



Contents lists available at ScienceDirect

## Journal of Organometallic Chemistry

journal homepage: [www.elsevier.com/locate/jorganchem](http://www.elsevier.com/locate/jorganchem)

# Selective *N*-cycle hydrogenation of quinolines with sodium borohydride in aqueous media catalyzed by hectorite-supported ruthenium nanoparticles

Bing Sun, Diego Carnevale, Georg Süß-Fink\*

Institut de Chimie, Université de Neuchâtel, CH-2000 Neuchâtel, Switzerland

## ARTICLE INFO

## Article history:

Received 17 December 2015

Received in revised form

18 July 2016

Accepted 19 July 2016

Available online xxx

Dedicated to Professor Heinrich Lang on the occasion of his 60th birthday.

## Keywords:

Ruthenium nanoparticles

Hectorite

Quinoline derivatives

Quinoline analogues

Hydrogenation

Isotope labeling

Catalyst recycling

## ABSTRACT

A new catalyst containing metallic ruthenium nanoparticles intercalated in hectorite (*nano*-Ru@hectorite) was found to catalyze the reduction of quinoline and quinoline derivatives by NaBH<sub>4</sub> in aqueous solution to give selectively the corresponding 1,2,3,4-tetrahydroquinolines (*N*-cycle hydrogenation). In most cases the reaction can be done under mild conditions (25–60 °C) without pressure equipment, conversion and selectivity being superior to 99%. In the case of sterically hindered derivatives, the reaction can be done in a pressure vessel under self-generated pressure (up to 9 bar). Isoquinoline and quinoxalines also undergo selective *N*-cycle hydrogenation, but 2-phenyl-quinoline is hydrogenated to give 2-phenyl-5,6,7,8-tetrahydroquinoline (*C*-cycle hydrogenation). Isotope labeling experiments combined with semi-empirical calculations of the electrostatic potentials support a heterolytic hydrogenation mechanism involving a hydride from NaBH<sub>4</sub> and a proton from H<sub>2</sub>O. The catalyst *nano*Ru@hectorite can be recycled and reused.

© 2016 Published by Elsevier B.V.

## 1. Introduction

The hydrogenation of quinoline (Q) and its derivatives is a fascinating area of research, since the hydrogenation products such as 1,2,3,4-tetrahydroquinoline (THQ) have various industrial applications ranging from the production of petrochemicals and fine chemicals to the development of heterocyclic skeletons for pharmaceuticals and agrochemicals [1]. Synthetic methods to obtain THQ include catalytic cyclization [2,3], Beckman rearrangement [4] and the direct partial hydrogenation of quinoline. Among these methods, the *N*-cycle-selective hydrogenation of quinoline is the most interesting process because of its reasonable atom utilization efficiency. A general problem in the selective hydrogenation of *N*-cycles is, however, the possible and sometimes irreversible adsorption of the amine formed at the surface of the metal catalyst [5,6], thus blocking the catalytic sites.

Precious metal complexes can be used for the catalytic

hydrogenation of quinoline to THQ, but most of these catalysts fail to give satisfactory results due to numerous complications associated with homogeneous catalysis [7–9]. Heterogeneous metal catalysts such as gold [10], palladium [11–13], rhodium [14,15], and ruthenium [16–18], supported on titania, alumina, silica, coal, hydroxyapatite or polymers have also been developed for this reaction. In most cases, elevated temperature and pressure are essential to convert quinoline into THQ, the selectivity being tuned by various organic solvents [19].

From the green chemistry point of view, water would be the most interesting solvent, because it is not only a green solvent in organic synthesis, but also plays a promoting role in enhancing the catalyst activity [20]. Only a few heterogeneous catalysts have been found active in the hydrogenation of quinoline in aqueous medium, such as ruthenium nanoparticles supported on silica spheres with an outer shell of microporous silica [21], palladium nanoparticles stabilized by black wattle tannin [22,23] and palladium nanoparticles supported by polymers [24]. Notably, graphene-supported Ru or Rh nanoparticles are found to catalyze the hydrogenation of aromatics efficiently even without solvents [25,26].

In our previous work, we developed a heterogeneous catalyst by

\* Corresponding author.

E-mail address: [georg.suess-fink@unine.ch](mailto:georg.suess-fink@unine.ch) (G. Süß-Fink).

intercalation of cationic benzene ruthenium complexes into hectorite, followed by reduction with molecular hydrogen to give a black solid containing metallic ruthenium nanoparticles intercalated in hectorite (*nanoRu@hectorite*) [27–29]. This material was found to catalyze the hydrogenation of quinoline with switchable selectivity, the reaction in water at 60 °C and 30 bar H<sub>2</sub> giving THQ, conversion and selectivity being at 99% [30]. However, high-pressure equipment is required for this reaction.

Inspired by a recent paper by M. M. Dell'Anna et al. on the hydrogenation of quinoline by sodium borohydride in water catalyzed by polymer-supported palladium nanoparticles [31], we modified our *nanoRu@hectorite* catalyst system, so that it also works with NaBH<sub>4</sub> and H<sub>2</sub>O as the hydrogen source for the hydrogenation of quinoline. The simple intercalation of RuCl<sub>3</sub> · n H<sub>2</sub>O in hectorite gives a black precatalyst, which is stable in air and which catalyzes the selective hydrogenation of quinoline to THQ with NaBH<sub>4</sub> in water under mild conditions in an open reaction vessel; no pressure equipment is required. The actual catalyst, metallic ruthenium nanoparticles intercalated in hectorite (*nanoRu'@hectorite*), can be recovered and reused. Herein, we report the preparation of the precatalyst, the characterization of the catalyst and its performance for *N*-cycle hydrogenation of quinoline and its derivatives including isoquinoline and quinoxalines.

## 2. Experimental

### 2.1. General

Deionized water was made from tap water by ionic exchange resins and degassed before use. All the *N*-cyclic chemicals were purchased from commercially available sources and used as received. RuCl<sub>3</sub> · n H<sub>2</sub>O was loaned by the Johnson Matthey Research Center. NaBH<sub>4</sub> and NaBD<sub>4</sub> (D, 98 atom %) were purchased from Aldrich, and D<sub>2</sub>O (D, 99.9%) from Cambridge Isotope Laboratories.

### 2.2. Preparation of the precatalyst

White sodium hectorite powder was synthesized according to the method of Bergk and Woldt [32]. The sodium cation exchange capacity, determined under the method of Lagaly and Tributh [33], was found to be 1.04 mEq/g. White hectorite powder (1 g) was degassed *in vacuo* for 1 h and followed by the N<sub>2</sub> saturation, then the calculated amount of RuCl<sub>3</sub> · n H<sub>2</sub>O (0.40 mmol) dissolved in 85 ml H<sub>2</sub>O (black solution) was transferred dropwise to the hectorite powder. The suspension was stirred for 3 h at room temperature, then treated by filtration and washing with deionized H<sub>2</sub>O (black solid) until no chloride ion was detected. The obtained solid product was dried *in vacuo* at 50 °C for 12 h and then ground to give a fine powder, containing 0.39 μmol/mg Ru (2 mol%) based on ICP-OES analysis.

### 2.3. Characterization of the catalyst *nanoRu'@hectorite* formed *in situ* during the catalytic hydrogenation reactions

The powder X-ray diffraction (PXRD) 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 [34]:

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

where *n* is an integer (herein *n* = 1),  $\lambda$  is the X-ray wavelength (for

the CuKα,  $\lambda = 1.5418 \text{ \AA}$ ).  $\theta$  is the angle between incident beam and scattering planes.

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 number of over 100 nanoparticles by using the software ImageJ [35].

Inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin-Elmer Optima 3300 DV) was employed to analyze the amount of *in situ* formed ruthenium in hectorite and ruthenium leaching in the centrifuged supernatant after the catalytic run.

### 2.4. Catalytic reactions

Precatalyst (50 mg), NaBH<sub>4</sub> (or NaBD<sub>4</sub>) (3–12 mmol), 1 mmol of the *N*-cyclic substrate and 5 ml deionized and degassed water (or D<sub>2</sub>O) were placed in a 25 ml three-necked flask equipped with a reflux condenser and a pressure release valve to discharge the hydrogen gas self-generated during the reactions. The operation was carried out under inert atmosphere. The reaction mixture was vigorously stirred at different temperatures (25–60 °C) for the time selected. The complete conversion of substrate was determined by submitting small samples to spot thin layer chromatography (TLC). After completion, the slurry was centrifuged to separate the catalyst. The solid phase obtained was washed with deionized H<sub>2</sub>O and then several times with ethyl acetate to remove all organic residue. The filtrate was collected, extracted with ethyl acetate and the extract dried over anhydrous MgSO<sub>4</sub>. After removal of the solvent *in vacuo*, the corresponding product was obtained. In some cases, a silica-gel column chromatography was used to purify the product (isolated yield). The product analysis and identification was conducted by comparing the NMR spectral data with those of the published pure substances (all analyzed by <sup>1</sup>H NMR and <sup>13</sup>C NMR on Bruker Avance II 400 MHz spectrometer). The reaction selectivities were obtained from the NMR spectra by integration of characteristic peaks for the product and reactant.

Alternatively, the reaction was performed in a magnetically stirred stainless-steel autoclave (100 ml) in cases where the reaction failed to be complete under atmospheric pressure. The loading procedure was the same as that in a flask. After purging three times with nitrogen, the autoclave was quickly fixed in the preheated oil bath. Once the reaction was complete, the autoclave was quenched in cold water, the pressure was released, and the product was isolated as described above.

Isotope labeling experiments were done for the hydrogenation of quinoline with NaBH<sub>4</sub>/D<sub>2</sub>O and with NaBD<sub>4</sub>/H<sub>2</sub>O (and for comparison with NaBH<sub>4</sub>/H<sub>2</sub>O and with NaBD<sub>4</sub>/D<sub>2</sub>O), under the same conditions as those of entry 7 in Table 1 (see below). All NMR spectra were recorded with a narrow-bore Bruker 400 spectrometer (9.4 T) operating at  $\omega_0/2\pi = 400.0$  and 100.6 MHz for <sup>1</sup>H and <sup>13</sup>C, respectively, and equipped with an AVANCE-II console and a 5 mm double-resonance probe. The *r*<sub>f</sub>-field strengths of all hard  $\pi/2$  and  $\pi$  pulses were  $\omega_1/2\pi = 26$  kHz and 27 kHz, for <sup>1</sup>H and <sup>13</sup>C channels, respectively. Quantitative proton spectra were acquired with a recycling delay  $d_1 = 5 \times T_1$ , with longitudinal relaxation time constraints  $T_1$  of the as measured inversion-recovery experiments. Semi-empirical calculations were performed with the PM7 method as implemented in MOPAC2012 [36]. The optimized geometries were used for calculations of the electrostatic potentials by means of the keyword ESP.

The recyclability of the *nanoRu'@hectorite* catalyst was examined for the hydrogenation of quinoline under atmospheric

Download English Version:

<https://daneshyari.com/en/article/5153294>

Download Persian Version:

<https://daneshyari.com/article/5153294>

[Daneshyari.com](https://daneshyari.com)