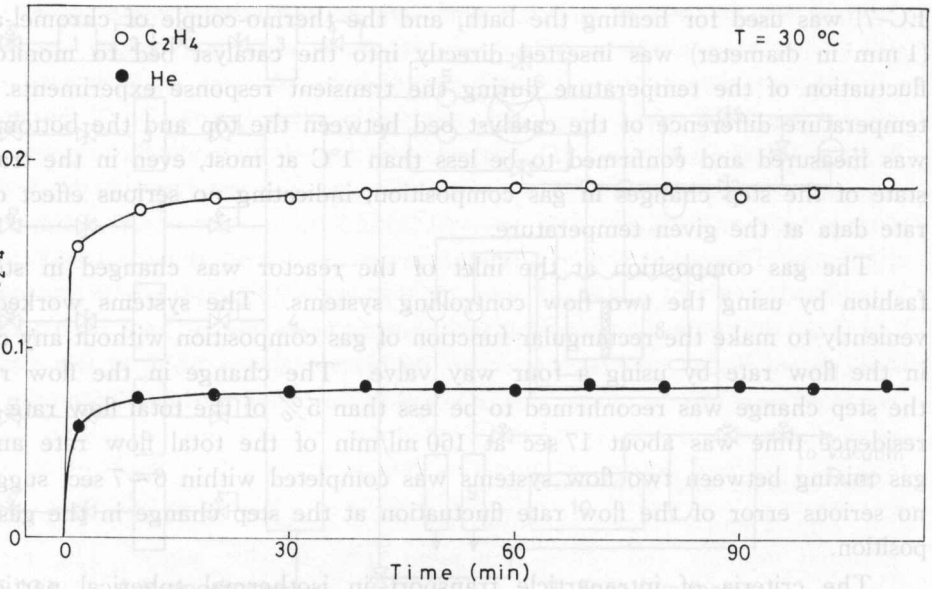

Fig. 4. Change in the concentration of He and C_2H_4 in the diffusion cell.

cell)[21]. Fig. 4 illustrates the responses of the mutual diffusion of C_2H_4 and He as an example. One can recognize that the diffusion reaches a steady state in about 90 min at most, and 120 min was taken for all the experiments.

3. Experimental Results and Discussion

3-1. Transient Behavior of Reaction Gas Components

S_{red} was prepared by reducing it with H_2 for 6 hrs after the surface was oxidized with O_2 (20%)-N_2 (80%). This reduction was always conducted prior to its use before the transient response experiment.

Fig. 5 illustrates the transient behavior of CO_2 and C_2H_4 on S_{red}. As can be seen from the mode of the instantaneous responses of the adsorpton and desorption curves, there was no delay, showing no adsorption of either gases on S_{red}.

The oxidized surface (S_{ox}) was prepared by oxidizing it with a mixture of O_2 (20%)-N_2 (80%) at 90°C for 24 hrs. Typical transient behavior of CO_2 and C_2H_4 are represented in Fig. 6. The response curves of adsorption and desorption clearly indicate delay, suggesting appreciable amounts of adsorption.

The surface treated with C_2H_4 (S_{In}) was prepared as follows. The catalyst surface was treated with a stream of O_2 (20%)-He (80%) mixture at 90°C for 24 hrs and then it was flushed with a pure He stream for 30 min. The He stream was switched in step fashion into a stream of C_2H_4 (5%)-He (95%) mixture containing no O_2. C_2H_4 can react with surface oxygen species to produce C_2H_4O, CO_2 and H_2O as shown in Fig. 7 by Run 1, where H_2O is not presented in the figure. The production of EO and CO_2 in small amounts was observed for long

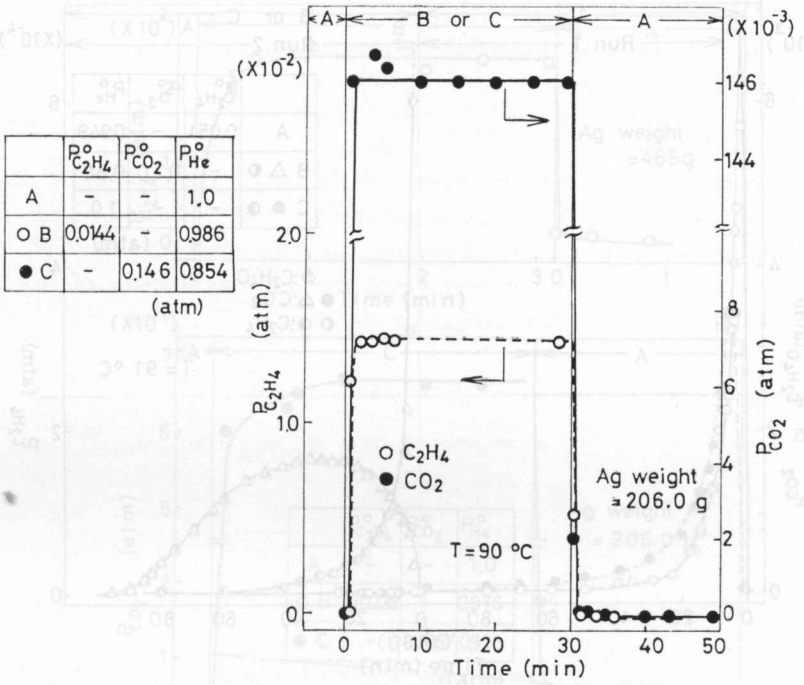

Fig. 5. C_2H_4–C_2H_4 and CO_2–CO_2 responses on the surface reduced with H_2 (S_{red}).

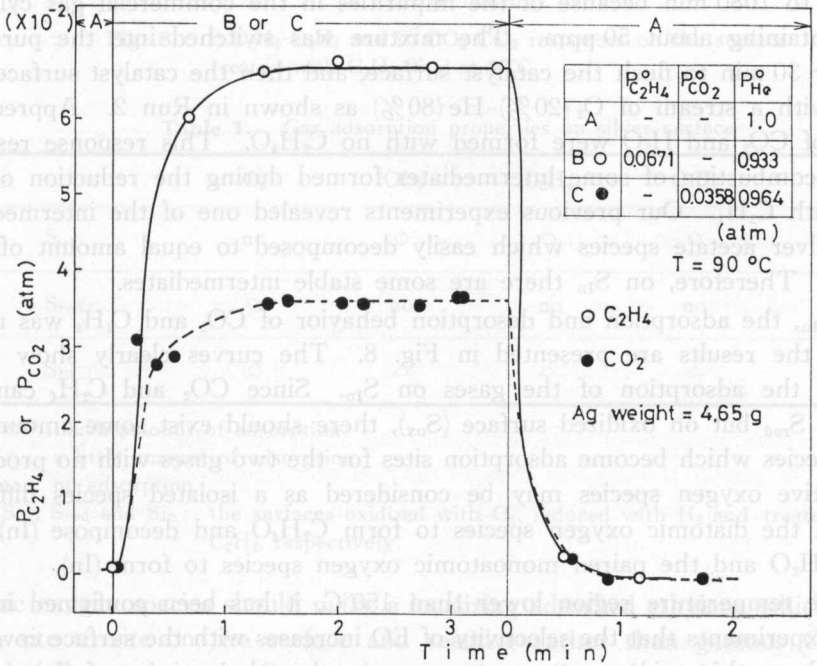

Fig. 6. C_2H_4–C_2H_4 and CO_2–CO_2 responses on the surface oxidized with O_2. (S_{ox}).

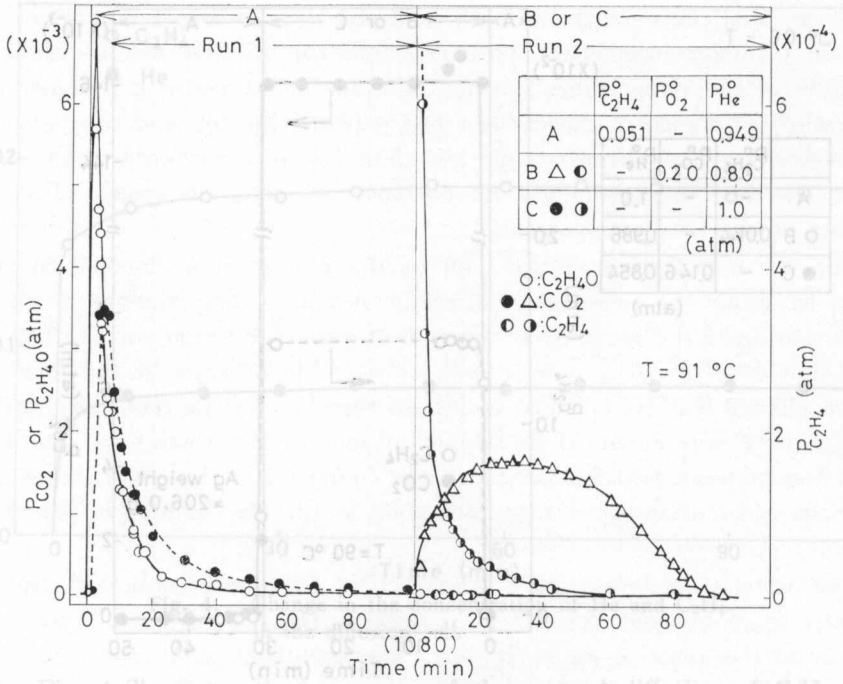

Fig. 7. Reactivity of the intermediate (In) during C_2H_4 oxidation on a silver catalyst.

period up to 1080 min because of the impurities in the commercial gas cylinder of He containing about 50 ppm. The mixture was switched into the pure He stream for 30 min to flush the catalyst surface, and then the catalyst surface was oxidized with a stream of O_2 (20%)-He (80%) as shown in Run 2. Appreciable amounts of CO_2 and H_2O were formed with no C_2H_4O. This response resulted from the combustion of some intermediates formed during the reduction of the surface with C_2H_4. Our previous experiments revealed one of the intermediates to be a silver acetate species which easily decomposed to equal amount of CO_2 and H_2O. Therefore, on S_{In} there are some stable intermediates.

On S_{In}, the adsorption and desorption behavior of CO_2 and C_2H_4 was measured and the results are presented in Fig. 8. The curves clearly show delay suggesting the adsorption of the gases on S_{In}. Since CO_2 and C_2H_4 can not adsorb on S_{red} but on oxidized surface (S_{ox}), there should exist some amounts of oxygen species which become adsorption sites for the two gases with no products. This inactive oxygen species may be considered as a isolated species differing from both the diatomic oxygen species to form C_2H_4O and decompose (In) into CO_2 and H_2O and the paired monoatomic oxygen species to form (In).

In the temperature region lower than 150°C, it has been confirmed in our separate experiments that the selectivity of EO increases with the surface coverage of (In). From this evidence, one may presume that the amount of (In) on the surface is one of the important parameters for the formation of EO. The isolated

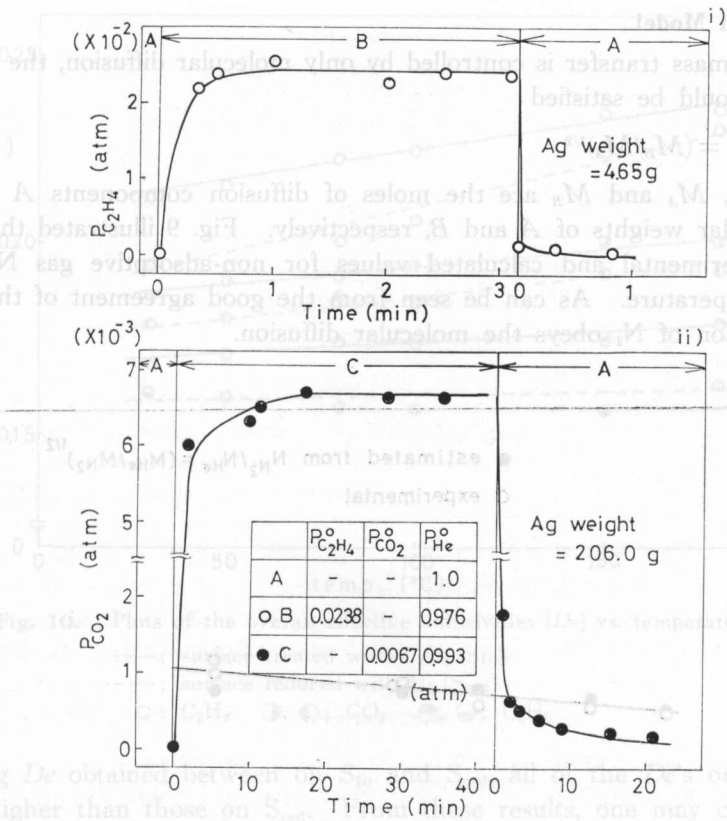

Fig. 8. i) C_2H_4–C_2H_4 and ii) CO_2–CO_2 responses on the surface treated with C_2H_4 (S_{In}) at 90°C.

Table 1. Gas adsorption properties on silver surface

	O_2	CO_2	C_2H_4	C_3H_6	CO
S_{ox}	no	○	○	○	○
S_{red}	○	no	no	no	no
S_{In}	○	△	△	△	△

○: much amount of adsorption.
△: a little amount of adsorption.
no: no adsorption.
S_{ox}, S_{red} and S_{In}: the surfaces oxidized with O_2, reduced with H_2 and treated with C_2H_4, respectively

atomic oxygen species should make a localizing adsorbed ethylene which is mobile from site to site on the surface and reactive rather than gaseous C_2H_4. This will be discussed in detail in a later section. Gas adsorption properties on a silver surface is summarized in Table 1.

3-2. Diffusion Model

When the mass transfer is controlled by only molecular diffusion, the following equation should be satisfied;

$$N_A/N_B = (M_B/M_A)^{1/2} \tag{2}$$

Where N_A, N_B, M_A and M_B are the moles of diffusion components A and B and the molecular weights of A and B, respectively. Fig. 9 illustrated the comparison of experimental and calculated values for non-adsorptive gas N_2 as a function of temperature. As can be seen from the good agreement of the both lines, the diffusion of N_2 obeys the molecular diffusion.

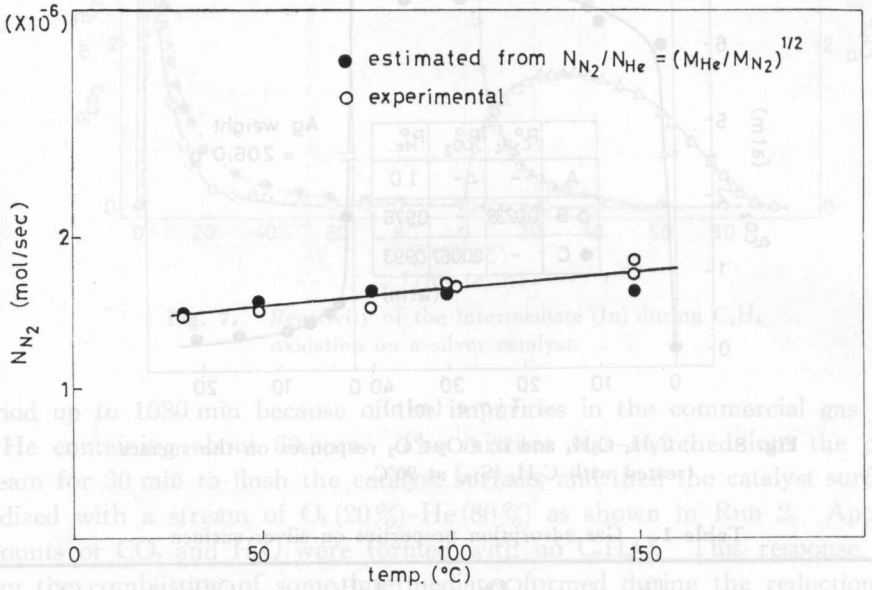

Fig. 9. Comparison of the diffusion rate of N_2 (N_{N_2}) between experimental and estimated on the surface oxidized with O_2 (S_{ox}).

For the adsorptive gases, the effective diffusivity De_A was evaluated by Equation (3);

$$N_A{}^T = -De_A(S/L)(C_{AV_1} - C_{AV_2}) \tag{3}$$

Where $N_A{}^T$ is the amount of total diffusion for adsorptive gas, De_A is effective diffusivity of A gas, S is diffusion area, L is diffusion length and C_{AV_1} and C_{AV_2} are the concentration of A gas on both sides. Eq. (2) can be rewritten as

$$De_A = -\frac{LRN_A{}^T T}{SP(y_{AV_1} - y_{AV_2})} \tag{4}$$

Where R is gas constant, P is total pressure, T is temperature, and y_{AV_1} and y_{AV_2} are mole fractions of A on both sides.

Fig. 10 illustrates De as a function of temperature for C_2H_4, CO_2 and C_3H_6.

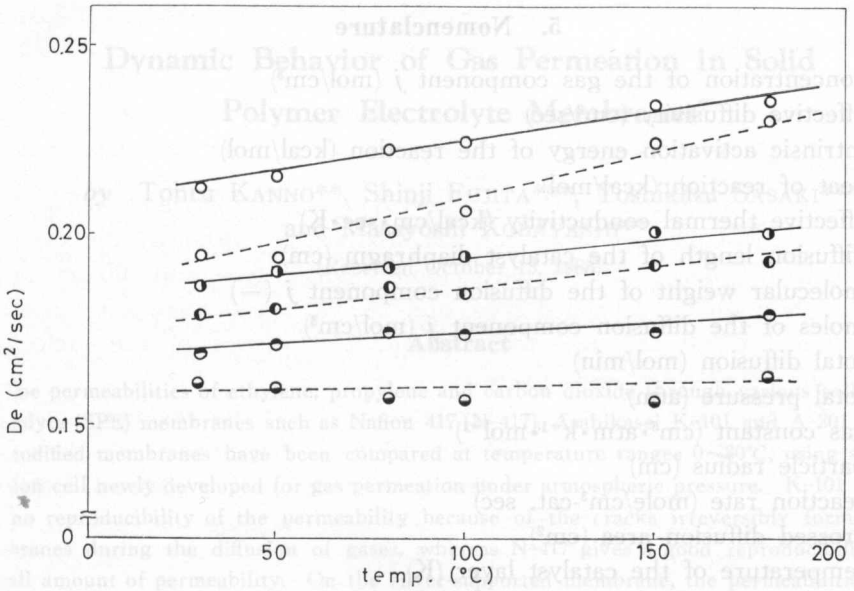

Fig. 10. Plots of the overall effective diffusivities (*De*) vs. temperature.
——; surface treated with C_2H_4 (S_{In}).
– – –; surface reduced with H_2 (S_{red}).
○; C_2H_4 ◑, ◐; CO_2 ◓, ◒; C_3H_6

Comparing *De* obtained between on S_{In} and S_{red}, all of the *De*'s on S_{In} are 10 or 20% higher than those on S_{red}. From these results, one may conclude that the adsorptive gases on S_{In} can transfer faster than on S_{red}. To explain this enhancement of diffusion, there are two possibilities. (1) cahnge in the porosity of the catalyst diaphragm due to the treatment with C_2H_4, and (2) contribution of surface diffusion on S_{In}. If (1) were the case, the experimental results would not be reproducible. In the present case, all the experimental results are confirmed to be reproducible. Case (2), therefore, must be acceptable.

4. Conclusions

A new experimental operation was developed to measure the gas diffusivity on a powdered silver catalyst. The nature of the catalyst surface is characterized by three different treatments with O_2, H_2 and C_2H_4. The surface reduced with H_2 indicates no adsorption of CO_2 and C_2H_4, and their diffusion follows the molecular diffusion mechanism. The surface treated with C_2H_4 shows the enhancement of the amount of gas adsorption and effective diffusivity, suggesting the possibility of participation of surface diffusion of adsorbed species, especially adsorbed C_2H_4 in C_2H_4 oxidation.

5. Nomenclature

C_V : concentration of the gas component j (mol/cm^3)
De : effective diffusivity (cm^2/sec)
E : intrinsic activation energy of the reaction (kcal/mol)
ΔH : heat of reaction (kcal/mol)
k_{eff} : effective thermal conductivity (kcal/cm·sec·K)
L : diffusion length of the catalyst diaphragm (cm)
M_j : molecular weight of the diffusion component j (−)
N_j : moles of the diffusion component j (mol/cm^3)
N^T : total diffusion (mol/min)
P : total pressure (atm)
R : gas constant (cm^3·atm·k^{-1}·mol^{-1})
R_p : particle radius (cm)
r : reaction rate (mole/cm^3-cat. sec)
S : crossed diffusion area (cm^2)
T : temperature of the catalyst layer (K)
T_0 : reaction temperature in gas bulk (K)
y_V : molar fraction of the gas on the both sides of the catalyst diaphragm (−)

6. References

1) D. N. Miller and R. S. Kirk, AIChE Journal, **8**, No. 2, 183 (1962).
2) Y. Horiguchi, R. R. Hudgins and P. L. Silveston, Canadian J. Chem. Eng., **49**, 76 (1971).
3) L. A. Roybal and S. I. Sandler, AIChE Journal, **18**, 39 (1972).
4) H. Sohn, R. Merrill and E. Petersen, Chem. Eng. Sci., **25**, 399 (1970).
5) P. Schneider and J. Smith, AIChE Journal, **14**, 886 (1968).
6) E. M. Read and J. B. Butt, J. Phys. Chem., **15**, 133 (1971).
7) F. Shadman-Yazdi and E. Petersen, Chem. Eng. Sci., **27**, 227 (1972).
8) J. H. Krasuk and J. M. Smith, IEC Fundamentals, **4**, 102 (1965).
9) H. H. Kung and M. C. Kung, Chem. Eng. Sci., **23**, 1003 (1978).
10) R. B. Grant and R. M. Lambert, JCS Chem. Commun., **59**, 662 (1983).
11) R. B. Grant and R. M. Lambert, J. Catal., **92**, 364 (1985).
12) M. Kobayashi, Catalysis, Under Transient Conditions, ACS Symposium Series, 178, Edited by L. L. Hegedus and A. T. Bell.
13) M. Koayashi, M. Yamamoto and H. Kobayashi, Proc. 6th ICC, A24 (1976).
14) M. Kobayashi, Chem. Eng. Sci., **37**, 4I03 (1982).
15) M. Kobayashi and T. Kanno, J. Catal., **90**, 24 (1984).
16) T. Kanno and M. Kobayashi, Proc. 8th ICC, III-277 (1984).
17) H. Kobayashi and M. Kobayashi, Catal. Reviews, **10**, 139 (1975).
18) C. O. Bennett, Catal. Rev. Eng. Sci., **12**, 121 (1976).
19) J. B. Butt, "Reaction Kinetics and Reactor Design", p 386, Prentice-Hall Inc., New Jersey (1980).
20) M. Kobayashi and H. Kobayashi., J. Catal., **27**, 100 (1972).
21) E. Wicke and W. Kallenbach, Die Oberflachen diffusion von Kohlendioxyd in Kolloid Z. **97**, 135 (1941).