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# Ru nanoparticles confined in Zr-containing spherical mesoporous silica containers for hydrogenation of levulinic acid and its esters into γ-valerolactone at ambient conditions

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ABSTRACT

Hydrogenation of levulinic acid and its esters to produce γ-valerolactone (GVL) was demonstrated over ruthenium nanoparticle (NP) catalyst supported on Zr-containing spherical mesoporous silicas as a bifunctional catalyst. The Ru NPs were found to be uniformly dispersed within the periodically ordered short mesopore channels with an average size of less than 1.5 nm without any agglomeration. They exhibited superior activity for the hydrogenation of both levulinic acid and its esters under mild reaction conditions (70 °C, 0.5 MPa $H_2$) compared to those supported on the conventional silica owing to their ultrasmall particle size and the acidity of Zr sites. In the hydrogenation of levulinate ester, addition of heterogeneous acids could afford a faster reaction rate in GVL production by accelerating the following intramolecular dealcoholation step. The catalyst was reusable over repeated catalytic cycles without a significant loss of catalytic performance, demonstrating its potential as a heterogeneous catalyst for GVL production under ambient reaction conditions.

## 1. Introduction

Efficient and sustainable biomass conversion technologies are being extensively studied to address worldwide concerns about the depletion of petroleum resources and energy problems for future energy production [1–7]. Utilization of biomass as renewable, ubiquitous carbon sources to produce valuable biofuels and feedstock chemicals is one of the promising alternatives to the current petroleum-based chemical industrial technologies. Among various chemicals synthesized from cellulosic biomass, γ-valerolactone (GVL) is gaining considerable attention as a versatile building block, since it can be used as a fuel additive [8], solvent for biomass processing [9], as well as an ideal precursor for the production of hydrocarbons [10–14], polymers [10,15,16] and other valuable chemicals [10], thus has a great potential to reduce the consumption of petroleum-derived fossil fuels. In an ideal process currently proposed, GVL is produced from cellulosic biomass via hydrogenation of levulinic acid (LA) and its esters and the following acid-catalyzed intramolecular dehydration/dealcoholation step. LA and its esters are intermediate compounds produced by acid-catalyzed solvolysis of various cellulosic biomass such as cellulose, glucose, fructose, as well as 5-hydroxymethylfurfural (HMF) in water [17,18] and alcohols [19–27], respectively. The hydrogenation reaction of LA and its esters is generally conducted by using various heterogeneous precious metal particle catalysts such as Ru [28–32], Pd [33,34] and Pt [35], which can afford GVL in excellent yields under the presence of pressurized $H_2$, but high reaction temperatures and high $H_2$ pressures are still required to achieve high activities [36,37]. For the establishment of economical and ecological biomass conversion process, the reaction needs to be operated at low temperature/pressure conditions and the consumption of precious metals needs to be minimized [38].

Precious metal nanoparticles (NPs) are important catalysts in various chemical reactions, such as hydrogenation, dehydrogenation and oxidation, because of their unique structures and activities originating from their metal–metal bonds [39–41]. Their activities are known to be dependent on their particle size, structures, composition and the nature of support materials [42,43]. In order to maximize the catalytic activity of metal NPs and improve their reusability, they are conventionally immobilized on appropriate support materials with retaining their small particle size. Among numerous kinds of supports, mesoporous silica is frequently chosen

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as an ideal support owing to its pore diameter (2–20 nm) similar to the size of the metal NPs and the defined porous arrangement that can spatially-isolate the NPs. However, the metal NPs supported on the conventional mesoporous silicas usually suffer from leaching and particle aggregation during reactions and low-accessibility of reactant molecules because of the two-dimensionally-aligned long mesopore channel systems. One of the key issues for achieving high catalytic activity for the supported metal NPs is to develop a new method to highly-disperse and stabilize them by manipulating the morphology, porous structure and surface environment of mesoporous silicas. In regard to this issue, we have recently developed a method to disperse and stabilize guest species within the channels of mesoporous silica, in which the heteroatoms (especially Zr) imbedded within the matrix of mesoporous silica provide a productive effect to anchor and stabilize the guest species via intermolecular acid–base interactions [44,45]. Such effects are expected to be beneficial for dispersing and stabilizing metal NPs as well, and thus improve the catalytic performances of the metal NPs.

Herein, we demonstrate hydrogenation of levulinic acid and its esters into γ-valerolactone by using Ru NP catalysts confined in Zr-containing spherical mesoporous silica as a bifunctional catalyst. The Zr site imbedded within spherical mesoporous silica may have an ability to disperse and stabilize the Ru NPs, which may offer an improved stability and reusability of the Ru NP catalysts. Furthermore, the imbedded Zr sites may contribute to GVL selectivity owing to their acidic property to catalyze the dehydration/dealcoholation reaction steps [46–48]. To this end, a series of Zr-containing spherical mesoporous silica having P6mm hexagonal mesoporous structure with varied Zr content were synthesized by sol–gel process using cetyltrimethylammonium bromide (CTAB) as a pore-directing agent and tetraethylorthosilicate (TEOS) as a silicon source. The influences of Zr incorporation on porous structures, size of Ru NPs and catalytic performances (including activity, selectivity and stability) were investigated in detail. The activities of the catalysts were examined by the hydrogenation of levulinic acid (LA) and methyl levulinate (ML) at ambient reaction conditions and were compared with Ru NPs supported on the conventional silica materials.

## 2. Experimental

### 2.1. Synthesis of Zr-containing spherical mesoporous silica

The Zr-containing spherical mesoporous silicas (ZrSMS) with different Zr contents were synthesized according to the reported method with minor modifications [49,50]. Into an aqueous solution containing cetyltrimethylammonium bromide (CTAB, Wako Pure Chemical Ind., Ltd.) and aqueous ammonia (28%, Wako Pure Chemical Ind., Ltd.), tetraethylorthosilicate (TEOS, 95%, Wako Pure Chemical Ind., Ltd.) diluted in ethanol (1.0 M) was added rapidly at 50 °C under stirring. After stirring for 1 h, a mixture of TEOS and zirconium(IV) tetrapropoxide ($Zr(O^nPr)_4$, 70% in 1-propanol, Tokyo Chemical Ind. Co., Ltd.) in ethanol (0.2 M) was added dropwise under vigorous stirring and the mixture was continuously stirred for another 2 h at 50 °C. The molar ratio of the initial synthesis solution was adjusted to $Si:Zr:NH_3:CTAB:H_2O = 1.0:(0–0.1):28:0.25:2540$. The solution was then transferred to a teflon bottle, sealed and hydrothermally treated at 100 °C for 24 h under static conditions. Then, the resulting particles were collected by centrifugation at 18,000 rpm, washed several times with deionized water and ethanol, dried overnight and finally calcined at 550 °C for 6 h to remove the organic template. The samples were denoted as Zr*x*SMS, where *x* represents the Zr/Si molar ratio in the initial solution.

For comparison, a conventional mesoporous silica with large particle size (MCM-41) was prepared by a hydrothermal synthesis method using CTAB as an organic template and TEOS as a silicon source with the molar ratio of $Si:NH_3:CTAB:H_2O = 1.0:3.3:0.1:66$.

### 2.2. Synthesis of supported Ru NP catalysts

The supported Ru NP catalyst was synthesized by a conventional impregnation method and a following reduction treatment in a flow of $H_2$. 1.0 g of support was dispersed in 50 mL of aqueous solution containing 3.51 g of ruthenium(III) nitrosyl nitrate solution ($Ru(NO)(NO_3)_x(OH)_y$, 1.5% as Ru, Aldrich) and subjected to ultrasonication for 5 min. After stirring for 24 h at room temperature, the slurry was then placed in a rotary evaporator, and the water was removed under vacuum to facilitate the incorporation of the Ru(III) ions into the support. After drying at 100 °C, the sample was reduced in a flow of 10% $H_2$ in $N_2$ (100 mL/min) at 350 °C for 5 h with a ramping rate of 4 °C/min. The Ru loading was adjusted to 5 wt.%. The conventional mesoporous silica (MCM-41), fumed silica ($S_{BET} = 279\ m^2/g$, Wako Pure Chemical Ind., Ltd.) and zirconia ($S_{BET} = 112\ m^2/g$, Daiichi Kigenso Kagaku Kogyo Co., Ltd.) were also used as supports.

### 2.3. Characterization

X-ray diffraction (XRD) patterns were recorded on a Bruker AXS D8 Advance X-ray diffractometer with CuKα radiation ($\lambda = 1.54056$ Å, 40 kV to 40 mA). Nitrogen adsorption–desorption isotherms were measured at −196 °C by using Micromeritics ASAP2020. The samples were degassed at 300 °C under vacuum for 4 h prior to the measurements. The specific surface area was calculated by the BET (Brunauer–Emmett–Teller) method by using adsorption data ranging from $p/p_0 = 0.05–0.30$. The pore size distributions were obtained from the adsorption branches of the isotherms by the BJH (Barret–Joyner–Halenda) method. Transmission electron microscope (TEM) observations were performed with a FEI TITAN80-300 operated at 200 kV. Infrared spectra were recorded on a JASCO FTIR-6300 instrument in the spectral range $2000–400\ cm^{-1}$ under vacuum with a resolution of $4\ cm^{-1}$ using samples diluted with KBr. Dynamic light scattering (DLS) study was carried out on a Malvern Zetasizer Nano ZS at 25 °C in ethanol solution.

Temperature programmed desorption of $NH_3$ ($NH_3$-TPD) was performed by using a BELCAT-B system (BEL Japan, Inc.) equipped with an on-line thermal conductivity detector. The samples were pretreated under a He flow (50 mL/min) at 600 °C for 1 h, allowed to cool to 50 °C and subsequently exposed to flowing 5% $NH_3$/He gas (50 mL/min) for 1 h. After purging at 50 °C for 30 min with He, $NH_3$-TPD was carried out between 50 and 600 °C under a He flow (30 mL/min) with a ramping rate of 10 °C/min.

### 2.4. Procedures for catalytic reactions

Hydrogenation of LA and ML was performed in a 60 mL cylindrical stainless steel autoclave reactor (EYELA, Inc.) equipped with a bourdon pressure gauge. In a typical reaction, catalyst (Ru 0.5 mol%), substrate (5 mmol) and solvent (water or methanol, 10 mL) were introduced into the reactor, which was then sealed, purged and pressurized with 0.5 MPa of $H_2$ and then heated at 70 °C with magnetic stirring. After the allotted reaction time, a portion of the reaction mixture was withdrawn by filtration and then analyzed by a gas chromatograph (Shimadzu GC-14B) with a flame ionization detector equipped with a capillary column (ULBON HR-20M; 0.53 mm × 30 m; Shinwa Chemical Ind., Ltd.). Conversion of substrate and yields of products were quantified by using bis(2-methoxyethyl)ether as an internal standard. To study the catalyst