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KINETIC ANALYSIS OF PARALDEHYDE DEPOLYMERIZATION FOR A CHEMICAL HEAT PUMP

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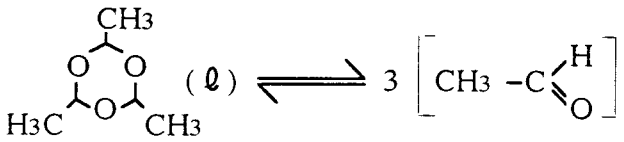
Abstract

A paraldehyde/acetaldehyde (Pa/A) chemical heat pump generates cold thermal energy. The purpose of this work is to investigate the depolymerization mechanism of paraldehyde involved in the chemical heat pump cycle. The depolymerization rate of paraldehyde has been measured in the range from 13 °C to 30 °C with Amberlyst 15E. The reaction rate equation of paraldehyde on Amberlyst 15E was described by the Langmuir-Hinshelwood kinetic model. Paraldehyde depolymerization consists of four elemental reactions. The rate-determining step is the ring-opening process of paraldehyde.

1. Introduction

A chemical heat pump (CHP) with paraldehyde/acetaldehyde (Pa/A) can generate low-temperature (10 - 13 °C) energy. The Pa/A system utilizes the reaction heat of the paraldehyde depolymerization and the vaporization heat of acetaldehyde. Paraldehyde is depolymerized with an acid catalyst as shown by Eq. (1) and the reaction heat is 110.3 kJ mol^{-1}. The vaporization heat of acetaldehyde is 26.4 kJ mol^{-1}.



$$\Delta H = 189.5 \text{ kJ mol}^{-1} \qquad (1)$$

The chemical heat pump with the Pa/A system consists of four parts: an endothermic reactor, an exothermic reactor, a compressor and an expansion valve. Cold thermal energy is generated in the endothermic reactor. Liquid paraldehyde in the endothermic reactor is depolymerized to acetaldehyde vapor. Acetaldehyde vapor is compressed and fed to the exothermic reactor. Acetaldehyde is trimerized on an acid catalyst to form liquid paraldehyde in the exothermic reactor. Liquid paraldehyde is returned to the original state by an expansion process.

Most chemical heat pumps with organic chemical reactions are expected to be alternative systems as non-CFC systems, and have advantages of continuous cycle and good heat exchange owing to utilization of fluid reactants. Chemical heat pumps with organic chemical reactions and the utilization of the reaction heat have been studied: the reaction systems of benzene hydrogenation (Murata *et al.*, 1993), 2-methyl-2-propanol/isobutene/water (Kato *et al.*, 1991) and acetone hydrogenation (Taneda *et al.*, 1993). The utilization of the reaction heat in a CHP for cooling is unusual owing to low reaction rate at low temperature. The Pa/A system and the system of acetal hydrolysis (Watanabe *et al.*, 1996) can generate cold thermal energy with organic reactions and the utilization of the reaction heat.

The purpose of this work is to investigate the mechanism of paraldehyde depolymerization with an acid solid catalyst for the CHP. A rate equation of the depolymerization was estimated from experiments. A cooling rate of the CHP was evaluated from the reaction rate equation.

2. Measurement of Depolymerization Rate

2.1 Experimental Apparatus

The depolymerization rate was measured with the experimental apparatus schematically shown in Fig. 1. The catalyst bed was set in an aluminum tube reactor with an inner diameter of 6.0 mm. Amberlyst 15E and aluminum particles were contained in the catalyst bed. The aluminum particles promote the heat transfer and reduce the temperature difference in the catalyst bed. Non-activity of the aluminum particles and the tube were confirmed experimentally.

The temperature of the reactor and the fed paraldehyde were set at 13, 20 or 30 °C within ± 0.3 °C. The temperature distribution in the catalyst bed was kept within ± 0.3 °C. Temperatures were measured by K-type thermocouples. The depolymerization rate was obtained from the change of the acetaldehyde concentration between inlet and outlet of the reactor. The concentrations of acetaldehyde and paraldehyde were analyzed by gas chromatography. Gas chromatographic measurements were made with Shimadzu GC-8A with flame-ionization detector. Amberlyst 15E was sieved with a particle size from 0.35 mm to 0.58 mm. The mean particle diameter of the catalyst was 0.49 mm. The catalyst was pretreated at 110 °C in Ar gas for 2 h.

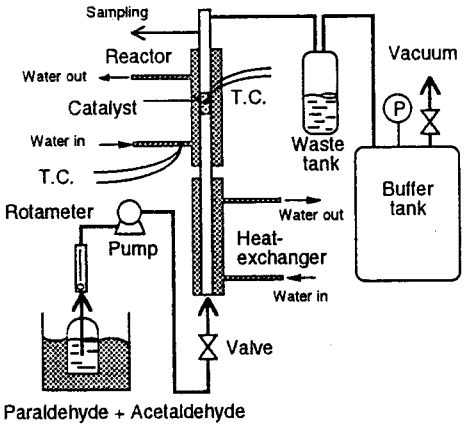


Fig. 1 Experimental apparatus of continuous reactor for measuring the reaction rate.

2.2 Result of the Depolymerization Rate

The feed rate to the reactor was kept constant at 12.4 m*l* min^{-1}. This feed rate was free from the mass-transfer restriction in the catalyst bed. Effects of mass-transfer were confirmed experimentally as shown in Fig. 2. The reaction rate increases with the feed rate up to 5.0 m*l* min^{-1}. The reaction rate over the feed rate of 5.0 m*l* min^{-1} is constant; the reaction rate is not restricted by the mass-transfer.

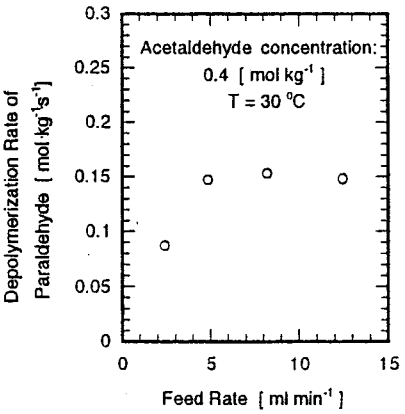


Fig. 2 Effects of the feed rate on the paraldehyde deolymerization rate.

The depolymerization rates were measured as a function of the acetaldehyde concentration. These rates were plotted in Fig. 3. The depolymerization rate decreases with an increase in the acetaldehyde concentration and with a decrease in the reaction temperature because of the endothermic reaction.

The ideal reaction rate was estimated from the effectiveness factor of the catalyst to analyze the reaction mechanism from the measured kinetic data. The ideal reaction rate is not restricted by intraparticle mass transport in a catalyst particle. The effectiveness factor of the Amberlyst 15E can be estimated from the Weisz modulus (Weisz and Hicks, 1962). The Weisz modulus is given by Eq. (2).

$$\Phi = (R_{pa} / 3)(d_p/6)^2 \rho_p / D_e(X_{AE} - X_A)\rho \tag{2}$$

The effective diffusivity is related to the pore-volume tortuosity factor by the following expression

$$D_e = \frac{\varepsilon_P}{\tau} D_{PaA} \tag{3}$$

The molecular diffusivity was evaluated by Wilke-Chang method (Wilke and Chang, 1955).

The Weisz modulus was calculated with the following data: the tortuosity factor was assumed to be 3, the porosity was 0.24, the molecular diffusivity was 1.52×10^{-9} m^2 s^{-1}. at 13 °C. The Weisz modulus of 0.87 was evaluated by above data substituted into Eqs. (2) and (3). The effectiveness factor was estimated with the relationship between the effectiveness factor and the Weisz modulus (Weisz and Hicks, 1962). The effectiveness factor decreases with an increase in the diameter of the catalyst as shown in Fig. 4. The effectiveness factor of mainly used the catalyst (d_p = 0.49 mm) was found to be 0.25 at 13 °C. This effectiveness factor means that the observed depolymerization rate is 0.25 times of the ideal depolymerization rate.

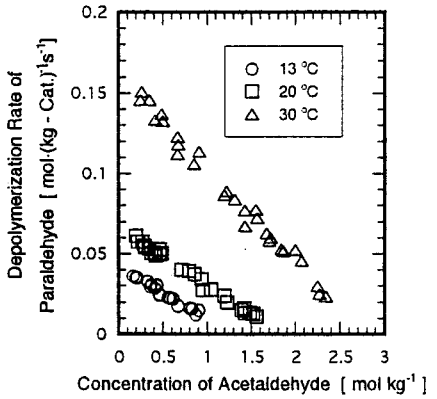


Fig. 3 Effects of the acetaldehyde concentration on the depolymerization rate.

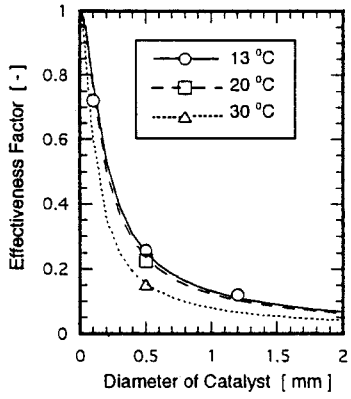


Fig. 4 Effects of the diameter of the catalyst on the effectiveness factor of the catalyst.

3. Reaction Mechanism of Paraldehyde Depolymerization

The depolymerization mechanism on the solid catalyst was assumed that four steps occur in series. The first step is an adsorption process of a paraldehyde molecule on a catalyst site. A proton transfers from H-bonding of the acid catalyst site to an oxygen atom in a paraldehyde molecule. The second step is a process of paraldehyde ring-opening and rearrangement of the vicinal-bond electrons; the acetaldehyde and the unstable species (a di-radical) are produced. The third step is a decomposition process of the unstable species. The fourth step is a desorption process of the acetaldehyde molecule from the site.

The reaction rate equation of paraldehyde on the solid catalyst was described by the

Langmuir-Hinshelwood kinetic model. The ring-opening step was assumed to be the rate-determining step from the previous works (Walvekar and Halgeri, 1972, Bell and Brun, 1954 and Cox and Yates, 1979) which will be discussed later. An activity of acetaldehyde and paraldehyde, instead of the concentrations, were used as variables in the reaction rate equation owing to some variations in the activity coefficients. The activities were estimated by the UNIFAC method (Gnehlling *et al.*, 1981). The following equations can be given.

First step $\theta_{Pa} = K_1 a_{Pa} \theta$ (4)

Second step $r = k_2 \theta_{Pa} - k_{-2} \theta_{AA} a_A$ (5)

Third step $\theta_{AA} = \theta_A a_A / K_3$ (6)

Fourth step $\theta_A = a_A \theta / K_4$ (7)

A fraction of vacant-sites to total sites on the catalyst can be expressed by

$$\theta = 1 - (\theta_{Pa} + \theta_{AA} + \theta_A) \tag{8}$$

The fraction of the free-sites is given by Eq. (9) with Eqs. (4),(6),(7) and (8), and with an assumption that the activation coefficients of the adsorbed substances are unity.

$$1/\theta = 1 + a_A / K_4 + a_A^2 / K_3 K_4 + K_1 a_{Pa} \tag{9}$$

The reaction rate of the second step is equal to the overall reaction rate owing to the rate-determining step. The depolymerization rate equation can be expressed as

$$R_{Pa} = k_2 \theta_{Pa} - k_{-2} \theta_{AA} a_A \tag{10}$$

Equation (10) can be rewritten with Eqs. (6) and (7)

$$R_{Pa} = (k_2 K_1 a_{Pa} - k_{-2} a_A^3 / K_3 K_4)\theta \tag{11}$$

The overall reaction rate can be represented by the reaction equilibrium constant to remove unknown constants.

$$R_{Pa} = k_2 K_1 (a_{Pa} - a_A^3 / K_{EQ})\theta \tag{12}$$

where the reaction equilibrium constant is given by Eq. (13).

$$K_{EQ} = k_2 K_1 K_3 K_4 / k_{-2} = a_E^3 / a_{PaE} \tag{13}$$

From Eqs. (9) and (12), the depolymerization rate can be expressed as

$$R_{Pa} = \frac{k_2 K_1 (a_{Pa} - a_A^3 / K_{EQ})}{1 + a_A / K_4 + a_A^2 / K_3 K_4 + K_1 a_{Pa}} \tag{14}$$

The kinetic constants, k_2, K_1, K_3 and K_4 can be determined from the rearrangement of Eq. (14). Equation (14) is rearranged and divided into two groups as shown in Eq.(15).

$$(a_{Pa} - a_A^3 / K_{EQ}) / R_{Pa} = (1 + a_A / K_4 + a_A^2 / K_3 K_4 + K_1 a_{Pa}) / K \tag{15}$$

where $K = k_2 K_1$. The left side in Eq (15) is a group of parameters which can be determined from the experimental kinetic data, the right side in Eq (15) is a group of the reaction rate constant and the equilibrium constants which will be investigated. The value of f is defined as

$$f = (a_{Pa} - a_A^3 / K_{EQ}) / R_{Pa} \tag{16}$$

The experimental data of the depolymerization rate were modified by Eq. (16). The right side in Eq (15) can be written without the paraldehyde activity. A paraldehyde activity can be expressed by

$$a_{Pa} = \gamma_{Pa} X_{Pa} = \gamma_{Pa}(1/M_{Pa} + M_A X_A / M_{Pa})$$
$$= \gamma_P / M_{Pa} + M_A \gamma_P (a_A / \gamma_A) / M_{pa}$$
$$= b_1 \gamma_{Pa} + b_2 (\gamma_{Pa} / \gamma_A) a_A \qquad (17)$$

The right side in Eq (15) can be rearranged with Eqs. (16) and (17).

$$f = a_A^2 / KK_3K_4 +$$
$$\{1/K_4 - b_2K_1(\gamma_{Pa} / \gamma_A)\}a_A / K +$$
$$(1 + b_1\gamma_{Pa}K_1) / K \qquad (18)$$

At the low acetaldehyde activity (< 0.3 mol kg^{-1}), a_A^2 / KK_3K_4 and $b_2K_1(\gamma_{Pa} / \gamma_A)$ can be negligible; Eq. (18) is reduced to Eq. (19).

$$f = (1/KK_4)\, a_A + (1+b_1K_1)/K \qquad (19)$$

The kinetic data at the low activity were used to evaluate the coefficients of the activity in Eq. (19). The f value obtained from Eq. (16) were plotted against the acetaldehyde activity in Fig. 5. The lines in Fig. 5 were fitted with the linear equation by of the least squares method; the coefficients of the activity in Eq. (19) was determined from the slope and the intercept of the lines. The kinetic data at the high activity were used to evaluate the coefficients in Eq. (18). The f values at the high activity were plotted again in Fig. 6. In this case, the curves in Fig. 6 were fitted by the quadratic equation with the known constants obtained at the low activity. All kinetic constants can be determined by the comparison of coefficients obtained from curve fitting to the terms in Eq. (18).

The calculated kinetic constants were shown in Arrhenius plotting in Fig. 7. Symbols in Fig. 7 were calculated from experimental kinetic data. The kinetic constants were fitted by linear equations as shown in Fig. 7. The kinetic constant of K_1 increases with a decrease in the reaction temperature because the adsorption step is the exothermic reaction. The kinetic constants of k_2, K_3 and K_4 decrease with an increase in reaction temperature owing to the endothermic reactions. The kinetic constants can be described as a function of temperature in Eqs. (20) - (23).

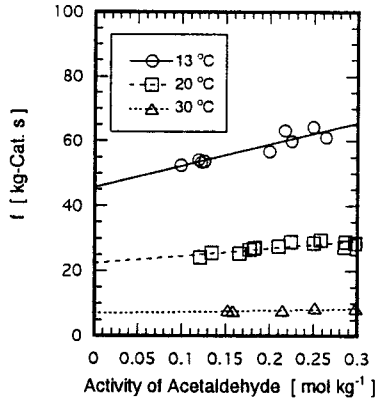


Fig. 5 Effects of the acetaldehyde activity on the f value defined by Eq. (16) at the low activity.

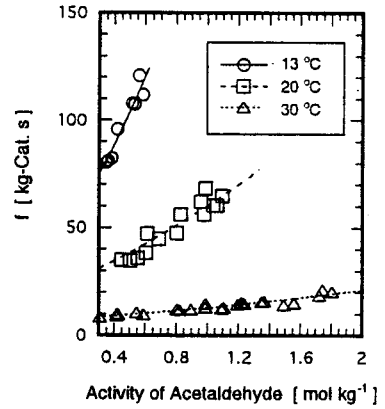


Fig. 6 Effects of the acetaldehyde activity on the f value defined by Eq. (16).

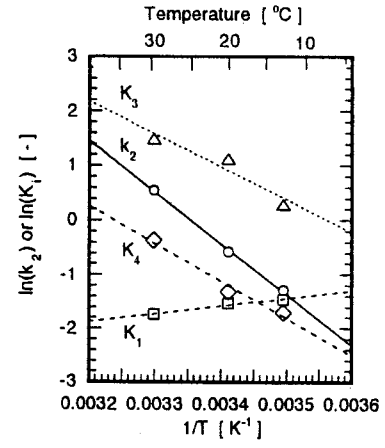


Fig. 7 Effects of temperature on the rate constant and on the chemical equilibrium constants.

$$k_2 = exp\{(-1.00\times10^4/T) + 33.8\} \quad (20)$$

$$K_1 = exp\{(2.18\times10^3/T) - 9.25\} \quad (21)$$

$$K_3 = exp\{(-7.00\times10^3/T) + 24.7\} \quad (22)$$

$$K_4 = exp\{(-7.11\times10^3/T) + 23.6\} \quad (23)$$

4. Discussion

Arrhenius activation energy can be calculated from the slope of the lines in Fig. 7. The calculated activation energy of the rate-determining step is 83.3 kJ mol^{-1}. Walvekar and Halgeri (1972) reported that the activation energy of the paraldehyde depolymerization on the solid catalysts ranges from 62 to 106 kJ mol^{-1}. The activation energy can not be compared simply with our calculated activation energy, because their reaction mechanism was based on the Michaelis-Menten kinetic model. The calculated activation energy, however, is within this range.

The rate-determining step was assumed to be the ring-opening step since the depolymerization rate depends on an acidity of a catalyst. Kinetic measurements (Bell and Brun, 1954) were reported on the paraldehyde depolymerization with homogeneous catalysts. The depolymerization rate depends upon the acidity of the homogeneous catalyst. Cox explained with the transition state theory that the reaction rate of the paraldehyde ring-opening step is slower than that of decomposition step of the unstable species (Cox and Yates, 1979). In our study, the activation energy of the paraldehyde ring-opening step is higher than the other steps. The highest activation energy of the ring-opening step agrees with the assumption.

The cooling rate with the Pa/A system was estimated at 13 °C in the endothermic reactor with Amberlyst 15E. The cooling rate increases with a decrease in the acetaldehyde concentration in the endothermic reactor. The acetaldehyde concentration is arrested by the compression ratio and the coefficient of performance (COP) which are restricted by the condition of the practical use. The acetaldehyde concentration of 1.2 mol kg^{-1} which was one of the reasonable concentration was settled by the restriction of the compression ratio and the COP. The cooling rate of 3.4 kW per unit catalyst-weight was estimated at this concentration.

Side reactions in the reaction system can not be allowed because of the continual reaction in the system. The side reaction most possibly occurs in the Pa/A system is the production of crotonaldehyde. Crotonaldehyde is produced from acetaldehyde in the presence of an alkaline catalyst or at high temperature. Any products of side reactions were not detected by gas chromatography in our measurement.

5. Conclusion

The depolymerization rate equation with Amberlyst 15E was estimated. The equation of the paraldehyde depolymerization rate on the catalyst was described by the Langmuir-Hinshelwood kinetic model. The paraldehyde depolymerization on the solid catalyst was assumed that four steps occur in series. The rate-determining step of the paraldehyde depolymerization on the solid catalyst is the paraldehyde ring-opening step. The cooling rate per unit catalyst-weight of 3.4 kW was evaluated at 13 °C and at 1.2 mol kg^{-1} of the acetaldehyde concentration.

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Nomenclature

a_i = activity of i [mol kg^{-1}]
b_i = constant defined in Eq. (17)
D_e = effective diffusivity [m^2 s^{-1}]
D_{PaA} = molecular diffusivity of cetaldehyde in paraldehyde [m^2 s^{-1}]
d_p = diameter of catalyst particle [m]
f = defined by Eq. (16)
ΔG = Gibbs function change [kJ mol^{-1}]
k_{-2} = rate coefficient of reverse reaction at second step [kg mol^{-1} s^{-1} (kg-Cat.)$^{-1}$]
k_2 = rate coefficient of forward reaction at second step [kg mol^{-1} s^{-1} (kg-Cat.)$^{-1}$]
K_i = equilibrium constant
M_i = molecular weight of i [kg mol^{-1}]
R = gas constant [kJ mol^{-1}K^{-1}]
R_{Pa} = depolymerization rate of paraldehyde [mol (kg-Cat.)$^{-1}$ s]
r = reaction rate at second step [kg mol^{-1} s^{-1} (kg-Cat.)$^{-1}$]
T = temperature [K]
X_i = concentration of i [mol kg^{-1}]
x_i = mole fraction of i

Greek symbols

ε_p = catalyst void fraction
Φ = Weisz modulus
γ = coefficient of activity
θ = fraction of vacant sites of catalyst
θ_i = fraction of active sites of catalyst adsorbed by i
ρ = density of liquid [kg m^{-3}]
ρ_p = catalyst solid density [kg m^{-3}]
τ = tortuosity factor

Subscripts

A = acetaldehyde
AE = acetaldehyde at the reaction equilibrium condition
Pa = paraldehyde
PaE = paraldehyde at the reaction equilibrium condition