Electronic Supplementary Material (ESI) for Catalysis Science & Technology
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Supporting Information

Cooperation between the surface hydroxyl groups of Ru-SiO_2@mSiO_2 and water for good catalytic performance for hydrogenation of quinoline

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1. To explore the conversion of quinoline during the heating time could be neglected?

1.0 mmoL quinoline, 2.0 mL water and 35 mg catalyst were transferred to a Teflon-lined autoclave and the hydrogen was charged to the desired pressure after removing the air. After the autoclave was heated to 363 K in about 25 min without stirring. The autoclave was cooled to room temperature. All the products were taken out and the autoclave was washed with ethanol for 3 times (3.0 mL×3) to collect the products. The catalyst was separated by centrifugation. The liquid phase was analyzed by GC.

2. To explore is the leached Ru nanoparticles as the catalytic species?

The followed experiments was designed: Exp. (1). 1.0 mmoL of quinoline, 2.0 mL of water and 3.0 MPa of hydrogen was introduced into the autoclave and reacted for 5 h at 363 K; Exp. (2). Ru-SiO_2@mSiO_2 (0.67 mol% Ru relative to quinoline), 2 mL water and 3.0 MPa of hydrogen was introduced into the autoclave and reacted for 5 h at 363 K, the catalyst was separated by filtration and the water was used as the solvent in the next experiment; Exp. (3). 1.0 mmoL of quinoline, 2.0 mL water which was collected in Exp. (2) and 3.0 MPa of hydrogen was introduced into the autoclave and reacted for 5 h at 363 K. The results were listed in **Table S1**. Exp. (1) shows that we could exclude the metal particles absorbed on the liner tube in the autoclave as the catalytic species. Result in Exp. (3) shows that although there was trace amount

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Ru leaching, the leached Ru was not as the catalytic species. (Note: the liner tube was bathed in chloronitrous acid at 303 K for 30 min, then bathed in concentrated nitric acid at 353 K for 3 h to remove all icons. The liner tube was washed by amount of water and dried at 353 K for 5 hours in vacuum before use.)

Entry	Reaction Components	Conversion (%)
Exp. (1)	quinoline, water and hydrogen	No reaction
Exp. (2)	catalyst, water and hydrogen	No reaction
Exp. (3)	quinoline, water [a] and hydrogen	No reaction

Table S1. Reaction performance in different reaction components

a. Collected from Exp. (2)

Reaction conditions: 5 h at 363 K

3 Synthesis of $Ru/SiO_2 \cdot xH_2O$ catalyst

In typically, 500 mg of silica with the size distribution about 300-400 meshes was dispersed in the mixture of 25 mL ethanol and 0.L ml $NH_3 \cdot H_2O$, then 10 mg Ru^{3+} was added and stirred for 24 h. After that, 5.0 mL of $NaBH_4$ solution was dropped into the suspension to reduce the Ru^{3+}. The solid was filtered and dried at 308 K in vacuum. The catalyst was denominated as $Ru/SiO_2 \cdot xH_2O$. The Ru-loading (2%) was determined by ICP-AES

4. Synthesis of Ru/SiO_2-spheres catalyst

In typically, 0.70 mL $NH_3 \bullet H_2O$, 30 mL ethanol and 2.5 mL deionized water were stirred for 1 h at ambient temperature, then 1.9 mL TEOS was added and stirred for 6 h to get the silica core. Then 20 mg Ru^{3+} was added and the stirring continued for another 3 h. After that, 5.0 mL $NaBH_4$ solution was dropped into the suspension to reduce the Ru^{3+}. The suspension was filtered and dried in vacuum. The product was denominated as Ru/SiO_2-Spheres. The Ru-loading (2%) was determined by ICP-AES.

5. Preparation of composite of quinoline adsorbed on the $Ru\text{-}SiO_2@mSiO_2$

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100 mg catalyst and 2.0 mL quinoline were mixed together and stirred for 24 h at room temperature, the excess quinoline was distilled under vacuum at 393K. The solid was dried at 333K under vacuum for 24 h before detected by IR and Solid-state ^{13}C NMR.

6. Computational method

The method was as follows: Geometry optimizations were performed using the density functional theory (DFT) with the Beck's three-parameter nonlocal exchange functional and the gradient-corrected functional of Lee, Yang, and Parr (B3LYP) [1, 2, 3] and 6-31++G(d,p) basis set. The harmonic vibrational frequencies were also calculated at the same level to characterize the nature of the stationary point as true minimum with no imaginary. The NMR was calculated at the same level using GIAO method. All calculations were carried out using Gaussian 03 program [4]. The mainnetwork structures of the silica were proved as $\{(HO)Si(OSi)_3\}$ and $\{(HO)_2Si(OSi)_2\}$ by solid-state ^{29}Si NMR The silica of the catalyst was built as $HOSi[OSi(OH)_3]_3$ in the computational model.

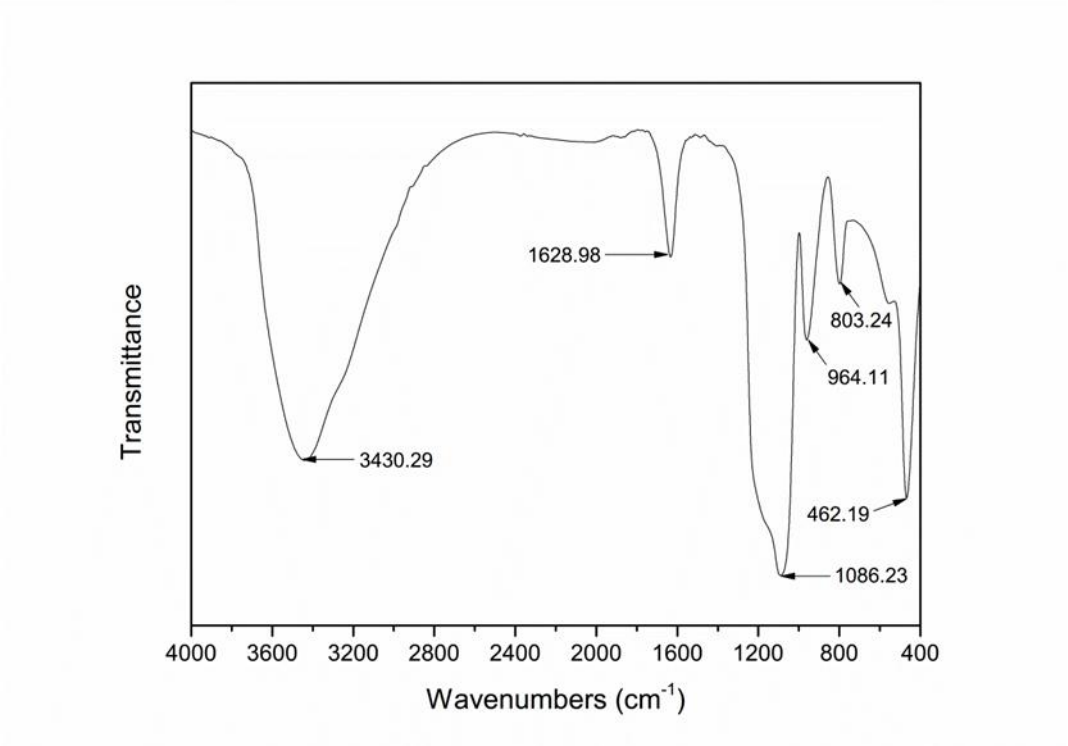

Fig. S1 FT-IR spectra of Ru-SiO_2@mSiO_2

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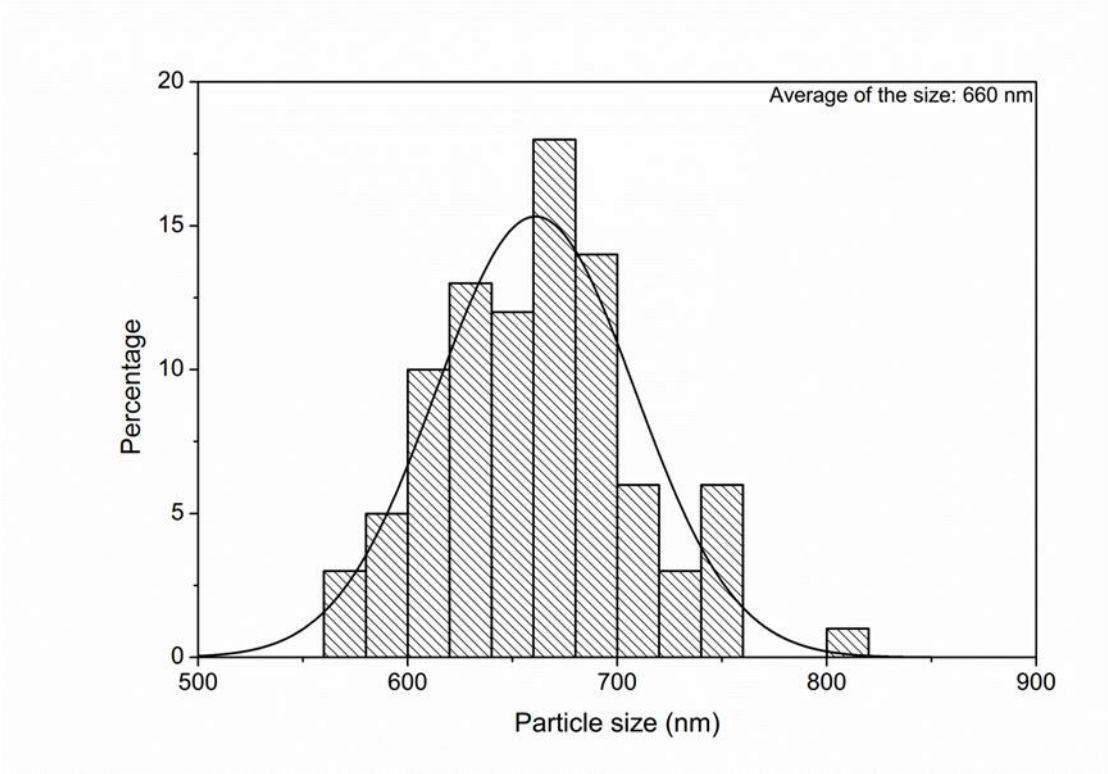
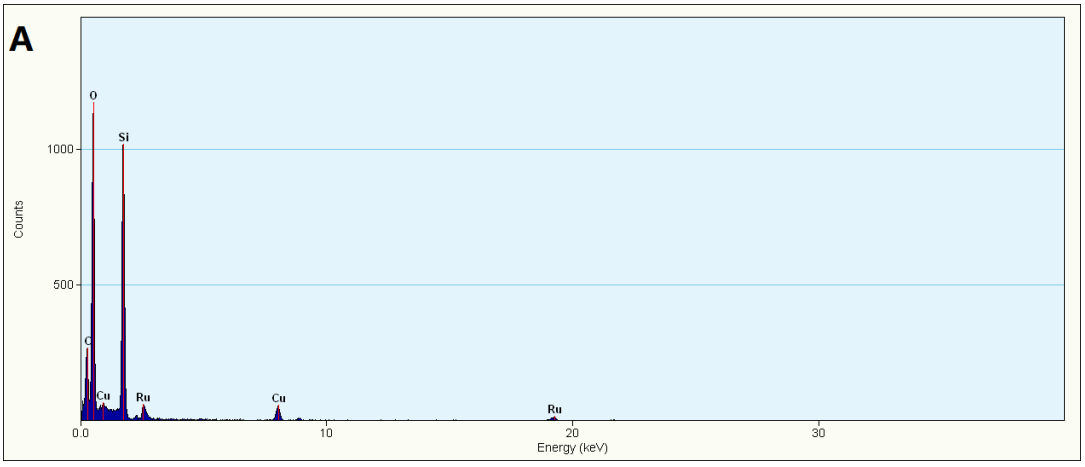


Fig. S2 Particle size distribution histogram of the Ru-SiO_2@mSiO_2 particles



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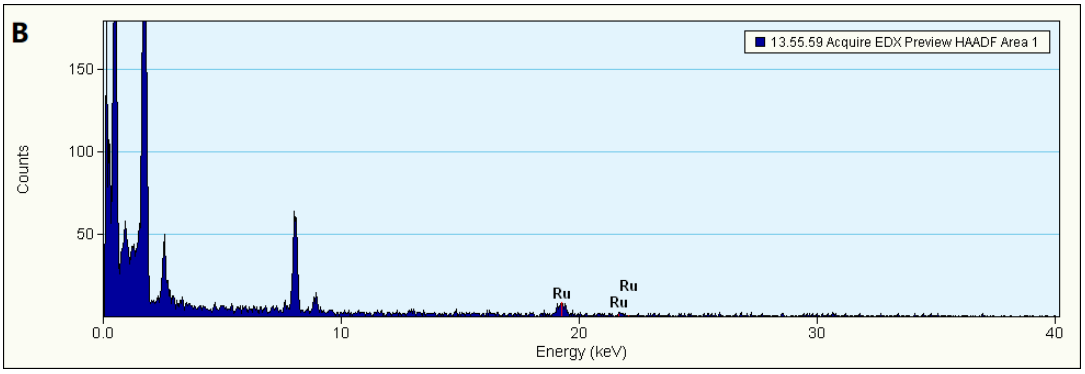
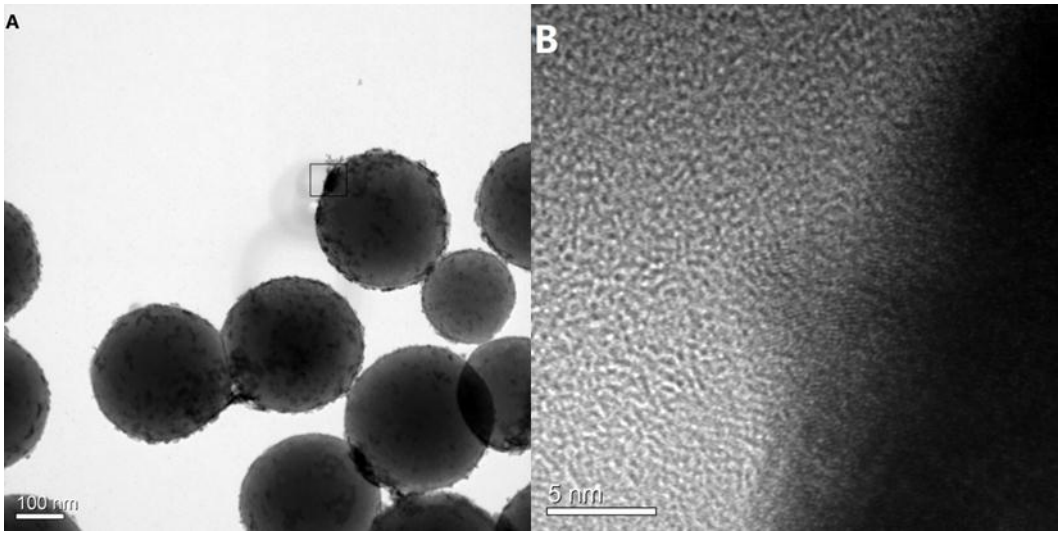


Fig. S3 Energy-dispersive X-ray analysis spectra of Ru-SiO_2 (A) and Ru-SiO_2@mSiO_2 (B)



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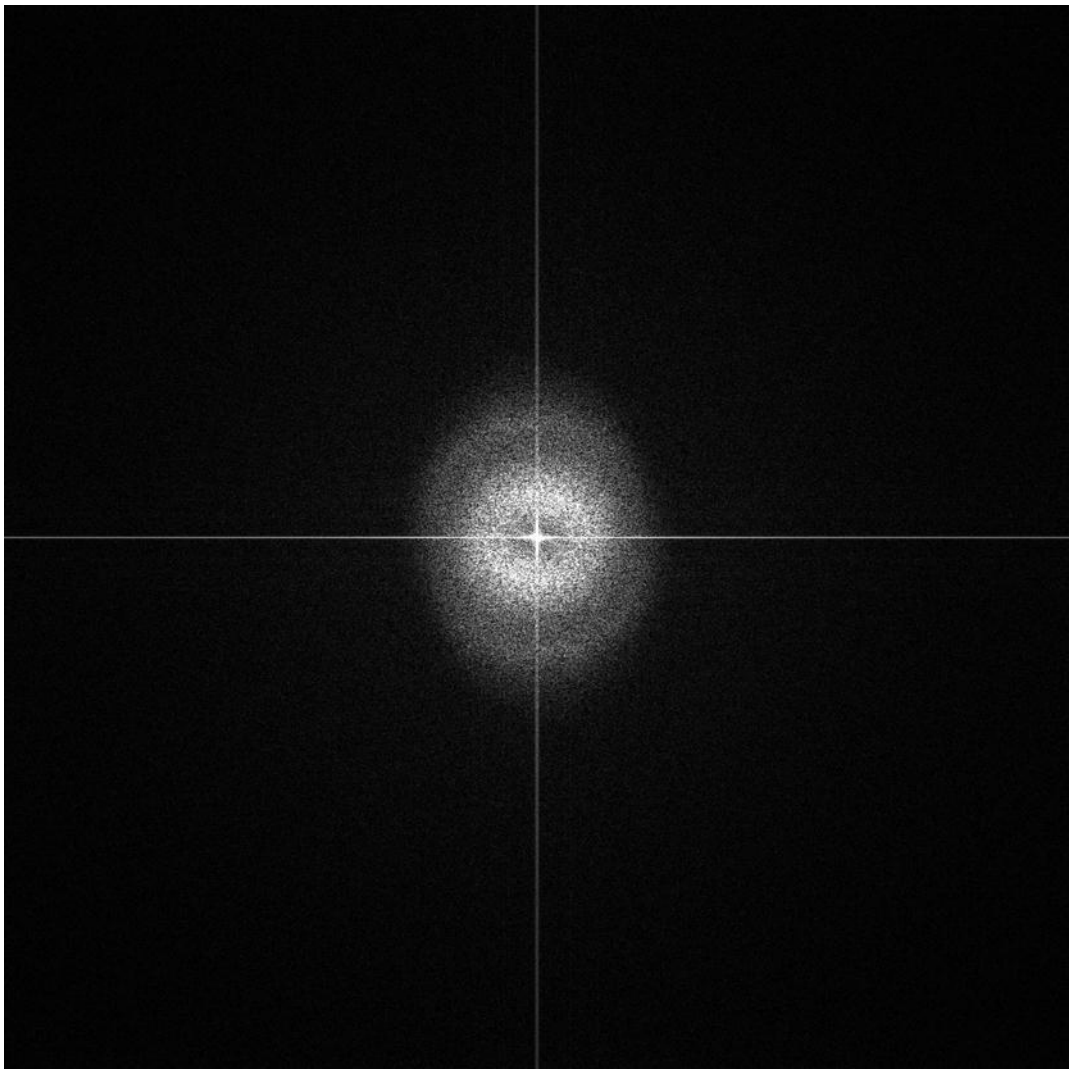

Fig. S4 TEM images the Ru-sSiO_2 (A) and HRTEM image of Ru-SiO_2 with selected area (B) and the live-FFT of image B

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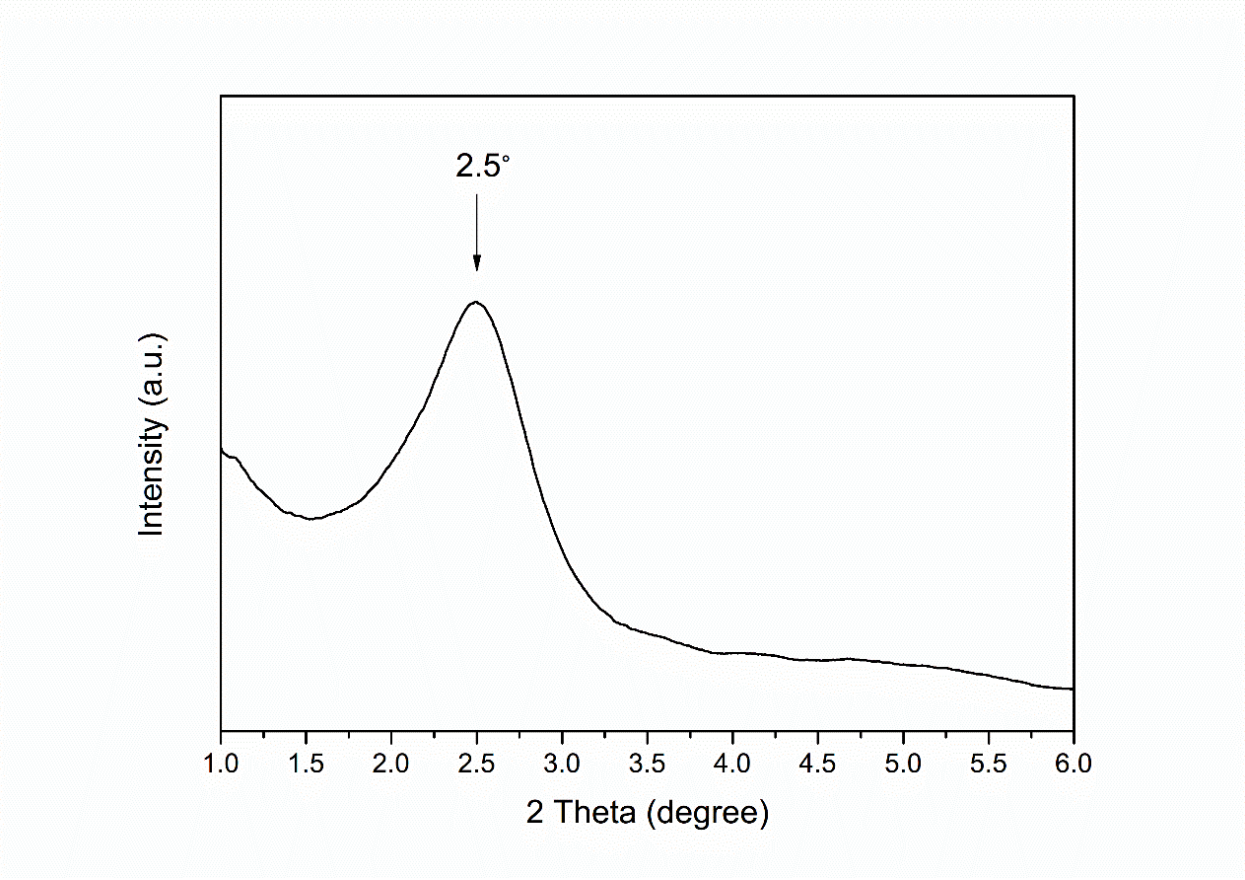

Fig. S5 Low-angle XRD patterns of the Ru-SiO_2@mSiO_2

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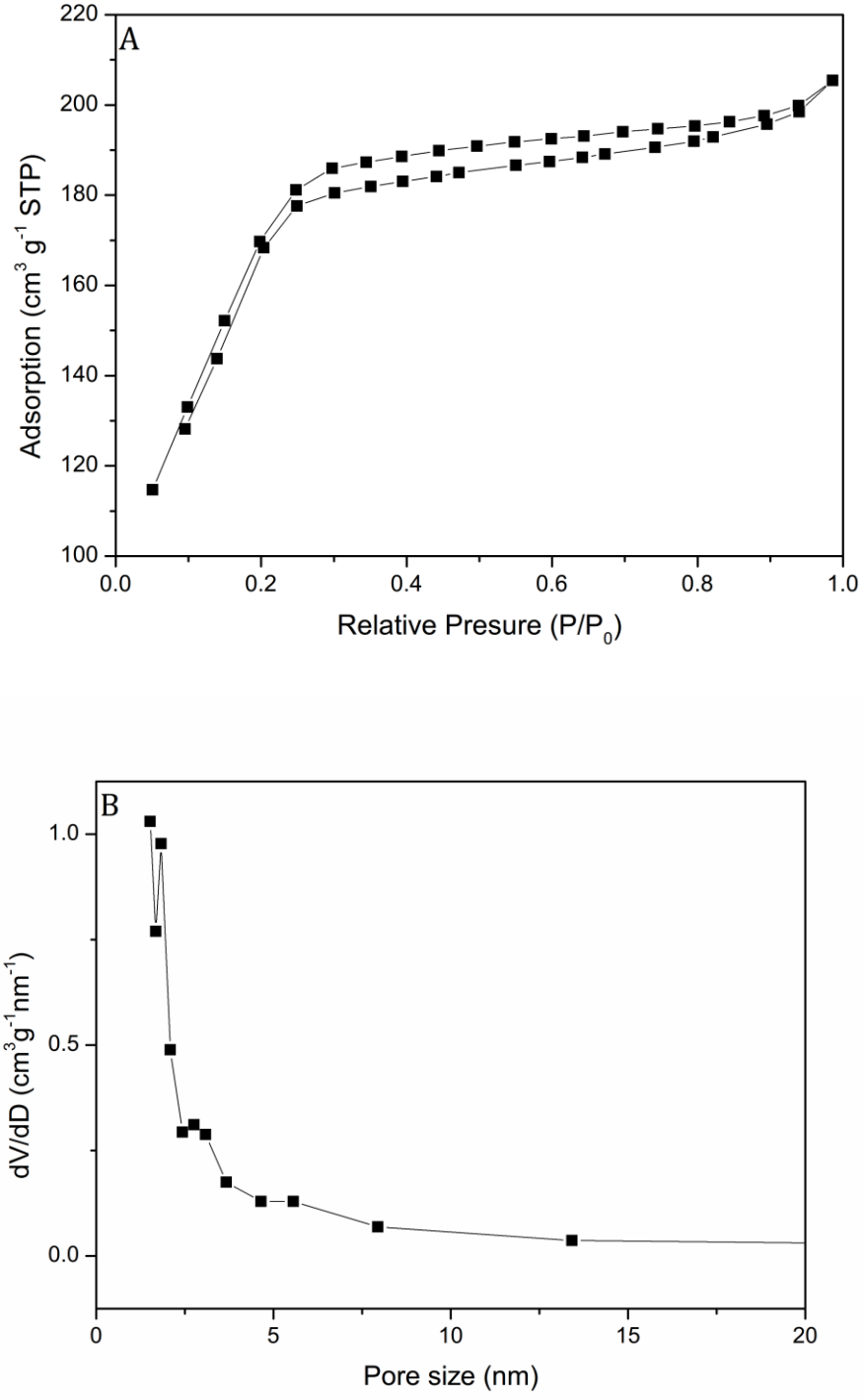

Fig. S6 Nitrogen adsorption-desorption isotherms (A) and pore distribution (B) of Ru-SiO_2@mSiO_2

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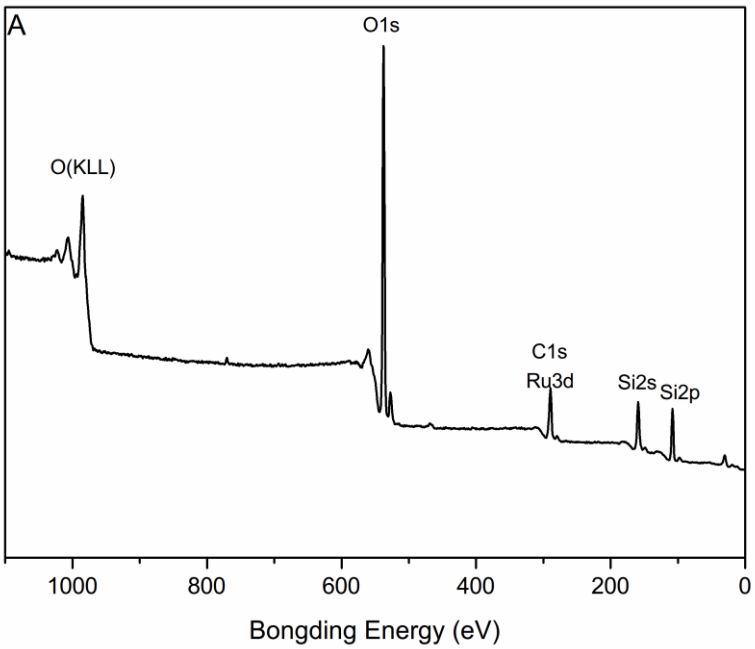

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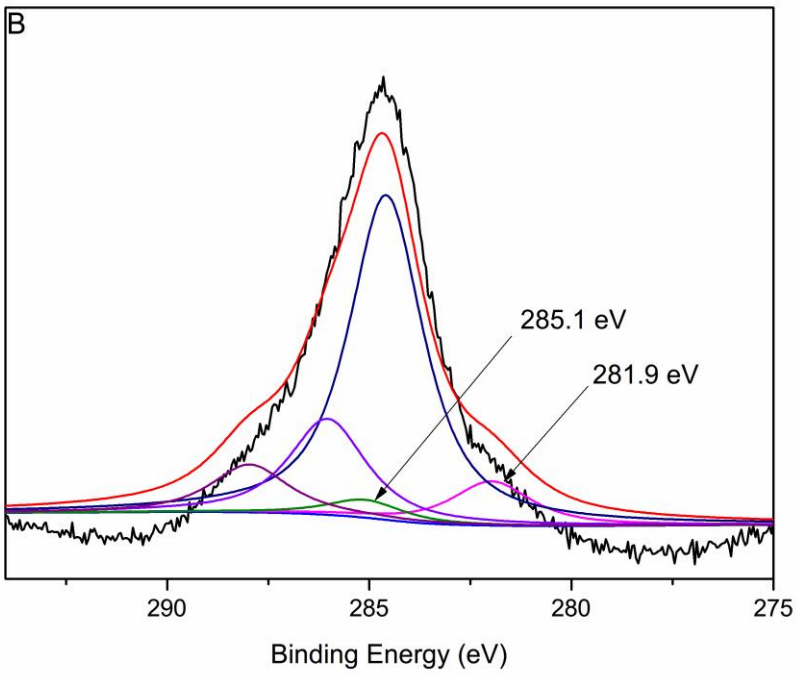

Fig. S7 XPS spectra of Ru-SiO_2@mSiO_2, A: survey spectra of Ru-SiO_2@mSiO_2, B: Ru 3d XPS of Ru-SiO_2@mSiO_2

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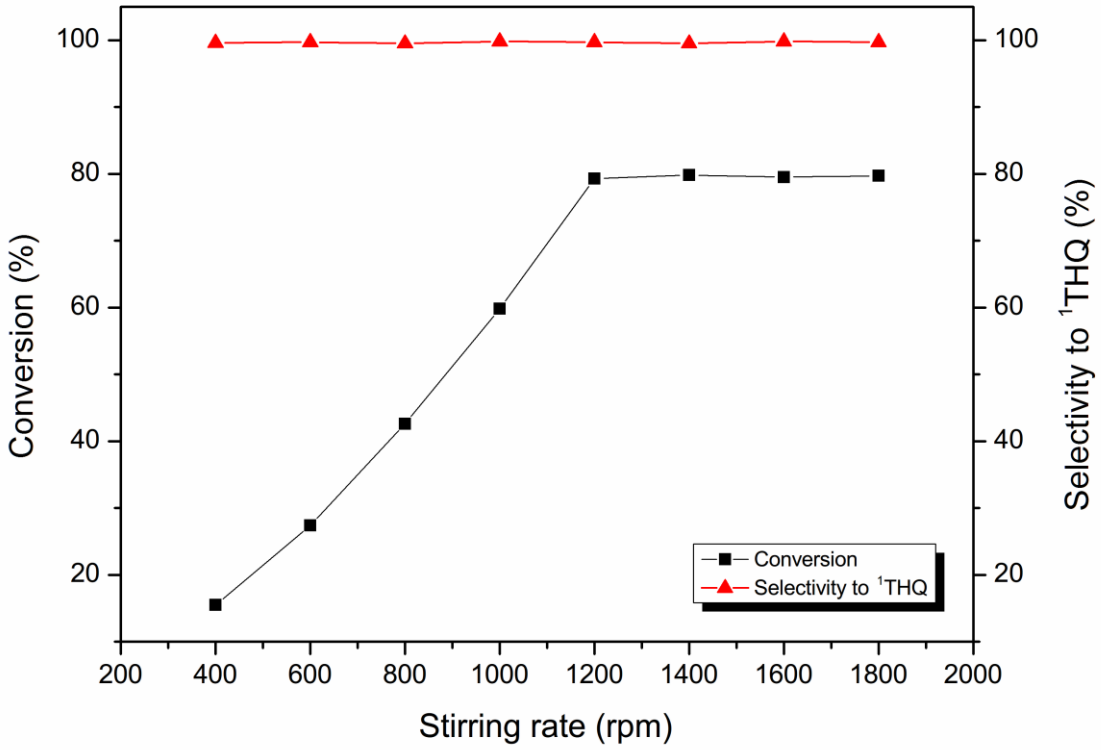

Fig. S8 Conversion of quinoline in different stirring rate

Reaction conditions: quinoline (1.0 mmoL), Ru (0.67 mol% relative to quinoline), 2.0 mL water, 363 K reaction temperature, 1.0 MPa hydrogen pressure, 5 h reaction time.

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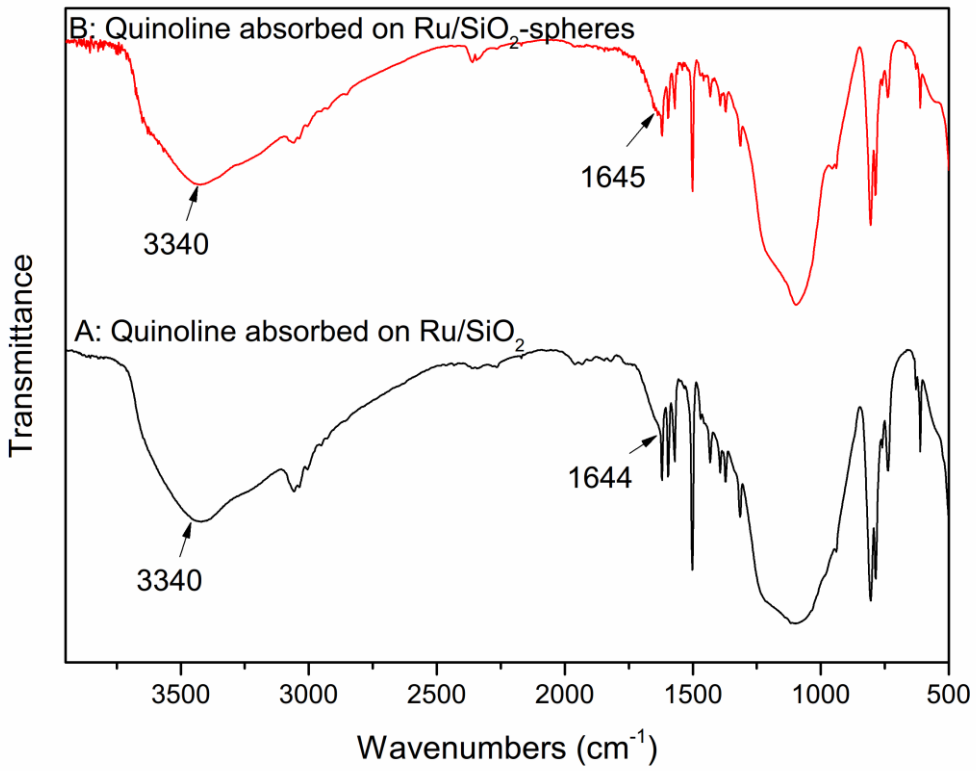

Fig. S9 The IR spectrum of quinoline absorbed on Ru/SiO_2 and quinoline absorption on Ru/SiO_2-spheres

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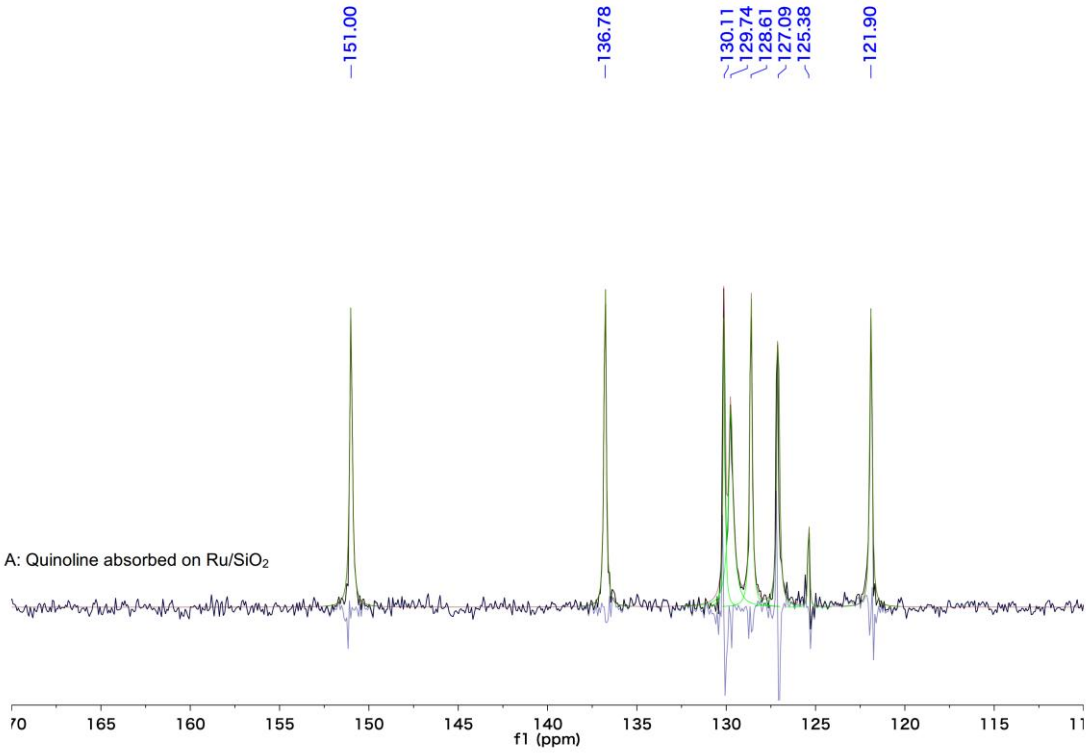

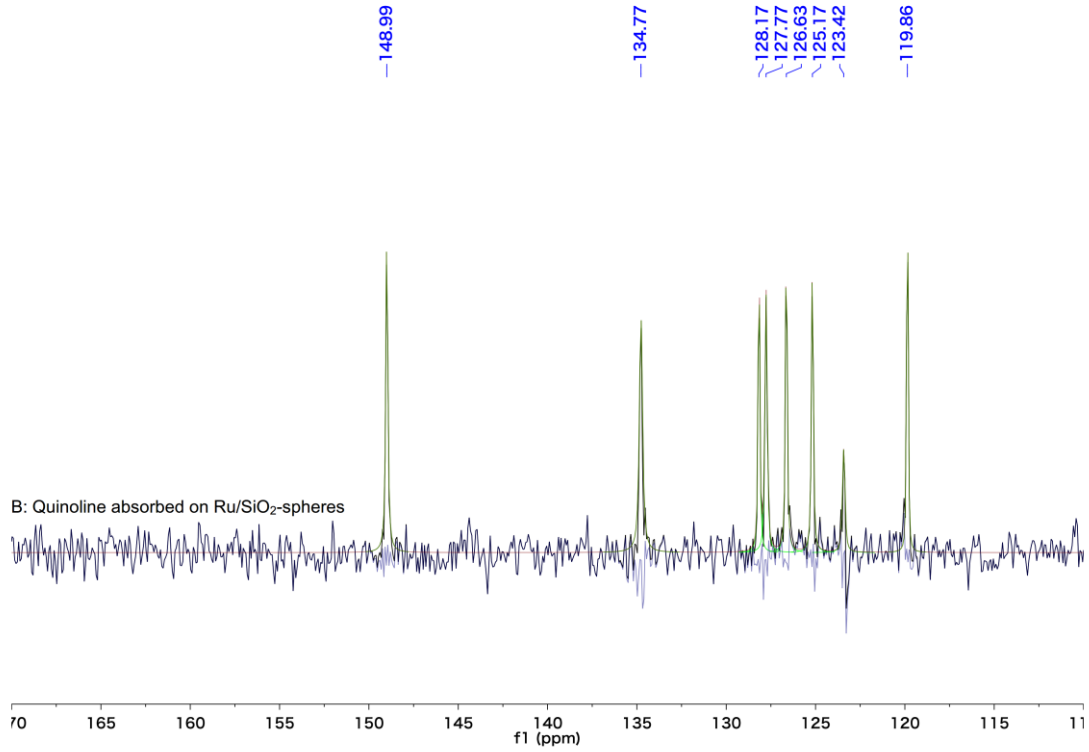

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Fig. S10 The ^{13}C NMR of ^{13}C CP/MAS NMR of quinoline absorbed on the $Ru/SiO_2.xH_2O$ (A) and quinoline absorbed on the Ru/SiO_2-spheres (B)

Reference

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