



Original article

Immobilization of chiral Rh catalyst on glass and application to asymmetric transfer hydrogenation of aryl ketones in aqueous media

Tan-Yu Cheng^{*}, Jing-Lan Zhuang, Hui Yao, Huai-Sheng Zhang, Guo-Hua Liu^{*}

Key Laboratory of Resource Chemistry of Ministry of Education, College of Life and Environmental Science, Shanghai Normal University, Shanghai 200234, China

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ABSTRACT

A chiral catalyst, Cp^{*}RhTsDPEN (Cp^{*} = pentamethyl cyclopentadiene, TsDPEN = substitutive phenylsulfonyl-1,2-diphenylethylenediamine), was synthesized and immobilized at the surface of glass. The immobilized catalyst exhibited good catalytic efficiency for asymmetric transfer hydrogenation of aromatic ketones in water with HCOONa as hydrogen source.

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1. Introduction

Self-assembled monolayers (SAMs) are an excellent tool to change surface properties of materials. The method has attracted a lot of interest and has developed rapidly in the past years. Nanotechnology has developed rapidly in recent decades, and it is widely used in several areas. SAMs are often used to prepare nanoparticles [1–3], because most nanoparticles need to be functionalized and have their biological toxicity reduced. Glass plates are also good supports for functional molecules. Fluorescent sensors were assembled on glass, which were used for the detection of nitroaromatic compounds in the vapor phase [4–6]. Fluorescent proteins were immobilized on glass surfaces, and they were very important for potential applications in bionanotechnology [7]. Some metal catalysts were supported on glass surfaces, which were used to catalyze oxidation reactions [8,9].

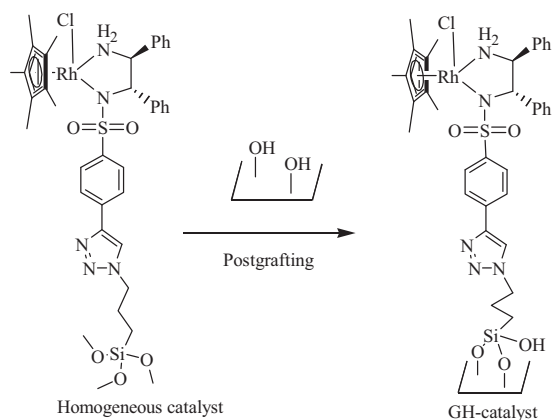
Chiral compounds are very important in our daily life, especially in medicinal chemistry, because different configurations have different drug activities. As such, enantioselective synthesis has attracted increasing interest from chemists during the past few decades. There are three main approaches to asymmetric synthesis, which are chiral pool synthesis, chiral auxiliaries, and

asymmetric catalysis. Asymmetric transfer hydrogenation (ATH) is one of the most important asymmetric catalytic reactions, and it is normally promoted by transition metal catalysts [10–17]. Noyori *et al.* found that chiral TsDPEN exhibited excellent catalytic activity and enantioselectivity in the asymmetric transfer hydrogenation of aromatic ketones [18], and they have made outstanding contributions in this area [19,20]. Compared with homogeneous catalysts, heterogeneous immobilization molecular catalysts at the surfaces of materials have several outstanding advantages, including facile product purification, easy catalyst recovery from reaction mixtures and reusability. Normally, the materials used for immobilizing molecular catalysts are mesoporous silica [21,22], magnetic materials [23], zeolites [24], organic polymers [25], or high surface area carbon [26]. However, to the best of our knowledge there is no chiral catalyst that is immobilized on a glass surface.

What we are interested in is material supported catalysts in an effort to achieve highly active and recyclable heterogeneous catalysts [27–31]. Herein, the ligand of TsDPEN (substitutive phenylsulfonyl-1, 2-diphenylethylenediamine) with ethynyl group was synthesized, and the ligand was conjuncted with a silica source *via* click chemistry. Then, the homogeneous catalyst was prepared through stirring the solution of the ligand and [Cp^{*}RhCl₂]₂ in dichloromethane at room temperature. At last, the obtained catalyst was immobilized at the surface of glass plates to form the heterogeneous catalyst, which showed good catalytic efficiency and enantioselectivity.

^{*} Corresponding authors.

E-mail addresses: tycheng@shnu.edu.cn (T.-Y. Cheng), ghliu@shnu.edu.cn (G.-H. Liu).



Scheme 1. Preparation of heterogeneous catalyst supported on glass.

2. Experimental

2.1. Preparation of the glass containing hydroxyl group

Microscope glass slides were used for monolayer preparation. The substrates were oxidized with piranha solution for 15 min (concentrated H_2SO_4 and 33% aqueous H_2O_2 in 3:1 ratio; caution: piranha should be handled carefully) and rinsed with MilliQ water (MQ). After drying with nitrogen stream, the substrates were used immediately to provide a freshly hydroxyl terminated surface on which to form the silanized monolayer.

2.2. Preparation of glass-supported heterogeneous catalyst (GH-catalyst)

As shown in Scheme 1, processed glass were immersed in the solution of silanizing homogeneous catalyst in CH_2Cl_2 until the solvent evaporated completely. To remove the unreacted homogeneous catalyst, the prepared glass were treated with ultrasound in CH_2Cl_2 and EtOH. The glass-supported heterogeneous catalyst (GH-catalyst) was obtained after the glass dried.

2.3. Typical catalytic procedure

A typical procedure was as follows [32]: GH-catalyst, HCOONa (20 mg, 0.3 mmol), ketones (2.0 mmol), and 2.0 mL water were added in a 10 mL round bottom flask. The mixture was allowed to react at 40 °C for 4 h. During the reaction, it was monitored constantly by TLC. The conversion and *ee* value could be determined by chiral GC using a Supelco β -Dex 120 chiral column (30 m \times 0.25 mm (i.d.), 0.25 μm film) or HPLC analysis

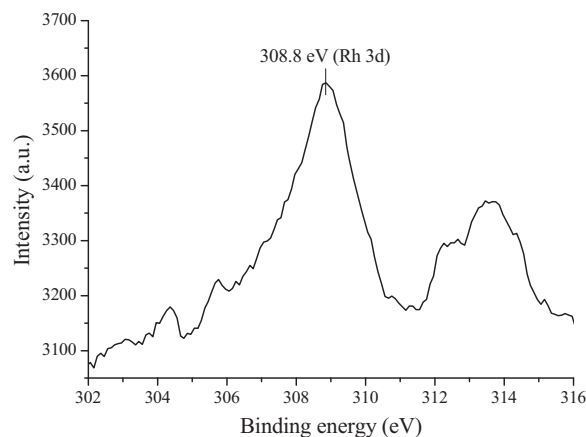


Fig. 1. XPS spectrum of the Rh active site within GH-catalyst.

with UV–vis detector using Daicel OJ-H chiral column (\varnothing 0.46 cm \times 25 cm).

3. Results and discussion

3.1. XPS analysis of GH-catalyst

The click reaction was used for the synthesis of the TsDPEN ligand with the trimethoxysilane group, which combined with Rh to form the homogeneous catalyst (see Supporting information). The heterogeneous catalyst was synthesized by grafting the homogeneous catalyst onto the oxidized glass with excess hydroxy groups. According to the XPS data, the O/Si ratio of normal glass was 1.53, and that of oxidized glass was 2.11. That indicated that excess hydroxy groups were obtained after the glass was oxidized. The content of sulfur increased from 0 to 0.61%. This was because a few sulfonic groups were produced when the glass was oxidized by sulfuric acid. The glass we used were normal slides, so there was plentiful carbon according to the XPS data. After grafting the homogeneous catalyst onto the slides, the XPS N1s and Rh3d signals indicated that the catalyst was immobilized successfully. As shown in Fig. 1, the binding energy of Rh3d was 308.8 eV, which was nearly the same with $\text{Cp}^*\text{RhTsDPEN}$ (309.3 eV).

3.2. AFM analysis of GH-catalyst

The resulting AFM images are shown in Fig. 2. The surface roughness exhibited by the root-mean-square (RMS) height value for glass was 2.60 nm. After grafting, the RMS value for the catalyst 6 decreased to 2.19 nm. This decrease in roughness can be

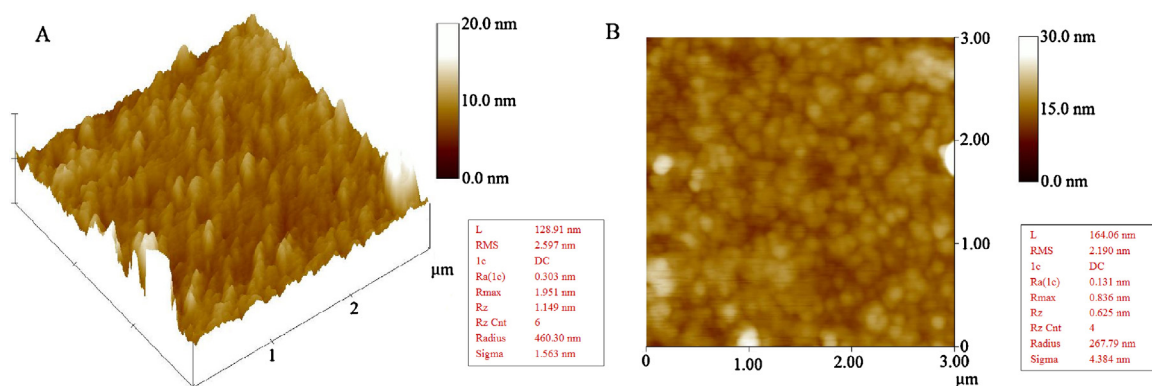


Fig. 2. AFM images of the glass (A) and GH-catalyst (B).

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