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Short communication

Silica-based helical rod supporting guanosine compounds catalyzed asymmetric hetero-Diels–Alder reaction

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ABSTRACT

A series of silica-based helical rods were prepared and functionalized for immobilization of guanosine compounds in catalytic asymmetric hetero-Diels–Alder reaction. Nitrogen physisorption, electron microscopy and amino acid adsorption revealed that helical rod has a hierarchical structure including morphology and internal channels, and doping of sodium lactate facilitates porosity and internal chirality of synthetic rods. Catalysis revealed that guanosine derivatives were catalytically active, combination of guanosine with *L*-sodium lactate-doped rod was more enantioselective than that with zero- or *D*-sodium lactate-doped samples, and recycling of supported Schiff-base-guanosine was stable during six cycles.

1. Introduction

Asymmetric hetero-Diels–Alder (hDA) reaction gives chiral six-membered heterocycles, which showed values in synthetic and pharmaceutical chemistry [1]. Taking into account optical purity of product, separation of catalyst, as well as environmental concerns, design of catalyst for hDA had become an important task for both academic and industrial demands [2]. Previously, metal catalysts provided high conversion and enantioselectivity, like metallosalen [3], Schiff-base [4] or BINOL complexes [5]. But leaching of metal ions into product would become an unfavorable factor to commercialization [6]. Organocatalysis attracted attentions due to relief of metal toxicity, tolerance of water and air, and operational simplicity [7]. The α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanol (TADDOL) [8], bis-sulfonamide derivatives [9] and oxazoline [10] brought about promising results, but heterogeneous catalysis was inadequate and deserved efforts [11].

Guanosine was composed of guanine and ribofuranose, which had unique biological [12] and material characters [13], but catalytic application was scarce. Actually, chiral centers of ribofuranose were hydroxylated and centralized, which were prone to inter- or intramolecular hydrogen bonds, eventually facilitating enantioselectivity. On the other hand, some nanosized helical silica had been applied as support in asymmetric catalysis [14], which confirmed chiral induction of helical configuration. Based on these progresses, this work aimed to develop helical silica for immobilization of guanosine as organocatalyst in asymmetric hetero-Diels–Alder reaction, and to test synergetic effects between molecular catalyst and support.

2. Experimental

2.1. General

Starting materials and reagents were obtained as shown in Supplementary data, and disodium 3-*tert*-butyl-salicylaldehyde 5-sulfonate was synthesized according to literature [15]. ^{1}H NMR, ESI-HRMS, FT-IR and particle size were recorded on Bruker ADVANCE III (400 MHz), microOTOF-Q II, Bruker Tensor 27, and Zetasizer Nano ZS90 respectively. BET surface area, pore volume, pore radius and pore size distribution were recorded on Micromeritics ASAP 2020. Low-angle X-ray diffraction (2θ at 0.5° to 10°) of powdered samples were reported on Philips X'Pert Pro diffractometer using Cu-Ka radiation (λ, 1.5418 Å), with 0.05°s^{-1} interval. X-ray photoelectron spectroscopy (XPS) was carried out on Kratos Axis Ultra DLD, using monochromatic Al Kα X-ray (1486.6 eV) as irradiation source. Scanning electron microscopy (SEM) was performed on JEOL JSM-6700F at 20.0 kV with Au coating. Transmission electron microscopy (TEM) was tested on JEOL JEM-200CX at 120 kV.

Configuration of channels of Z, L and D was determined by enantioselective adsorption of chiral valine in aqueous solution (Scheme 1) [16]. In practice, sample (20 mg) and *L*-(or *D*-)valine (50 mg) were added to distilled water (20 mL), then vigorously 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.

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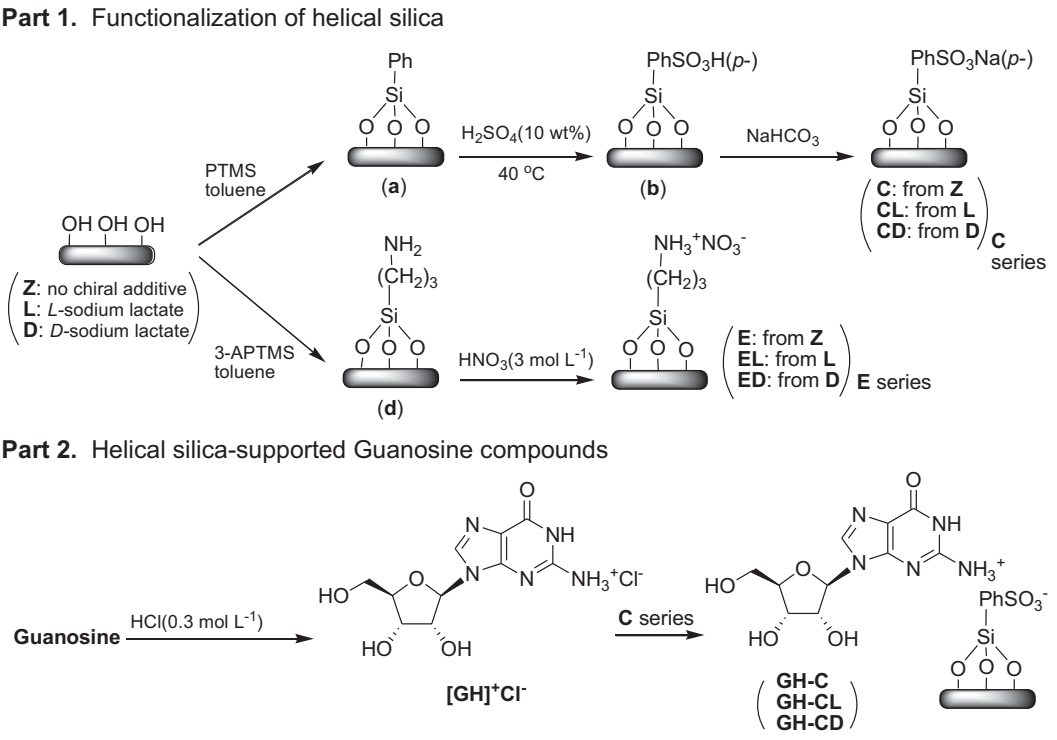

Scheme 1. Synthesis of catalysts.

Adsorption percentage was calculated on Lambert–Beer's Law, then plotted as a function of time.

Thin layer chromatography (TLC) was tested on glass plates coated with GF_{254} silica gel, coloration in phosphomolybdic acid (PMA)/ethanol solution (5 wt.%). Conversion and e.e. were determined by HPLC. System controller: Waters 1525, binary hplc pump; UV–vis detector: Waters 2998, photodiode array detector; UV: 254 nm for 2,3-dihydro-2-phenyl-4*H*-pyran-4-one (benzaldehyde), 2-(*p*-chlorophenyl)-2,3-dihydro-4*H*-pyran-4-one (4-chlorobenzaldehyde), 2-hexyl-2,3-dihydro-4*H*-pyran-4-one (heptaldehyde), 2-ethoxyformyl-2,3-dihydro-4*H*-pyran-4-one (ethyl glyoxylate), obtained after scanning 200–400 nm. Daicel Chiralcel OD-H, size: 150 mm × 4.6 mm; particle: 5 μm; mobile phase: *n*-hexane/2-propanol, 90/10, v/v; rate: 0.5 mL min^{-1}; column temperature: 300 K; pressure: 3.0–3.5 MPa; sample concentration: 0.5 mg mL^{-1} in *n*-hexane; injection: 10 μL.

2.2. Synthesis

2.2.1. Synthesis of supports

Sample Z was synthesized when hexadecyltrimethylammonium bromide and ammonia solution (25 wt.%) were used as surfactant and

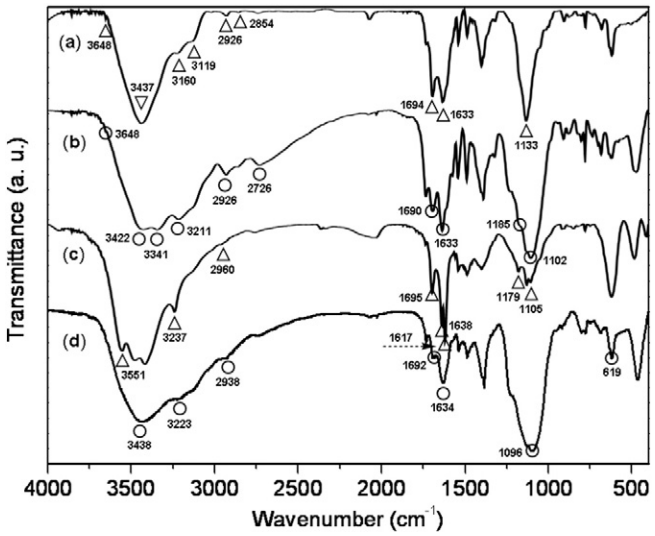

Fig. 1. FT-IR of guanosine (a), GH-CL (b), SG (c) and SG-EL (d).