Supporting Information

Highly Stable Ru/LaCO$_3$OH Catalyst Consisting of Support-coated Ru Nanoparticles in Aqueous-Phase Hydrogenolysis Reactions

Bulong Li, Lulu Li and Chen Zhao*

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, China

Email: czhao@chem.ecnu.edu.cn
Experiment section

Chemicals
All chemicals were received from commercial suppliers without further purification: Guaiacol (Sinopharm Chemical Reagent Co., Ltd, AR assay), glycerol (Sinopharm Chemical Reagent Co., Ltd, AR assay), Ruthenium(III) chloride Hydrate (Shanxi Kaida Chemical Engineering Co., Ltd, Ru≥37.0% AR assay), Sodium hydroxide (Sinopharm Chemical Reagent Co., Ltd, ≥96% AR assay), aqueous ammonia solution (Sinopharm Chemical Reagent Co., Ltd., 28 wt%), Lanthanum nitrate hexahydrate (Shanghai Aladdin Bio-chem Technology Co., Ltd, 99% AR assay), Zirconium(IV) oxynitrate hydrate (Shanghai Aladdin Bio-chem Technology Co., Ltd, 99.99% AR assay), Sodium Carbonate anhydrous (Shanghai Reagent Co., Ltd, ≥99.8% AR assay), silicon dioxide (Shanghai Macklin Biochemical Co., Ltd, 99.5%, particle size: 15 ± 5 nm), Air, H₂, and N₂ gases (99.999 vol.%) were supplied by Shanghai Pujiang Specialty Gases Co., Ltd.

Synthesis of LaCO₃OH
The procedure to synthesis of LaCO₃OH as described in a previous literature. In a classical synthesis, 0.189 g NaOH and 1.431 g Na₂CO₃ were dissolved in 60 ml deionized water under magnetic stirring. Then the gained alkaline solution was added rapidly into 60 ml solution containing 0.779 g La(NO₃)₃∙6H₂O under vigorous stirring. The mixed solution was subsequently transferred into a 200 ml Teflon autoclave and maintained at 230 ℃ for 8 h. After cooled to room-temperature, the precipitate was washed with deionized water and absolute ethanol, and finally dried at 60 ℃ overnight.

Synthesis of ZrO₂
ZrO₂ was prepared by a conventional precipitation method. 4.0 g zirconium oxynitrate hydrate was dissolved in 100 ml deionized water under stirring, then the pH of solution was adjusted to 9.5 by dropwise addition of aqueous ammonia solution. After stirring for 8h, the white precipitates was washed with deionized water, and dried at 110 ℃ overnight followed by calcination at 400 ℃ in air for 2h.

Preparation of 5 % wt Ru/SiO₂, 5 % wt Ru/ZrO₂, 5 % wt Ru/LaCO₃OH catalysts
All these Ru based supported catalysts were prepared by the incipient impregnation method. In a typical procedure, 1.0 g supports was added into 10 ml deionized water respectively. Then an appropriate amount of RuCl₃·3H₂O solution was dripped into the suspension of supports under stirring. Then the suspension samples were further dried at 60 ℃ for 12 h, followed by air-calcination at 350 ℃ for 4 h and hydrogen-reduction at 350 ℃ for 4 h.

Catalyst characterization
Nitrogen sorption isotherms were recorded at 77 K on a BELSORP-MAX instrument after degassing the samples for 10 h under vacuum at 573 K. The surface areas were calculated by the Brunauer-Emmett-Teller (BET) method.

The Ru content was quantified by inductively coupled plasma (ICP) on a Thermo IRIS Intrepid II XSP atomic emission. Transmission electron microscopy (TEM) images were obtained on a JEOL JEM-2100 microscope operating at an accelerating voltage of 200 kV. STEM-mapping was observed by transmission electron microscopy (TEM, JEM-2100, JEOL, Japan) and energy
dispersive X-ray (EDX, Oxford, UK). For the TEM sample preparation, the samples were ground, dispersed in ethanol, and deposited on the copper grids prior to observation.

X-ray diffraction (XRD) patterns were recorded with a Rigaku Ultima IV X-ray diffractometer (35 kV and 25 mA) using Cu Kα radiation (λ = 1.5405 Å) over a 2θ ranging from 10° to 80° at a scanning speed of 60° min⁻¹ operating at 35 kV and 25 mA.

The temperature programmed reduction (TPR) analysis of catalysts was performed by using TP5080 (Xuanquan Instrument, Tianjin) apparatus equipped with a thermal conductor detector (TCD), using a 5% H₂/N₂ mixture (flowing rate: 30 mL·min⁻¹) and a heating rate of 10 K·min⁻¹.

The X-ray photoelectron spectroscopies (XPS) spectra were obtained using Al Kα (hv = 1486.6 eV) radiation on a Thermo Scientific K-Alpha spectrometer. Charging effects were corrected using the C 1s peak due to adventitious carbon with E_B fixed at 284.8 eV.

In situ diffuse reflectance infrared Fourier transform spectra (DRIFTS) were acquired with a BRUKER TENSOR 27 spectrometer equipped with a MCT detector and operated at a resolution of 4 cm⁻¹. All spectra were obtained at room temperature. Before the experiment, the samples in a powder form were treated at 350 °C for 1 h with N₂. After cooled to room temperature, the background spectrum was recorded and then the CO gas was introduced into the reaction cell at a total flow rate of 50 mL·min⁻¹. After adsorption for 30 min, the spectra under purge of N₂ were collected at room temperature.

**Catalytic reaction**

A typical experiment with guaiacol was carried out as followed: 1g guaiacol, 0.75g catalyst and 150 ml deionized water were introduced into a batch autoclave reactor (Beijing Senlang Instrument, 250ml). To remove the residual air, the reactor was firstly flushed with N₂ for three times, then 0.2 MPa H₂ was pursed into the reactor at ambient temperature. The reaction was performed at 240 °C with a stirring speed of 500 rpm. After reaction, the products were extracted using ethyl acetate and then analyzed by a Shimadzu GC coupled with GC-MS and equipped with a Rtx-5Sil MS capillary column (30 m × 0.25 mm × 0.25 μm). Dodecane acted as an internal standard to calculate the yields of liquid products. Conversion = (changes of reactant / total amount of reactant) × 100%. Selectivity = (C atoms in each product / total C atoms in the products) × 100%.

For the experiment with glycerol, 0.4 g glycerol, 0.1 g catalyst and 80 ml deionized water was introduced a batch reactor (Beijing Senlang Instrument, 250ml). After removed the residual air by flushing N₂, 3 MPa H₂ was purged in to the reactor at ambient temperature, then the reactor was heated up to 200 °C and maintained for 3h. After reaction, the catalyst was removed by filtering, and the liquid-phase products were analyzed by Waters HPLC system equipped with a Phenomenex Rezex RQA-Oganic Acid H⁺ (8%) column and a differential refractive index detector (RID). HPLC analysis was conducted at a column temperature of 60°C using water as the mobile phase. The samples were injected with injection volume of 10 μL. The yield and the conversion were analyzed by the standard curve method. Conversion = (changes of reactant / total amount of reactant) × 100%. Selectivity = (C atoms in each product / total C atoms in the products) × 100%.

The catalyst used in recycling reaction was collected by filtration and drying in oven at 60 °C overnight.
Figure S1. $N_2$ adsorption and desorption isotherms of Ru/SiO$_2$, Ru/ZrO$_2$ and Ru/LaCO$_3$OH samples.
Figure S2. XPS spectra of Ru/SiO$_2$, Ru/ZrO$_2$ and Ru/LaCO$_3$OH samples.
Figure S3. Ru 3d XPS spectra in Ru/LaCO$_3$OH after reduction at 500 °C with H$_2$ for 4 h.

Figure S4. Four-run recycling tests on hydrogenolysis of guaiacol over (a) Ru/ZrO$_2$ and (b) Ru/SiO$_2$. Conditions: 1.0 g guaiacol, 0.75 g catalyst, H$_2$O (150 mL), 0.8 MPa N$_2$ and 0.2 MPa H$_2$, 150 min.
Figure S5. Eight-run recycling tests on hydrogenolysis of guaiacol over hydrothermally-reduced Ru/LaCO$_3$OH. Conditions: 1.0 g guaiacol, 0.75 g catalyst, H$_2$O (150 mL), 0.8 MPa N$_2$ and 0.2 MPa H$_2$, 150 min.

Figure S6. Matlab fitting curve for hydrogenolysis of guaiacol over Ru/LaCO$_3$OH. Reactions conditions: 1.0 g guaiacol, 0.75 g catalyst, H$_2$O (150 mL), 0.2 MPa H$_2$. 
Figure S7. TEM image of Ru/LaCO₃OH with chloride free.

Reference