

UNIQUE CONFORMATION OF Rh(I) PILLAR COMPLEXES IMMOBILIZED ON TAENIOLITE

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ABSTRACT

UNIQUE CONFORMATION OF RH(I) PILLAR COMPLEXES IMMOBILIZED ON TAENIOLITE. Rhodium pillar complex with chiral diamine ligands, Rh-Cn(-)-CHDA, were synthesized and intercalated with various loading amounts in the range of 19 - 26% CEC, *Cation Exchange Capacity (CEC)* into Lithium Taeniolite (LiTN). These pillared catalysts (Rh-Cn(-)-CHDA/TN) were characterized by XRD, elementary analysis, and FT-IR. Results of XRD analysis showed that the clearance space of the catalyst interlayer increased proportionally with the alkyl chain length of the ligand with the slope of 0.14 nm/CH₂.

Key words: Rh(I) pillar complex, Taeniolite

ABSTRAK

KONFORMASI KOMPLEKS RH(I) DIIMOBILISASI PADA TAENOLIT. Proses pilarisasi pada kompleks Rhodium menggunakan ligan diaminkiral, Rh-Cn(-)-CHDA, telah berhasil dilakukan. Kompleks yang terbentuk kemudian diinterkalasikan ke dalam Litium Taenolit dengan jumlah *loading* divariasikan antara 19 % hingga 26% *Cation Exchange Capacity (CEC)*. Katalis yang telah pilarisasi, (Rh-Cn(-)-CHDA/TN) dikarakterisasi dengan *XRD*, *elementary analysis* dan *FT-IR*. Hasil *XRD* menunjukkan bahwa jarak antara dua layer meningkat seiring dengan penambahan panjang alkil pada ligan dengan peningkatan 0,14 nm/CH₂.

Kata kunci: Rh(I) pillar complex, Taeniolite

INTRODUCTION

Host guest interactions between inorganic layer compounds and organic compounds provide suitable construction for heterogeneous catalysts. Large surface area, high cation exchange capacity, swelling, and intercalation ability of layer compounds, such as clay minerals, give a great potential for catalyst support [1].

A unique conformation of pillar complexes was detected, i.e., all-trans conformation for the alkyl groups of the pillar complexes in the smectite layer was reported [2]. Therefore, enhancement of molecular recognition reactions such as shape selective, regioselective, and stereoselective reaction can be expected due to the controllable interlayer space and the regulation of the active species stereochemistry in smectite clays as a host.

This current study will be focused in synthesis of effective chiral sites by intercalation of Rh(I) pillar complexes. In order to get high performance of the

catalyst and develop greener systems utilizing heterogeneous catalysis, rhodium pillar complex catalysts were intercalated on lithium taeniolite via simple ion exchange method and applied for stereoselective hydrogenation of 4-methylcyclohexanone.

EXPERIMENTAL METHOD

Materials

Pillared complex catalyst precursor of (R,R)-1,2-cyclohexanediamine was obtained from Aldrich, while n-aldehydes, silver perchlorate, potassium carbonate, and sodium borohydrate were purchased from Wako Pure Chemical Ind., Ltd (Wako) without any further purification. Rhodium chloride hydrate was purchased from N.E. CHEMCAT and solid supports LiTN was purchased from Topy Ind. Ltd. Substrate toward

stereoselective hydrogenation reaction, 4-methyl cyclohexanone, was purchased from Tokyo Chemical Industry (TCI). Solvents, such as methanol, ethanol, n-hexane, dichloromethane, diethyl ether, acetone, and toluene were commercially purchased from Wako and purified by literature procedures. Silica gel, silica plates, hexane and ethyl acetate for column chromatography were obtained from Wako

Synthesis of Trans-N,N'-dialkyl Cyclohexane-1,2-Diamine(Cn-CHDA)

Trans-cyclohexane-1,2-diamine (1 g, 8.8 mmol) was charged into a schlenk tube, dried by purified toluene (15 mL) and evaporated under 30 °C. Molecular sieves 4A (2 g) and n-aldehyde (16 mmol) were added into the dried *trans*-cyclohexane-1,2-diamine. The reaction mixture was stirred for 17 hours at 30 °C to obtain the corresponding imine. The imine as an intermediate product was reduced by addition of dried methanol (15 mL) and 1 mol equivalent of NaBH₄ (0.66 g, 16 mmol). The mixture was then stirred for 1 hour at 30 °C. Reduction reaction was terminated by addition of deionized water (20 mL). Molecular sieve were removed by filtration and the filtrate was extracted with dichloromethane (CH₂Cl₂) (3 x 30 mL). The organic layer was washed with saturated aqueous NaCl and dried overnight with potassium carbonate (K₂CO₃). K₂CO₃ was removed by filtration and the crude product was obtained by evaporation of the filtrate. The crude product was then purified further by silica-chromatograph with ethyl acetate-hexane (1-1) eluent. The collected fractions were analyzed by FT-IR and ¹H NMR to obtain the pure fraction with 20-50% yield.

Synthesis [Rh(μ-Cl)(cod)]₂

Degassed ethanol (30 mL) was charged into a schlenk tube and bubbled by N₂ flow for 30 minutes. Rhodium (III) chloride (RhCl₃) (1 g, 3.8 mmol) and 1,5-cyclooctadiene (cod) (2 mL) was added to the schlenk tube. The mixture was refluxed for 3 h at 85 °C. The reaction mixture was then cooled in the refrigerator for 1 hour and orange crystal product was precipitated. The orange crystal was filtered off and washed with cold ethanol and dried in vacuo for 24 hours to obtain 80% yield. The product was analyzed by FT-IR and NMR.

Synthesis of Rh-Cn-(-)-CHDA

[Rh(μ-Cl)(cod)]₂ (0.2 g, 0.4 mmol) and silver (I) perchlorate (0.168 g, 0.8 mmol) were charged into schlenk tube and degassed by N₂ flow. Acetone (10 mL) was then added to the mixture. The mixture was stirred for 1 hour at 30 °C. Silver chloride was removed from the solution by filtration. To the filtrate, acetone (5 mL) was added and stirred for 1 hour at

30 °C. The solvent was removed by vacuum evaporation to yield pale yellow crystal. The crystal was washed with hexane and stirred for 15 minutes at 40°C. The hexane was removed by decantation and washing was repeated three times. The rhodium pillar complexes were analyzed by NMR.

Intercalation of Rh-Cn-(-)-CHDA into Clay

A suspension of LiTN (0.1 g) in deionized H₂O (15 mL) was placed in a 250 mL flask and stirred for swelling for 2 hour at 30 °C. An amount of rhodium pillar complex (0.27 mmol) dissolved in methanol (45 mL) was then added and the mixture was stirred for 48 hour at 30 °C. The suspension was filtered, washed with methanol and dried in vacuo for 24 hour. The intercalated pillar complex catalysts were then analyzed by FT-IR, XRD, and elemental analysis.

General Procedure for Stereoselective Hydrogenation of 4-Methylcyclohexanone Derivatives

Stereoselective hydrogenation reactions were conducted in a glass autoclave packed with a magnetic stirrer. The catalyst complexes of Rh-Cn-(-)-CHDA/TN (0.0116 g, 6.25x10⁻⁴mmol) and KOH (0.0183 g, 0.32 mmol) were introduced into the autoclave tube and degassed. Mixture was dissolved with the degassed methanol (3 mL). The 4-methylcyclohexanone (0.625 mmol) was then added and the reaction line was allowed to be charged with H₂ (3 MPa). The hydrogenation reactions were performed for 24 hours at 10 °C. After carefully releasing the hydrogen gas, the reaction mixture was centrifuged and analyzed by capillary Gas Chromatography Rt-βDEXsm.

Product Stereoselectivity Determination

The product stereoselectivity was determined as the fraction of the absolute difference of the each stereoisomer product as described by the following Equation (1):

$$\text{stereoselectivity} = \frac{|\text{cis} - \text{trans}|}{\text{cis} + \text{trans}} \times 100\% \quad \dots (1)$$

RESULT AND DISCUSSION

Chiral Ligands Cn-(-)-CHDA

FT-IR spectra of diamine chiral ligands in the 4000-500 cm⁻¹ region can be observed in Figure 1. Successful alkylation of the diamine was detected by the appearance of the secondary amine vibration spectrum.

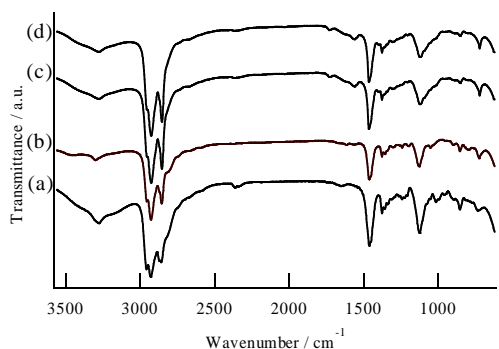


Figure 1. FT-IR spectra of Cn(-)-CHDA with n equal to (a) 4, (b) 7, (c) 9 and (d) 10

From FT-IR analysis of diamine chiral ligand Cn(-)-CHDA with n = 4, 7, 9, and 10 that is shown in Figure 7, the methyl and methylene groups both have asymmetric and symmetric C-H stretching vibration modes, giving absorption bands just below 3000 cm⁻¹. C-H stretching vibration of CH₃ showed absorption peak at 2924-2928 cm⁻¹ region of the spectrum. Meanwhile, data of the FT-IR absorption peaks showed that C-H stretching vibration of CH₂ gave bands at 2854-2856 and 2924-2928 cm⁻¹ region of the spectrum. Secondary amine stretching vibration showed one band at 3280-3302 cm⁻¹ region of the spectrum due to the single N-H stretching vibration. This N-H bond assignment is very important to confirm that the alkylation of two amines were successful. If only one amine alkylated, there should be two peaks of N-H stretching vibration which reveal primary amine.

Pillar complexes Rh-Cn(-)-CHDA

FT-IR analysis of Rh-Cn(-)-CHDA was conducted to observe the successfulness of metal complexes synthesis. FT-IR spectra of pillar complexes Rh-Cn(-)-CHDA in the 4000-500 cm⁻¹ region is shown in Figure 2. Successful synthesis of pillar complexes was detected by appearance of the counter anion peaks.

As can be observed, the spectrum changed after metal complexes were synthesized by the appearance of counter anion ClO₄⁻ stretching vibration at 1090 cm⁻¹ and

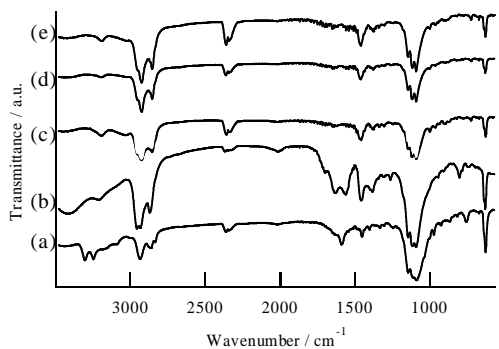


Figure 2. FT-IR spectra of Rh-Cn(-)-CHDA with n equal to (a) 0, (b) 4, (c) 7, (d) 9 and (e) 10

625 cm⁻¹. New peaks were also observed in the range 3003-3037 cm⁻¹ region assigned to the C-H (sp²) stretching vibration of 1,5-cyclohexanediamine. In addition, the peaks of N-H stretching vibration shifted to the lower IR frequency at 3190 cm⁻¹. This shift frequency indicates that the new coordination bond of N-H and rhodium might cause the attached bond to absorb at lower frequencies. Therefore, it can be concluded that metal complexes were successfully formed.

Intercalated Pillar Complexes Rh-Cn(-)-CHDA into LiTN

Fourier Transform-Infra Red

FT-IR spectra of intercalated pillar complexes into LiTN (Rh-Cn(-)-CHDA/TN) in the 4000-500 cm⁻¹ region can be observed in Figure 3. Successful intercalation was detected by the disappearance of the counter anion peaks and the appearance of new peak assigning the host structure peak.

Results revealed that all intercalated pillar complexes showed band at 2953-2964, 2926-2941, and 2854-2860 cm⁻¹ region that can be associated with $\nu_{as}CH_3$, $\nu_{as}CH_2$ and ν_sCH_2 of the chiral diamine ligands respectively. Meanwhile ν_{Si-O} due to the host structure was observed at 999-1001 cm⁻¹ region. In addition, the peaks for ClO₄⁻ at 1090 and 625 cm⁻¹ assigned to the counter anion were no longer observed. These Si-O bond and disappearance of counter anion bond assignments are very important to confirm that the intercalation of Rh-Cn(-)-CHDA into LiTN successfully proceeded by simple cation exchange method.

X-Ray Diffractometer

XRD patterns of the intercalated rhodium pillar catalysts, Rh-Cn(-)-CHDA/TN, are shown in Figure 4. The d₀₀₁ and the C.S. of LiTN after the intercalation of pillar complexes were summarized in Table 1.

XRD measurements revealed that all intercalated rhodium pillar catalysts showed shifts to the lower angle

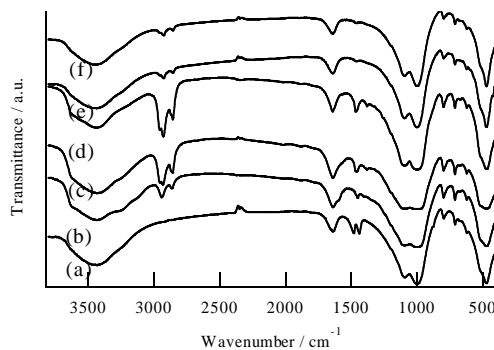


Figure 3. FT-IR spectra of (a) LiTN and Rh-Cn(-)-CHDA/LiTN with n equal to (b) 0, (c) 4, (d) 7, (e) 9 and (f) 10

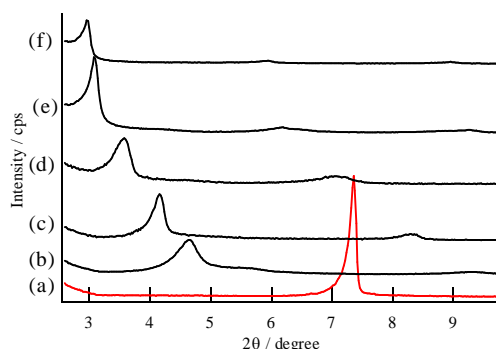


Figure 4. XRD pattern of (a). LiTN and Rh-Cn(-)-CHDA/LiTN with n equal to (b). 0, (c). 4, (d). 7, (e). 9 and (f). 10

Table 1. XRD parameters of LiTN and Rh-Cn(-)-CHDA/TN

| Carbon number | 2θ / degree | d_{001} / nm | C.S. ^a / nm |
|---------------|--------------------|----------------|------------------------|
| LiTN | 7.36 | 1.18 | 0.22 |
| 0 | 4.64 | 1.87 | 0.91 |
| 4 | 4.16 | 2.09 | 1.13 |
| 7 | 3.56 | 2.44 | 1.48 |
| 9 | 3.08 | 2.82 | 1.86 |
| 10 | 2.96 | 2.93 | 1.97 |

$$^a \text{C.S.} = 0.96 \text{ nm} - d_{001}$$

in the range of 2.9-4.6. Thus, the C.S., d_{001} – thickness of the silicate layer, of Rh-Cn(-)-CHDA/TN expanded to 0.91-1.97 nm range after the intercalation. This indicates that rhodium pillar complex catalysts were fixed in interlayer of LiTN. These C.S. well agreed with the molecular size of Rh-Cn(-)-CHDA where the alkyl chain conformation of ligands in the interlayer is presumed to be all-trans [2]. It is presumed that the square planar sheet of each rhodium complexes is arrayed parallel to the LiTN layer [5]. Further investigation of the C.S. correlation with the alkyl chain length can be seen in Figures 4 and 5. It is shown that the C.S. depended on the alkyl chain length. The C. S. calculated from XRD was proportional to the length of alkyl groups with the 0.14 nm increment per CH_2 .

Elemental Analysis

In order to determine the catalysts loading amount, intercalated rhodium pillar complex was analyzed by elemental analysis. CHN weight percentage was obtained and used to calculate the loading amount of the catalysts. Loading amount was calculated based on fraction of nitrogen weight percentage in the observed data and model compound. Elemental analysis data of the intercalated catalyst, Rh-Cn(-)-CHDA/LiTN, is showed in Table 2.

Intercalation of 100% mol/mol feeding amount of rhodium pillar complexes/LiTN in methanol/ H_2O solvent yielded loading amount 0.43-0.75 mmol g^{-1} . It can be observed that loading amount was diverse with different

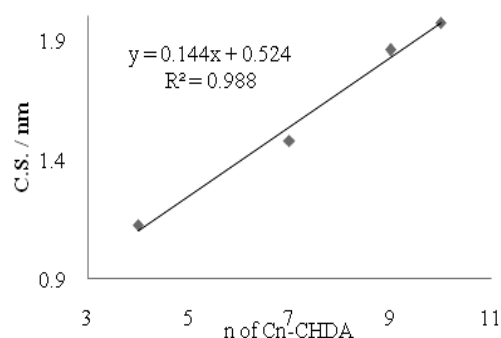


Figure 5. Correlation of C.S. with alkyl chain length

Table 2. Elemental analysis for Rh-Cn(-)-CHDA/LiTN

| Sample | L.A. / mmol g^{-1} | Exchange rate / % ^a |
|----------------|-----------------------------|--------------------------------|
| C0(-)-CHDA/TN | 0.74 | 26 |
| C4(-)-CHDA/TN | 0.43 | 15 |
| C7(-)-CHDA/TN | 0.54 | 19 |
| C9(-)-CHDA/TN | 0.75 | 26 |
| C10(-)-CHDA/TN | 0.53 | 19 |

^aBased on cation exchange capacity (LiTN: 2.682 mequiv g^{-1})

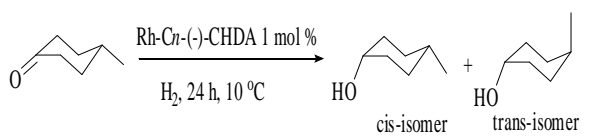
alkyl chain length of ligands. The diverse results demonstrate that intercalation of various alkyl chain length ligands of the catalysts did not affect intercalation exchange rate. Therefore, all of the intercalation conducted with 100% mol/mol feeding amount of rhodium pillar complexes/LiTN. The intercalation exchange rate might be affected by intercalation condition, such as stirring rate.

Stereoselective Hydrogenation of 4-Methyl Cyclohexanone by Rhodium Pillar Complex Catalysts

Stereoselective hydrogenation of 4-methyl cyclohexanone by homogeneous and heterogeneous rhodium pillar complex catalysts is summarized in Table 3.

The results of 4-methylcyclohexanone hydrogenation in homogeneous system indicate that the stereoselectivity tend to decrease by increasing the length of the alkyl chain. This demonstrates that the stereoselective hydrogenation by homogeneous catalysts depend on the flexibility of the alkyl chain. In the longer alkyl chain more, the alkyl chains are more flexible and thus the orientation of the pillar complex catalysts would be in random conformation. Therefore the stereochemistry of the active species of the catalysts might be changed, the substrate can approach the catalyst active site via the both sides of the molecular plane and resulting in more racemic cis and trans products. Meanwhile, heterogeneous system toward stereoselective hydrogenation of

Table 3. Stereoselective hydrogenation of 4-methyl cyclohexanone ^a



| Entry | Carbon number (n) | Homogeneous ^b | Heterogeneous ^c |
|-------|-------------------|--|--|
| | | Stereoselectivity (cis) % ^d | Stereoselectivity (cis) / % ^d |
| 1 | 0 | 30 | 13 |
| 2 | 4 | 32 | 20 |
| 3 | 6 | 34 | 24 |
| 4 | 7 | 26 | 27 |
| 5 | 8 | 25 | 29 |
| 6 | 9 | 23 | 30 |
| 7 | 10 | 23 | 36 |

^a4-methylcyclohexanone, 0.625 mmol; Rh catalyst, 6.25 x 10⁻³ mmol; KOH, 0.313 mmol; methanol, 3 mL; H₂ pressure, 3MPa, reaction time, 24 h. ^bRh-Cn(-)-CHDA was used as catalyst. ^cRh-Cn(-)-CHDA/TN was used as catalyst. ^dDetermined by GC-MS Rt-βDEXsm using an internal standard method

4-methyl cyclohexanone showed that the cis selectivity increased along with the alkyl length, as the rhodium pillar complexes orientated in a fix position to maintain the stereochemistry of the active site. The longer the alkyl chain length, the C.S. of the catalysts was wider and the substrate would be easy to enter the active site of the catalysts. The highest stereoselectivity was achieved by utilizing Rh-C10(-)-CHDA/TN to obtain 36% (cis).

CONCLUSIONS

Rhodium pillar complexes, Rh-Cn(-)-CHDA, with various alkyl chain length were successfully synthesized and intercalated in cationic exchange lithium taeniolite (Li[(Mg₂Li)(Si₄O₁₀)F₂]) via simple ion exchange method. XRD measurements revealed that all intercalated rhodium pillar catalysts showed the C.S. of the clay catalyst was expanded to 0.91-1.97 range after intercalation. This indicates that rhodium pillar complex catalysts were fixed in interlayer of LiTN with expansion of C.S. was proportional to the length of the alkyl groups with 0.14 nm/CH₂.

The heterogeneous stereoselective hydrogenation of 4-methylcyclohexanone gave higher stereoselectivity than of the homogeneous one. The highest stereoselectivity was achieved by utilizing Rh-C10(-)-CHDA/TN to obtain 36% (cis).

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