



Helical silica immobilizing ruthenium complexes for highly asymmetric addition of diethylzinc to aldehydes

Le Li, Fang Guan, Xiaoyong Li, Chao Fan, Aqun Zheng, Benhua Huang, Junjie Zhang, Yang Sun*

Department of Applied Chemistry, School of Science, Xi'an Jiaotong University, No. 28 Xianning West Road, Xi'an 710049, PR China

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ABSTRACT

A new series of helical silica were synthesized by doping of L-sodium hydrogen glutamate in a sol-gel procedure. Characterizations revealed doping of L-sodium hydrogen glutamate improved porosity, morphology, hydrolysis resistance and internal chirality of silica matrix. Meanwhile, chiral ruthenium complexes were synthesized and immobilized into helical silica in order to catalyze asymmetric addition of diethylzinc to aryl aldehydes. Catalysis revealed chiral induction synergy of multiple chiral centers on one ruthenium complex was existent. Ruthenium complexes immobilized over the glutamate-doped helical silica showed much better ee values and yields than those over blank-doped one. Immobilization of helical silica-supported ruthenium complex into imidazolium ionic liquid was efficiently recycled during three times. This work not only provided new chiral silica, but also studied their application in asymmetric catalysis.

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1. Introduction

Asymmetric addition of dialkyl zinc to aldehyde contributed to stereoselective formation of carbon-carbon bond, which had showed values in synthesis of many pharmaceutical molecules [1]. In the early years, chiral leucinol and dimethylaminoisobornenol were used to catalyze this transformation, proving coordination of ligand to dialkyl zinc would not only activate Zn-C bond, but also increase nucleophilicity of zinc alkyl [2-4]. From then on, an increasing number of homogeneous catalysts provided high conversions and enantioselectivities, including organic ligands like diazole [5], imine [6], pyrrolidine [7], phosphoramidate [8] and sulfamide [9], as well as metal complexes like Zn-Binol [10] and Ti-Binol [11]. Meanwhile, heterogeneous catalysts came into sight, such as silica-supported chiral alcohol [12] and helical silica [13,14], which brought about satisfactory heterogeneity and recycling outputs. Currently, topics on cleaner production and broader substrate scope attracted attentions [15]. Overall, taking into account reaction rate, optical yield, as well as environmental pressure, design of efficient and green catalysts became a popular choice for both academic and industrial interests. Furthermore, key issues like relationship between chirality of catalyst and enantioselectivity

of products, substrate scope and heterogenization deserved more endeavors.

Chiral silica attracted attentions in asymmetric catalysis, probably due to their potential roles as active supports for chiral induction [16]. Homogeneous catalytic components could be immobilized into chiral silica, so as to improve both heterogeneity and chiral induction. However, synthesis of chiral silica was not very easy, where templates played an important role. In practice, Che et al. [17] synthesized mesoporous helical silica by using chiral template. Some non-chiral templates could also construct helical silica under sol-gel condition [18]. Based on advances in the last decade, there was a big room for exploration of new chiral silica [19].

In recent years, immobilization of silica-based catalyst into ionic liquid (IL) had found promising applications, because IL could be confined in pore system of silica, stabilizing large-scale catalytic centers [20]. Nevertheless, a few ILs containing anions like BF_4^- or PF_6^- would hydrolyze slowly under exposure to water, releasing HF [21]. Therefore, ILs containing greener anions deserved attentions, which would facilitate both post-treatment and environmental protection.

In this work, chiral ruthenium-sulfamide complexes were synthesized in order to study chiral induction synergy of multiple chiral centers on one catalyst. Meanwhile, helical silica was synthesized by doping of chiral glutamate in sol-gel, and then functionalized to immobilize ruthenium complexes for better chiral induction and

* Corresponding author. Fax: +86 29 82668559.
E-mail address: sunyang79@mail.xjtu.edu.cn (Y. Sun).

heterogeneity in catalytic asymmetric addition of diethylzinc to aldehydes. At last, ruthenium catalysts would be recycled in combination with an imidazolium ionic liquid. This work would not only produce new chiral silica, but also show their application in asymmetric catalysis.

2. Experimental

2.1. Starting materials

Hexadecyltrimethylammonium bromide ($C_{16}TAB$), tetraethyl orthosilicate (TEOS), L-sodium hydrogen glutamate ($C_5H_8NNaO_4 \cdot H_2O$, abbreviated as L-glutamate), ammonia solution (25 wt.%), phenyltrimethoxysilane (PTMS), 3-aminopropyltrimethoxysilane (3-APTMS), (R)-1-(naphthalen-1-yl) ethanamine, D-(+)-10-camphorsulfonyl chloride (97%), L-(-)-10-camphorsulfonyl chloride (98%), dichloro (*p*-cymene) ruthenium(II) dimer (**Ru0**, 98%), diethylzinc (2 mol L^{-1} in toluene), benzaldehyde (98%), *o*-tolualdehyde (98%, 0.1% hydroquinone stabilizer), *p*-tolualdehyde (99%), *p*-chlorobenzaldehyde (98%) and 1-*n*-butyl-3-methylimidazolium chloride (BMImCl) were purchased from Acros, Adamas, Accela or Alfa, and used without purification. The (*R,R*)- and (*S,S*)-1,2-diammoniumcyclohexane mono-(+/-)-tartrate salt (*R,R*- and *S,S*-DMTS) were synthesized according to literature [22]. The 1-*n*-butyl-3-methylimidazolium nitrate (BMImNO₃) was prepared by ion exchange of BMImCl with AgNO₃ in distilled water (Section A1, Supplementary data).

2.2. Instruments

¹H NMR were tested on Bruker ADVANCE III (400 MHz). ESI-HRMS was detected on microOTOF-Q II, Bruker.Daltonics. The C, H, N elemental analysis was reported on Elementar VarioEL III. Ruthenium contents were measured on inductively coupled plasma atomic emission spectrometry (ICP-AES), ICPE-9000, Shimadzu. FT-IR were detected in KBr pellets on Bruker Tensor 27, with wave numbers of 400–4000 cm^{-1} .

BET surface area, pore volume, pore radius and pore size distribution were measured on Micromeritics ASAP 2020, using N₂ adsorption isotherms at 77.35 K. Samples were degassed at 150 °C in vacuum before testing. Surface area was calculated using the multi-point Brunauer–Emmett–Teller (BET) method based on adsorption data with relative pressure P/P_0 of 0.06–0.3. Total pore volume was obtained from N₂ adsorbed at $P/P_0 = 0.97$. Pore volume and pore radius were determined using Barrett–Joyner–Halenda (BJH) method.

Low-angle X-ray diffraction ($2\theta = 0.5^\circ - 10^\circ$) of powdered samples was performed on Philips X'Pert Pro diffractometer using Cu-K α radiation (λ , 1.5418 Å), with interval of $0.05^\circ \text{ s}^{-1}$. Scattering signals at $2\theta = 0.5^\circ - 2.0^\circ$ were omitted for clarity. X-ray photoelectron spectroscopy (XPS) was carried out on Kratos Axis Ultra DLD, using monochromatic Al K α X-ray (1486.6 eV) as irradiation source. Scanning electron microscopy (SEM) was tested on JEOL JSM-6700F at 20.0 kV with Au coating. Transmission electron microscopy (TEM) was tested on JEOL JEM-200CX at 120 kV.

Internal configurations of silica samples were determined by enantioselective adsorption of valine in water [23]. In practice, sample (20 mg) and L-(or D-) valine (50 mg) were added to distilled water (20 mL), then stirred at 25 °C for 120 min. Concentration of L-(or D-) valine was measured by UV (210 nm, UV 1800, Shimadzu) under sampling at regular intervals. Adsorption percentage was determined by Lambert–Beer's Law, plotted as a function of time.

Thin layer chromatography (TLC) was performed on glass plates coated with GF₂₅₄ silica gel. Yields were determined by GC–MS, and ee values by chiral HPLC. GC–MS was tested on

GCMS-QP2010 Plus, Shimadzu, with Rxi-5 ms capillary column (length 30 m, internal diameter 0.25 mm). For chiral HPLC, system controller: Waters 1525, binary hplc pump; UV–vis detector: Waters 2998, photodiode array detector; UV: 220 nm for 1-phenyl-1-propanol (benzaldehyde as substrate), 1-(2'-tolyl)-1-propanol (*o*-tolualdehyde), 1-(4'-tolyl)-1-propanol (*p*-tolualdehyde) and 1-(4'-chlorophenyl)-1-propanol (*p*-chlorobenzaldehyde), determined by scanning 200–400 nm. Daicel Chiralcel OD-H, size: 150 mm \times 4.6 mm; particle: 5 μm ; mobile phase: *n*-hexane/2-propanol, 97/3, v/v; rate: 1.0 mL min^{-1} ; column temperature: 300 K; pressure: 5.5 MPa; sample concentration: 0.5 mg mL^{-1} in *n*-hexane; injection: 10 μL .

2.3. Synthesis of sulfamide ligands (**L1** and **L2**)

L-(-)-10-camphorsulfonyl chloride (0.25 g, 1.0 mmol) and (R)-1-(naphthalen-1-yl) ethanamine (0.17 g, 1.0 mmol) were combined into dichloromethane (100 mL) at 25 °C. Triethylamine (1.01 g, 10 mmol) was introduced, and the mixture was further stirred for 6 h at 25 °C. The organic solution was washed carefully with distilled water ($3 \times 30 \text{ mL}$) and brine ($3 \times 30 \text{ mL}$), then concentrated under reduced pressure. The residue was purified by flash chromatography (SiO₂; petroleum ether/ethyl acetate, 2/1, V/V), to provide brown oil (**L1**, 0.16 g, 41% yield). ¹H NMR (400 MHz, CDCl₃) δ : 8.23 (d, $J = 3.0 \text{ Hz}$, 1H), 7.86 (d, $J = 8.4 \text{ Hz}$, 1H), 7.77 (d, $J = 8.0 \text{ Hz}$, 1H), 7.57 (dd, $J = 6.8, 7.2 \text{ Hz}$, 2H), 7.50 (dd, $J = 7.6, 7.2 \text{ Hz}$, 1H), 7.44 (dd, $J = 8.0, 7.2 \text{ Hz}$, 1H), 6.32 (d, $J = 8.8 \text{ Hz}$, 1H), 5.63–5.61 (m, 1H), 2.55–2.75 (m, 2H), 2.19–2.20 (m, 1H), 1.96–1.93 (m, 2H), 1.73 (d, $J = 6.8 \text{ Hz}$, 2H), 1.57 (s, 3H), 1.25 (s, 6H). Anal. Calcd for C₂₁H₂₅NO₃S: C, 67.89; H, 6.78; N, 3.77. Found: C, 68.16; H, 6.99; N, 3.76. ESI-HRMS (positive, m/z): 372.3175 (Calcd. for $[M+H]^+$ 372.5000). **L2** was synthesized according to the same process except for using D-(+)-10-camphorsulfonyl chloride. ESI-HRMS (positive, m/z): 372.3376 (Calcd. for $[M+H]^+$ 372.5000).

2.4. Synthesis of **Ru1** and **Ru2**

$[\text{RuCl}_2(\textit{p}\text{-cymene})]_2$ (**Ru0**, 0.31 g, 1 mmol for Ru) and **L1** (or **L2**; 0.38 g, 1 mmol) were combined into *i*-PrOH (10 mL) at 25 °C, and triethylamine (1.01 g, 10 mmol) was introduced. The mixture was stirred at 25 °C for 5 h, and then concentrated under reduced pressure. The orange solids were collected as **Ru1** (0.37 g, 55% yield; or as **Ru2**, 0.44 g, 65% yield). Anal. Calcd. for C₃₁H₃₉NSO₃Cl₂Ru·NEt₃ (**Ru1**): C, 57.05; H, 6.98; N, 3.59. Found: C, 57.65; H, 6.55; N, 3.85. Anal. Calcd. for C₃₁H₃₉NSO₃Cl₂Ru·3NEt₃ (**Ru2**): C, 60.43; H, 8.62; N, 5.70. Found: C, 59.96; H, 9.01; N, 5.39.

2.5. Synthesis of **Ru3** and **Ru4**

The *R,R*-DMTS (0.26 g, 1.0 mmol) and anhydrous K₂CO₃ (0.27 g, 2.0 mmol) were combined into distilled water (5 mL) with stirring at 25 °C. Then, absolute ethanol (1 mL) was introduced. The solution was vigorously stirred at 75 °C for 2 h, then cooled to room temperature. Free diamine was carefully extracted by CH₂Cl₂ ($4 \times 5 \text{ mL}$), then slowly added to an solution of **Ru1** (1.0 mmol, in 3 mL ethanol). The mixture was stirred at room temperature for 3 h, then concentrated under reduced pressure. **Ru3** was obtained as brown oily substances (0.73 g, 90% yield). **Ru4** was synthesized according to the same procedure except for using *S,S*-DMTS (0.66 g, 82% yield). Anal. Calcd. for C₃₁H₃₉NSO₃Cl₂Ru·C₆H₁₄N₂ (**Ru3**): C, 56.13; H, 6.74; N, 5.30. Found: C, 56.57; H, 7.09; N, 5.29. Anal. Calcd. for C₃₁H₃₉NSO₃Cl₂Ru·C₆H₁₄N₂ (**Ru4**): C, 56.13; H, 6.74; N, 5.30. Found: C, 56.30; H, 6.39; N, 4.95.

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