Microporous Rhodium(II) 4,4′,4″,4‴-(21*H*,23*H*-porphine-5,10,15,20-tetrayl)tetrakisbenzoate. Synthesis, Nitrogen Adsorption Properties, and Catalytic Performance for Hydrogenation of Olefin

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(Received June 20, 2003; CL-030556)

A novel microporous rhodium(II) coordination polymer, $[Rh_2(H_2TCPP)]$ (**1**) (H_2TCPP = 4,4′,4″,4‴-(21*H*,23*H*-porphine-5,10,15,20-tetrayl)tetrakis benzoic acid) was synthesized. The complex **1** showed high porosity of the micropores of 7.3 Å. The amount of nitrogen adsorbed by **1** was 2.87 mole per mole of Rh, which is about three times that of rhodium(II) fumarate and rhodium(II) terephthalate. Complex **1** also showed high turnover frequencies for the hydrogenation of ethylene and propene at ca. 200 K.

Microporous materials based on transition coordination polymers have attracted much attention because of their molecular adsorption,[1–7] ion-exchange, and catalysis properties.[8] Among a number of coordination polymers, we have focused on the synthesis of rhodium(II) carboxylate coordination polymers because of their high gas adsorption properties and high thermal stabilities.[9,10] Recently, we also reported on the high catalytic activities of dinuclear rhodium carboxylate coordination polymers, rhodium(II) fumarate (**2**) and rhodium(II) terephthalate (**3**), for the hydrogenation of ethylene, propene, and butene at 255 K.[11]

In this study, we were interested in the synthesis of a new microporous rhodium(II) coordination polymer, $[Rh_2(H_2TCPP)]$ (**1**) (H_2TCPP = 4,4′,4″,4‴-(21*H*,23*H*-porphine-5,10,15,20-tetrayl) tetrakis benzoic acid) (Figure 1). The nitrogen adsorption property and the catalytic activity of complex **1** for the hydrogenation of ethylene and propene were also reported.

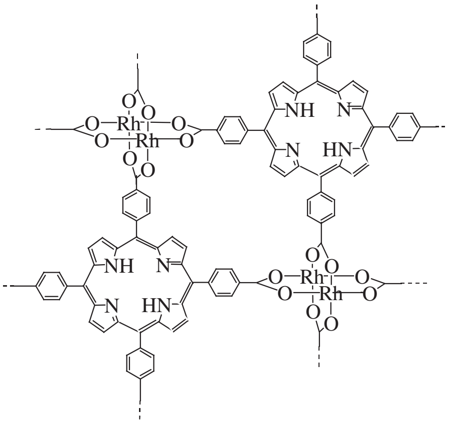

Figure 1. Deduced molecular structure of complex **1**.

Complex **1** was synthesized as follows. A mixture of $Rh_2(CH_3COO)_4{\cdot}2H_2O$ (50 mg, 0.105 mmol) and H_2TCPP (82.8 mg, 0.105 mmol) in MeOH (25 mL) was heated to 453 K at 5 K/min and kept for 3 h in an autoclave, then cooled to room temperature at a rate of 0.5 K/min. A dark brown precipitate was collected, washed with methanol, and dried at 323 K under vacuum for 3 h. Yield 59%. Elemental Anal. Found: C, 56.39; H, 3.39; N, 4.94%. Calcd for $C_{50}H_{35}N_4O_{10.5}Rh_2$ = $[Rh_2(C_{48}H_{26}N_4O_8)(CH_3OH)_2]{\cdot}0.5H_2O$: C, 56.35; H, 3.31; N, 5.26%. TG/DTA data: 6.8 wt % loss observed below 423 K, suggesting $0.5H_2O$ (0.75%) and $2CH_3OH$ (6.0%). Decomposition began at around 553 K with an exothermic peak at 558 K.

The temperature dependence of magnetic susceptibilities was measured by a SQUID magnetometer (Quantum Design, MPMS-5S) in the temperature range of 2 to 300 K. The temperature dependence of magnetic susceptibilities of **1** obeyed the Bleaney–Bowers equation[12] for $S = 1/2$ Heisenberg model of dimer structure with $2J = -1920\,\mathrm{cm^{-1}}$, $g = 2.09$ and monomer impurity = 1.2% (Figure 2), showing the same magnetic behavior as rhodium(II) acetate[13,14] which has the well-known structure of dinuclear rhodium(II).

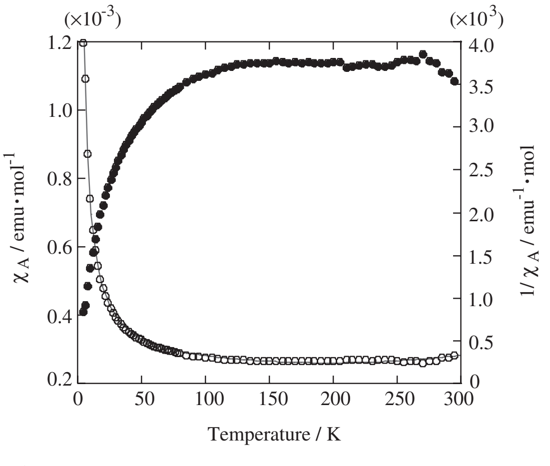

Figure 2. Temperature dependence of magnetic susceptibilities (empty circles) and inverse of magnetic susceptibilities (filled circles) of $[Rh_2(H_2TCPP)]$ (**1**) versus temperature. The solid lines indicate the best fit curve of the Bleaney-Bowers equation with $g = 2.09$, $2J = -1920\,\mathrm{cm^{-1}}$, and monomer impurity = 1.2%.

Analysis of argon isotherm for complex **1** yielded a BET surface area of 290.0 m^2/g and an effective pore size of 7.3 Å (using the Horvath–Kawazoe (HK) method[15]). A sharp peak was observed at 7.3 Å for complex **1**, indicating that the obtained coordination polymer had uniform micropores. Such a large surface area and a high micropore porosity might be due to the stacking of two-dimensional layers on each other, similar to other carboxylate coordination polymers.[1,16]

The temperature dependence of the amount of adsorbed nitrogen was measured by a Cahn 1000 electric balance at 20 Torr, where 1 Torr = (101325/760) Pa. The adsorption of complex **1** occurred at temperatures below 200 K. The maximum amount of adsorbed nitrogen was 2.87 mole per mole of Rh at 77 K, which was about three times that of complexes **2** (0.87) and **3** (1.11) at the same temperature (Table 1).[11,16]

Hydrogenation of olefin (ethylene and propene) catalyzed by complex **1** was conducted at 194 and 197 K, respectively. The high activity of complex **1** necessitated reaction at a low temperature in order to secure a low initial rate and the resulting freedom from complications arising from the influence of mass and heat transport. Complex **1** was put into a reaction vessel, which was connected to a conventional closed gas circulation system (350 mL). After evacuation at room temperature, reaction gas consisting of 30-Torr olefin and 60-Torr H_2 was introduced. Product analysis was conducted by a gas chromatograph equipped with a thermal conductivity detector (TCD) (Porapak Q) and activated alumina columns). For ethylene hydrogenation, the product was ethane with 100% selectivity; no induction period was observed. The conversion reached 100% after 40 min. The turnover frequency (TOF) of **1** was 2.13×10^{-2} [(mol of product)$\cdot s^{-1} \cdot$(mol of complex)$^{-1}$], which was about 329 times that of complex **2** (6.47×10^{-5}) (Table 2). For propene hydrogenation, the product was propane with 100% selectivity. The conversion reached 80% after 300 min. The TOF for complex **1** was 3.26×10^{-4}, which was about 15 times that of complex **2** (2.17×10^{-5}). Various rhodium-containing materials, e.g., Rh foil with TiO_2 overlayers[17] and Rh/polyphosphine metal catalyst,[18] were used as catalysts for the hydrogenation reaction but a higher temperature of 323 K was required. Magnetic susceptibility for complex **1** after pretreatment under hydrogen at 373 K for 1 h showed the same results as that of **1** before pretreatment, suggesting that the dinuclear rhodium(II) centers in **1** were stable active centers under our reaction conditions. This data suggests that the dinuclear rhodium coordination polymer with porphyrin-containing carboxylate is an effective material for gas adsorption and the catalytic hydrogenation of olefin.

Table 1. Maximum amount of occluded nitrogen for Rh-containing complexes

Complexes	Amount of occluded N_2[a]	Pore diameter(Å)	Refs.
$Rh_2(H_2TCPP)$ (**1**)	2.87[a](5.74)[b]	7.3	This work
Rh fumarate (**2**)	0.87[a]	5.4	11
Rh terephthalate (**3**)	1.11[a]	6.0	11
H_2TCPP	0.66[b]	—	This work

[a] mol/mol of Rh. [b] mol/mol of porphyrin.

Table 2. Catalytic activities for hydrogenation of ethylene and propene catalyzed by Rh-containing materials[a]

Catalysts	TOF(E)[b]	TOF(P)[c]	Refs.
$Rh_2(H_2TCPP)$ (**1**)	2.13×10^{-2}	3.26×10^{-4}[d]	This work
Rh fumarate (**2**)	6.47×10^{-5}	2.17×10^{-5}	This work

[a] Reaction conditions: catalyst 0.12 mmol, olefin (ethylene and propene) 30 Torr, H_2 60 Torr, reaction temperature at 194 K. [b] TOF(E) = Turnover number (TON = mol of product/mol of complex)/s for hydrogenation of ethylene. [c] TOF(P) = TON/s for hydrogenation of propene. [d] reaction temperature at 197 K.

This work was supported by a Grant-in-Aid for Specially Promoted Research (No. 15350088) from the Ministry of Education, Culture, Science, Sports and Technology, Japan. CNK is grateful for the support of The Association for the Progress of New Chemistry.

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Published on the web (Advance View) August 18, 2003; DOI 10.1246/cl.2003.854