Water-assisted one-pot synthesis of N-doped carbon supported Ru catalysts for heterogeneous catalysis

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Experimental Section:

Materials

RuCl₃·xH₂O (Ru content: 35.0~42.0wt%), Chitin (practical grade), quinoline (AR, 99%), 6-chloroquinoline (AR, \geq 98%), and 6-methylquinoline (AR, 98%) were purchased from Shanghai Aladdin Chemistry Co., Ltd. 6-fluoroquinoline (AR, 95%), 6-bromoquinoline (AR, 96%), 6-methoxyquinoline (AR, 96%), 8-hydroxyquinoline (AR, 99%), and 1,2,3,4-tetrahydroquinoline (AR, 97%) were purchased from Shanghai Macklin Biochemical Co., Ltd. All of them were used directly without further purification.

Catalyst preparation

The preparation of Ru/CN catalysts involved one-pot pyrolysis of chitin and RuCl₃·xH₂O with the assistance of water. In a typical experiment, chitin (6 g) and 4 mL of an aqueous solution of RuCl₃·xH₂O (10 mg/mL) were added into an ethanol solution, and then the as-made solution was heated by oil bath at 60 °C until completely drying to form a powder. Subsequently, the dried powder was transferred into a furnace and heated at 350 °C for 2 h, and then increased the temperature to the desired temperature (500 °C, 600 °C, 700 °C, or 800 °C) for the desired time (0.5 h, 1 h, 2 h, 3 h, or 4 h) under nitrogen flow with the presence of water. Finally, the obtained black powder was washed with water several times and dried under vacuum at 60 °C overnight. The Ru/CN-700-1h sample was prepared by similar procedure except for without the presence of water during the pyrolysis process. For comparison, chitin was directly pyrolyed at 350 °C for 2 h, and then increased the temperature to 700 °C for 1 h under nitrogen flow with the presence of water, hereafter referred to as CN-700H2O-1h. For acid leaching experiment, CN-700H2O-1h sample was soaked in hydrochloric acid solution (3 M) at 80 °C for 24 h to remove the impurity existed in carbon support, and the sample obtained here denoted as CN-700H₂O-1h-HCl.

Characterizations

Powder X-ray diffraction (XRD) was carried out in a Shimadzu XRD-600 diffractometer with Cu K α irradiation. Textural properties were determined by

Nitrogen adsorption experiment at -196 °C using an 3Flex instrument from Micromeritics. BET (Brunauer-Emmett-Teller) equation was used to calculate the BET surface area and pore volume. The size and dispersity of particles in the samples analysis were performed using transmission electron microscopy (TEM) with a JEM-3010. More than 200 particles in the TEM images were chosen to calculated the mean particles size and size distribution. Inductively coupled plasma mass spectrometer (ICP-MS) was employed to analyze the actual Ru content in the prepared catalysts on a USA Perkin Elmer NexION 350D instrument. The pulse CO chemisorption experiments were performed using an Auto Chem 2920 instrument (Micromeritics, USA) at 40 °C with a pulse of 10%CO/90%He (volume ratio). Assuming CO/Ru stoichiometry of 1:1, the CO uptake and metal area were calculated using following equations:

$$C0 \ uptake = \frac{n_{C0}}{m_{Ru}} = \frac{n_{C0}}{m_{Cat.} \times Ru \ loading} \tag{1}$$

$$metal \ area = S_{Ru} \times \frac{n_{CO} \times N_A}{m_{Ru}} \times 10^{-18} = S_{Ru} \times \frac{n_{CO} \times N_A}{m_{Cat.} \times Ru \ loading} \times 10^{-18}$$
(2)

where n_{co} is the mole amount of adsorbed CO, $m_{Cat.}$ is the weight of catalyst used in the experiment, Ru loading is the actual Ru loading in the catalyst (wt%), S_{Ru} is the cross-sectional area of Ru (0.0821 nm²), and N_A is Avogadro's constant (6.022 × 10²³ mol⁻¹).

Catalytic tests

The hydrogenation reaction was carried out in a 50 mL stainless-steel autoclave with a Teflon inner layer. Typically, quinoline (0.5 mmol), catalyst (20 mg), and ethanol (5 mL) were introduced into the stainless-steel autoclave, and then the reactor was purged with H₂ several times. After that, the reactor was filled with 2 MPa hydrogenation pressure at room temperature and finally heated to a desired temperature with a magnetic stirring (1000 rpm). The collected sample solution was quantified by a gas chromatograph (GC, FULI GC9720) with SE-54 capillary column (30 m × 0.32 mm × 0.5 µm). The GC detecting conditions were as follows: nitrogen as carrier gas; injection port temperature: 250 °C; detector (FID) temperature: 250 °C;

column temperature: holding at 70 °C for 1 min, then increasing from 70 to 240 °C with a heating rate of 12 °C/min, finally holding at 240 °C for 0.5 min.

In order to examine stability of the catalysts, they were recycled in repeated runs. First, quinoline (0.5 mmol), ethanol (5 mL) and an excess amount of Ru/CN-700H₂O-1h (150 mg) were added into the batch reaction and the catalytic hydrogenation was carried out at 80 °C and 2 MPa H₂ for 1.5 h. After the reaction, the recovered catalyst was washed with ethanol and dried overnight at 40 °C under vacuum condition. Afterward, 20 mg of catalyst was taken from them and was tested under same reaction conditions: quinoline (0.5 mmol), ethanol (5 mL), and Ru/CN-700H₂O-1h (20 mg), at 80 °C and 2 MPa H₂ for 1.5 h (this is second cycle). Meanwhile, the remanent recovered Ru/CN-700H₂O-1h catalyst was tested under same reaction conditions: Ru/CN-700H2O-1h, quinoline (0.5 mmol), ethanol (5 mL) at 80 °C and 2 MPa H2 for 1.5 h. Afterward, the recovered catalyst was washed with deionized water and dried overnight at 40 °C under vacuum, and then 20 mg of catalyst was taken from them and was used for the next run under same reaction conditions: quinoline (0.5 mmol), ethanol (5 mL), and Ru/CN-700H₂O-1h (20 mg), at 80 °C and 2 MPa H₂ for 1.5 h (this is third cycle). Subsequent reusability tests were performed on the same material by following the same procedure.

Catalyst	Ru loading (wt%)
Ru/CN-500H ₂ O-2h	0.68
Ru/CN-600H ₂ O-2h	0.69
Ru/CN-700H ₂ O-2h	0.68
Ru/CN-800H ₂ O-2h	0.65
Ru/CN-700H ₂ O-0.5h	0.68
Ru/CN-700H ₂ O-1h	0.64
Ru/CN-700H ₂ O-1h-used	0.61
Ru/CN-700-1h	0.67
Ru/CN-700H ₂ O-3h	0.78
Ru/CN-700H ₂ O-4h	0.80

Table S1. The actual Ru loading of various Ru-based catalysts

^aCalculated by ICP-MS.



Figure S1. XRD patterns of CN-700H₂O-1h before and after HCl leaching.



Figure S2. TEM images of CN-700H₂O-1h.



Figure S3. N₂ adsorption-desorption isotherms of various Ru catalysts prepared with different pyrolysis temperatures (A) and pyrolysis times (B)



Figure S4. TEM images and particle size distribution of Ru/CN-500H₂O-2h (A and B), Ru/CN-600H₂O-2h (C and D), Ru/CN-700H₂O-2h (E and F), and Ru/CN-800H₂O-2h (G and H)



Figure S5. TEM images and particle size distribution of Ru/CN-700H₂O-0.5h (A and B), Ru/CN-700H₂O-1h (C and D), Ru/CN-700H₂O-3h (E and F), and Ru/CN-700H₂O-4h (G and H)



Figure S6. XPS spectra of Ru 3p (A) and N 1s (B) in the different Ru/CN catalysts.



Figure S7. The kinetic curve of quinoline hydrogenation over the $Ru/CN-700H_2O-1h$ catalyst. Reaction conditions: catalyst 20 mg, quinoline 0.5 mmol, ethanol 5 mL, 80 °C, 2 MPa H₂.



Figure S8. Catalyst recycling for the hydrogenation of quinoline over Ru/CN-700H₂O-1h catalyst. Reaction conditions: quinoline 0.5 mmol, catalyst 20 mg, ethanol 5 mL, 80 °C, 2 MPa H₂, 1.5 h.



Figure S9. N_2 adsorption-desorption isotherms of reused Ru/CN-700H₂O-1h catalyst. S_{BET:} BET surface area. Vt: total pore volume. D_p: average pore size.



Figure S10. TEM images and particle size distribution of Ru/CN-700H₂O-1h catalyst after six cycles