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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 (*nano*Ru@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.

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 α,β-unsaturated aldehydes. Ruthenium-supported hectorite catalysts have been reported by Shimazu et al. using $[Ru(NH_3)_6]^{3+}$ as precursor [8] and by our group using $[(C_6H_6)Ru(H_2O)_3]^{2+}$ cations [9–14] or $[(C_6H_6)_4Ru_4H_4]^{2+}$ cations [15] as precursors for the intercalation. In particular, metallic ruthenium nanoparticles (3–27 nm) intercalated in hectorite (*nano*Ru@hectorite) proved to be a highly active and selective catalyst for the hydrogenation of benzene [9–11], furfuryl alcohol [12], α,β-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 Al_2O_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 $Pd(OH)_2$ 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_2O_3 [27]. Among these catalytic systems, only Rh on carbon seems to be recyclable.

Herein, we report metallic ruthenium nanoparticles intercalated in hectorite (*nano*Ru@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 *nano*-Ru@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 $[(C_6H_6)RuCl_2]_2$ 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 $[(C_6H_6)RuCl_2]_2$ (83.8 mg, 0.17 mmol) was dissolved in distilled and N_2-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_2-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_2 (50 bar) at 100 °C for 14 h. After pressure release and cooling, the *nano*Ru@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 CuKα 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 $n = 1$), λ is the X-ray wavelength (for the CuKα, $\lambda = 1.5418$ Å). θ 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 λ is the X-ray wavelength ($\lambda = 1.5418$ Å), K is a constant related to crystallite shape, here taken as 0.94. β is the full width at half maximum (FWHM) of the peak profile, and θ 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 *nano*Ru@hectorite (0.01592 mmol Ru, 10 ml H_2O) and the appropriate amount of the substrate were carefully transferred into the autoclave under inert atmosphere, and then the autoclave was charged with H_2 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 μm, 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 ^1H and ^{13}C NMR in methanol-d_4 or D_2O 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 *nano*Ru@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_2 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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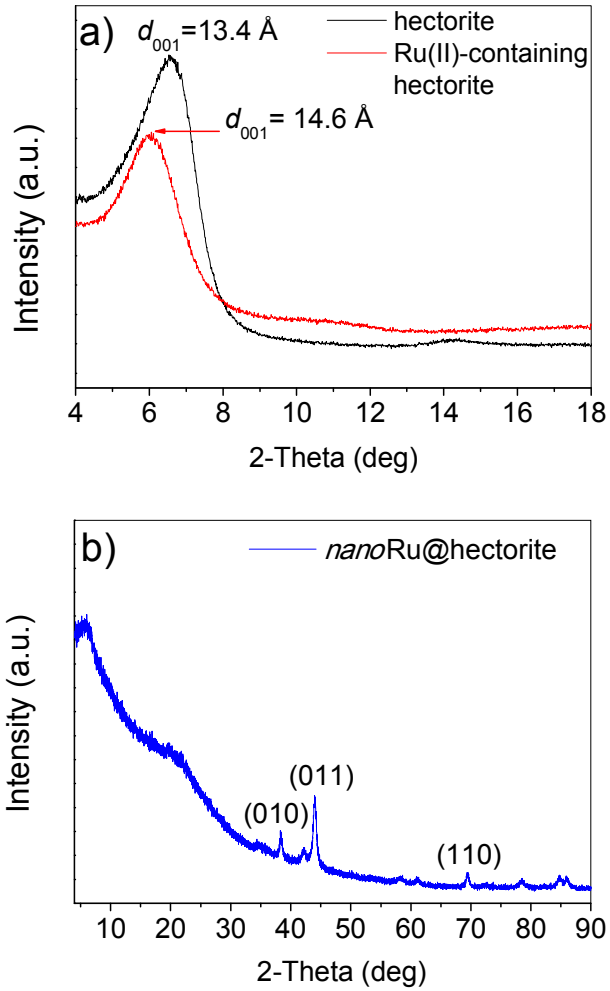

Fig. 1. (a) XRD patterns of the sodium hectorite and Ru(II)-containing hectorite in a scan range from 4° to 18°, in which the broad peak refers to the hectorite(001) X-ray reflection. The calculated d-spacing (d_{001}) of hectorite and Ru(II)-containing hectorite is 13.4 Å and 14.6 Å, respectively. (b) XRD pattern of Ru(0) nanoparticles intercalated in hectorite (*nano*Ru@hectorite) obtained under a H_2 pressure of 50 bar at 100 °C for 14 h in water (10 ml).

3. Results and discussion

3.1. Catalyst characterization

The *nano*Ru@hectorite catalyst is accessible from synthetic sodium hectorite, a white solid presenting an idealized cell formula of $Mg_{5.5}Li_{0.5}Si_8O_{20}(OH)_4Na\cdots nH_2O$ [40] and an aqueous solution of benzene ruthenium dimers containing the aqua complexes $[(C_6H_6)RuCl_2(H_2O)]$, $[(C_6H_6)RuCl(H_2O)_2]^+$ and $[(C_6H_6)Ru(H_2O)_3]^{2+}$ in equilibrium [15]. The yellow material is obtained by ion exchange of the sodium cations against benzene ruthenium aqua cations in the interlaminar space. The d-spacing (d_{001}) of the sodium hectorite and Ru(II)-containing hectorite are 13.4 Å and 14.6 Å, respectively (Fig. 1a). The swelling layers distance refers to the interaction between the adsorbed ruthenium complexes and the intercalant in hectorite [2]. The yellow Ru(II)-containing catalyst precursor is stable in the air that can be isolated and stored. When suspended in the appropriate solvent, this precursor can be then reduced by molecular hydrogen to give the active *nano*Ru@hectorite catalyst, an air-sensitive black powder [10].

The ruthenium loading of *nano*Ru@hectorite is assumed to be 3.2 wt% [9], based upon the molar ratio of $[(C_6H_6)RuCl_2]_2$ used (corresponding to 75% of the experimentally determined [35] cation exchange capacity) and the presence of metallic ruthenium is evidenced by its typical reflections in the XRD pattern (Fig. 1b) and by EDS analysis (Supplementary Material). Calculated from the line broadening of Ru(011) X-ray reflection using the Scherrer equation, the crystal system being assumed hexagonal (see Fig. 2), the crystallite size is approximately 15 nm. However, a typical TEM micrograph with a statistical diameter calculation (Fig. 2a and c) results in a mean particle size of 24 nm and the standard deviation of 3.5 nm. The different diameters from XRD and TEM suggest that the ruthenium nanoparticles are partially polycrystalline, which is shown by Selected Area Electron Diffraction (SAD) (Fig. 2a inlet).

3.2. Catalysis

The hydrogenation of chiral aromatic amino acids often requires mild conditions in order to avoid racemization. The protection of the benzylic C—N bond and carboxylic group is a common method to avoid the hydrogenolytic cleavage of C—N bond [27]. Water as a solvent allows the variation of the pH, which can be used to dissolve the tested amino acids, because in acidic or basic solution amino acids are present in cationic or anionic form. With *nano*Ru@hectorite as catalyst, the hydrogenation of aromatic amino acids into corresponding cyclohexyl-substituted amino acids are listed in Scheme 1.

Since the *nano*Ru@hectorite catalyst is prepared from the ruthenium(II)-containing hectorite precursor by hydrogen reduction in aqueous solution, the suspension of *nano*Ru@hectorite in water is slightly basic (pH = 9). Table 1 shows activity and selectivity of the catalyst for L-phenylalanine (**1a**) hydrogenation under different reaction conditions. Under a H_2 pressure of 40 bar with a low substrate to metal ratio (Table 1, entry 1), the catalytic

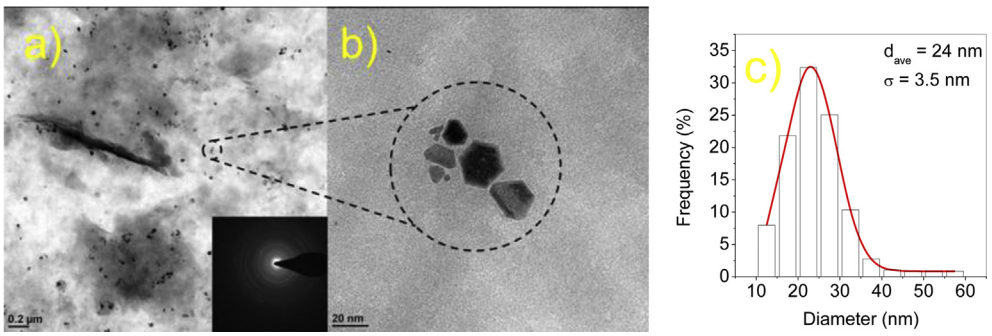

Fig. 2. (a) A TEM micrograph (the scale bar 0.2 µm) of the dispersed ruthenium nanoparticles in hectorite, in which the inlet SAD pattern displayed a series of bright rings relevant to the polycrystalline. (b) The enlarged TEM micrograph (the scale bar 20 nm) for ruthenium nanoparticles clearly shows a hexagonal morphology. (c) The size distribution of the ruthenium nanoparticles is presented in the histogram, the diameter ranging from 10 to 60 nm with a mean particle size of 24 ± 3.5 nm.

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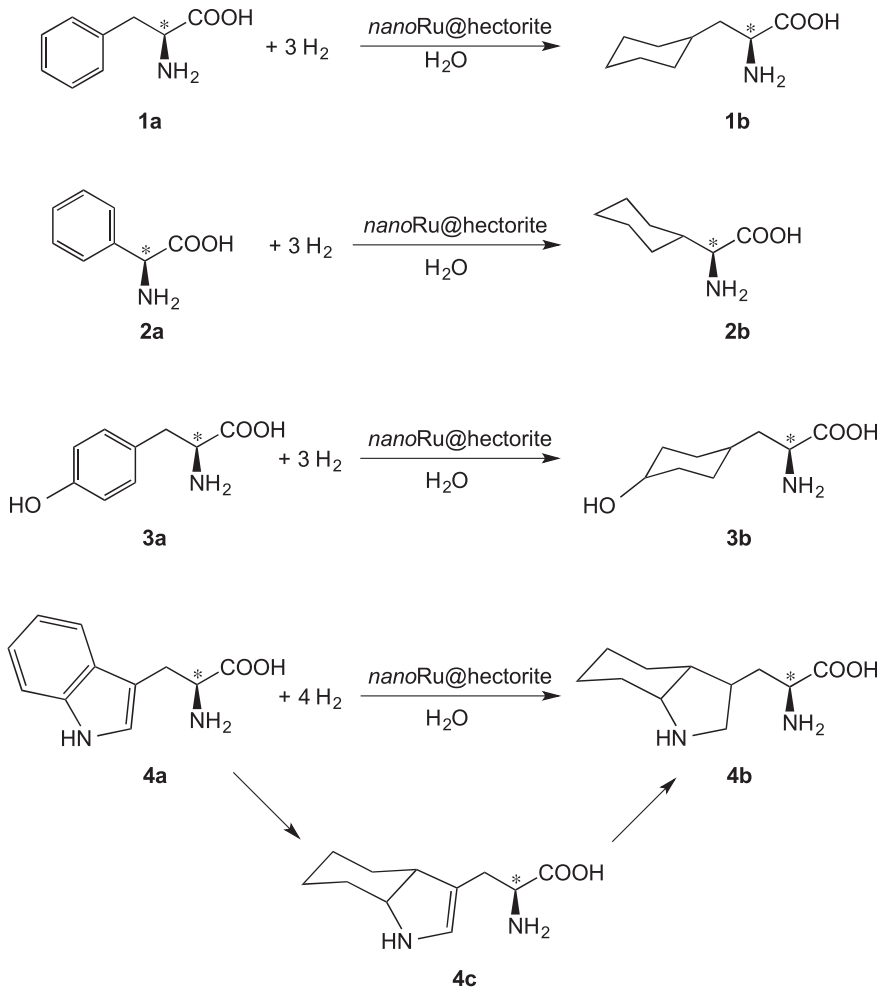

Scheme 1. Hydrogenation of the aromatic amino acids catalyzed by *nano*Ru@hectorite in aqueous solution.

hydrogenation of **1a** to give **1b** is complete in 120 h at room temperature without racemization, the selectivity being over 99%. With a higher substrate to metal mole ratio of 76, the conversion is only 52% under the same conditions, although the selectivity is still high (Table 1, entry 2), the main reason being that the aqueous solution at pH = 9 does not fully dissolve the substrate at room temperature. The solubility can be improved by higher temperature and the best conditions are 60 °C and 40 bar H_2 with a substrate to metal mole ratio of 106, which gives full conversion and high selectivity (Table 1, entry 4). A higher loading of substrate does not lead to full conversion even at higher temperature for 24 h (Table 1, entry 6, 7). A blank experiment was carried out without a catalyst (Table 1, entry 5). No conversion was observed, which proves the activity of *nano*Ru@hectorite.

We varied the pH of the aqueous solution from 1 to 14 by adding appropriate amount of acid (2 N HCl or 1 N H_2SO_4) or base (1 N NaOH or KOH). As shown in Table 2, **1a** can be hydrogenated exclusively to **1b** in all cases (Entry 3 to 7). Unlike Ru on carbon

Table 1
Hydrogenation of L-phenylalanine (**1a**) over *nano*Ru@hectorite in aqueous solution.

Entry[a]	S/M[b]	T, °C	p_{H2}, bar	t, h	C[c], %	S[d], %
1	38	20	40	120	>99	>99
2	76	20	40	120	52	>99
3	106	60	30	24	96	>99
4	106	60	40	18	>99	>99 (92)
5[e]	106	60	40	18	0	0
6	114	90	40	24	64	>99
7	114	100	40	24	87	>99

[a] The catalysts (50 mg) for all the entries were prepared under a H_2 pressure of 50 bar at 100 °C for 14 h in water (10 ml). The pH value of all the aqueous solution is 9.
[b] S/M = substrate to metal mole ratio.
[c] C = conversion of **1a**.
[d] S = selectivity for **1b**, the value in parentheses being the isolated yield.
[e] No catalyst in the system.

Table 2
Hydrogenation of L-phenylalanine (**1a**) over *nano*Ru@hectorite in water at different pH.

Entry[a]	pH	S/M	T, °C	p_{H2}, bar	t, h	C[b], %	S[c], %
1	1[d]	114	100	40	24	60	>99
2	9	114	100	40	24	87	>99
3	1[d]	106	60	40	12	>99	>99
4	4[d]	106	60	40	18	>99	>99
5	7[d]	106	60	40	18	>99	>99
6	9	106	60	40	18	>99	>99 (92)
7	14[e]	106	60	40	12	>99	>99

[a] The catalysts (50 mg) for all the entries were prepared under a H_2 pressure of 50 bar at 100 °C for 14 h in water (10 ml).
[b] C = conversion of **1a**.
[c] S = selectivity for **1b**, the value in parentheses being the isolated yield.
[d] pH adjusted by adding 2 N HCl or 1 N H_2SO_4.
[e] pH adjusted by adding 2 N NaOH or KOH.

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Table 3
Hydrogenation of a series of amino acids over *nano*Ru@hectorite in water.

Substrate[a]	pH[b]	S/M	T, °C	p_{H2}, bar	t, h	C[c], %	S[d], %
2a	1	118	60	40	12	>99	>99
2a	9	118	60	40	48	89	>99
2a	11	118	60	40	24	89	>99
2a	13	118	60	40	24	90	>99
2a	14	118	60	40	12	>99	>99 (94)
3a[e]	1	106	60	40	18	76	65
3a	1	78	100	50	24	93	50
3a	14	106	60	40	24	0	0
3a	14	106	100	50	24	0	0
4a[f]	1	53	60	40	24	33	50
4a	1	53	80	40	24	53	50
4a	1	78	100	50	24	65	77
4a	14	78	100	50	24	>99	63
4a	14	106	100	50	24	91	58

[a] The catalysts (50 mg) for all the entries were prepared under a H_2 pressure of 50 bar at 100 °C for 14 h in water (10 ml).
[b] pH adjusted by adding 2 N NaOH or KOH, and 2 N HCl or 1 N H_2SO_4.
[c] C = conversion of aromatic amino acid.
[d] S = selectivity for the cyclohexyl derivative, the value in parentheses being the isolated yield.
[e] The found byproduct in the hydrogenation of **3** being cyclohexylalanine.
[f] The found byproduct being **4c**.

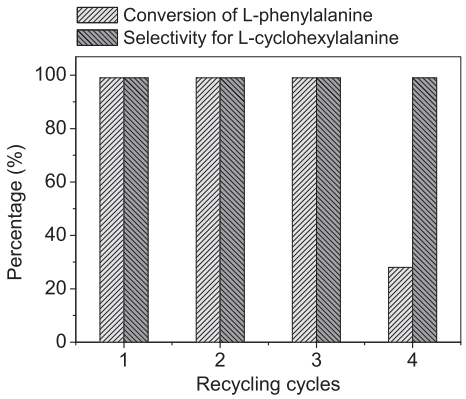

Fig. 3. The recyclability of the *nano*Ru@hectorite catalyst for four catalytic runs of **1a**. The first recycling was conducted following the regular catalytic run with fresh catalyst under the conditions of 40 bar H_2 at 60 °C for 18 h (as entry 4 in Table 1). All the recycling runs were performed under the same conditions as those with fresh catalyst.

[24,26] and Rh on Al_2O_3 [27], *nano*Ru@hectorite catalyzes the hydrogenation of L-phenylalanine even under neutral aqueous solution, which offers a good opportunity for a scale-up production.

We also examined other aromatic amino acids containing aromatic substituents for the hydrogenation over *nano*Ru@hectorite in aqueous solution. It turned out that the reaction works well when the substrate contains an unsubstituted phenyl group as in **1a**. Thus, L-phenylglycine (**2a**) is converted into L-cyclohexylglycine (**2b**) with more than 99% conversion and selectivity, either in very acidic (pH = 1) or basic condition (pH = 14). However, incomplete conversion of **2a** was observed over pH range from 2 to 13, the reason being the low solubility of **2a** in a less acidic or basic solution.

We also extended our study to L-tyrosine (**3a**), which contains a hydroxyl group at the aromatic ring. Initially studied by Waser et al. [41], the hydrogenation of tyrosine under acidic conditions (1 N HCl) produced a mixture of hexahydrotyrosine (10%) and β-cyclohexylalanine (90%) catalyzed by PtO_2. The stability of the hydroxyl-substituted phenyl group is higher than that of the phenyl ring, since the hydroxyl function increases the electron density of the phenyl ring. Therefore, harsher conditions are required to activate the hydrogenation process in tyrosine. As shown in Table 3, with *nano*Ru@hectorite as catalyst, the conversion of **3a** only proceeds under acidic and harsh conditions (100 °C, 50 bar H_2, 24 h) to give a maximum conversion of 93% with a selectivity of 50%, the byproduct being cyclohexylalanine. The selectivity for **3b** can be increased to 65% but at the expense of the conversion (76%) by lowing pressure and temperature.

L-3-(octahydroindolyl)alanine (**4b**) is an important unusual amino acid in the synthesis of peptides. Therefore the catalytic hydrogenation of L-tryptophan (**4a**) to produce **4b** is an attractive process. To date, there is no heterogeneous catalyst reported for this reaction. We examined the *nano*Ru@hectorite catalyst into the hydrogenation of **4a** in aqueous solution with different pH. Both acidic and basic conditions are possible for the hydrogenation of **4a**, but complete conversion was obtained at pH = 14 with 63% selectivity. Under all these conditions, the byproduct **4c** was always formed, which may be explained by the poisoning effect of the amine group in the indole moiety to the catalyst [42,43], which hampers the further hydrogenation of the pyrrole ring.

3.3. Recovery and recycling

The recyclability of the catalyst for four consecutive catalytic runs by separating the catalyst after each run and reactivating it under hydrogen pressure has been examined in the case of **1a** (Table 2, Entry 3). As shown in Fig. 3, the recycled catalyst remains highly active and selective in the first three runs, giving exclusively **1b** without racemization. However, in the fourth recycling process, the diameter of the ruthenium nanoparticles increased from 24 nm to 45 nm in average, resulting in hexagonal nanoparticles with a broader size distribution (Fig. 4). Furthermore, partial aggregation of the ruthenium nanoparticles is observed, which leads to a drop in the catalytic activity, the conversion being decreased to 28%, the

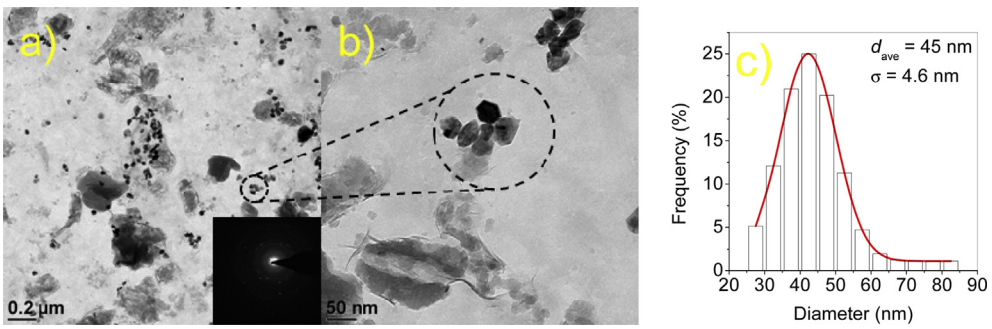

Fig. 4. TEM micrographs of the *nano*Ru@hectorite catalyst after three catalytic runs of **1a** (a, b), showing hexagonal ruthenium nanoparticles with partial aggregation. (c) The mean particle size is 45 ± 4.6 nm.

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selectivity being still over 99% (Fig. 3). Ruthenium leaching (2 ppm) is negligible, as shown by ICP-OES analysis of the filtrate. The catalyst deactivation, caused by aggregation of the ruthenium nanoparticles, may be avoided by modifying the reactivation conditions of *nano*Ru@hectorite [10].

4. Conclusion

In conclusion, the activity and selectivity of *nano*Ru@hectorite catalyst in the hydrogenation of chiral aromatic amino acids under different reaction conditions has been studied. *Nano*Ru@hectorite is a highly active catalyst that can catalyze the hydrogenation of L-phenylalanine in aqueous solution even at room temperature. The pH value plays an important role in varying the activity of the catalyst. Aromatic amino acids are hydrogenated to give the corresponding cyclohexyl-substituted amino acids without racemization. Recycling experiments show *nano*Ru@hectorite to be a stable catalyst that can be recovered and reused at least three times without loss of activity and selectivity.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2015.09.011.

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