Bull. Chem. Soc. Jpn., *61*, *973—981 (1988)*

Alumina-Anchored Cobalt Porphine Catalysts for the Conversion of Quadricyclane to Norbornadiene

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(Received August 27, 1987)

Methods are described for the preparation of cobalt(II) deuteroporphyrin and cobalt(II) tetrakis(*p*-sulfonatophenyl)porphine anchored on alumina beads coated with polyaminesulfone-A. Wavelength dispersive X-ray microanalysis showed that the cobalt(II) porphine distributes within the catalyst outer surface layer of ca. 100 μm depth. The catalysts are highly active for the cycloreversion of quadricyclane to norbornadiene. A detailed kinetics of the isomerization using an isothermal recycle reactor gave a rate expression of Langmuir–Hinshelwood type. The catalysts gradually lose their activity, which can be regenerated completely by heating the catalysts at 200 °C in vacuo.

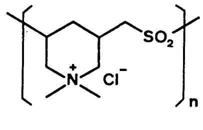
Heterogeneous catalysts have merit to eliminate disadvantages of homogeneous catalysts, the difficulties in separation of catalyst from product as well as the loss of expensive catalyst by entrainment. Solar energy storage system based on photochemical formation of highly strained molecules coupled with catalyzed reversion of the photoproduct is the case.[1–8] In the connection with the recent importance of solar chemical latent energy system, several heterogeneous catalysts have been developed for the conversion of quadricyclane (Q) to norbornadiene (NBD),[9–12] and the criteria for an ideal catalyst have been pointed out by King and Sweet.[9] A serious problem for the catalysts reported so far seems to be loss of catalyst activity upon repeated use and its regeneration.

This paper describes our new method for preparation of heterogeneous catalyst by immobilizing cobalt(II) porphine derivatives on alumina beads.

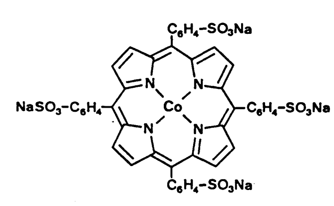
In evaluating the catalysis system, it is essential to know the kinetic profiles over a wide range of substrate concentration. Most of kinetic studies reported so far have been carried out at low quadricyclane concentrations (e.g., 0.1 mol·L^{-1})[9]. Here, we have examined kinetics of our heterogeneous catalysis system over a range of the substrate concentration of 0.1—1.0 mol·L^{-1} using an isothermal recycle reactor. Furthermore, energy releasing process (Q→NBD) has been run on an adiabatic fixed bed reactor and the temperature profiles of the system are discussed based on the kinetic studies.

Results and Discussion

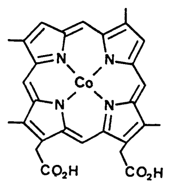
Preparation of the Catalysts, Co(II)TPPS/PAS/Alumina (1) and Co(II)DPIX/PAS/Alumina (2). By soaking activated alumina beads (mean diameter of 3 mm) in aqueous solution of polyaminesulfone-A (PAS, 3, MW=2×10^5), 3 was adsorbed on the alumina beads, and the alumina beads were modified to have the anion binding ability. Thus, upon contact with a solution of cobalt(II) sodium tetrakis(*p*-sulfonatophenyl)porphine (Co(II)TPP(*p*-SO_3Na)$_4$, 4) in methanol the alumina beads coated with PAS adsorbed the porphynato cobalt(II) to afford the catalyst Co(II)-TPPS/PAS/Alumina (1). The adsorption was effective, and in typical run using 9.1 g of 4, the complete disappearance of the color of 4 in the liquid phase was observed by the PAS/Alumina (190 g). For cobalt(II) deuteroporphyrin (Co(II)DPIX, 5), pyridine was used as solvent. In this case, by the rapid adsorption of 5 by PAS/Alumina Co(II)DPIX/PAS/Alumina (2) was obtained. Four kinds of heterogeneous catalysts, A—D of 2 were prepared, which incorporated 19 mmol, 39 mmol, 72 mmol, and 139 mmol of 5 per 1 kg of the resulting catalyst, respectively. In each case adsorption of cobalt(II) porphines was carried out under unaerobic conditions. These cobalt contained catalysts are, however, stable to air in dry state. The conditions for the preparation of each catalysts are shown in Table 1.



PAS, 3



Co(II)TPP(p-SO_3Na)$_4$, 4



Co(II)DPIX, 5

Table 1. Preparation of the Modified Alumina-Anchored Cobalt(II) Porphine Catalysts

Catalyst (batch)	Co(II) porphine	PAS/alumina	Solvent	Catalyst obtained	Co(II) porphine[a)] incorporation
		g		g	mmol·kg^{-1}
1	9.12 g Co(II)TPP(*p*-SO_3Na)$_4$	190	2000 mL Methanol	194	43
2(A)	0.75 g Co(II)DPIX	69	160 mL Pyridine	70	19
2(B)	2.6 g Co(II)DPIX	114	500 mL Pyridine	116	39
2(C)	0.2 g Co(II)DPIX	4.67	40 mL Pyridine	4.9	72
2(D)	0.4 g Co(II)DPIX	4.60	80 mL Pyridine	5.0	139

a) Evaluated based on the weight of catalyst obtained and the amount of Co(II) Porphine used, because almost complete adsorption of the metal porphine was observed in each case.

Table 2. Activities of Cobalt(II) Porphines Anchored on Alumina Beads Modified by PAS for the Conversion of Q to NBD[a)]

Catalyst[b)]	Mol of Co(II) Porphine	$k_w \times 10^6$	k_p
	mol·g^{-1}	L·s^{-1}·g^{-1}	L·s^{-1}·mol^{-1}
1	0.043	2.45	0.57
2-A	0.019	2.95	1.6
2-B	0.039	6.00	1.5
2-C	0.072	7.93	1.1
2-D	0.14	10.8	0.77

a) Kinetic studies were carried out using pentane solution of Q, initially 0.02 mol·L^{-1} and ca. 70 mg of the catalysts at 21±1°C. b) A—D refer to the batch numbers in Table 1.

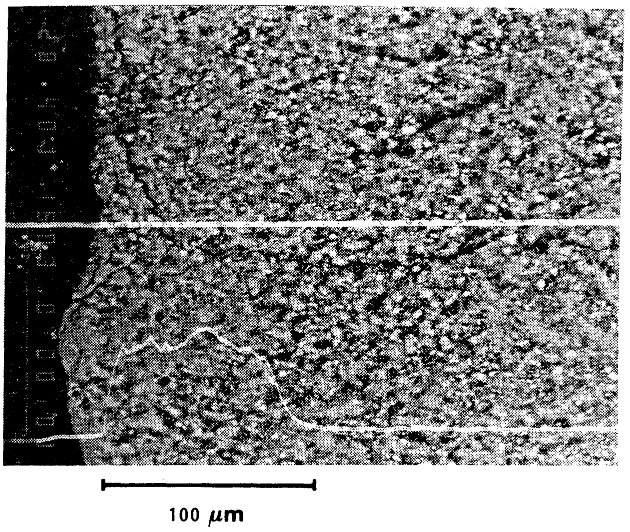


Fig. 1. SEM photograph as well as distribution of Co atoms for the cross section of the bead of Co(II)-TPPS/PAS/Alumina. The waved line shows the distribution of Co atoms along the corresponding white straight line.

Scanning Electron Microscopy (SEM) and Wavelength Dispersive X-Ray Microanalysis on Cross Section of Beads of Co(II)TPPS/PAS/Alumina (1). Figure 1 depicts SEM photograph of the cross section of the beads of **1**. The white waved line refers to distribution of Co atoms along the diameter on the cross section of the bead corresponding to the white straight line. As depicted by the waved line in Fig. 1, the distribution of Co atoms was found to be within a catalyst surface layer of 100 μm depth.

Activities of Co(II)TPPS/PAS/Alumina and Co(II)DPIX/PAS/Alumina as Catalysts. The catalysts **1** and **2** showed remarkably large catalytic activities for the reversion of Q to NBD. As one exmple, when a solution of 4 ml of Q in 6 ml of benzene was treated with 1 g of **2**-A, the exothermic reaction occurred immediately within 5 s, and the solution began to boil vigorously. After 1 min, more than 99% conversion of Q was observed by a GC analysis.

The conversion of Q to NBD catalyzed by these catalysts was followed kinetically in an isothermal batch reactor. The disappearance of Q (initial concentration=0.02 mol·L^{-1}), in pentane and the concomitant formation of NBD at 21±1 °C were monitored by GC. At such a low concentration of Q, a first order kinetic plots gave a straight line, whereas the reaction at higher concentration of Q could not be expressed by pseudo-first-order kinetic treatment. As the catalytic activities we use the values k_w L·s^{-1}·g^{-1} which are the first order kinetic constants normalized to 1 g of catalyst in 1 L of solution. The values were obtained from runs with ca. 70 mg of catalyst in 5 mL of solution (Table 2). In Table 2, k_p is the activity based on cobalt(II) porphine content. Table 2 shows the variation of the activity of **2** when the amount of Co(II)DPIX adsorbed was changed. At the low content of the cobalt(II) porphine below 39 mmol·g^{-1}, catalytic activity is proportional to the amount of Co(II)DPIX adsorbed. On the contrary, at higher content no correlation is observed, where k_w varies

Table 3. Pseudo-First-Order Kinetic Constants of Catalyzed Reversion of Q to NBD at Various Temperatures[a)]

Catalyst	Temperature	$k_{obsd} \times 10^4$
	°C	s^{-1}
1	19	3.27
1	24	3.65
1	29	4.10
1	34	4.65
2-A	16	3.88
2-A	21	4.46
2-A	25	4.69
2-A	30	5.65

a) First order kinetic constants were measured in an isothermal batch reactor using 5 mL of pentane solution of Q, initially 0.02 mol·L^{-1}, with 70 mg of the catalysts.

only from 6.00 to 10.8 L·s^{-1}·g^{-1} while the amount of Co(II)DPIX adsorbed varies from 39 to 140 mmol·g^{-1}. Although the reason of the lack of the correlation at higher amount of Co(II)DPIX is not apparent, it seems likely that the distribution of the catalyst monomer to deeper layer of the catalyst particle and the correspondingly occurring inner mass diffusion limitation might reduce the apparent activity of the catalyst monomer at its high content.

Temperature dependence of the pseudo-first-order kinetic constant is shown in Table 3. An Arrhenius plots corresponding to Table 3 gave energy of activation of the reaction of 16.9 and 18.8 kJ mol^{-1} for **1** and **2**-A, respectively, indicating that the active species for each catalyst is fairly effective for the cycloreversion of Q to NBD.

Kinetic Study at High Quadricyclane Concentration by an Isothermal Recycle Reactor. A more detailed analysis was undertaken of the kinetics of the conversion of Q to NBD catalyzed by **1** and **2**, i.e., kinetic profiles with respect to Q concentration and the retention of catalytic activities. These subjects are difficult to be examined by an usual batch type reactor. Here, the reaction rate was measured by an isothermal recycle reactor (batch of solid and flow of fluid, Fig. 2)[13)] which eliminates the external mass transfer resistance. Isooctane was used as a solvent in this case.

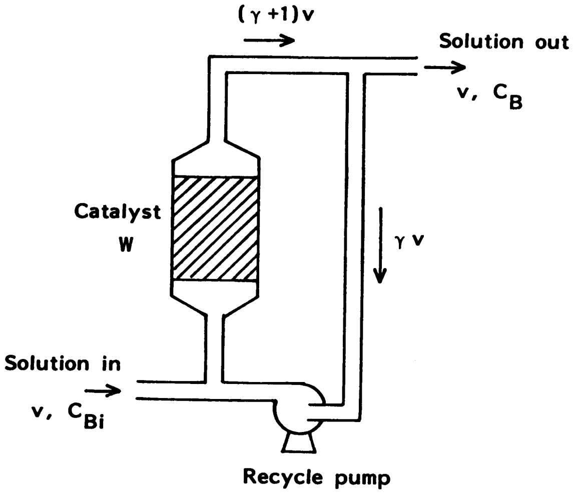


Fig. 2. Recycle reactor.

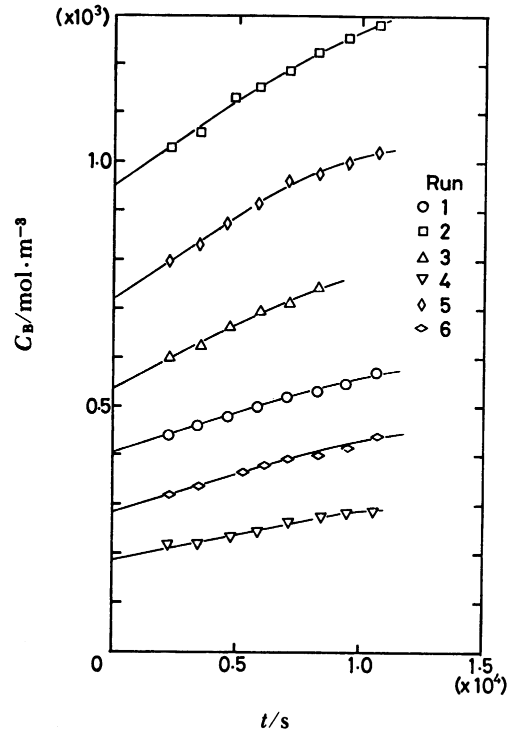


Fig. 3. Concentration of Q as a function of time. Run numbers refer to the experimental run given in Table 4.

In Fig. 2 C_{Bi} and C_B are concentrations of Q for inlet and outlet of the reactor, respectively. The solution was fed by steady rate of v m^3·s^{-1}. Catalyst of the weight of W kg was used. The value γ is recycle ratio, which was set large enough to treat the reactor as an ideal CSTR (continuous stirred tank reactor). Thus, we can set up Eq. 1 for the material balance

$$vC_{Bi} - vC_B - rW = 0 \quad (1)$$

where r denotes the reaction rate over catalyst (mol·s^{-1}·kg^{-1}). Thus the reaction rate normalized to 1 kg of catalyst is given by Eq. 2.

$$-r = v(C_{Bi} - C_B)/W \quad (2)$$

A description of the experimental conditions for Co(II)TPPS/PAS/Alumina **1** is given in Table 4.

After the reaction system reached to pseudo-steady state, Q concentration (C_B) was monitored at appropriate time intervals. Figure 3 shows the C_B as a function of time for Runs 1—6 for example, and the corresponding reaction rates ($-r$) are plotted vs. time

Table 4. Experimental Conditions for the Kinetic Study of the Reversion of Q Catalyzed by **1**[a)]

Run	$C_{Bi}\times10^{-3}$ mol·m^{-3}	$W\times10^{3}$ kg	$v\times10^{7}$ m^{3}·s^{-1}	T °C	Catalyst
1	0.76	1.02	1.64	11.0	Fresh
2	1.53	1.05	1.65	11.0	Fresh
3	0.97	0.99	1.71	11.0	Fresh
4	0.44	1.00	1.61	11.0	Fresh
5	1.23	1.02	1.63	11.0	Fresh
6	0.59	1.01	1.68	11.0	Fresh
7	0.34	1.03	2.89	42.0	Fresh
10	1.64	1.03	2.68	42.0	Fresh
11	1.03	0.99	2.74	42.0	Fresh
12	1.36	0.78	2.46	42.0	Fresh
13	0.73	0.79	2.44	42.0	Fresh
14	0.45	0.74	2.35	42.0	Fresh
15	1.61	0.75	1.75	25.0	Fresh
16	1.12	0.78	1.78	25.0	Fresh
17	0.39	0.78	1.73	25.0	Fresh
18	1.24	0.74	1.79	25.0	Fresh
19	0.78	0.75	1.80	25.0	Fresh
20	0.54	0.83	1.73	25.0	Fresh
21	1.24	0.74	2.09	25.0	Reactivated (Used in Run 18)
22	0.55	0.73	1.81	25.0	Reactivated (Used in Run 20)
23	1.26	0.73	1.80	25.0	Reactivated (Used in Run 21)

a) Values C_{Bi}, W, and v refer to symbols in Fig. 2, (see text).

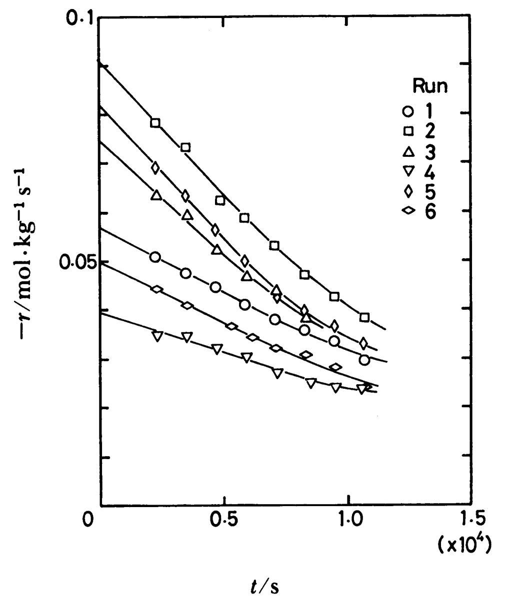


Fig. 4. Reaction rate as a function of time. Run numbers refer to the experimental run given in Table 4.

in Fig. 4. The decrease in the reaction rate arises from the partial loss of activity of the catalyst. The value r_0 estimated by extrapolation at t=0 was adopted as a reaction rate for the corresponding Q concentration C_{B0}. Plots of $-r_0$ vs. C_{B0} are shown in Fig. 5 for three different temperatures. If the reaction were first order with respect to Q the plots should be linear. The plots shown in Fig. 5 can be expressed by equations indicated in the same figure for each temperature. The equations can be correlated to Langmuir–Hinshelwood type rate expression

$$-r = kKC_B/(1 + KC_B) \tag{3}$$

Kinetic constant k mol·kg^{-1} s^{-1} and absorption constant K m^3·mol^{-1} were obtained from experimental correlation shown in Fig. 5 and are summarized in Table 5. Figure 6 shows Arrhenius Plots for k and K which gave temperature dependences of these values as indicated in the same figure. Thus, reaction rate of the reversion of Q to NBD catalyzed by **1** can be written as following.

$$-r = \frac{0.406\exp(-2062/T)C_B}{1 + 1.01 \times 10^{-3}\exp(213/T)C_B} \tag{4}$$

In the case of Co(II)DPIX/PAS/Alumina (**2-B**), the similar experiments gave qualitatively the same results as the case of **1**. The kinetic profiles for **2-B** are shown in Table 5, and the rate expression is

$$-r = \frac{0.539\exp(-1832/T)C_B}{1 + 1.58 \times 10^{-4}\exp(593/T)C_B} \tag{5}$$

The retension of the catalytic activity of **2-B** after

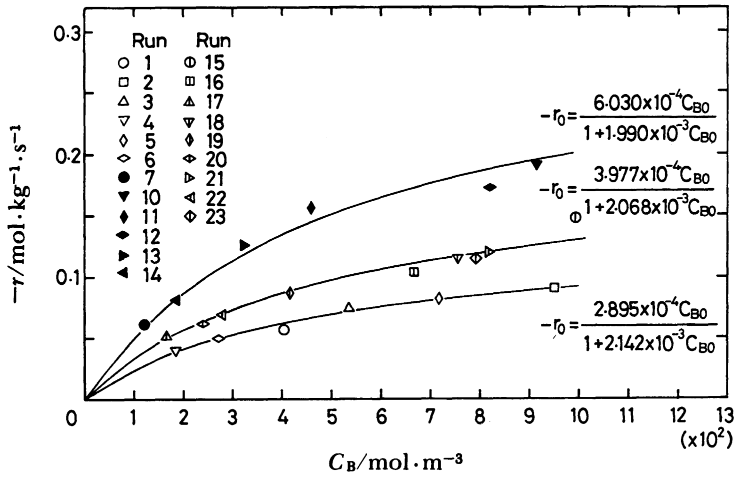


Fig. 5. Plots of reaction rates vs. Q concentration at $t=0$. Run numbers correspond to the experimental conditions given in Table 4. Upper curve is for 42.0 °C (Runs 7—14), middle curve for 25.0 °C (Runs 15—23) and bottom curve for 11.0 °C (Run 1—6).

Table 5. Kinetic Parameters for the Reversion of Q to NBD Catalyzed by Co(II)TPPS/PAS/Alumina (**1**) and Co(II)DPIX/PAS/Alumina (**2-B**)[a]

Catalyst	Temp	k	10^3K	E_a	ΔH
	°C	$\text{mol}\cdot\text{kg}^{-1}\cdot\text{s}^{-1}$	$\text{m}^3\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
	11.0	0.135	2.14		
1	25.0	0.192	2.07	18.9	−1.77
	42.0	0.303	1.99		
	11.0	0.714	1.24		
2-B	20.0	0.833	1.20	20.2	−4.93
	40.0	1.51	1.04		

a) k and K refer to the symbols in Eq. 3. E_a is energy of activation obtained based on an Arrhenius plots for k and ΔH heat of adsorption for K.

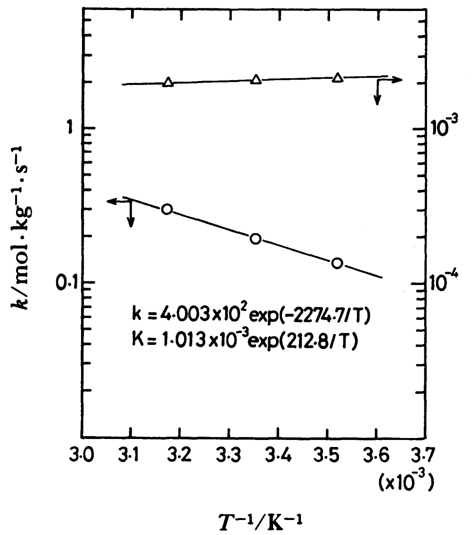


Fig. 6. Arrhenius plots for the kinetic constant k and adsorption constant K given in Table 5 for the Co(II)TPPS/PAS/Alumina catalyzed reversion of Q.

repeated use was examined by an isothermal (30±1 °C) batch reactor according to the method described by King and Sweet.[9] A 0.17 g charge of catalyst **2-B** ($6.6\times10^{-4}\ \text{mol}\cdot\text{L}^{-1}$ Co) was examined for loss of activity upon repeated recycling using 10 mL of $0.1\ \text{mol}\cdot\text{L}^{-1}$ Q in pentane. After five times batch of repeated use, ca. 40% loss of activity was observed while they reported ca. 50% loss of activity when 0.107 g of their polystyrene-anchored Co(II)TPP ($8.1\times10^{-4}\ \text{mol}\cdot\text{L}^{-1}$ Co) was used. The deactivation of catalytic activity was examined quantitatively based on the kinetic studies by the use of the isothermal recycle reactor. For this purpose, fractional activity (a) is defined as

$$a = -r(C_B,t)/-r(C_B,0) \tag{6}$$

where $-r(C_B,0)$ is the initial rate expressed by Eq. 4 or Eq. 5 corresponding to the fresh catalyst, and $-r(C_B,t)$ denotes the reaction rate corresponding to catalyst which has worked for t s being exposed in Q solution of the concentration C_B. Numerical treatments

Table 6. Values, α and β, in Eq. 7 Characterizing the Retension of Activities of Catalysts **1** and **2-B**

Catalyst	Temperature °C	$10^3\alpha$	$10^6\beta$
1	11	31	2.9
1	20	31	3.3
2-B	11	3.7	0.27
2-B	20	3.7	0.27
2-B	40	16	1.1

Table 7. Experimental Conditions and Physical Properties of Isooctane Solution of Q

Flow rate	$0.157\,\mathrm{cm\cdot s^{-1}}$ [a)]
Solution	
Q concentration	$1.09\,\mathrm{mol\cdot L^{-1}}$ [b)]
Mean value of heat capacity at constant pressure	$2.28\,\mathrm{J\cdot g^{-1}\cdot K^{-1}}$ [c)]
Density	$0.793\,\mathrm{g\cdot cm^{-3}}$
Heat of reversion of Q	$96.2\,\mathrm{kJ\cdot mol^{-1}}$ [d)]

a) Superficial velocity. b) Initial concentration. c) Heat capacity of isooctane at 55 °C was employed. d) Determined by a microcalorimetry of the isomerization catalyzed by $Rh_2Cl_2(NBD)_2$.

afforded the expression of the fractional activity as a function of C_B and t

$$a = \exp[(-\beta C_B/1 + \alpha C_B)t] \tag{7}$$

where the values, α and β, for **1** and **2-B** at various temperatures are reported in Table 6.

Although the mechanism of the loss of activity is not clear, Eq. 7 indicates that Q molecule should be included in the mechanism. King and Sweet reported[9] that the loss in catalytic activity of their polystyrene-anchored Co(II)TPP arised from partial oxidation of the cobalt metal, and they demonstrated that the loss could be partially regenerated by the treatment with a strong reducing agent. In our case of cobalt(II) porphine anchored on PAS/Alumina, the decrease in the activity could be regenerated by heating the used catalyst at 200 °C in vacuo. In the Runs 21 and 22 seen in Table 4, used catalysts reactivated by this method were employed. As shown in Fig. 5 the plots for these runs is on the line obtained for the runs with fresh catalysts, which indicates the complete recovery of the catalytic activity. Even in the case of Run 23 in which the catalyst used has experienced two times reactivations, an almost complete regeneration of the catalytic activity was observed. The same reactivation procedure was effective for Co(II)DPIX/PAS/Alumina. These results indicate that the loss of catalytic activity of **1** and **2** should be due to fouling which arises from a kind of reaction of Q molecule and which can be eliminated by heating in vacuo.

A Bench-Scale Examination of Energy-Releasing Process, Q→NBD, Catalyzed by Co(II)DPIX/PAS/Alumina, 2-B. The feature of the heat-releasing process based on the reversion of Q catalyzed by **2-B** was examined by using a bench scale fixed bed reactor. A schematic of the flow system is shown in Fig. 7. The reactor was made of Pyrex glass, 2 cm in inner diameter and 70 cm in length, and packed with solid catalyst **2-B** of ca. 200 cm^3 in volume. Measurement of the axial temperature distribution in the reactor was made by the twenty thermocouples fixed at the axis of the reactor. Isooctane solution of Q at room temperature was introduced into the reactor by means of a roller pump. Table 7 lists the experimental conditions and the physical properties of the solution.

At the experimental conditions, both conversions and temperature rise were close to equilibrium. That is, Q in the inlet solution was isomerized to NBD during the flow through the catalyst bed with a concomitant evolution of heat and with no detectable by-products. Conversion at the exit of the reactor was unity, and maximum temperature rise was 58.5 °C which agrees well with the adiabatic temperature rise calculated based on the values in Table 7.

Figure 8 shows the axial temperature profiles along the reactor. With increasing distance Z, the temperature T rapidly increases and reaches a constant value. This system could conceivably have external mass transport resistance with Damköhler number being 11.5 at 40 °C. Therefore one-dimensional heterogeneous model accounting for interfacial gradient was used to predict the longitudinal distribution of temperature in the adiabatic fixed bed.[14] Here, the rate expression, Eq. 5, includes the internal mass transfer resistance. Although measurements show a little larger rate of the catalyst deactivation, they are well represented by the solid lines.

Conclusion

Polyaminesulfone modified alumina beads adsorbed cobalt(II) porphine derivatives possessing acidic group through ionic linkages, which provides an very easy method to immobilize cobalt(II) porphines on solid support. Using cobalt(II) tetrakis(*p*-sulfonatophenyl)porphine and cobalt(II) deuteroporphyrin, the method provides active catalysts for the valence isomerization of Q to NBD. The catalysts reveal prominent properties; high activity, small deactivation rate and moreover ability of regeneration of activity by heating the catalyst at 200 °C in vacuo. Furthermore, the distribution of the active species in the catalyst particle is restricted to a thin layer on the surface of the support. The catalyst showed strong resistivity against temperature (250 °C).

The reaction rate of the catalyzed isomerization of Q

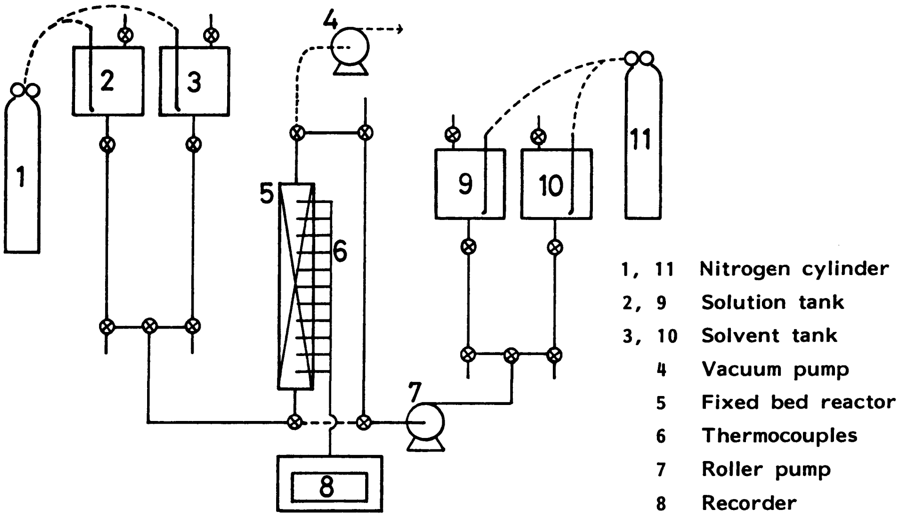


Fig. 7. Schematic of flow system.

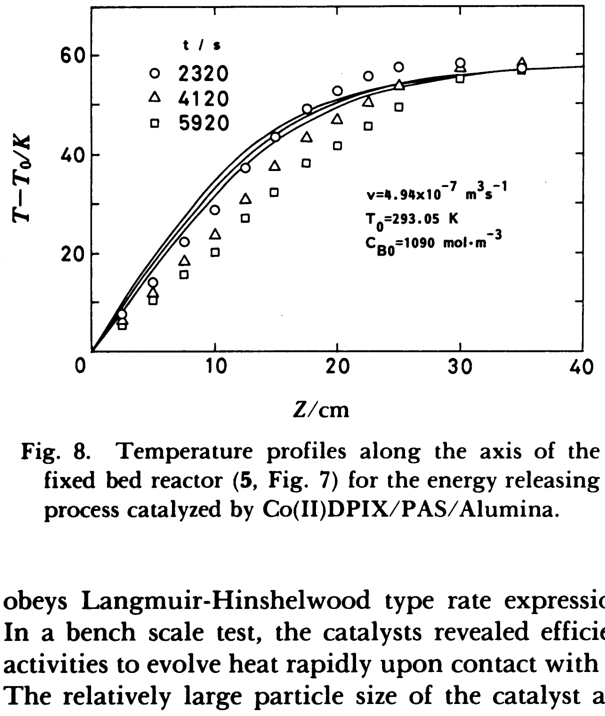


Fig. 8. Temperature profiles along the axis of the fixed bed reactor (**5**, Fig. 7) for the energy releasing process catalyzed by Co(II)DPIX/PAS/Alumina.

obeys Langmuir-Hinshelwood type rate expression. In a bench scale test, the catalysts revealed efficient activities to evolve heat rapidly upon contact with Q. The relatively large particle size of the catalyst and correspondingly the small pressure drop when packed in a column is presumably a preferable property in practical process. Furthermore, the catalysts did not swell up upon contact with any solvent.

Experimental

Materials. Polyaminesulfone-A (PAS) and activated alumina beads (Sumitomo Alumi NKH-1) were offered by Nittobo Co. Ltd. and Sumitomo Aluminium Smelting Co. Ltd., respectively. Deuteroporphyrin IX was prepared from protohemin according to the method of Fischer.[15] Incorporation of cobalt(II) was performed by the method of Yamamoto.[16] Pyridine was distilled over KOH under argon. Quadricyclane was prepared by a modification of King's method.[9] Pentane and isooctane used in kinetic studies were guaranteed grade commercially available and were used without further purification.

Analytical Method. Gas chromatographic analyses were carried out on a GC system composed of a Shimadzu GC-7A with TCD detector and a Shimadzu Chromatopac C-E1B. A Pyrex glass column, 5 mm in inner diameter and 1 m in length, was packed with Silicone DC-550. Helium was used as a carrier with flow rate of 50 mL·min^{-1}. Treatment of the packed column with five times injections of 50 μL triethylamine followed by baking out for 3 h at 150 °C eliminated the isomerization of Q in the column. Samples were analyzed using an injector temperature of 120 °C and a column temperature of 70 °C.

Sodium Tetrakis(*p*-sulfonatophenyl)porphinatocobalt(II) Complex (Co(II)TPPS, 4). A solution of 9.95 g (8 mmol) of sodium tetrakis(*p*-sulfonatophenyl)porphine and 1.99 g (8 mmol) of cobalt acetate in 100 mL of DMF was refluxed for 5 min. After cooling the reaction mixture, addition of benzene afforded 10 g (98%) of **4**.

PAS Modified Alumina Beads. To a 1 L solution of polyaminesulfone-A (PAS, **3**) (mean MW=2X10^5, Nittobo Co. LTD.) in water (10 wt%) was added 200 g of activated alumina beads (mean diameter of 3 mm, Sumitomo Aluminium Smelting Co. Ltd., NKH-1). The mixture was stood for 12 h with occasional swirling. Separation of the beads by filtration with a stainless steel net, air-drying at 100 °C for 2 days and drying at 80 °C in vacuo for 3 h afforded 245 g of the PAS modified alumina beads, PAS/Alumina.

Co(II)TPPS/PAS/Alumina (1). A two-necked round-bottomed flask equipped with a septum rubber stopper and three way valve was charged with a 190 g of PAS/Alumina, air in the flask was replaced with argon by means of a pump and argon balloon. To this was added a solution of 9.12 g (7.2 mmol) of **4** in a 2 L of degassed methanol by means of a canalation by positive argon pressure using a teflon tubing with 3 mm in inner diameter. The mixture was stood for 2 days under positive argon pressure with occasional swirling. After 2 days the color of the cobalt(II) porphine of the supernant was disappeared almost completely. The catalyst beads were filtered under nitrogen atmosphere and dried for

6 h at 120 °C in vacuo to give 174 g of the title catalyst. The catalyst was stocked under positive argon pressure.

Co(II)DPIX/PAS/Alumina (2). A solution of 0.75 g (1.3 mmol) of cobalt(II) deuteroporphyrin (Co(II)DPIXCo, **5**) in 160 ml of dry pyridine degassed by freeze and pumping was introduced onto a 69 g of PAS/Alumina beads under argon atmosphere. After the color of the cobalt(II) porphyrin was disappeared from the supernant, the beads were separated by filtration under argon and dried for 5 h at 150 °C in vacuo to give 70 g of **2** of batch-A. Batch-B, C, and D of **2** were prepared by similar manner. The specific quantities of materials and the solvent employed in the preparation of each batch are shown in Table 1.

Scanning Electron Microscopy and Wavelength Dispersive X-Ray Microanalysis. Scanning electron microscopy and the wavelength dispersive X-ray microanalysis on catalyst **1** were simultaneously carried out by the use of a JXA-733 of JOEL Co. Ltd. The specimen for the analysis of the cross section of the bead was prepared by dividing a bead into two hemispheres.

Measurements of Catalytic Activities and Studies on the Recycling Catalytic Run. A reaction cell of 20 mL in volume mantled with a jacket was equipped with a magnetic stirring bar and a septum rubber stopper. Thermostated water was circulated through the jacket in order to regulate the temperature of the reaction cell. The cell was charged with a weighed catalyst (ca. 70 mg) under argon atmosphere and was added a Q solution in pentane being set at reaction temperature by a syringe and the timing begun. Samples of the reaction solution (10 μL) were withdrawn for GC analyses. The initial sample was withdrawn at 30 s with subsequent samples at 120 s intervals, and more than 15 samples were analyzed.

The recycling study was carried out in a similar manner. At the end of the reaction period (more than 90% conversion), the reaction solution was decanted. The employed catalyst was washed two times with 5 mL of pentane and was dried up for 5 min under reduced pressure before using it for the next catalytic run.

Kinetic Studies Using an Isothermal Recycle Reactor. A schematic illustration of a recycle reactor is shown in Fig. 2. As shown in Table 4, around 1 g of catalyst was charged in the batch of the reactor. The whole system was immersed in a water bath thermostated at desired temperature. Solution of Q in isooctane was introduced into the reactor with precise control of the flow rate. In the experimental runs, recycling ratio γ was set above 67 so that the reactor could be treated as an ideal CSTR.[13] The superficial velocity in the catalyst fixed bed reactor above 4.2 cm·s^{-1} was employed in order to eliminate external diffusion resistance.[17] Samples of the reaction solution were withdrawn at the exit of the reactor and were analyzed on a GC system. After the reaction system reached to pseudo-steady state samplings were carried out at such time intervals indicated in Fig. 4.

Bench Scale Examination of the Catalytic Energy-Releasing Process on Co(II)DPIX/PAS/Alumina 2-B. A schematic of the flow system is shown in Fig. 7. The apparatus was made of teflon except a glass reactor and a rubber (Biton) tubing in pump. Each tank was 5 L in volume and the pipeline which connects a reactor with tanks was 6 mm in diameter. Feed was introduced into the reactor by means of a roller pump which provides very precise control of flow rate over the range of 120—1200 mL·h^{-1}. A cylindrical reactor was used, which is made of Pyrex glass, 2 cm in inner diameter and 70 cm in length. The reactor was packed with **2-B** of 200 cm^3 in volume. The active catalytic portion was contained between inert fore and aft sections of glass beads. The reactor was thermally insulated from its surroundings with asbestos. The twenty copper–constantan thermocouples were fixed at the axis of the reactor to measure the axial temperature distribution in the reactor. A hybrid recorder was used to record the outputs of the thermocouples. The concentrations of both Q and NBD were measured with a GC. Isooctane was used as a solvent.

In operation, feed at room temperature (20.1 °C) was introduced into the reactor by means of a roller pump at a constant flow rate. The solvent feed was initially passed through the reactor, establishing a steady flow. Once steady flow was achieved a three way valve was switched, sending the solution stream through the reactor. Temporal changes in temperature were measured by the thermocouples and samplings of the solution were made at the exit of the reactor. Their compositions were analyzed with the GC. During the experiments, the solution and solvent in tank has been bubbling by nitrogen gas from a cylinder to prevent a polymerization of NBD by dissolved oxygen. Reaction periods of about 1—2 h were employed. Table 7 lists the experimental conditions and the physical properties of the solutions.

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14) The steady state equations are:

Fluid

$$-u\cdot \mathrm{d}C_{\mathrm{B}}/\mathrm{d}Z = \rho_{\mathrm{b}}\cdot k_{\mathrm{c}}\cdot a_{\mathrm{s}}\cdot (C_{\mathrm{B}} - C_{\mathrm{BW}})$$

$$u\cdot \rho\cdot C_{\mathrm{pm}}\cdot \mathrm{d}T/\mathrm{d}Z = \rho_{\mathrm{b}}\cdot h\cdot a_{\mathrm{s}}\cdot (T_{\mathrm{W}} - T)$$

Solid

$$-r = k_{\mathrm{c}}\cdot a_{\mathrm{s}}\cdot (C_{\mathrm{B}} - C_{\mathrm{BW}})$$

$$(-\Delta H)\cdot(-r) = h\cdot a_{\mathrm{s}}\cdot (T_{\mathrm{W}} - T)$$

where u: superficial velocity
C_B: molar concentration of quadricyclane
C_{BW}: molar concentration of quadricyclane at catalyst pellet surface
Z: axial distance coordinate in fixed bed reactor
ρ_b: bulk catalyst density
k_c: liquid–solid mass transfer coefficient
a_s: external surface area of catalyst particle per unit mass
ρ: liquid density
C_{pm}: specific heat capacity of liquid
T: bulk liquid temperature
T_W: liquid temperature at catalyst pellet surface
h: liquid–solid heat transfer coefficient
$-r$: reaction rate
$-\Delta H$: heat of reaction

The model is extended to the pseudo-steady state by introducing the fractional activity of catalyst, a.

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