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Alumina-anchored Cobalt(II) Schiff Base Catalyst for the Isomerization of Trimethyldicyanoquadricyclane to the Norbornadiene

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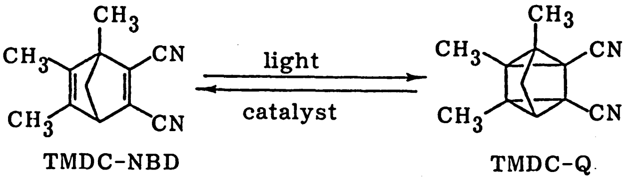
N,N'-Disalicylidene-4-carboxy-1,2-phenylenediiminatocobalt(II) supported on polyaminesulfone modified alumina beads has been prepared. The immobilized complex revealed efficient catalysis for the conversion of trimethyldicyanoquadricyclane (TMDC-Q) to the corresponding norbornadiene (TMDC-NBD). Using a bench-scale fixed bed reactor, TMDC-Q in chlorobenzene (1 mol dm^{-3}) isomerized to TMDC-NBD quantitatively during the flow through catalyst bed of only 20 cm with the temperature increase from 24.5 °C to 75 °C.

We presented a pair of valence isomers, donor-acceptor norbornadienes (DA-NBD) and the corresponding quadricyclanes (DA-Q) as an excellent solar-chemical-latent-heat system.[1)] Developing an efficient catalyst for the reverse energy-releasing process remained to be solved, and thus we have been studying on the catalysis of metal complexes for the cycloreversion of DA-Q, especially, trimethyldicyanoquadricyclane(TMDC-Q) to trimethyldicyanonorbornadiene(TMDC-NBD), which is a typical donor-acceptor system.



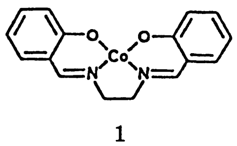
Although cobalt(II)porphyrins are widely appreciated to be a good catalyst for the isomerization of quadricyclane derivatives,[2-4)] the complexes revealed low activity for polysubstituted quadricyclanes such as TMDC-Q.[4)] What is worse is that activity of catalysts generally decreases upon immobilization, and as an extreme case, a heterogeneous catalyst anchoring cobalt(II)porphyrins[3)] was found to have no effect on the isomerization of TMDC-Q. It is disclosed that nortricyclanyl radical possessing Co-C bond is a key intermediate in the isomerization of quadricyclane derivatives catalyzed by tetraphenylporphinatocobalt(II), (TPPCo(II)).[4)] For the design of an effective Co(II) chelate catalyst, eliminating the steric repulsion between the equatorial ligand and the polysubstituted nortricyclanyl moiety is necessary. Thus, we have chosen here cobalt(II) complexes ligated with more flexible ligand than porphyrins, e.g., N,N'-disalicylideneethylenediiminatocobalt(II) (1),[5a] N,N'-disalicylidene-1,2-phenylenediiminatocobalt(II) (2a),[5b] and its methyl- (2b)[5c] and methoxycarbonyl- (2c)[5c] derivatives. A heterogeneous catalyst was prepared by immobilizing the 4-carboxy derivative (2d)[5d] on alumina beads.[6] For the assessment of the heterogeneous catalyst including formulations for activity, selectivity, and deactivation, heterogeneous catalytic process (TMDC-Q TMDC-NBD) was run using a fixed bed integral reactor as well as a batch reactor.

The isomerization reactions catalyzed by 1 and 2a-c were carried out in benzene under nitrogen. For all the catalysts, quantitative isomerization of TMDC-Q to TMDC-NBD was observed. The catalyzed isomerizations in the homogeneous systems were followed kinetically, and results are shown in Table 1. The complexes 2a-c revealed higher catalytic activity than TPPCo(II). The substitution with electron withdrawing group enhanced the activity. Among the catalysts listed in Table 1, 2c showed the highest activity, and therefore immobilization was made for the corresponding acid, Co(II)(Salphen-CO_2H) 2d.

Table 1. Activities of Cobalt(II) Schiff Base Complexes for the Conversion of TMDC-Q to TMDC-NBD[a]

Catalysts	10^4 [cat.]	Temp	$10^5 k_1$ [b]	$10^2 k_2$ [c]
	mol dm^{-3}	°C	s^{-1}	s^{-1} mol^{-1} dm^3
1	2.45	27.0	0.16	0.64
2a	2.18	27.0	0.27	1.2
2b	2.10	27.0	0.23	1.1
2c	1.86	27.0	0.27	1.4
2c	1.86	34.5	0.52	2.8
TPPCo(II)	10.0	27.0	0.11	0.11

a) TMDC-Q solutions of 0.1 mol dm^{-3} in benzene were used for 1 and 2, and 0.2 mol dm^{-3} for TPPCo(II). b) Apparent pseudo-first-order kinetic constants. c) Pseudo-first-order kinetic constants normalized to catalyst concentration of 1 mol dm^{-3}.



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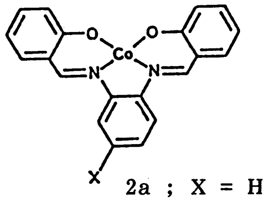
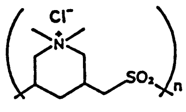


2a ; X = H
2b ; X = CH_3
2c ; X = CO_2CH_3
2d ; X = CO_2H



3
(PAS)

According to the method reported formerly[3] activated alumina beads (mean diameter of 0.2 mm)[6] was modified by treating with aqueous solution of polyaminesulfone(PAS). Upon contact with a solution of 72 g of 2d in 1.5 dm^3 pyridine the modified alumina beads (570 g) adsorbed 2d to afford the heterogeneous catalyst Co(II)(Salphen-CO_2H)/PAS/Alumina with the 2d incorporation of 0.27 mol kg^{-1}. A quantitative isomerization of TMDC-Q to TMDC-NBD was observed for this catalyst. The catalyzed reactions were followed using an isothermal batch reactor. The rate of the reaction ($r_A = -\,d[\text{TMDC-Q}]/dt$, mol s^{-1} g^{-1}) normalized to the amount of the catalyst (1 g dm^{-3}) for the temperatures ranging from 0 °C to 50 °C could be represented by

$$r_A = \{\ 120\cdot C_0^{0.5}C^{0.5}/(\ 1 + C_0\ )\ \}\exp(-45.3 \times 10^3/RT) \qquad (\ 1\ )$$

where C_0 is initial concentration of TMDC-Q and C is concentration of TMDC-Q. Within conversion lower than 20%, pseudo-first-order kinetic plots gave almost straight lines, and the pseudo-first-order kinetic constants thus obtained are summarized in Table 2. Noteworthy is that Co(II)(Salphen-CO_2H) immobilized on the support still keeps ca. 20% of the homogeneous catalytic activity of the corresponding ester <u>2c</u>.

Table 2. Catalytic Activity of the Co(II)-(Salphen-CO_2H)/PAS/Alumina for the Isomerization of TMDC-Q[a)]

Temp[b)]	[TMDC-Q][c)]	10^6k_w[d)]	10^2k_{Co}[e)]
°C	mol dm^{-3}	s^{-1} g^{-1} dm^3	$s^{-1}mol^{-1}$ dm^3
19.0	0.1	1.6	0.61
19.0	0.25	1.0	0.37
0.3	0.5	0.14	0.050
8.3	0.5	0.3	0.11
19.0	0.5	0.68	0.25
34.5	0.5	1.3	0.39

a) Reaction in chlorobenzene. b) ± 0.5 °C. c) Initial concentration. d) Pseudo-first-order kinetic constants normalized to catalyst amount of 1 g dm^{-3}. e) The kinetic constants normalized to Co(II)(Salphen-CO_2H) content, 1 mol dm^{-3}.

The kinetic formulation of the catalytic cycloreversion of TMDC-Q was examined also by using an integral reactor on an adiabatic operation. The apparatus used was similar to that described formerly.[3)] A cylindrical reactor of 4 cm in inner diameter and 58 cm in length was packed with the solid catalyst and was thermally insulated efficiently. The thirty copper-constantan thermocouples were fixed at the axis of the reactor. In operation, 0.5 mol dm^{-3} solution of TMDC-Q in chlorobenzene at room temperature was introduced into the reactor at a constant superficial velocity of 0.0151 cm s^{-1}. Temporal changes in temperature were measured by the thermocouples. Reaction periods of 4-8 h were employed. At the experimental condition, both conversion and temperature rise were close to equilibrium. That is, TMDC-Q in the inlet solution isomerized to TMDC-NBD during the flow through the catalyst bed with a concomitant evolution of heat and with no by-products. Conversion at the exit was unity.

Figure 1 shows an axial temperature profile along the reactor. With increasing distance Z, the temperature T rapidly increases and reaches a constant value. The maximum temperature rise (27.7 °C) agrees well with the adiabatic temperature rise (27.3 °C), which is calculated on the basis of the values; heat capacity of the solution $C_p = 1.5$ J g^{-1} K^{-1}, density of the solution 1.085 g cm^{-3} and the heat of the reversion of TMDC-Q $\Delta H = -88.7$ kJ mol^{-1}. To predict the longitudinal distribution of temperature, a one-dimensional heterogeneous model accounting for interfacial gradient was used with the reaction rate, Eq. 1. Evidently, the measurement shows fairly well agreement with the prediction which is depicted by a broken line in Fig. 1.

Figure 2 shows an axial temperature profile for the inlet concentration of 1 mol dm^{-3} under the same flow condition as before. Apparently, the temperature of the solution rapidly increases from 24.5 °C to 75.0 °C, during the flow through catalyst bed of only 20 cm depth.

Although the catalyst lost the part of its activity upon using, the deactivation rate was small, and the rate of the avarage active front was only 0.3 cm h^{-1} in even the case that the TMDC-Q solution of 1.0 mol dm^{-3} was used. It might be noteworthy that the loss of catalytic activity can be restored almost completely by heating the used catalyst at 200 °C in vacuo.

Mechanistic studies on the catalysis of cobalt(II) schiff base complexes are under way and will be reported elsewhere.

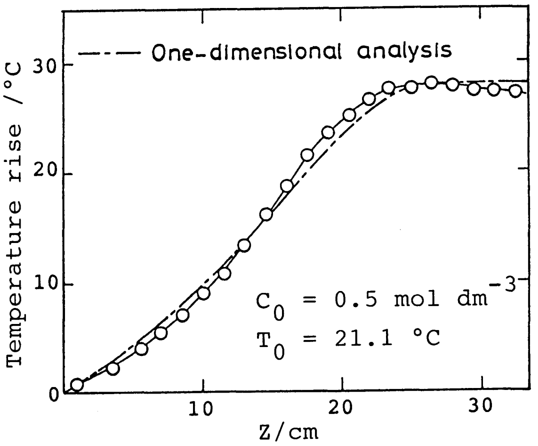


Fig. 1. Axial temperature profile along the reactor at a pseudo-steady state. Initial concn.= 0.5 mol dm^{-3}.

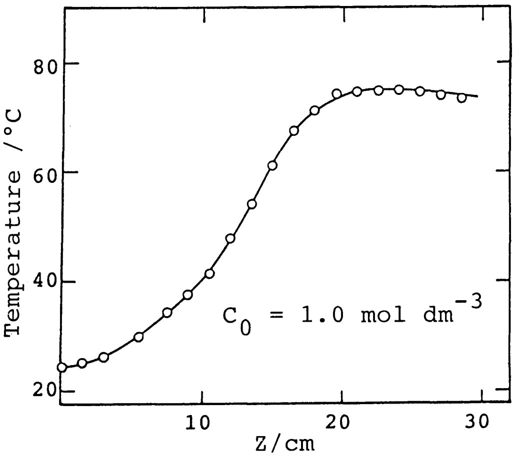


Fig. 2. Axial temperature profile along the reactor for the run with TMDC-Q solution initially 1.0 mol dm^{-3}.

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References

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6) Activated alumina KGO-1442 available from Sumitomo Chem. Co., Ltd.

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