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Synthesis of Diethyl Oxalate by a Coupling-Regeneration Reaction of Carbon Monoxide

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Abstract: This article describes a process for the synthesis of diethyl oxalate by a coupling reaction of carbon monoxide, catalyzed by palladium in the presence of ethyl nitrite. The kinetics and mechanism of the coupling and regeneration reaction are also discussed. This paper presents the results of a scale-up test of the catalyst and the process based on an a *priori* computer simulation.

Key words: CO coupling, diethyl oxalate, kinetics and mechanism, simulation, scale-up test

1. Introduction

The use of carbon monoxide to produce organic chemicals is an important research area of C1 chemical technology. In particular, the coupling reaction of carbon monoxide for producing diethyl oxalate can take place under moderate reaction conditions and with low consumption of energy. This chemical is a useful feedstock for the synthesis of ethylene glycol and oxalate acid, as well as for the preparation of dyestuff, pharmaceuticals, useful solvents, extraction agents and various intermediates [1]. Accordingly, this synthesis route for diethyl oxalate from carbon monoxide over supported palladium catalysts has been studied by several groups [2–8].

Two chemical reactions taking place simultaneously are involved in the process: the coupling reaction and the regeneration reaction. The coupling reaction performs the synthesis of diethyl oxalate from carbon monoxide and ethyl nitrite in the presence of a coupling catalyst.

$$2CO + 2EtONO \rightarrow (COOEt)_2 + 2NO \qquad (a)$$

In the regeneration reaction, the nitrogen monoxide produced in the coupling reaction reacts with alcohol and oxygen to form ethyl nitrite. The ethyl nitrite so formed is then recycled as the feed to the coupling reaction.

$$2NO + 2EtOH + 1/2O_2 \rightarrow 2EtONO + H_2O \qquad (b)$$

The overall equation is:

$$2CO + 2EtOH + 1/2O_2 \rightarrow (COOEt)_2 + H_2O \qquad (c)$$

As is clear from the above description, a match of the coupling-regeneration rates is vital to successfully running the process. With an effective control, there will be a reasonable utilization of NO, EtONO and EtOH, without any toxic emissions from the system. In this way, no hazardous gases are emitted and a self-cycling, non-polluting, and closed system is established.

2. Kinetics and mechanism of the coupling and regeneration reaction

2.1. Kinetics and mechanism of the coupling reaction

The kinetic characteristics of the catalytic coupling of carbon monoxide to diethyl oxalate in the

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gas phase over a supported palladium catalyst were studied in previous experiments [2,9]. Our research revealed that the rate-controlling step is the adsorption of carbon monoxide. Moreover, it was considered that the alkoxycarboxide intermediate (COOEt) possibly exists, and associates further to diethyl oxalate on the surface of the catalyst. The results also indicated that the catalytic reaction of carbon monoxide coupling occurs via a redox mechanism. The resulting Langmuir-Hinshelwood type rate expression is shown in equation (1). The kinetic parameter K_i in the rate express is a function of the reactor temperature, as shown in equation (2). The values of K_{i0} and E_i are listed in Table 1.

$$\begin{aligned} -r_{\rm co} = \; & (K_7 P_{\rm CO} - K_8 K_1 \frac{P^{0.5}_{\rm (COOEt)_2} P_{\rm NO}}{P_{\rm EtONO}})/ \\ & (1 + K_1 \frac{P^{0.5}_{\rm (COOEt)_2} P_{\rm NO}}{P_{\rm EtONO}} + K_2 P_{\rm EtONO} + \\ & K_3 P^{0.5}_{\rm (COOEt)_2} + K_4 P_{\rm (COOEt)_2} + \\ & K_5 P_{\rm NO} + K_6 P_{\rm EtOH}) \end{aligned} \tag{1}$$

$$K_i = K_{i0} \exp(E_i/RT) \tag{2}$$

Table 1. Values of K_{i0} and E_i

i	K_{i0}	E_i
1	534.4	991
2	0.00183	37570
3	379.4	3840
4	20340	–17835
5	20269	–16770
6	4618	1026
7	1604.5	–21427
8	0.0844	–18561

2.2. *Kinetics and mechanism of the regeneration reaction*

The kinetics of the regeneration reaction was studied for the sake of matching with the carbon monoxide coupling reaction [10]. The macroscopic kinetic model was established to be in the form of

$$R_{\rm A} = K_{\rm R} P_{\rm NO} \tag{3}$$

with an activation energy of 19.46 kJ·mol^{-1} and a frequency factor of 0.341 mol·m^{-3}·Pa^{-1}·s^{-1}. Characteristic parameters of the rate equation and the regeneration column were obtained on the basis of the two-film theory of gas-liquid reactions. An inspection of the results shows that the regeneration reaction is a first order fast reaction and the rate-determining step is the liquid film resistance.

3. Selection of optimum operating conditions by simulation of the reaction system

An outline of the synthesis process for $\rm (COOEt)_2$ is shown in Figure 1. The coupling reactor was a single tube, 1.5 m long and 2.7 cm in diameter, packed with a supported bimetallic catalyst Pd-Me/$\rm Al_2O_3$. It was jacked to allow heat exchange with a coaxial flow of a YD-300 heat-transfer oil. The ratio of $L/d_{\rm t}$ was 55.6 and $d_{\rm t}/d_{\rm p}$ was 90, so that the reactor could be assumed to behave as a plug flow reactor (PFR). A basic two-dimensional pseudohomogeneous model was used to represent the reactor behavior. Assuming that the pressure drop across the reactor was negligible, the steady state mass balance and heat balance are:

$$\begin{aligned} \frac{\partial X_{\rm CO}}{\partial Z} = \; & \frac{d_{\rm p}}{P_{\rm er}}(\frac{\partial^2 X_{\rm CO}}{\partial r^2} + \frac{\partial X_{\rm CO}}{r \partial r}) \\ & + \frac{(-r_{\rm CO})\rho_{\rm B}\frac{\pi}{4}d_{\rm t}^2}{F_{\rm CO}} \end{aligned} \tag{4}$$

$$\begin{aligned} \frac{\partial T}{\partial Z} = \; & \frac{\lambda_{\rm er}\frac{\pi}{4}d_{\rm t}^2}{F_{\rm t}C_{\rm Pg}}(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r}) \\ & + \frac{r_{\rm CO}\rho_{\rm B}\Delta H\frac{\pi}{4}d_{\rm t}^2}{F_{\rm t}C_{\rm Pg}} \end{aligned} \tag{5}$$

And the boundary conditions are:

$$\begin{array}{ll} Z = 0, \;\; 0 \le r \le \frac{d_{\rm t}}{2}, & X_{\rm CO} = 0, \;\; T = T_0 \\ r = 0, \;\; 0 \le Z \le L, & \frac{\partial X_{CO}}{\partial r} = \frac{\partial T}{\partial r} = 0 \\ r = 1, \;\; 0 \le Z \le L, & \frac{\partial X_{\rm CO}}{\partial r} = 0, \\ & \frac{\partial T}{\partial r}\,|_{r=\frac{d_{\rm t}}{2}} = \frac{wC_{\rm Pc}}{\pi d_t \lambda_{\rm er}}\frac{\partial T}{\partial Z} \end{array}$$

The regeneration was performed in a two-phase reactor — a bubble column filled with θ-ring stuffing. The internal diameter and height of the bubble-column amounted to 6 cm and 36 cm, respectively. The gas and the liquid all flowed in from the bottom of the column and out from the top. From the calculation we found that the liquid phase Peclet number was 0.0034, which was less than 0.1, and the gas phase Peclet number was 25.4, *i.e.*, greater than 10.

Therefore, a CSTR model could be used to represent the liquid phase behavior, and the PFR for gas phase behavior. The differential and overall mass balances are:

$$G_{\mathrm{t}}\mathrm{d}Y_{\mathrm{NO}} = (R_{\mathrm{A}})A_{\mathrm{t}}\mathrm{d}h \tag{6}$$

$$G_{\mathrm{t}}(Y_{\mathrm{NO_2}} - Y_{\mathrm{NO_1}}) = 2L_{\mathrm{t}}(C_{\mathrm{W2}} - C_{\mathrm{W1}})A_{\mathrm{t}}\mathrm{d}h \tag{7}$$

Steady-state simulation and optimization on the basis of industrial application were carried out with the Sequential Modular Approach with the aid of Aspen and PRO/II software. The simulation results are shown in Figures 1–4. The parameters considered included the inlet temperature of the coupling reactor, the fresh gas feed flow rate, the inert gas flow rate, the coolant flow rate and direction, the inlet temperature, the reaction pressure, the alcohol concentration, the residence time, the heat exchange coefficient, and the component concentration.

As shown in Figure 2, being an exothermic reaction, the reaction temperature of the coupling reaction at a finite axial reactor position exhibited a peak or "hot spot". Figure 3 illustrates that the difference in radial concentration was negligible. Figures 4 and 5 demonstrate that both the inlet concentration of carbon monoxide and the flow direction of the coolant had a strong influence on the reactor bed temperature. On the basis of the simulation, suitable operation conditions are as follows:

(1) Inlet temperature of the coupling reactor: 353–373 K;

(2) Temperature of the bubble column: 303–313 K;

(3) CO feed rate: 7–9 mol/h;

(4) O_2 flow rate into the regeneration column: 2 mol/h;

(5) The ratio of recycling gas volume to fresh gas volume: 5–8;

(6) Composition of the feed entering the coupling reactor (mol%): CO 20%–25%, EtONO 20%, N_2 40%–45%.

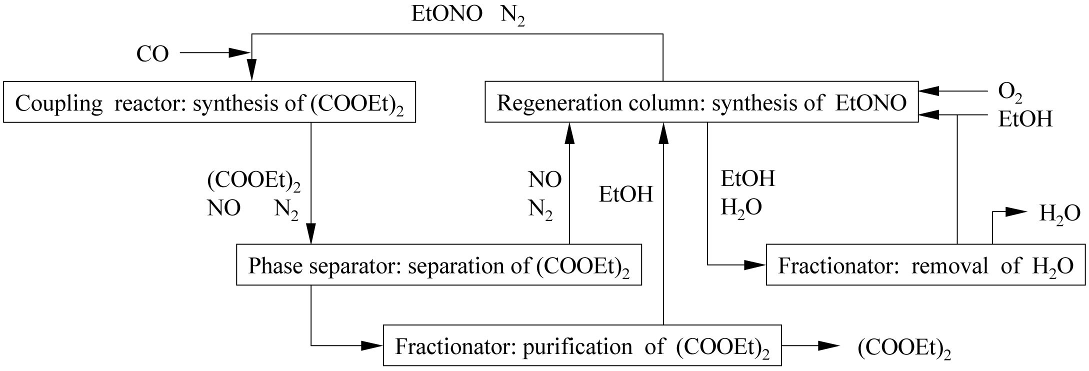

Figure 1. Flow diagram for the synthesis of $(COOEt)_2$ from carbon monoxide

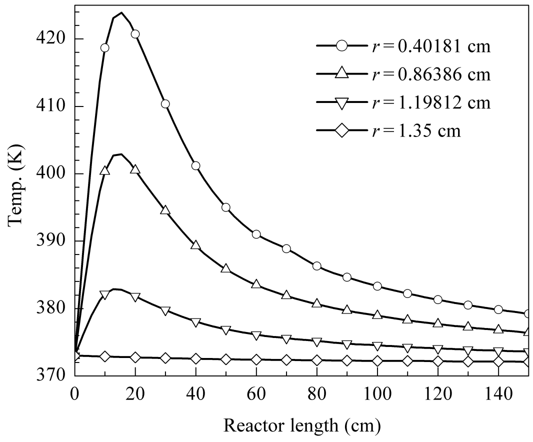

Figure 2. Profiles of temperature along the reactor length.

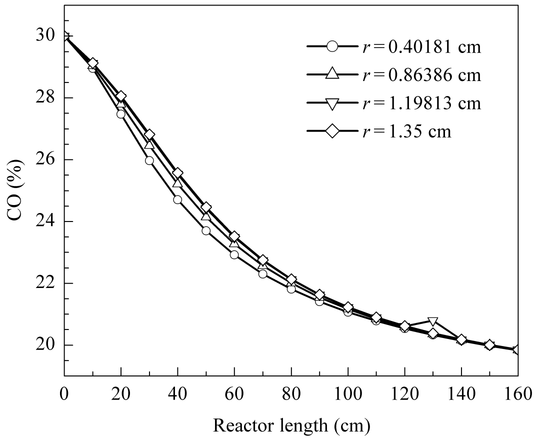

Figure 3. CO concentration *vs.* the reactor length.

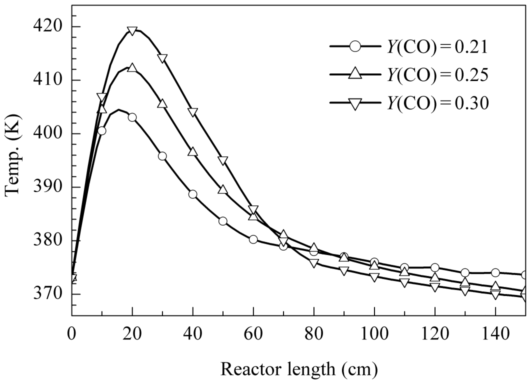

Figure 4. Sensitivity of inlet CO concentration.

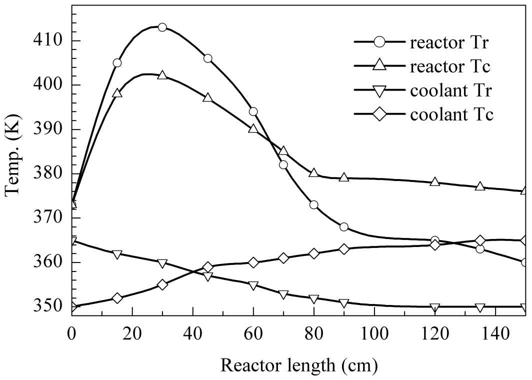

Figure 5. Influence of the flow direction of the coolant.

4. Scale-up test and engineering development

A scale-up test was carried out based on the above research results. The objective was to examine the stability of the catalyst, the matching ability of the coupling-regeneration reactions, and the influence factors. The automatic scale-up equipment was outfitted with an online monitor, computer controller and in-time recorders. During the scale-up test, the coupling reactor and the regeneration column were preheated to 353 K and 305 K, respectively. NO, N_2 and EtOH were fed into the regeneration column. The flow rate of EtOH was 1.7 ml/min, and the mole ratio of NO, O_2 and EtOH was equal to the stoichiometric ratio of the regeneration reaction. Carbon monoxide was fed into the coupling reactor with a flow rate of 8 mol/h. The EtONO produced by the regeneration reaction was cycled into the coupling reactor, where it reacted with carbon monoxide to form $(COOEt)_2$. There was a condenser and a phase separator at the inlet of the coupling reactor where the desired product, $(COOEt)_2$, was condensed into liquid and separated from NO, N_2 *etc.*. NO and all other gases, after being pressurized, were fed into the regeneration column to react with EtOH to form EtONO for recycling.

4.1. Scale-up test of catalyst preparation

Figures 6 and 7 indicate the relationship of the scale-up factor of catalyst preparation to reaction performance and space time yield (STY) of $(COOEt)_2$. As can be seen from the figures, the process of catalyst preparation in our study demonstrated excellent repetition, negligible scale-up effects, and results that can meet the requirements of industrialization.

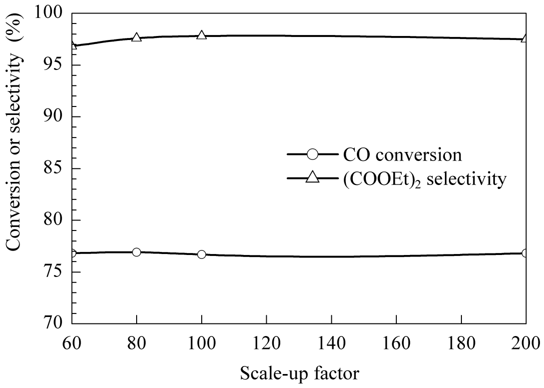

Figure 6. Reaction performance *vs.* catalyst scale-up factor.

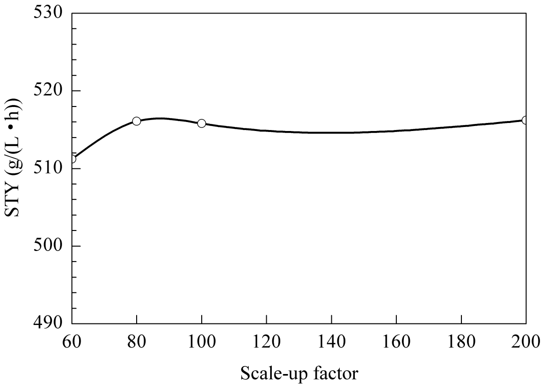

Figure 7. Space time yield (STY) of $(COOEt)_2$ *vs.* scale-up factor.

4.2. 1000-hour scale up duration test

Reaction parameters were collected during the test run with the aid of a computer. The concentrations of the key components in the reaction system were analyzed by an online gas chromatograph. The change in concentration of the ethyl nitrite during the entire run time was negligible (Figure 8). This means that the amount of EtONO produced by the regeneration reaction was equal to the amount consumed by the coupling reaction. Figure 9 shows that the concentration of the desired product, diethyl oxalate, remained nearly unchanged within the range of 93%–98%, and its selectivity was never less than 90%.

The exhaust rate of the tail gas was never more than 0.09%, also indicating that the rate of the coupling reaction principally matched up with the rate of the regeneration reaction during the run time.

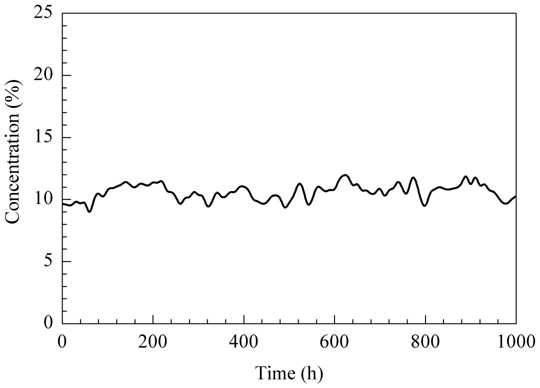

Figure 8. Ethyl nitrite concentration in cycling gas as a function of on-stream time.

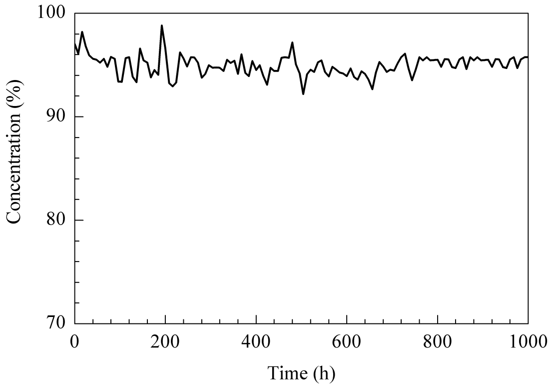

Figure 9. Diethyl oxalate concentration as a function of on-stream time.

5. Conclusions

(a) Based on the coupling and regeneration kinetics and from simulating the carbon monoxide coupling-regeneration reaction for diethyl oxalate, the problem of rate-matching of the complex reaction system has been solved, and suitable operating conditions for the process have been obtained.

(b) A 1000-hour scale-up test was carried out in a continuous process development unit to study the matching of operating parameters between the coupling and regeneration reactions based upon the simulation results. With a proper choice in the operating conditions and by effective controlling, the rates between these two reactions could be roughly balanced with each other so that the process could realize practically no emission of poisonous substances.

(c) The stability of the catalyst was also tested and verified in the scale-up test. The results proved that the catalyst prepared could meet the requirement of industrialization for the carbon monoxide coupling reaction.

A pilot plant test for diethyl oxalate production with a capacity of 300 t/year is already in progress.

Nomenclature

$A_{\rm t}$ — cross-sectional area of bubble column, $\rm m^2$

$C_{\rm Pc}$ — specific heat of coolant, $\rm J{\cdot}K^{-1}{\cdot}kg^{-1}$

$C_{\rm Pg}$ — mean specific heat of reactant mixture, $\rm J{\cdot}K^{-1}{\cdot}kg^{-1}$

$C_{\rm W1}$ — $\rm H_2O$ concentration at the outlet of bubble column, $\rm kmol{\cdot}m^{-3}$

$C_{\rm W2}$ — $\rm H_2O$ concentration at the inlet of bubble column, $\rm kmol{\cdot}m^{-3}$

$d_{\rm p}$ — diameter of the catalyst pellets, mm

$d_{\rm t}$ — reactor diameter, m

E_i — coupling kinetic constant

$F_{\rm CO}$ — CO flow rate at the reactor inlet, $\rm kmol{\cdot}m^{-2}{\cdot}h^{-1}$

$F_{\rm t}$ — overall flow rate of reactant mixture, $\rm kmol{\cdot}m^{-2}{\cdot}h^{-1}$

G_t — inert gas flow rate in bubble column, $\rm kmol{\cdot}h^{-1}$

h — axial coordinate of bubble column, m

$K_{\rm R}$ — regeneration macrokinetic constant, $\rm mol{\cdot}m^{-3}{\cdot}Pa^{-1}{\cdot}s^{-1}$

K_i — coupling kinetic constant

K_{i0} — coupling kinetic constant

L — length of catalyst bed, m

$L_{\rm t}$ — liquid flow rate in bubble column, $\rm m^3{\cdot}h^{-1}$

M — mean molecular weight of reactant mixture, $\rm kg{\cdot}kmol^{-1}$

P_i — partial pressure of the i^{th} component, kPa

r — radial coordinate of reactor, m

$r_{\rm CO}$ — CO reaction rate, $\rm mol{\cdot}m^{-3}{\cdot}s^{-1}$

R — universal gas constant, $\rm J{\cdot}mol^{-1}{\cdot}K^{-1}$

$R_{\rm A}$ — regeneration reaction rate, $\rm mol{\cdot}m^{-3}{\cdot}s^{-1}$

T — temperature of reactor bed, K

$T_{\rm c}$ — temperature of reactor bed or coolant(cocurrent), K

$T_{\rm r}$ — temperature of reactor bed or coolant (countercurrent), K

$X_{\rm CO}$ — CO conversion,%

$Y_{\rm NO}$ — ratio of NO to inert gas in bubble column, v/v

$Y_{\rm NO1}$— ratio of NO to inert gas at the outlet of bubble column, v/v

$Y_{\rm NO2}$— ratio of NO to inert gas at the inlet of bubble column, v/v

Z — axial coordinate of reactor, m

Greek letters

ΔH — heat of reaction, $J \cdot mol^{-1}$
λ_{er} — radial heat transfer coefficient, $J \cdot m^{-2} \cdot s^{-1} \cdot K^{-1}$
ρ_B — density of catalyst bed, $kg \cdot m^{-3}$

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