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# Ruthenium-catalyzed hydrogenation of aromatic amino acids in aqueous solution

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## ABSTRACT

A catalyst containing metallic ruthenium nanoparticles intercalated in hectorite (*nanoRu@hectorite*) was found to catalyze the hydrogenation of aromatic amino acids in aqueous solution. Thus, L-phenylalanine and L-phenylglycine can be converted exclusively into the corresponding L-cyclohexyl amino acids with retention of chirality under mild conditions (60 °C, 40 bar), conversion and selectivity being superior to 99%. The catalyst can be recycled and reused at least three times without loss in activity and selectivity.

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## 1. Introduction

The design of nanocomposites consisting of functional metals and proper matrices is a very active field of research for the development of recyclable catalysts. Highly active metallic nanoparticles must be stabilized by a suitable support in order to prevent aggregation to bulk metal [1]. Hectorite is a naturally occurring clay that belongs to the class of smectite minerals possessing the features of cation exchange, intercalation and swelling properties [2]. It can be defined as layers of negatively charged two-dimensional aluminosilicate sheets held together by sodium cations in the interlaminar space, which are susceptible to ion exchange [2–4]. There have been a number of reports on the immobilization of transition metal particles or metal complexes by hectorite involving rhodium [5,6] and platinum [7] for the catalytic hydrogenation of olefins and  $\alpha,\beta$ -unsaturated aldehydes. Ruthenium-supported hectorite catalysts have been reported by Shimazu et al. using  $[\text{Ru}(\text{NH}_3)_6]^{3+}$  as precursor [8] and by our group using  $[(\text{C}_6\text{H}_6)\text{Ru}(\text{H}_2\text{O})_3]^{2+}$  cations [9–14] or  $[(\text{C}_6\text{H}_6)_4\text{Ru}_4\text{H}_4]^{2+}$  cations [15] as precursors for the intercalation. In particular, metallic ruthenium nanoparticles (3–27 nm) intercalated in hectorite

(*nanoRu@hectorite*) proved to be a highly active and selective catalyst for the hydrogenation of benzene [9–11], furfuryl alcohol [12],  $\alpha,\beta$ -unsaturated ketones [13] and quinoline [14].

Unnatural amino acids are important structural motifs for peptides, peptidomimetics, synthetases and pharmaceuticals [16–18]. The synthesis of unnatural amino acids has received a tremendous impact from homogeneous [19–21], heterogeneous [22–28] and enzymatic catalysis [29–32]. Featured by high efficiency and enantioselectivity as well as by comparatively mild operating conditions, homogeneous catalysis and enzymatic catalysis show advantages as compared with their heterogeneous counterpart. However, considering the increasing demand of unnatural amino acids and the possibility of the contamination by the catalyst to the product in the separation section, a heterogeneous process for the manufacturing of these compounds would be more attractive. From this point of view, supported metal catalysts for the synthesis of optically pure unnatural amino acids have been developed.

A number of heterogeneous catalytic systems have been exploited to selectively convert phenyl rings into saturated cyclohexyl rings. Noble metals, such as Pd [22,33], Pt [23], Ru [24,26] and Rh [25,27,28] supported on carbon or  $\text{Al}_2\text{O}_3$ , are the most widely studied catalysts. The solubility of the aromatic amino acids in water is low, but it can be improved in acidic or basic medium. Depending on the catalyst employed, the pH plays an important

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role in the hydrogenation of aromatic amino acids. For example, for the hydrogenation of (R)-phenylglycine, palladium on charcoal under basic conditions gave only phenylacetic acid [33], however, the expected (R)-cyclohexylglycine can be formed over Pd(OH)<sub>2</sub> on charcoal in the pH range of 4.5–8.0 with 66% conversion and 84% *e.e* [22]. To the best of our knowledge, a very limited number of supported catalysts have been reported to selectively hydrogenate phenyl-substituted amino acids into cyclohexyl-substituted amino acids with high *e.e.*, such as Ru on carbon [24,26], Rh on carbon [25] and Rh on Al<sub>2</sub>O<sub>3</sub> [27]. Among these catalytic systems, only Rh on carbon seems to be recyclable.

Herein, we report metallic ruthenium nanoparticles intercalated in hectorite (*nanoRu@hectorite*) as a highly active and selective catalyst for the hydrogenation of aromatic amino acids, a reaction which works in aqueous solution. The effect of the pH on the hydrogenation processes is thoroughly studied. The *nanoRu@hectorite* catalyst can be recovered and reused for further runs.

## 2. Experimental

### 2.1. Syntheses

White sodium hectorite powder was synthesized according to the method of Bergk and Woldt [34]. The sodium cation exchange capacity, determined under the method of Lagaly and Tributh [35], was found to be 104 mEq per 100 g. The dimeric complex [(C<sub>6</sub>H<sub>6</sub>)RuCl<sub>2</sub>]<sub>2</sub> was synthesized following the procedure reported by Arthur and Stephenson [36].

#### 2.1.1. Preparation of the ruthenium(II)-containing catalyst precursor

The neutral complex [(C<sub>6</sub>H<sub>6</sub>)RuCl<sub>2</sub>]<sub>2</sub> (83.8 mg, 0.17 mmol) was dissolved in distilled and N<sub>2</sub>-saturated water (50 ml), giving a clear yellow solution after vigorous stirring for 1 h. The pH of this solution was adjusted to 8 (using a glass electrode) by adding the appropriate amount of 0.1 M NaOH. After filtration this solution was added to 1 g of finely powdered and degassed (1 h under high vacuum, then N<sub>2</sub>-saturated) sodium hectorite. The resulting suspension was stirred for 4 h at 20 °C. Then the yellow ruthenium(II)-containing hectorite was filtered off and dried *in vacuo* for 12 h.

#### 2.1.2. Preparation of the *nanoRu@hectorite* catalyst

The ruthenium(0)-containing hectorite was obtained by reacting a suspension of the yellow ruthenium(II)-containing hectorite (50 mg, 0.01592 mmol Ru) in water (10 ml) in a magnetically stirred stainless-steel autoclave (volume 100 ml) under a pressure of H<sub>2</sub> (50 bar) at 100 °C for 14 h. After pressure release and cooling, the *nanoRu@hectorite* catalyst was isolated as a black material.

### 2.2. Methods

The powder X-ray diffraction (XRD) patterns of the catalysts were collected by XRD Application LAB in CSEM (Switzerland). The samples were measured in air at 20 °C on a STOE STADIP high-resolution X-ray diffractometer using CuK $\alpha$  radiation. D-spacing (*d*) determination of the interlamellar spacing in hectorite, based on hectorite (001) reflection, was calculated from Bragg's law [37]:

$$n\lambda = 2d \sin \theta$$

where *n* is an integer (herein *n* = 1),  $\lambda$  is the X-ray wavelength (for the CuK $\alpha$ ,  $\lambda$  = 1.5418 Å).  $\theta$  is the angle between incident beam and scattering planes. Based on the Ru(011) reflection with the Si standard as a reference for the instrument peak broadening, the crystallite size *L* was calculated using the Scherrer equation [38]:

$$L = K\lambda/(\beta \cos \theta)$$

where  $\lambda$  is the X-ray wavelength ( $\lambda$  = 1.5418 Å), *K* is a constant related to crystallite shape, here taken as 0.94.  $\beta$  is the full width at half maximum (FWHM) of the peak profile, and  $\theta$  is the Bragg angle.

Transmission electron microscopy (TEM) was conducted in CSEM on a Philips CM 200 Transmission Electron Microscope (operating at 200 kV) coupled with Energy Dispersive X-ray spectrometry (EDS) for chemical analysis. The solid catalyst samples are thoroughly dispersed in ethanol and deposited on carbon film coated square mesh copper grids. The calculation of the nanoparticle size was obtained from TEM images with a total number of 100 nanoparticles by using the software ImageJ [39].

### 2.3. Catalysis

The selective hydrogenation of the optically active phenyl amino acid was carried out in a magnetically stirred stainless-steel autoclave (100 ml). Prior to the loading of the catalyst, the autoclave was purged three times with hydrogen to expel the air. Typically, a freshly prepared suspension of *nanoRu@hectorite* (0.01592 mmol Ru, 10 ml H<sub>2</sub>O) and the appropriate amount of the substrate were carefully transferred into the autoclave under inert atmosphere, and then the autoclave was charged with H<sub>2</sub> to the desired pressure. The autoclave was placed into the pre-heated heating mantle and the magnetic stirring was started for the indicated reaction time. After the reaction, the autoclave was cooled down and the pressure was released. The reactor was thoroughly rinsed with 2 N NaOH solution to wash out the entire product (in the case of acidic system, 2 N HCl was used). All the collected solutions were filtered (0.22  $\mu$ m, PTFE) to remove the catalyst and then treated with diluted HCl (or NaOH) solution to adjust the pH to 5.5, which caused the partial precipitation of the product. The suspension was then reduced *in vacuo* to 10 ml in order to complete the precipitation. The precipitate was filtered off, washed with distilled water and dried *in vacuo* for 24 h.

The white product was analyzed through <sup>1</sup>H and <sup>13</sup>C NMR in methanol-d<sub>4</sub> or D<sub>2</sub>O using a Bruker Avance II 400 MHz spectrometer using tetramethylsilane (TMS) as internal standard. IR spectra were recorded with a PerkinElmer FT-IR 1720 X spectrometer. Optical rotation was measured by a SCHMIDT HAENSCH Polartronic H532 polarimeter. The optical purity of the product was further examined by HPLC-UV technique (Ultimate 3000RS Dionex system with Acquity UPLC® BEH HILIC column). Electrospray ionization mass spectra (ESI-MS) were obtained in negative ion mode on a Bruker FTMS 4.7T BioAPEX II mass spectrometer. Inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin-Elmer Optima 3300 DV) was used to analysis the ruthenium leaching after the catalytic run.

### 2.4. Catalyst recycling and recovery

After a catalytic run, the *nanoRu@hectorite* catalyst was separated by decantation from the centrifuged reaction mixture. The supernatant was analyzed by ICP-OES to detect the Ru leaching. The catalyst was washed with 2 N NaOH (in the case of acidic system, 2 N HCl was used) solution and then with degassed water to extract traces of the catalytic product. After drying *in vacuo* for 12 h, the recycled catalyst was dispersed in the reaction medium under ultrasonic conditions and reactivated in the autoclave under a H<sub>2</sub> pressure of 50 bar at 100 °C for 14 h. After pressure release and cooling, the amino acid substrate, the amount of which was calculated from the weight of the corresponding recycled catalyst, was added for the next catalytic run.

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