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Author(s)	SUZUKI, Isao; KANEKO, Yoshihisa
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Instructions for use

PRESSURE-JUMP IN HETEROGENEOUS CATALYSIS

II. Dehydrogenation of Propane over a Cr_2O_3-Al_2O_3-K_2O Catalyst

By

Isao SUZUKI[*] and Yoshihisa KANEKO[*]

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Abstract

The pressuere-jump method was applied to the dehydrogeneration of propane over a Cr_2O_3-Al_2O_3-K_2O catalyst at 443°C in a closed static reactor. The rate equation $r = (k_1 K_1 P_{C_3H_8} - k_2 K_2 K_3 P_{C_3H_6} P_{H_2})/(1 + K_1 P_{C_3H_8} + K_2 P_{C_3H_6})(1 + K_3 P_{H_2})$ proposed previously for initial kinetics was verified by the pressure-jump method.

Introduction

The chamical relaxation method pioneered by Eigen *et al.*[1] gives the rate constants of forward and reverse reactions independent of the equilibrium constant. By application of the chemical relaxation method to a reaction, plausible rate equations can be tested in two ways : by examining the relation between the observed relaxation curves and those predicted by the proposed rate equation, and by comparing the observed equilibrium constant with that calculated from the following equation ;

$$\frac{\overrightarrow{k}}{\overleftarrow{k}} = K^{1/\nu}, \tag{1}$$

where $\overrightarrow{k}$ and $\overleftarrow{k}$ are the forward and backward rate constants, respectively, K is the equilibrium constnat of the over-all reaction, and ν is the stoichiometric number of the rate determining step of a sequence of elementary steps comprising the over-all chemical reaction.[2] The pressure-jump method, one of the chemical relaxation method, has been used successfully for the investigation of the catalytic reaction between NO and Cl_2 over H-mordenite.[3]

This paper concerns with the application of the pressure-jump method applied to the dehydrogenation of propane over a Cr_2O_3-Al_2O_3-K_2O catalyst.

*) Department of Chemistry, Utsunomiya University, 350 Mine-machi, Utsunomiya, 320 Japan.

I. SUZUKI and Y. KANEKO

Dehydrogenation and the hydrogenation of hydrocarbons are important processes in the petrochemical industry, and they have been extensively investigated from the industrial and scientific points of view.[4] We elected to study the kinetics of C_3 hydrocarbons because the dehydrogenation and the hydrogenation occur in an easily accessible temperature range and none of isomers could be formed in the reaction. In our previous paper,[5] many possible reaction steps were logically written down and the corresponding rate equations were derived. The applicability of these equations was tested for three types of reactions; (i) the hydrogenation of propylene, (ii) the dehydrogenation of propane in the absence of propylene or hydrogen, and (iii) the dehydrogenation in the presence of propylene or hydrogen. A rate expression that adequately described the observed rate was the following Langmuir-Hinshelwood equation as

$$r = \frac{k_1 K_1 P_{C_3H_8} - k_2 K_2 K_3 P_{C_3H_6} P_{H_2}}{(1 + K_1 P_{C_3H_8} + K_2 P_{C_3H_6})(1 + K_3 P_{H_2})} \, . \tag{2}$$

The purpose of the present paper is to test this equation by the pressure-jump method.

Experimental

Catalyst :

A Cr_2O_3-Al_2O_3-K_2O catalyst was prepared from alumina sol, chromic nitrate, and potassium nitrate; the contents of Cr_2O_3 and K_2O were 7.15 wt% and 2.75 wt%, respectively.[5] BET surface area determined by nitrogen adsorption was 184 m²/g. 8.98 g of the catalyst was heated at 500°C under a vacuum for 2 hr, reduced with 200 Torr of hydrogen for 1 hr, and finally evacuated for 2 hr all at the same temperature.

Reactant :

Hydrogen from Takachiho Chem. Ind. Co. Ltd. was purified by passage through copper powder heated at 400°C and then through a liquid nitrogen trap. Propane and propylene from Takachiho Chem. Ind. Co. Ltd. were purified by repeated distillations. None of impurity was detected by gas-solid chromatography (GSC) analyses.

Apparatus :

The apparatus consists of 3000 mℓ of Pyrex glass bulb equipped with a cavity for the catalyst bed, a preheater, an oil manometer, and a gas handling device for GSC analyses (Fig. 1). The oil manometer is connected with the bulb through a narrow tube filled with helium in order to prevent

the oil from direct contact of oil with reacting gases. The oil used was a diffusion pump oil (Dow Corning, 704 diffusion pump fluid) and its vapor pressure is negligibly small. In order to measure a small change of the pressure, the temperature of the bulb was carefully kept constant during the course of the reaction. The bulb, except the cavity, was surrounded with a metal jacket filled with water maintained at a constant temperature. Furthermore, a tube is immersed in the jacket and is connected to the reference side of the oil manometer. The tube is filled with helium and any change of the pressure in the reaction bulb caused by a change of the tem-

Fig. 1. Schematic diagram of apparatus.

perature of water in the metal jacket is compensated with the accompanying change of the pressure of helium. The volume of the tube is so large that the change of the pressure caused by the change of the oil level is negligibly small.

Gas analyses:

Analyses of the hydrocarbons were performed by GSC with a 60 cm-columm of silica gel at 60°C. Helium was used as a carrier, and its flow rate was about 40 cc/min. The partial pressure of hydrogen, propylene, and propane at equilibrium were obtained as follows. A mixture of propane, propylene, and hydrogen was introduced into the reaction bulb where it was allowed to equilibrate for several hours. The partial pressure of hydrogen $P_{H_2}^e$ was determined by measuring the pressure decrease after traping the condensable gases in a liquid nitrogen trap, evacuating the non-condensable gases (mainly H_2), and allowing the trapped gases to refill the reaction bulb. A small amount of methane and ethane was not trapped, and it was corrected with reference to GSC results. The partial pressures of propylene $P_{C_3H_6}^e$, propane $P_{C_3H_8}^e$, methane, and ethane were obtained by GSC analyses. The sum of the pressures of hydrogen, methane, ethane, propylene, and propane thus obtained agreed with the total pressure obtained by the manometer. The equlibrium constant obtained by the dehydrogenation of propane was equal to that obtained with the hydrogenation of propylene.
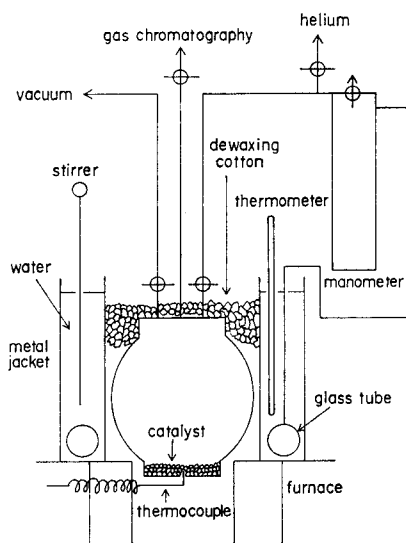
The constant $K = P_{H_2}^e P_{C_3H_6}^e / P_{C_3H_8}^e$ was 7.3 Torr at 443°C and agrees with the value reported in the literature.[6]

Procedure :

A known mixture of hydrogen, propylene and propane with composition in or near equilibrium was introduced to the reaction bulb. The total pressure was, thereafter, followed with the oil manometer. The pressure changed slightly and gradually became constant or increased slightly. The slight increase in total pressure was caused by the cracking of propylene. The partial pressures of reactants were obtained from the total pressure and GSC results, and they agreed with the pressures obtained by the method mentioned above. Then, a perturbation was accomplished by an introduction of hydrogen into the system, and the relaxation to a new equilibrium state was followed by the oil manometer.

Fig. 2. Pressure-jump relaxation curve. The curve was obtained by the introduction of hydrogen ($\Delta P_{H_2} = 3.1$ Torr) into the system with the equilibrium pressures of $P_{C_3H_6}^e = 11.4$ Torr, $P_{C_3H_8}^e = 8.1$ Torr and $P_{H_2}^e = 10.2$ Torr over a Cr_2O_3-Al_2O_3-K_2O at 443°C.

Results and Discussion

A typical relaxation curve is shown in Fig. 2. The linear increase in the total pressure observed at 40 min after the introduction of hydrogen was due to the formation of methane and ethane as shown in Fig. 3. The corrected pressure change caused by the hydrogenation alone of propylene was obtained from the difference between the pressure changes given in Fig. 2 and that in Fig. 3. The relaxation equation of the corrected pressure change may
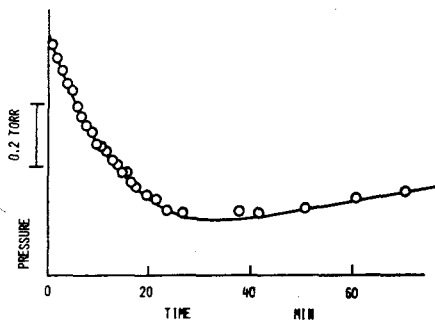

Fig. 3. The change in the pressure of methane (○) and ethane (●) at 443°C over a Cr_2O_3-Al_2O_3-K_2O.

be expressed as

$$P_0 - P = (P_0 - P_\infty)\left(1 - \exp\left(-t/\tau\right)\right),\qquad(3)$$

where P_0 and P_∞ are the pressures at time 0 and time ∞, respectively. Equation 3 can be written as follows;

$$\ln\left\{\frac{P - P_\infty}{P_0 - P_\infty}\right\} = -\frac{t}{\tau},\quad(4)$$

which given a linear relation between $\ln\{(P - P_\infty)/(P_0 - P_\infty)\}$ and t. Such a plot is given in Fig. 4 and the slope shows $-1/\tau$. These procedures were repeated and the relaxation times τ were obtained for various equilibrium pressures. The equilibrium pressures of hydrogen, propylene and propane; the pressures of hydrogen introduced for perturbation; and the observed relaxation times are summarized in Table 1.

The relaxation time τ may be written as a function of the equilibrium pressures depending on the rate equation applied. If the rate equation as-
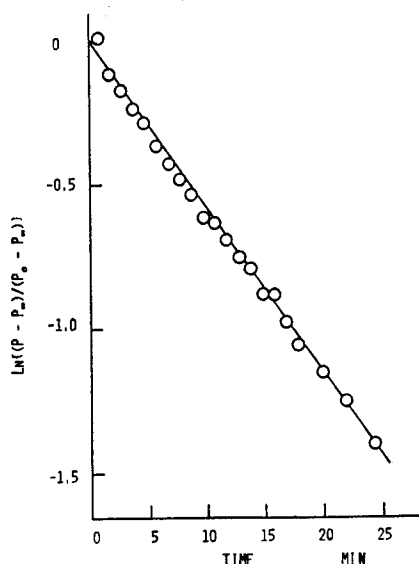

Fig. 4. Linear plot of corrected pressure for the pressure-jump relaxation curve. P: pressure at time t, P_0: pressure extrapolated to time 0, P_∞: pressure extrapolated to time ∞.

TABLE 1.　Summary of Kinetic Data

No.	$P^e_{C_3H_8}$ Torr	$P^e_{C_3H_6}$ Torr	$P^e_{H_2}$ Torr	ΔP_{H_2} Torr	$K^{a)}$ Torr	$1/\tau$ min^{-1}	$X^{b)}$ Torr	$Y^{b)}$ min^{-1}
1	11.4	8.1	10.2	3.1	7.2	0.0580	20.4	0.126
2	14.5	5.6	19.1	4.3	7.4	0.0538	27.8	0.142
3	4.5	5.3	6.2	2.5	7.3	0.0581	13.4	0.097
4	12.0	8.3	10.5	2.0	7.3	0.0592	20.1	0.128
5	15.9	11.1	10.5	2.8	7.3	0.0543	23.2	0.133
6	12.3	6.2	14.5	2.6	7.3	0.0463	22.7	0.106
7	8.7	7.9	8.0	2.9	7.3	0.0433	17·9	0.086
8	6.9	12.7	4.0	2.6	7.4	0.0530	17.9	0.103
9	4.4	5.1	6.4	2.4	7.4	0.0433	13.4	0.072

a)　$K = P^e_{C_3H_8} P^e_{H_2} / P^e_{C_3H_6}$
b)　X and Y are shown in Eqs. (11) and (12).

sumed is a simple power law, the relaxation time can be expressed with only two kinetic parameters, the forward and the reverse rate constants. Both of these kinetic parameters and the apparent reaction orders can be obtained from the linear plots of data generated by the pressure-jump method.[3]

Unfortunately, the initial rate of the hydrogenation or the dehydrogenation reaction does not follow a simple power law kinetics with respect to pressures of hydrogen, propylene and propane, but in fact obey a complex rate equation that includes several kinetic parameters.[5] It is, therefore, not easy to obtain a set of the best fit kinetic parameters and to select the most plausible rate equation for the reaction. In the present work we have assumed a rate equation previously proposed for the dehydrogenation of propane over the same catalyst and investigated the applicability of the same equation for the present data. The rate equation has been proposed on the basis of the following mechanism.[5]

$$C_3H_8 + S(1) \rightleftharpoons C_3H_8S(1) \tag{I}$$

$$C_3H_8S(1) + S(2) \rightarrow C_3H_6S(1) + H_2S(2) \tag{II}$$

$$C_3H_6S(1) \rightleftharpoons C_3H_6 + S(1) \tag{III}$$

$$H_2S(2) \rightleftharpoons H_2 + S(2) \tag{IV}$$

where $S(1)$ and $S(2)$ are the different vacant sites, and $C_3H_8S(1)$ and $H_2S(2)$ represent propane adsorbed on the site 1 and hydrogen adsorbed on the site 2, respectively. The mechanism proposed gives rise to the rate equation as ;

$$r = \frac{k_1 K_1 P_{C_3H_8} - k_2 K_2 K_3 P_{C_3H_6} P_{H_2}}{(1 + K_1 P_{C_3H_8} + K_2 P_{C_3H_6})(1 + K_3 P_{H_2})}, \tag{2}$$

where k_1 : forward rate constant of the rate determining step (II) ;

k_2 : reverse rate constant of the rate determining step (II) ;

K_1 : adsorption equilibrium constant for propane ;

K_2 : adsorption equilibrium constant for propylene ;

K_3 : adsorption equilibirum constant for hydrogen ;

The relaxation time τ can be related to the equilibrium pressures by applying rate equation (2). The pressures of propane, propylene and hydrogen can be written as

$$\left. \begin{aligned} P_{C_3H_8} &= P_{C_3H_8}^e + \Delta, \\ P_{C_3H_6} &= P_{C_3H_6}^e - \Delta, \\ P_{H_2} &= P_{H_2}^e + \Delta P_{H_2} - \Delta, \end{aligned} \right\} \tag{5}$$

where ΔP_{H_2} is the pressure of hydrogen for perturbation and Δ is the pressure which decreases after the addition of hydrogen. Substituting equation (5) into the rate equation (2) and expand the resulting equations (neglecting terms of higher order of Δ), we obtain the following equation:

$$\frac{d\Delta}{dt} = -\frac{1}{\tau}(\Delta - \Delta_0),$$ (6)

where

$$\Delta_0 = \frac{P_{C_3H_6}^e P_{C_3H_8}^e \Delta P_{H_2}}{P_{C_3H_6}^e P_{H_2}^e + P_{C_3H_8}^e (P_{C_3H_6}^e + P_{H_2}^e + \Delta P_{H_2})},$$ (7)

$$\frac{1}{\tau} = \left[\frac{1}{(1+K_1 P_{C_3H_8}^e + K_2 P_{C_3H_6}^e)\{1+K_3(P_{H_2}^e + \Delta P_{H_2})\}}\right] \times$$

$$\left[k_1 K_1 + k_2 K_2 K_3 \left\{P_{C_3H_6}^e + P_{H_2}^e + \Delta P_{H_2} + \right.\right.$$

$$\left.\left.\frac{(K_1-K_2) P_{C_3H_6}^e \Delta P_{H_2}}{1+K_1 P_{C_3H_8}^e + K_2 P_{C_3H_6}^e} - \frac{K_3 P_{C_3H_6}^e \Delta P_{H_2}}{1+K_3(P_{H_2}^e + \Delta P_{H_2})}\right\}\right].$$ (8)

Integration of equation (6) gives

$$\Delta = \Delta_0 \left(1 - \exp(-t/\tau)\right).$$ (9)

Equation (9) is equal to equation (3) since Δ and Δ_0 are equal to (P_0-P) and (P_0-P_∞), respectively and it gives the relaxation curve as shown in Fig. 4. Equation (8) can be written as follows;

$$Y = k_1 K_1 + k_2 K_2 K_3 X,$$ (10)

where

$$X = P_{C_3H_6}^e + P_{H_2}^e + \Delta P_{H_2} +$$
$$\frac{(K_1-K_2) P_{C_3H_6}^e \Delta P_{H_2}}{1+K_1 P_{C_3H_8}^e + K_2 P_{C_3H_6}^e} - \frac{K_3 P_{C_3H_6}^e \Delta P_{H_2}}{1+K_3(P_{H_2}^e + \Delta P_{H_2})},$$ (11)

$$Y = \frac{(1+K_1 P_{C_3H_8}^e + K_2 P_{C_3H_6}^e)\{1+K_3(P_{H_2}^e + \Delta P_{H_2})\}}{\tau}.$$ (12)

If the adsorption equilibrium constants are known, X and Y can be calculated from the values tabulated in Table 1. We used $K_1 = 0.0153$ Torr^{-1}, $K_2 = 0.037$ Torr^{-1} and $K_3 = 0.036$ Torr^{-1} which have been obtained with the dehydrogenation of propane or the hydrogenation of propylene over the same catalyst at the same temperature.[5] If the reaction is expressed adequately with equation (2), there should be a linear relation between X and Y as

shown in Fig. 5. The ratio of the intercept $k_1 K_1$ to the slope $k_2 K_2 K_3$ should be equal to the equilibrium constant (stoichiometric number $\nu = 1$) according to equation (1). The intercept $k_1 K_1$ observed was 0.0284 min^{-1} and the slope $k_2 K_2 K_3$ was 0.00417 Torr^{-1}min^{-1}; the ratio was 6.8 Torr. This is nearly equal to the observed equilibrium constant $K = 7.3$ Torr.

Fig. 5. Linear plot of pressure-jump kinetic data. X and Y are shown in Eqs. (11) and (12).

The rate constant obtained here is consistent with that obtained in previous work[5] as follows. The intercept $k_1 K_1$ in Fig. 5 is converted as

$$k_1 K_1 = 0.0284 \text{ min}^{-1} = 0.0284 \text{ Torr min}^{-1} \text{ Torr}^{-1}$$

$$= 0.0284 \times \frac{3000}{22400} \times \frac{1}{760} \times 6.023 \times 10^{23} \times \frac{1}{60} \times$$

$$\frac{1}{8.98 \times 184 \times 10^4} \text{ molecules sec}^{-1}\text{cm}^{-2}\text{ Torr}^{-1}$$

$$= 2.79 \times 10^9 \text{ molecules sec}^{-1}\text{cm}^{-2}\text{ Torr}^{-1} . \tag{13}$$

Then, we have $k_1 = (2.79 \times 10^9 / 0.0153)$ molecules sec^{-1}cm^{-2} = 1.81×10^{11} molecules sec^{-1}cm^{-2}. This value nearly equal to the rate constant $k_1 = 2.11 \times 10^{11}$ molecules sec^{-1}cm^{-2} reported in Fig. 2 of our earlier paper.[5]

The catalyst was located at the bottom of the reaction bulb as shown in Fig. 1 and hence, the mass transport of the species through the gas phase to and from the catalyst occurs by convection. The following arguments support the belief that convection was so fast that the rate was not limited by mass transport effects. If the over-all reaction rate was controlled by mass transport, the rate should be proportional to the pressure of the reacting gas. The rates observed for both the dehydrogenation of propane and the hydrogenation of propylene were not proportional to the pressures of the reacting gases, but rather could be expressed with the Langmuir-Hinshelwood kinetics. Furthermore, we obtained 33.9 Kcal/mole and 10.0 Kcal/mole as the activation energy of the dehydrogentation of propane and the adsorption enthalpy of propane, respectively. These values are much higher than those would be expected for a mass transpor process.
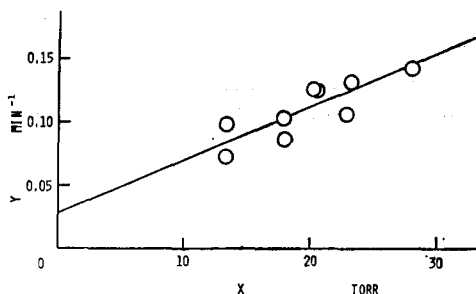
Acknowledgement

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