

Structural change of cerium oxide-supported ruthenium catalyst during the biorefinery of platform chemicals

Current requirements to reduce carbon dioxide emissions have been the driving force for biorefinery utilizing renewable resources, such as plant biomass, as carbon-neutral feedstocks for commodity chemicals [1]. To utilize biomass feedstocks in place of fossil resources, the development of highly efficient catalytic methods is strongly desired [2]. To date, much effort has been devoted to the direct carbon–oxygen (C–O) bond cleavage of high-oxygen-containing biogenic polyols to produce valuable chemicals by hydrogenolysis and deoxydehydration. For example, there have been many attempts to achieve the selective hydrogenolysis of glycerol, which is readily obtained from fats and oils, to 1,2-propanediol and 1,3-propanediol as valuable polyester monomers and solvents using copper- and platinum-based heterogeneous catalysts, respectively. On the other hand, selective cleavage of carbon–carbon (C–C) bonds has not yet been widely researched despite its great potential for extending the utility of biomass-derived oxygenates to obtain the desired carbon chain length. However, these reactions often suffer from low selectivity toward the desired chemicals, limited substrate scope, and high reaction temperatures. Therefore, the development of selective and versatile C–C bond scission catalysts that can work under milder conditions is highly desired to open new routes for industrially important chemicals from a wide range of biomass derivatives.

Recently, we have found that cerium oxide-supported ruthenium (Ru/CeO₂) nanoparticles efficiently promoted the selective C–C bond scission of levulinic acid to 2-butanol in water [3]. Levulinic acid is one of the versatile platform chemicals obtained from biomass. There are many reports on the catalytic transformation of levulinic acid to valuable C5 chemicals, e.g., γ -valerolactone, 1,4-pentanediol, and 2-methyltetrahydrofuran. However, C–C bond

scission reactions into valuable C4 chemicals such as 2-butanol have seldom been reported. Furthermore, Ru/CeO₂ showed high generality for the cleavage of C–C bonds of oxygenated compounds. The results provide a simple and more environmentally friendly method for the refinery of platform chemicals from biomass that are currently produced from petroleum feedstock.

The reaction of levulinic acid to 2-butanol was conducted using Ru/CeO₂ in water at 423 K under 3 MPa of H₂. To clarify the origin of the novel catalysis of Ru/CeO₂, several physicochemical analyses such as electron microscopy, X-ray diffraction (XRD), and X-ray absorption spectroscopy (XAS) were carried out. The XAS experiments were conducted at SPing-8 **BL14B2** and **BL01B1**.

The morphology of Ru/CeO₂ was determined by field-emission scanning electron microscopy (FE-SEM) analysis, which clearly showed the drastic change in the morphology after the catalytic reaction. The fresh Ru/CeO₂ nanoparticles (Ru/CeO₂_fresh) of 3–5 μ m diameters were converted into an agglomeration of rodlike structures (Fig. 1(a)) on the used Ru/CeO₂ (Ru/CeO₂_used).

From the high-resolution TEM images of Ru/CeO₂_used, Ru nanoparticles of ca. 3 nm diameter were observed on CeO₂ nanorods (Figs. 1(b,c)). The nanorods consist of fine crystalline nanowires having a line spacing of 0.27 nm, which is consistent with the {002} reflection plane of CeO₂.

In situ XRD analysis of Ru/CeO₂ catalysts showed that the pristine CeO₂ support was transformed into Ce(OH)₃ (Fig. 2). No diffraction peaks derived from crystalline Ru oxide and Ru metal were observed in the fresh and used catalysts, suggesting the high dispersity of Ru species, respectively. The diffraction pattern of the Ru/CeO₂_used catalyst without exposure to air was similar to that of Ce(OH)₃

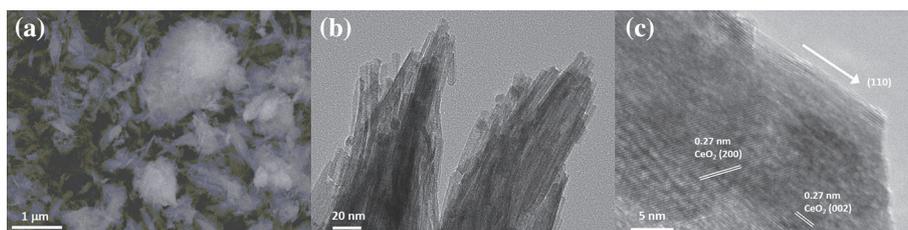


Fig. 1. FE-SEM image of Ru/CeO₂_used (a) and TEM images of Ru/CeO₂_used (b) and (c).

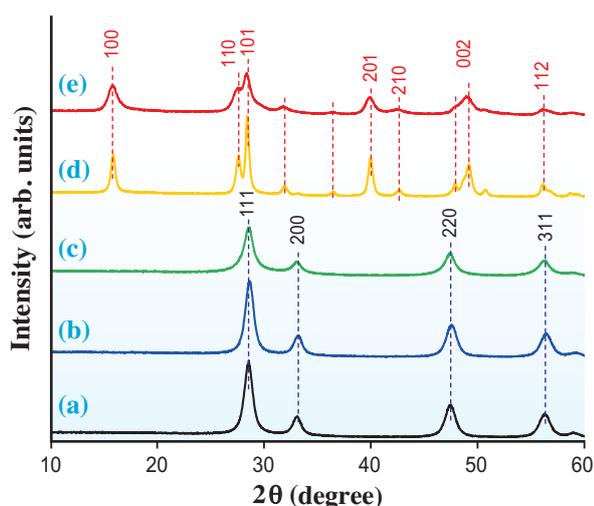


Fig. 2. XRD patterns of (a) pristine CeO_2 , (b) Ru/CeO_2 _fresh, (c) Ru/CeO_2 _used after exposure to air and (d) Ce(OH)_3 and (e) Ru/CeO_2 _used without exposure to air.

(Figs. 2(d) and 2(e)), indicating reduction and a phase transition from CeO_2 to Ce(OH)_3 . After exposure to air, the Ce(OH)_3 was oxidized back to CeO_2 (Fig. 2(c)).

Ru K -edge XAS analysis revealed that the Ru oxide in the fresh catalyst was reduced under the operating conditions to afford metallic Ru species

(Fig. 3(a)). FT-EXAFS and curve-fitting analysis of the peak at approximately 0.22 nm for the Ru-Ru shell revealed a Ru-Ru atomic distance of 0.267 nm and a coordination number of 8.6, indicating the formation of Ru nanoparticles with a mean diameter of ca. 3 nm [4]. The estimated particle size agreed well with that obtained from TEM observation (Figs. 3(b) and 1(b)).

Ce L_3 -edge XANES analysis also confirmed the complete reduction of Ce^{4+} to Ce^{3+} species under the reaction conditions (Fig. 3(c)). After exposing the used Ru/CeO_2 to air, the Ce(OH)_3 nanorods were easily oxidized to CeO_2 nanorods [5]. On the other hand, neither the Ru/CeO_2 catalysts used in organic solvents nor the CeO_2 sample without the use of Ru suggested that CeO_2 was reduced to Ce(OH)_3 during the reaction.

Considering the above results, we proposed the following reaction mechanism. A particular type of CeO_2 was reduced to Ce(OH)_3 nanorods under H_2 pressure in water at 423 K. The RuNPs formed on the cerium nanorods activate molecular hydrogen, and the spillover hydrogen and water promote the reduction of Ce^{4+} to Ce^{3+} to form Ce(OH)_3 nanorods. Water is necessary to promote the reduction of Ce species under the relatively mild conditions. The selective C–C bond cleavage was promoted by the concerted effect of the RuNPs with the basic Ce(OH)_3 nanorods.

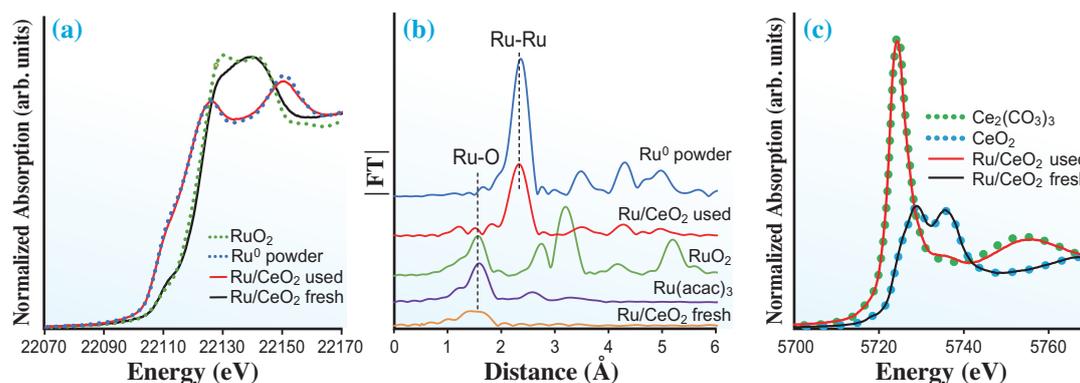


Fig. 3. Ru K -edge XANES (a) and FT of Ru K -edge EXAFS (b) of Ru/CeO_2 catalysts before and after catalytic reactions (H_2 3 MPa, 423 K in water). Ce L_3 -edge XANES of Ru/CeO_2 catalyst (c). (acac = acetylacetonate)

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References

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