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Highly Stable Ru/LaCO₃OH Catalyst Consisting of Support-coated Ru Nanoparticles in Aqueous-Phase Hydrogenolysis Reactions

Bolong Li, Lulu Li, Chen Zhao*^a

Hydrothermal reduction under aqueous conditions is widely used to convert biomass into more valuable products. However, the harsh conditions inherent in the process can irreversibly alter the intrinsic structure of the support, as well as dissolve the metal ions into the aqueous solution. In this contribution, for the fisrt time we have synthesized a new highly hydrothermally stable Ru/LaCO₃OH catalyst mostly consisting of Ru nanoparticles partially encapsulated by the LaCO₃OH support with strong metal-support interaction (SMSI), which confers high stability and activity to the catalyst under hydrothermal reduction conditions in the hydrogenolysis of biomass model molecules guaiacol and glycerol. During impregnation, the RuCl₃·3H₂O precursor initially reacts with LaCO₃OH to form a LaRu(CO₃)₂Cl₂ complex and LaOCl. XPS demonstrated that Ru was present in an oxidized state, TEM and XRD showed the absence of Ru⁰, and the XRD pattern illuminated the presence of the characteristic lattice fringe of LaOCI. While the LaRu(CO₃)₂Cl₂ complex was resistant to H₂ reduction at 350 °C, the complex underwent facile reduction to Ru⁰ under hydrothermal conditions at 240 °C. In the subsequent process, LaRu(CO₃)₂Cl₂ and LaOCI underwent hydrolysis, forming crystalline LaCO₃OH (confirmed by Ag⁺ titration and XRD patterns), Ru(OH)₃, and HCl. The Ru(OH)₃ was reduced in situ to Ru⁰ nanoparticles, as revealed by XPS and TEM analysis. The simultaneous hydrothermal reduction of Ruⁿ⁺ species and formation of crystalline LaCO₃OH results in the formation of Ru nanoparticles encapsulated by a protective LaCO₃OH layer, as evidenced by HRTEM and DRIFTS CO adsorption measurements. The preparation of catalysts with this unique structure comprising protected metal nanoparticles by the support itself which confer additional stability, is a novel strategy to prepare hydrothermal-stable catalysts.

Introduction

Bio-oils derived from the fast pyrolysis or liquefaction of sustainable biomasses such as cellulose, lignin, chitin, and lipid have attracted great attention as partial replacements of traditional nonrenewable fossil fuels.¹⁻⁹ However, these bio-oils are highly oxygenated due to the high oxygen contents of the precursor macromolecular biomass, and hence cannot be used directly as fuel sources without prior reduction with metal catalysts.^{10, 11} Due to the polar and hydrophilic nature of bio-liquids which contain multiple oxygen-containing functional groups, and meanwhile water is ubiquitous in biomass utilization, therefore, water is an attractive solvent for the conversion of bio-liquids into useful biofuels. In addition, the acidic or basic properties of water can be adjusted by controlling the pH. Indeed, there are many reports involving metal catalyzed reactions conducted in the aqueous phase for the conversion of substrates obtained from biomass into more useful products, such as hydrogenolysis of C-C and C-O bonds, hydrogenation, aldol condensation, isomerization, selective oxidation, and aqueous phase reforming reactions.¹²⁻¹⁶

It should be noted that the ionization constant of water (K_w) is highly dependent on temperature¹⁷, and hence a reaction catalyzed with a supported metal catalyst at elevated temperatures leads to enhanced H^+ and OH^- concentrations which can degrade the catalyst support structure. Thus, the stability of catalysts at elevated temperatures is an important factor that should be taken into consideration for the conversion of biomass. For example, Ravenelle et al. reported that the y-Al₂O₃ support gradually hydrated to böhmite when $Pt/\gamma-Al_2O_3$ was treated in aqueous conditions at 225 °C, resulting in a dramatic decrease in the surface area, and an increase in the size of the Pt nanoparticles from 4.3 nm to 7.8 $\mbox{nm.}^{\rm 18-19}$ Similarly, the surface area of SiO_2 was shown to decrease after treatment under aqueous conditions at 200 °C for 12 h (from 280 cm³ \cdot g⁻¹ to 70 cm³ \cdot g⁻¹).²⁰ With respect to mesoporous SBA-15 with highly ordered structures, the specific surface area decreased from 740 cm³ · g⁻¹ to 30 cm³ · g⁻¹ after treatment under similar conditions due to the high temperature induced alteration of the mesoporous structure of the catalyst support in aqueous phase.²⁰ These destructive effect of the catalyst structure caused by hydrothermal condition greatly decrease the catalytic activities. Hence, there is a strong need to synthesize catalysts with high

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

E-mail: czhao@chem.ecnu.edu.cn (C. Zhao)

⁺ Footnotes relating to the title and/or authors should appear here.

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hydrothermal stabilities, which would in particular increase the efficiency of biofuels or biochemicals production under aqueous conditions.

Great efforts have been made recently in order to enhance the hydrothermal stability of supported metal catalysts. To protect the hydrothermally-unstable catalysts, a strategy involving coating a carbon layer onto the metal surface of the support by introducing glucose as a carbonization agent was developed by Datye's group.^{20,} ²¹ In addition, the same group reported a chemical vapor deposition (CVD) method that formed graphitic carbon coated Pt/y-Al₂O₃, which showed excellent stability for reforming and hydrogenation reactions in the liquid phase. In addition, the atomic layer deposition (ALD) method has been used to prevent leaching/reoxidation of non-noble metal catalysts, thereby enhancing the stability of catalysts for aqueous phase reactions^{22, 23}. These methods enhance the hydrothermal stability of the supported metal catalysts by introducing an inert outer layer coat on the support surface.

The rare earth element lanthanum oxides, such as La₂O₃, LaO₂CO₃ and LaCO₃OH have been frequently used as supports in metal catalyzed ammonia synthesis, dry reforming, and oxidation reactions^{24,25}. Importantly, the rather harsh aqueous conditions used during its preparation demonstrate that LaCO₃OH exhibits high hydrothermal stability. Hence, LaCO₃OH could be an appropriate hydrothermally stable support for the metal catalyzed hydrogenolysis of C-O bonds of biomass derived material under aqueous conditions.

In our former work, Ru/C was found to be more selective than Pd/C and Pt/C for hydrogenolysis of C-O bond of lignin model compounds in the aqueous phase.^{13,14} Herein, we report a new Ru/LaCO₃OH hydrothermally stable catalyst formed as a result of successive procedures consisting of incipient impregnation, aircalcination, and hydrothermal reduction, which forms protected Ru nanoparticles encapsulated by LaCO₃OH with strong metal-support interaction (SMSI), and this catalyst is highly stable and leads to high hydrogenolysis rates for the conversion of the model biomolecules guaiacol and glycerol to the corresponding reduced products. In order to understand the relationship between catalytic activities and structural properties, extensive characterization of the catalyst and studies on the hydrogenolysis reaction were carried out; in addition, the two processes involved into impregnation of the Cl⁻ containing Ru precursor to the support and hydrothermal reduction of as-formed Ru complex were investigated in-depth.

Results and discussion

Three separate catalysts were prepared to study and compare their morphology and catalytic properties, and were initially prepared by loading a Ru metal precursor with metal contents of 5 wt%, as determined by inductively coupled plasma spectroscopy (ICP-AES), via the impregnation method to different supports (SiO₂, ZrO₂ and LaCO₃OH) with respective Brunner–Emmet–Teller (BET) surface areas of 231.5, 114.0, and 8.2 m²·g⁻¹. After impregnation,

the high temperatures involved during air calcination and hydrogen reduction processes led to a decrease in the BET surface areas of the catalysts to 160.0, 69.4, and 3.5 m²·g⁻¹, respectively (as shown in Fig. S1). The XRD diffractograms of the reduced samples are shown in Fig. 1. While the characteristic Ru⁰ peaks (JCPDS 06-0663) appeared on the Ru/SiO₂ catalyst, these peaks were absent in the Ru/ZrO₂ and Ru/LaCO₃OH catalysts, probably due to the presence of smaller Ru nanoparticles on the surface of the ZrO₂ and LaCO₃OH supports. Notably, in the Ru/LaCO₃OH catalyst apart from the intense peaks assigned to LaCO₃OH (JCPDS 26-0815), two broad peaks appeared at 25.2 ° and 33.9 ° which were assigned to characteristic LaOCI species (JCPDS 08-0477). The formation of lanthanide oxychloride (LnOCl, Ln=La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, and Er) in lanthanide-supported catalysts has been previously reported in the literature when chloride salts have been used as the metal precursors. For example, Basinska et al²⁶ detected the presence of tetragonal LaOCI phase after conducting the water-gas shift reaction at 350 °C in a Ru/La_2O_3 catalyst prepared with a chlorine containing precursor and the corresponding rare earth oxide. Similarly, Normand et al²⁷ found that using a palladium chloride salt as the metal precursor and rare earth oxides (La₂O₃, Pr₂O₃, and Tb₂O₃) during the impregnation step led to the formation of a stable oxychloride phase (LaOCI, PrOCI, and TbOCI). In our case, the LaOCI phase was formed from the RuCl₃·3H₂O precursor and the LaCO₃OH support after sequential impregnation and calcination procedures. On the Ru/LaCO₃OH sample, the intensity of the peaks corresponding to LaCO₃OH decreased in intensity, while new broad peaks corresponding to the LaOCI crystalline phase appeared. This suggests that LaOCI forms on the external surface of the support as the RuCl₃·3H₂O precursor reacts with the LaCO₃OH support.



Figure 1. XRD patterns of Ru/SiO_2 , Ru/ZrO_2 , and $Ru/LaCO_3OH$ catalysts.

Transmission electron microscopy (TEM) was used to characterize the particle information of the catalysts (Ru/SiO₂, Ru/ZrO₂, and Ru/LaCO₃OH) after H₂-reduction of the calcined samples at 350 °C (Fig. 2). In Ru/SiO₂, the catalyst has Ru particles with a mean size of 7.0 nm (Fig. 2a). The TEM image of the Ru/ZrO₂ catalyst showed little contrast between Ru and ZrO₂, and only a few Ru particles (d = ca. 3.2 nm) can be seen at the edge of the ZrO₂ (Fig.

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Figure 2. TEM images of (a) Ru/SiO₂, (b) Ru/ZrO₂, (c) Ru/LaCO₃OH, and (d) HRTEM image of Ru/LaCO₃OH samples with a fringe lattice of LaOCl after hydrogen reduction at 350 °C.

2b). The LaCO₃OH support in the Ru/LaCO₃OH catalyst consisted of large crystals with irregular shapes (Fig. 2c). In addition, the HRTEM image shows that while LaOCI (001) with visible lattice fringes (0.68 nm) was present (Fig. 4d), no Ru⁰ particles were found in this catalyst, which is consistent with the XRD result (Fig. 1). It is suggested that Cl⁻ ions from RuCl₃ may help to disperse Ru on the LaCO₃OH support, or that RuCl₃ in the metal precursor may react with the LaCO₃OH support to form a new Ru complex species that is highly dispersed on the external surface of the support. The energy dispersive spectroscopy (EDS) mapping on the Ru/LaCO₃OH catalyst demonstrated that Ru, Cl, La were evenly dispersed throughout the support (Fig. 3a-3c). The high angle annular dark field-scanning TEM (HAADF-STEM) showed that no Ru nanoparticles were present on the detected regions of the catalyst (Fig. 3d).



Figure 3. TEM-EDS mapping for the elements in Ru/LaCO₃OH (a) La, (b) Cl, (c) Ru, and (d) HAADF-STEM image.

X-ray photoelectron spectroscopy (XPS) was carried out to characterize the Ru 3d oxidation state of the three Ru catalysts after hydrogen reduction at 350 °C (Figure 4a). The Ru $3d_{3/2}$ peak

and the C 1s peak at 284.8 eV partially overlap, and the binding energies were calculated taking as reference the C 1s (284.8 eV) peak of carbon contamination.²⁸ In the XPS spectra of Ru/SiO₂ and Ru/ZrO₂ catalysts, clearly visible asymmetric peaks corresponding to Ru $3d_{5/2}$ were present at 280.2 eV and 280.1 eV respectively, while the Ru $3d_{3/2}$ peaks were observed at 284.3 eV and 284.2 eV respectively. The presence of the typical peaks corresponding to Ru⁰ indicates that the SiO₂ and ZrO₂ catalysts undergo facile reduction at 350 °C.²⁹

With respect to the Ru/LaCO₃OH catalyst, after deconvolution a C=O signal from the CO_3^{2-} group was able to be observed at 289.3 eV.²⁸ In the calcined Ru/LaCO₃OH catalyst, a Ru 3d_{5/2} signal is observed at 282.7 eV (Fig. 4b), which can be attributed to Ru (III) species; this value is very close to that measured by Mazzieri et al. for the Ru/Al₂O₃ catalyst (282.9 eV).³⁰ In the hydrogen reduced catalyst, a Ru 3d_{5/2} signal appeared at 281.6 eV corresponding to an electron deficient ruthenium species (Ruⁿ⁺), which was assigned to ruthenium (II) with chloride counterions (Fig. 4b).^{29,30} This result and the XRD data together demonstrate that the Ru/LaCO₃OH catalyst is incompletely reduced even after hydrogen reduction, perhaps resulting from the influence of residual chloride in the RuCl₃·3H₂O precursor. Indeed, the XPS experiment determined that chloride was present as evidenced by the XPS signals with a binding energy of 199.58 eV and 197.98 eV, assigned to $2p_{1/2}$ and $2p_{3/2}$ respectively of Cl in LaOCl species (Fig. 4c and Fig. S2).³¹ The intermediate Ru (II) oxidation state is likely to be highly stable in the presence of a LaCO₃OH supports and residual Cl⁻ ions. Moreover, it has previously been reported that chloride containing precursors may induce incomplete hydrogen reduction of Ru.³² Mazzieri et al.³⁰ reported that the hydrogen reduction of a Ru/Al₂O₃ catalyst using a RuCl₃ precursor led to partial reduction, with signals at 281.5 eV assigned to oxidized Ru, and a signal at 280.0 eV assigned to Ru⁰ also present. To reduce the sample in hydrogen at a higher temperature of 500 °C for 4 h, the in-completely reduced Ru²⁺ still existed with the Cl⁻ residue, as confirmed by the signal at 281.5 eV in XPS spectrum (Fig. S3). This is in accordance with the finding of Faroldi et al.³³ that Ru²⁺ was the dominant species with the typical Ru 3d_{5/2} signal at 281.8 eV from XPS spectrum, when reducing of Ru/La_2O_3 with H_2 at 550 °C using $RuCl_3 \cdot 3H_2O$ as precursor.



Figure 4. (a) XPS spectra of Ru/SiO₂, Ru/ZrO₂ and Ru/LaCO₃OH after hydrogen reduction at 350 °C with H2; (b) XPS spectra of Ru/LaCO₃OH after air-calcination and hydrogen-reduction at 350 °C; (c) XPS spectra of Cl in Ru/LaCO₃OH after air-calcination and hydrogen-reduction at 350 °C.

The reducibility of the three air-calcined supported Ru catalysts was investigated by hydrogen temperature-programmed reduction (H₂-TPR), as shown in Fig. 5. The H₂-TPR profile of the Ru/SiO₂ catalyst exhibited two reduction peaks at 149 °C and 190 °C. The two temperatures were attributed to the reduction of different

Page 4 of 11

particle sized RuO_x to Ru^0 metal, suggested by Yan et al³⁴. In comparison, Ru/ZrO2 showed one reduction peak at 134 °C, assigned to the reduction of RuO2 to Ru metal. The slightly lower reduction temperature is attributed to the smaller Ru particle sizes and the higher dispersion of Ru on ZrO₂, which is supported by the XRD pattern and the TEM image results as well. Surprisingly, Ru/LaCO₃OH exhibited a broad reduction peak from 260 to 420 °C, with a smaller peak at 341 °C, and the main peak at 382 °C. Taking into consideration the XPS results which confirm the presence of Ru in the +2 and +3 oxidation states, and the fact that less energy is required to reduce the higher oxidation state, the lower reduction peak at 341 °C can be ascribed to the reduction of (Ru (III)) to an intermediate oxidation state (Ru (II)), while the peak at 382 °C may be ascribed to the reduction of Ru (II) species to Ru metal. The reduction temperatures of the Ru/LaCO₃OH catalyst were far higher than those of the Ru/ZrO₂ and Ru/SiO₂ samples, indicating that Ru formed very stable complex species rather than discrete RuOx particles after air calcination.



Figure 5. H_2 -TPR profiles of air-calcined Ru/SiO₂, Ru/ZrO₂, and Ru/LaCO₃OH samples.

Considering the observed experimental data, we suggest that during impregnation Cl^- ions from the $RuCl_3 \cdot 3H_2O$ precursor participate in a surface reaction with the LaCO₃OH support to form crystalline LaOCI (as detected by XRD and TEM experiments), and the Ru^{3+} ions react strongly with the support to form a complex-like species. According to the TEM, XPS, and H₂-TPR results, ruthenium was found to be in a complex chemical environment (Scheme 1), and based on the stoichiometry of the surface reaction, the ruthenium complex species is inferred to be LaRu(CO₃)₂Cl₂ (Equation I):

 $2LaCO_3OH + RuCl_3 \rightarrow LaOCl + LaRu(CO_3)_2Cl_2 + H_2O$ (Equation I)

The high reduction temperature of ruthenium as determined by the TPR-H₂ profile confirms the highly stable nature of the LaRu(CO₃)₂Cl₂ complex. However, when the chloride counterions were removed from the LaRu(CO₃)₂Cl₂ complex by washing with ammonia, there was observed a marked decrease in the reduction



 $2\text{LaCO}_{3}\text{OH} + \text{RuCl}_{3} \rightarrow \text{LaOCI} + \text{LaRu}(\text{CO}_{3})_{2}\text{Cl}_{2} + \text{H}_{2}\text{O}$

Scheme 1. The surface reaction between $RuCl_3 \cdot _3H_2O$ precursor and LaCO₃OH support.

temperature to 166 °C (as shown in Figure 5), further confirming the hypothesis that chloride participates in the surface reaction during impregnation to form a highly stable Ru complex species.

Hydrothermal reduction of Ru complex on LaCO₃OH to Ru^0 in presence of H_2

Thus far, the TPR-H₂ experiment has determined the difficulty of reducing the Ru/LaCO₃OH catalyst after calcination, while other experimental data (TEM, XPS, and XRD) suggest that RuCl₃ reacts with LaCO₃OH to form a new La species (LaOCl) and a complex Ru species (LaRu(CO₃)₂Cl₂) on the external surface of LaCO₃OH (Scheme 1). Next, we attempted to reduce the calcined Ru/LaCO₃OH catalyst under hydrothermal conditions (240 °C, and H₂ at 2 bar pressure for 3 h. During hydrothermal treatment, the pH value gradually decreased from 6.89 to 4.45 (180 min), suggesting that hydrolysis may release HCl (Fig. 6a). The addition of Ag^{+} ions led to the precipitation of white AgCl (inset of Fig. 6a), showing that chloride ions are released into the aqueous phase during hydrothermal treatment. This suggests that the harsh conditions during hydrothermal treatment induce the hydrolysis of chloride containing species in the solid phase, releasing chloride ions into the aqueous phase as HCI (Scheme 2).

In addition, after hydrothermal treatment XRD analysis determined that the Ru/LaCO₃OH catalyst contained a highly crystalline LaCO₃OH phase (JCPDS: 26-0815, Fig. 6b) while the LaOCI lattice disappeared. This indicated that the LaOCI phase was no longer present after hydrolytic removal of surface chloride species, and the La³⁺ was reconstituted and recrystallized into LaCO₃OH under hydrothermal conditions. Notably, no Ru species were observed in the XRD pattern, perhaps due to overlap with the strong crystal peak of LaCO₃OH. Subsequently, XPS was used to characterize the electronic character of Ru after hydrothermal treatment of Ru/LaCO₃OH in the presence of hydrogen (Fig. 6c). Under hydrothermal conditions, the Ru $3d_{5/2}$ signal shifted from 281.6 eV (H $_{\rm 2}$ reduction at 350 °C) to the well-known signal indicative of Ru⁰ at 280.1 eV Ru⁰. Hence, under hydrothermal conditions after elimination of surface chloride species on the Ru/LaCO₃OH catalyst, there is facile reduction of oxidized ruthenium in the calcined catalyst to Ru^{0} .



Figure 6. (a) The variation of pH values during hydrothermal treatment at 240 °C in the presence of H_2 , (b) XRD patterns of LaCO₃OH, Ru/LaCO₃OH after H_2 -reduction, and Ru/LaCO₃OH after hydrothermal reduction in the presence of hydrogen, (c) XPS spectra of Ru/LaCO₃OH after H_2 reduction, and Ru/LaCO₃OH after hydrothermal reduction in the presence of H_2 .

Therefore, while in the LaRu(CO₃)₂Cl₂ complex the reduction of ruthenium in the presence of H₂ to Ru⁰ in flowing H₂ at 350 °C was minimal, under hydrothermal conditions the reduction occurs under much milder conditions (240 °C). During the hydrothermal process, Cl⁻ ions in both LaRu(CO₃)₂Cl₂ and LaOCl are removed from

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 $\label{eq:label} \begin{array}{l} \mbox{LaOCI} + \mbox{LaRu}(\mbox{CO}_3)_2\mbox{CI}_2 + 4\mbox{H}_2\mbox{O} \rightarrow 2\mbox{LaCO}_3\mbox{OH} + 3\mbox{HCI} + \mbox{Ru}(\mbox{OH})_3 \\ \mbox{2Ru}(\mbox{OH})_3 + 3\mbox{H}_2 \rightarrow 2\mbox{Ru} + 6\mbox{H}_2\mbox{O} \end{array}$

Scheme 2. The evolution of $Ru/LaCO_3OH$ under hydrothermal treatment in the presence of H_2 .

the catalyst surface into the aqueous solution, and LaCO₃OH is formed by recrystallization (confirmed by Ag⁺ titration and XRD patterns). Under hydrothermal conditions, the Ruⁿ⁺ species in the LaRu(CO₃)₂Cl₂ complex is hydrolyzed to Ru(OH)₃, which is then subsequently reduced to Ru⁰ nanoparticles (confirmed by XPS). The overall process for the hydrolysis of LaRu(CO₃)₂Cl₂ and LaOCl, and the *in situ* reduction of Ru(OH)₃ occurring on the surface of the catalyst is summarized by equations II and III:

LaOCl + LaRu(CO₃)₂Cl₂ + 4H₂O \rightarrow 2 LaCO₃OH + 3HCl + Ru(OH)₃ (Equation II)

 $2Ru(OH)_3 + 3H_2 \rightarrow Ru + 6H_2O$ (Equation III)

Since the reduction of Ru^{n+} species to Ru^{0} and the recrystallization of LaCO₃OH occurred simultaneously, it is possible that the LaCO₃OH could be interacting with the hydrothermally reduced Ru nanoparticles. To confirm the specific nature of the interaction and the morphology of the hydrothermally reduced catalyst, HRTEM and diffuse reflectance infrared Fourier Transform spectroscopy (DRIFTS) of CO adsorption experiments were carried out. As direct evidence, the TEM and HRTEM images of the Ru/LaCO₃OH catalyst after hydrothermal hydrogen reduction are shown in Figs. 7a and 7b. From these images it is clear that the lattice fringe for LaOCI and the LaRu(CO₃)₂Cl₂ species both disappeared after hydrothermal H₂ reduction, while newly formed Ru appeared as dark spots on the LaCO₃OH crystal surface. Ru particles with crystal facets were observed with a mean diameter of 2.8 ± 0.3 nm (Fig. 7a). After hydrothermal treatment, the newly formed LaCO₃OH layer partially coated Ru particles with a fringe lattice of Ru (100) (d spacing: 0.234 nm), as clearly shown in Fig. 7b and 7c. Such structural protection may significantly impede the particle growth and enhance the stability of the Ru/LaCO₃OH catalyst under the harsh hydrothermal conditions.

It is expected that the presence of a LaCO₃OH coat surrounding Ru particles on the hydrothermally hydrogen-reduced Ru/LaCO₃OH catalyst would change the surface adsorption characteristics, which can be confirmed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements of CO adsorption. The IR spectra for CO desorption on the Ru catalysts with three different





Figure 7. (a) TEM image and particle distribution and (b) the HRTEM image of hydrothermally H_2 -reduced Ru/LaCO₃OH, (c) the Ru (100) fringe lattice of hydrothermally H_2 -reduced Ru/LaCO₃OH.

supports under a purge of N₂ at room temperature is shown in Figures 8a-8c. The strong bands at 2171 cm⁻¹ and 2117 cm⁻¹ on the three Ru catalysts disappeared after a prolonged purge, and were attributed to gaseous CO rather than the adsorption of multicarbonyl species on Ru^{n+.33} In the initial stage of the purge, four bands are detected on the Ru/SiO₂ catalyst at 2171 cm⁻¹, 2125 cm^{-1} , 2117 cm^{-1} and 2065 cm^{-1} . After purging for 1500 seconds, the bands at 2171 cm⁻¹ and 2117 cm⁻¹ disappeared. The band at 2125 cm^{-1} is assigned to muticarbonyl species bound to $Ru^{n+}(Ru^{n+}(CO)_n)$, which lies in the high-frequency 1 (HF_1) region (2020-2156 cm⁻¹), while the band at 2065 cm⁻¹ corresponds to CO bound linearly to ${\rm Ru}^{n+}$, and lies in the ${\rm HF}_2$ region (2060-2110 ${\rm cm}^{-1}).^{36}$ No band corresponding to bridge-bonded CO was observed in Ru/SiO₂. The CO desorption pattern on the Ru/ZrO₂ catalyst was guite similar to that of Ru/SiO₂, except that the bands in the HF_1 (2127 cm⁻¹) and HF_2 (2071 cm⁻¹) regions are slightly shifted to higher wavenumbers. The blue shift of the bands may be due to the electronic deficient



Figure 8. The DRIFT spectra of CO adsorption on (a) H_2 -reduced Ru/SiO₂, (b) H_2 -reduced Ru/ZrO₂, and (c) hydrothermally-reduced Ru/LaCO₃OH in the presence of hydrogen.

character of Ru on Ru/ZrO₂, which may be induced by the Lewis acidic Zr atoms on ZrO₂. However, in the Ru/LaCO₃OH catalyst the bands in the region of CO adsorption on Ru (2040-2069 cm⁻¹) and the gaseous CO peak rapidly decreased to near baseline levels. It might be caused by the partial exposure of the Ru particles and the weak adsorbed CO on Ru particles, which is in line with the HRTEM image (Fig. 7b) showing that Ru nanoparticles are partially coated by a LaCO₃OH support layer. This result was similar to that observed for Au/HAP-500, where the IR spectra of CO adsorption confirmed that Au nanoparticles were wrapped by hydroxyapatite (HAP).³⁵ Therefore, the characterization of the catalyst with both HRTEM and DRIFT of adsorbed CO both suggest the presence of a LaCO₃OH

support layer partially coat around Ru nanoparticles showing a strong metal-support interaction (SMSI).

Combining the results obtained thus far (XRD patterns, changes in pH, XPS, HRTEM, and DRIFT of adsorbed CO), allows a determination of the various species formed during the hydrothermal reduction of the Ru/LaCO₃OH calcined catalyst. Under hydrothermal conditions the surface species LaOCI and LaRu(CO₃)₂Cl₂ are hydrolyzed (as confirmed by XRD), and the chloride ions that are released in the process lead to a reduction of the pH via the formation of HCl, while the lanthanum side-product LaOCI is recrystallized into LaCO₃OH (as determined by XRD). As shown in Scheme 2, hydrolysis of LaRu(CO₃)₂Cl₂ also leads to the formation of the Ru intermediate Ru(OH)₃, and was sequentially reduced to Ru⁰ nanoparticles in the presence of H₂ (as demonstrated by XPS). We propose that during the hydrothermal reduction, the Ru nanoparticles are partially coated with a support layer of LaCO₃OH, since the formation of reduced Ru nanoparticles occurs simultaneously with the release of LaCO₃OH, formed via the hydrolysis of the initially present LaRu(CO₃)₂Cl₂. The HRTEM image and DRIFT of adsorbed CO further validated the idea of the presence of a LaCO₃OH support partially coating around Ru nanoparticles. This support-wrapped metal catalyst is expected to exhibit high stability and activity in aqueous phase hydrogenolysis reactions at high temperatures.

High stability of hydrothermally reduced Ru/LaCO₃OH catalyst for aqueous phase hydrogenolysis reactions

To test the hydrogenolysis activity and stability of the novel hydrothermally prepared reduced Ru/LaCO₃OH catalyst, the reduction of guaiacol and glycerol (substrates widely available from bio-feedstocks) under aqueous conditions were chosen as model reactions, and their activities were compared with the conventionally prepared Ru/SiO₂ and Ru/ZrO₂ catalysts. The product distributions resulting from guaiacol hydrogenolysis in aqueous conditions at 240 °C and 0.2 MPa H₂ pressure with the three catalysts are summarized in Fig. 9a. The conversion of guaiacol reached 38.6%, 95.4%, and 95.6%, while the yield of benzene was 2.4%, 30.6%, and 75.8%, for the Ru/SiO₂, Ru/ZrO₂, and Ru/LaCO₃OH catalysts, respectively. As shown in Fig. 9b, the kinetic of guaiacol hydrogenolysis on hydrothermal-reduced Ru/LaCO₃OH was displayed. Accompanied with the rapid decrease of the guaiacol reactant, the maximum phenol yield reached 60.0% at 30min with an initial hydrogenolysis rate of 3.24 g·g⁻¹·h⁻¹, and then gradually decreased since then. The yield of benzene gradually increased to 75.8% at the reaction time of 150 min. This result have suggested that the hydrogenolysis of the methoxy group in guaiacol occurs as the first step in the reduction process, and is followed by the hydrogenolysis of phenol to benzene as the second step, which was determined to be the rate-limiting step according to kinetics modeling (Fig. S4). This result indicates that the newly developed Ru/LaCO₃OH catalyst shows high activity and selectivity in the hydrogenolysis of guaiacol to benzene under hydrothermal conditions.



Figure 9. (a) Hydrogenolysis of guaiacol over Ru/SiO₂, Ru/ZrO₂, and hydrothermally-reduced Ru/LaCO₃OH, Conditions: 1.0 g guaiacol, 0.75 g catalyst, H_2O (150 mL), 0.8 MPa N₂ and 0.2 MPa H₂, 150 min. (b) kinetic for hydrogenolysis of guaiacol on hydrothermally-reduced Ru/LaCO₃OH.

Glycerol hydrogenolysis in the aqueous phase was conducted over these three Ru catalysts at 200 °C and 3 MPa H₂ pressure. The glycerol conversion attained 10%, 21%, and 62%, while the selectivity to 1,2-propanediol reached 2%, 5%, and 46% with the Ru/SiO₂, Ru/ZrO₂, and Ru/LaCO₃OH catalysts, respectively (Fig. 10a). A kinetic curve for glycerol conversion (Fig. 10b) over hydrothermalreduced Ru/LaCO₃OH revealed that the primary product was 1,2propanediol with an initial hydrogenolysis rate of 2.0 g·g⁻¹·h⁻¹. With reaction time prolongs, the C-C cleavage products of ethylene glycol and methanol slightly increased to 5%, while the yield of 1,2propanediol increased to nearly 40%. These results further confirm the superiority of the Ru/LaCO₃OH catalyst for achieving high activity and selectivity for aqueous phase hydrogenolysis reactions.

In the recycling tests for guaiacol hydrogenolysis in water, Ru/LaCO₃OH showed much higher durable capability than Ru/SiO₂ and Ru/ZrO₂, as displayed in Fig. S5 and Fig. S6. Ru/LaCO₃OH still maintained high conversion (>95%) and benzene selectivity (> 70%) even after eight runs, but Ru/ZrO₂ and Ru/SiO₂ only attained respective 70% and 10% conversion after four runs with 22% and 1% benzene selectivity after four runs. A dramatic activity loss was observed on unprotect Ru nanoparticles on Ru/ZrO₂ and Ru/SiO₂ DOI: 10.1039/C7GC02414B Green Chemistry

Page 8 of 11

catalysts when recycling at high temperature water phase.

In order to test the influence of the protector layer towards the hydrogenolysis reaction, Ru/LaCO₃OH without a support layer (5 wt% Ru loading, identical to the metal loading of Ru/LaCO₃OH with Cl⁻) was synthesized subsequently. To obtain the Cl⁻ free catalyst, the RuCl₃·3H₂O metal salt was impregnated with the basic agent of NH₃·H₂O solution. Thus, Ru(OH)₃ precursor was formed after impregnation, and NH₄Cl stayed in the aqueous phase as confirmed by Ag⁺ titration. In contrast to the Ru/LaCO₃OH catalyst with Cl⁻ ions, in the Cl⁻ free catalyst Ru nanoparticles were not protected by a support layer, as demonstrated by the HRTEM image in Fig. S7. Accordingly, the as-formed unprotected Ru nanoparticles were comparatively easily reduced with H₂ at a relatively low temperature (166 °C), as shown from the TPR-H₂ profile in Fig. 5.



Figure 10. (a)hydrogenolysis of glycerol over Ru/SiO_2 , Ru/ZrO_2 , and hydrothermally-reduced $Ru/LaCO_3OH$, conditions: 0.4 g glycerol, 0.1 g catalyst, H_2O (80 mL), 3 MPa H_2 , 3 h; (b) kinetic for hydrogenolysis of glycerol on hydrothermally-reduced $Ru/LaCO_3OH$.

The hydrogenolysis of guaiacol was conducted over four recycling runs to determine the stability of two Ru/LaCO₃OH samples. In Ru/LaCO₃OH with Cl⁻ ions, a constant conversion of 95% and benzene yields of 76% were obtained for four recycling runs (Fig. 11). The leaching of Ru ions into the solution in the recycling tests was not detected by ICP measurement. Under identical conditions, the hydrogenolysis of guaiacol with the Cl⁻ free catalyst took place with 96% conversion and a benzene yield of 35% in the first run. The successive recycling tests led to gradual decreases in activity

Green Chemistry Accepted Manuscript

Green Chemistry

and selectivity, with a conversion of 94% and benzene yield of 12.19 in the fourth run. The slightly higher conversion in the first run of the Cl⁻ free catalyst may be due to the presence of greater amounts of unprotected Ru active sites. The marked difference in the capacity to undergo hydrodeoxygenation between these two catalysts demonstrates the importance of the protective coating around Ru with SMSI, and suggests that the Cl⁻ containing species may hold great potential as a robust catalyst for reactions conducted under hydrothermal conditions.



Figure 11. Four-run recycling tests on hydrogenolysis of guaiacol over hydrothermally-reduced Ru/LaCO₃OH with and without Cl⁻ ions. Conditions: 1.0 g guaiacol, 0.75 g catalyst, H₂O (150 mL), 0.8 MPa N₂ and 0.2 MPa H₂, 150 min.

Conclusions

We have synthesized a new highly hydrothermally-stable Ru/LaCO₃OH catalyst with a structure comprising support partially coated Ru nanoparticles, via sequential incipient impregnation, air-calcination, and hydrothermal reduction procedures. This catalyst exhibited superior performance in terms of stability and activity compared to Ru/SiO₂ and Ru/ZrO₂ catalysts as determined by the conversion and yields obtained in the hydrogenolysis of biomass model molecules guaiacol and glycerol under hydrothermal conditions. The structure of the hydrothermally reduced Ru/LaCO₃OH catalyst (the support coating around Ru particles) was maintained even after multiple reaction runs, and the leaching of Ru ions was negligible.

In contrast to the Ru/SiO₂ and Ru/ZrO₂ catalysts, under standard (non-aqueous) conditions, H₂-reduction of the Ru/LaCO₃OH sample at 350 °C did not lead to the formation of Ru⁰ species. The reduction of the Ru/LaCO₃OH catalyst is hindered by the presence of the stable RuLa(CO₃)₂Cl₂ complex and LaOCl, which are formed instead of RuO_x during the impregnation procedure when the RuCl₃·3H₂O precursor reacts with LaCO₃OH. However, upon hydrothermal H₂ reduction at 240 °C, LaOCl and RuLa(CO₃)₂Cl₂ were hydrolyzed into highly crystalline LaCO₃OH and Ru⁰ particles. The HRTEM image and DRIFT CO adsorption experiments suggested

and selectivity, with a conversion of 94% and benzene yield of 12.1% that the Ru nanoparticles were partially encapsulated by $LaCO_3OH$ in the fourth run. The slightly higher conversion in the first run of layers.

The strong interaction between the Ru nanoparticles and the partially coated LaCO₃OH support layers impeded the further growth of metal nanoparticles under harsh reduction conditions. Our developed new methodology, wherein the metal center is partially protected by support layers itself during an in-situ hydrothermal-hydrogen reduction process, is a novel strategy that offers the potentials of synthesizing hydrothermally-stable catalysts.

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Green Chemistry

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Green Chemistry, 2017, 00, 1-3 | 11

Green Chemistry Accepted Manuscript