Ru Single Atoms on One-Dimensional CF@g-C$_3$N$_4$ Hierarchy as Highly Stable Catalysts for Aqueous Levulinic Acid Hydrogenation

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Abstract: Herein, we report a stable catalyst with Ru single atoms anchored on a one-dimensional carbon fiber@graphitic carbon nitride hierarchy, by assembling wet wipes composed of fiber-derived carbon fiber (CF), melamine-derived graphitic carbon nitride (g-C$_3$N$_4$) and RuCl$_3$ before NaBH$_4$ reduction. The atomically dispersed Ru species (3.0 wt%) are tightly attached via N-coordination provided by exterior g-C$_3$N$_4$ nanosheets, and further stabilized by the interior mesoporous CF. The obtained CF@g-C$_3$N$_4$–Ru SAs catalyst can be cycled six times without notable leaching of Ru or loss of GVL yield in the acidic media. This catalyst is more stable than Ru nanoparticles supported on CF@g-C$_3$N$_4$, as well as Ru single atoms anchored on CF and g-C$_3$N$_4$, and proves to be one of the most efficient metal catalysts for aqueous LA hydrogenation to γ-valerolactone (GVL). The isolated Ru atoms by strong N-coordination, and their enhanced electron/mass transfer afforded by the one-dimensional hierarchy, can be responsible for the excellent durability of CF@g-C$_3$N$_4$–Ru SAs under harsh reaction conditions.

Keywords: Ru single atom; one-dimensional hierarchy; levulinic acid; γ-valerolactone; stability

1. Introduction

The gradual consumption of fossil resources and the growing attention directed toward global climate change have stimulated the efforts for the sustainable production of materials, chemicals and fuels [1]. The hydrogenation of cellulosic biomass-derived levulinic acid (LA) into γ-valerolactone (GVL) is a key reaction included in many biorefinery schemes for the production of renewable chemicals and fuels [2]. GVL is not only a key and safe intermediate for fine chemical and liquid fuel synthesis, but also a building block for polymers, a solvent and a flavoring agent [3]. However, achieving a high yield of GVL repeatedly is very difficult, since upgrading cellulosic LA is usually operated in aqueous media at a high temperature (>130 °C). Besides the impurities (such as sulfuric acid and formic acid) in LA feeds, abundant H$^+$ produced by the dissociation of LA and the ionization of subcritical water from the solvent/co-product makes the reaction media very acidic (pH ≈ 1), as the conversion of LA proceeds at a high temperature [4]. The reaction medium is normally oxygen functionalized, polar and even corrosive. In this case, the catalysts are easily deactivated owing to metal sintering, leaching, support collapse/destruction as well as the formation of carbonaceous deposits and process-derived impurities to poison active sites [5]. Such a tough reaction environment raises a significant challenge for the durability of the metal catalysts. Ru-based catalysts prove to be more persistent in acidic media as compared to non-precious metal sites. However, the durability of Ru catalysts under aqueous and acidic reaction conditions remains a concern to be addressed. It has been demonstrated that the supported Ru species are thermodynamically unstable and tend to sinter into larger particles in the presence of water, even at room
temperature [6]. Additionally, these Ru sites can be poisoned in the presence of acids and oxidants, also leading to the deactivation of the Ru catalysts as they are involved in the aqueous LA hydrogenation [7,8]. In this regard, it is highly desirable to construct persistent Ru sites that are active under repeated reactions, even exposed to water, acid and/or oxidant.

With the emergence of the concept of single-atom catalysis, it is anticipated that stable Ru catalysts will be developed by constructing atomically dispersed Ru sites on a certain supporting matrix via a strong metal–support interaction (SMSI). These Ru atoms can be isolated by the low Z elements surrounding, and the concerned aggregation, leaching, poisoning and oxidation would be alleviated toward aqueous LA hydrogenation [9]. Several Ru single-atom catalysts (SACs) have been fabricated by confinement of Ru single atoms into carbon nitride [10,11], N-doped graphene [12] and a metal–organic framework (such as ZIF, UiO-66, etc.)-derived carbons [13–15], showing excellent stability in catalytic reactions such as electrocatalytic \( \text{H}_2/\text{O}_2 \) evolution, \( \text{O}_2 \) reduction and quinoline/vanillin hydrogenation. The construction of single-atom sites to enhance catalytic stability has been recently demonstrated in biomass valorization. It was found that the Ni-N-C SAC delivered excellent stability towards the direct conversion of cellulose into ethylene glycol in water, and no metal aggregation or leaching was detected after seven consecutive runs [16]. Another SAC with Co atoms incorporated into the sulfur vacancies of MoS\(_2\) monolayer sheets displays enhanced stability compared to traditional CoMoS\(_2\) for the hydrodeoxygenation of 4-methylphenol into toluene. Deactivation cannot be found for this Co SAC, even when cycled seven times [17]. Nevertheless, highly stable metal SACs for LA hydrogenation under harsh reaction conditions are scarcely reported. To the best of our knowledge, only one stable SAC for aqueous LA hydrogenation was reported by Zhang and co-workers. The Ru single atoms (0.85 wt%) were dispersed on nanotetragonal ZrO\(_2\) and embedded in the amorphous carbon, which was achieved by the impregnation of RuCl\(_3\) into UiO-66 derived ZrO\(_2\)@C support [14]. This catalyst exhibits excellent stability with no apparent drop in catalytic performance observed in six consecutive runs in water and three consecutive runs in acidic media (pH \( \approx 1 \)).

Great progress has been made to develop stable Ru catalysts by constructing Ru single-atom sites. However, few investigations give importance to the supporting matrix and its synergism in single atoms to enhance the stability of catalysts under harsh reaction conditions. The low porosity of metal oxide supports and their vulnerability under acidic/hydrothermal conditions deactivate Ru single atoms. This calls for a persistent supporting matrix that not only stabilizes Ru single atoms, but also provides mesoporous arrays to facilitate mass transfer to extend catalyst life. Mesoporous carbons are chemically inert and stable, but the absence of coordination sites may lead to the leaching of loosely attached metal species during reactions. Graphitic C\(_3\)N\(_4\) can stabilize single atoms by N-coordination, but the sheet-like g-C\(_3\)N\(_4\) is less porous and tends to aggregate during repeated reactions. An ideal supporting matrix for a stable Ru SAC can not only regulate the geometric and electronic structure of single-metal sites based on SMSI, but also provide persistent porosity and inertness under harsh conditions to guarantee the durability of the entire catalyst. However, for aqueous LA hydrogenation, the rational design of an inert support with well-defined coordination sites and a mesoporous structure to construct stable Ru SACs has never been achieved.

Herein, we report a stable Ru catalyst with atomically dispersed Ru species (3.0 wt%) anchored on a one-dimensional CF@g-C\(_3\)N\(_4\) hierarchy. What deserves to be mentioned is the construction of the core–shell structured CF@g-C\(_3\)N\(_4\) supporting matrix. Such a one-dimensional hierarchy provides precise N-coordination sites to stabilize/regulate Ru single atoms, by the dispersion of exterior g-C\(_3\)N\(_4\) nanosheets. Additionally, the mesoporous structure of the CF@g-C\(_3\)N\(_4\) hierarchy accelerates the electron/mass transfer and survives in repeated reactions under harsh conditions. As expected, the obtained CF@g-C\(_3\)N\(_4\)–Ru SAs exhibits outstanding durability towards aqueous LA hydrogenation in acidic media.
2. Experimental

2.1. Chemicals

All of the chemicals were commercially obtained and were used without further purification. Ruthenium trichloride (RuCl$_3$$\cdot$ xH$_2$O, 38 wt%) was purchased from Aladdin Industrial Corporation, Shanghai. Melamine (AR, 99%) and sodium borohydride (NaBH$_4$, 99%) were purchased from Tianjin Guangfu Technology Development Co. Ltd. Nitric acid (HNO$_3$, 68 wt%), hydrochloric acid (HCl, 36 wt%), ethanol (EtOH, 95%) and acetone (AR, 99%) were purchased from Beijing Chemical Works. The wet wipes fiber was purchased from the market, produced by PHILIPS and containing a small quantity of titanium (0.27 wt%).

2.2. Sample Preparation

The wet wipes fiber (WWF, 2 cm $\times$ 2 cm) obtained for daily wipe were cleaned by acetone, hydrochloric acid (0.1 M), ethanol and deionized water under ultrasonic treatment in turn, and the obtained WWF was immersed into the HNO$_3$ aqueous solution (2.0 M) at 60 $^\circ$C for 1 h to ensure a clean surface. The dried WWF was then pyrolyzed at 500 $^\circ$C for 2 h in N$_2$ atmosphere, yielding the carbon fiber, CF (40% yield). The melamine was calcinated at 550 $^\circ$C in a furnace for 3 h, affording graphitic carbon nitride, g-C$_3$N$_4$ (65% yield, 99% purity). Subsequently, 0.1 g of g-C$_3$N$_4$ combined with 0.1 g of CF was dispersed in 1000 mL of water using sonication for 30 min. Then, 20 mg of RuCl$_3$$\cdot$xH$_2$O was introduced and the obtained mixture was stirred for 12 h, followed by addition of 0.5 g NaBH$_4$. The resulting mixture was further stirred for 6 h to produce CF@g-C$_3$N$_4$–Ru SAs catalyst. The synthesis of CF@g-C$_3$N$_4$–Ru NPs was performed according to the procedure mentioned above with slight modification. Typically, 0.1 g of g-C$_3$N$_4$ combined with 0.1 g of CF was dispersed in 1000 mL of water using sonication for 30 min, followed by introduction of 20 mg of RuCl$_3$, and the resulting mixture was stirred for 12 h. The Ru$^{3+}$-impregnated CF@g-C$_3$N$_4$ was obtained and then pyrolyzed at 500 $^\circ$C under N$_2$ atmosphere for 1 h, yielding CF@g-C$_3$N$_4$–Ru NPs. The synthesis of g-C$_3$N$_4$–Ru and CF–Ru was also performed as the procedure mentioned for CF@g-C$_3$N$_4$–Ru SAs synthesis, but without CF or g-C$_3$N$_4$ involved.

2.3. Characterization

Powder X-ray diffraction patterns of samples were obtained on a Rigaku D/Max 2500PC X-ray powder diffractometer using a Cu K$\alpha$ radiation ($\lambda$ = 0.15418 nm). TEM images were recorded on a Hitachi-7700 worked at 100 kV. High-resolution TEM images were obtained by a FEI Tecnai G2 F20 S-Twin HRTEM working at 200 kV. Atomic resolution HAADF-STEM images were obtained by using a Titan 80–300 scanning/transmission electron microscope operator at 300 kV, equipped with a probe spherical aberration corrector. Surface area analysis was performed on a JW-BK100 static volumetric gas adsorption instrument and the surface area was calculated by using the Brunauer–Emmett–Teller (BET) method. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific Escalab 250Xi X-ray photoelectron spectrometer. The Ru content was estimated by ICP-OES analysis conducted on a Thermo Icap 6300 emission spectrometer. Before the test, a certain amount of vacuum-dried sample was placed in a microwave digestion tank, and dissolved in 4 mL of aqua fortis solution mixed with 1 mL hydrogen peroxide. Microwave digestion was carried out for 30 min to completely dissolve the metal species. After cooling, each solution was filtered through a 0.45 $\mu$m poly-ethersulfone filter. X-ray absorption fine structure (XAFS) was carried out on the 20-BM-B beamline of Advanced Photo Source (APS) at Argonne National Laboratory. The XAFS data were obtained in the transmission mode at the Ru K-edge (22,117.0 eV). The XAFS data were processed using the Athena software for background removal, post-edge normalization and X-ray absorption near edge structure (XANES) analysis. The extended X-ray absorption fine structure (EXAFS) was analyzed using Artemis software, which implemented FEFF. The EXAFS data reduction was conducted by utilizing the standard procedures. The EXAFS function, $\chi$, was obtained.
by subtracting the post-edge background from the overall absorption and then normalized with respect to the edge jump step. Subsequently, k²-weighted χ(k) data in k space were Fourier transformed to r space in order to separate the EXAFS contributions from the different coordination shells.

2.4. Catalytic Test

The LA hydrogenation reactions were carried out in a magnetically stirred Parr 4560 autoclave. In a typical procedure, 30 mg of catalyst, 40 mL of H₂O and 0.12 g of LA were introduced into the autoclave. The sealed autoclave was charged and deflated with N2 three times before it was pressurized with H₂ to 4.5 MPa at room temperature and heated at 150 °C for 2 h. The separated liquid solution was quantitatively analyzed with gas chromatography (SP-6890) using 1, 4-dioxane as the internal standard.

3. Results and Discussion

The schematic description of CF@g-C₃N₄–Ru SAs synthesis is shown in Scheme 1. As illustrated, the wet wipes fiber (WWF) and melamine were utilized as precursors and pyrolyzed in N₂ atmosphere to produce carbon fiber (CF) and graphic nitride (g-C₃N₄), respectively. The ultrasonic treatment of g-C₃N₄ and CF in water not only exfoliates g-C₃N₄ in favor of capturing more Ru³⁺ in the subsequent impregnation, but also facilitates the formation of a core–shell structured CF@g-C₃N₄ hierarchy. Considering the aggregation tendency of Ru species at a high temperature, the reduction in Ru³⁺-impregnated CF@g-C₃N₄ was performed using NaBH₄ at room temperature to synthesize CF@g-C₃N₄–Ru SAs. Otherwise, the nanoparticle catalyst, denoted as CF@g-C₃N₄–Ru NPs, was formed by heating of the Ru³⁺-coordinated CF@g-C₃N₄ intermediate at 500 °C in an N₂ flow. Atomic Ru species anchored on a single CF and g-C₃N₄ support, denoted as CF–Ru and g-C₃N₄–Ru, respectively, were also prepared for comparison (please refer to the supporting information).

![Scheme 1. Schematic illustration of the synthetic process for CF@g-C₃N₄–Ru SAs.](image)

The WWF-derived CF is very smooth and has an average diameter of ca. 2 μm based on the transmission electron microscopy (TEM) observation (Figure 1a). g-C₃N₄ originated from melamine contains thin layers as shown in Figure 1b, which were then coated on the surface of CF and followed by RuCl₃ impregnation and NaBH₄ reduction. The resulting CF@g-C₃N₄–Ru SAs has a core–shell configuration with g-C₃N₄ nanosheets around the fibrous core, and no obvious Ru clusters or nanoparticles can be observed (Figure 1c), whereas the existence of homogeneously distributed Ru species can be revealed by the high-angle annular dark field scanning TEM (HAADF-STEM) image and elemental maps (Figure 1d,e). The HAADF-STEM image along with the line scanning profile across a CF@g-C₃N₄–Ru SAs fiber shows that both the N and Ru elements are located on the surface, while carbon is distributed inside (Figure 1f,g). These results further demonstrate the core–shell configuration and preliminarily indicate the well-dispersed Ru species on the exterior g-C₃N₄. In order to reveal the Ru structure, an observation was performed by aberration-corrected scanning TEM (AC-STEM). As shown in Figure 1h, bright dots with atomic
resolution can be detected and are homogeneously distributed. Due to the remarkable
difference in Z-contrast between Ru and N/C, these bright dots can be determined to
be atomically dispersed Ru species, indicating the formation of Ru single atoms. We
also observed some Ru atoms that are embedded into the (101) plane of TiO₂ (Figure 1i),
marked by the yellow circles. In this study, CF@g-C₃N₄–Ru NPs was also examined, and it
displays a core–shell configuration decorated with numerous Ru nanoparticles showing
an average diameter of 10.1 nm (Figure S1). This strongly suggests the critical role of NaBH₄
reduction in the synthesis of Ru SACs. The Ru mass loading for CF@g-C₃N₄–Ru SAs is
determined to be 3.0% by ICP-OES analysis (Table S1), which is twice more than that for
CF@g-C₃N₄–Ru NPs (1.3 wt%), and lower than that for CF–Ru (4.1 wt%) and g-C₃N₄–Ru
(4.5 wt%).

![TEM images](image)

**Figure 1.** TEM images of (a) CF, (b) g-C₃N₄ and (c) CF@g-C₃N₄–Ru SAs, (d,f) HAADF-STEM images
and (e,g) the corresponding elemental maps and line scanning profiles of CF@g-C₃N₄–Ru SAs, and
(h,i) aberration-corrected STEM image of CF@g-C₃N₄–Ru SAs.

The crystalline structure of different samples was investigated by X-ray diffraction
(XRD). As shown in Figure 2, the XRD pattern of CF@g-C₃N₄–Ru SAs shows two obvious
diffraction peaks at 13.4° and 27.5°, which can be indexed to the (100) and (002)
planes of g-C₃N₄ (JCPDS No.: 87-1562), respectively, and another weak diffraction at 43.3°
which can be ascribed to the (002) facet of the hexagonal carbon [18,19]. Characteristic
diffractions corresponding to crystalline Ru cannot be detected, in accordance with the
atomically dispersed Ru species observed by AC-STEM. Comparatively, the XRD pattern of
CF@g-C₃N₄–Ru NPs provides broad but clear (100), (002) and (101) diffractions that can be
ascribed to hcp-structured Ru NPs (JCPDS No.: 06-0663) [20]. The particle size is determined
to be 9.8 nm, calculated using the Scherer equation, and confirming the TEM observation. A
sharp diffraction at 25.2° combined with several weak peaks at 37.8°, 47.8°, 53.7°, 55.1° and
62.6° is also detected as those for CF, referring to the (101), (004), (200), (105), (211) and (204)
lattice planes of TiO$_2$ (JCPDS No.: 71-1167), respectively [21]. This is because WWF contains 0.27 wt% of Ti, which was transformed into TiO$_2$ after pyrolysis. It is noteworthy that as the activation/reduction was performed a high temperature in N$_2$ flow, TiO$_2$ was retained for CF@g-C$_3$N$_4$–Ru NPs. Otherwise, it was mostly removed for CF@g-C$_3$N$_4$–Ru SAs as it was reduced by NaBH$_4$. We also noticed that two diffraction peaks assigned to g-C$_3$N$_4$ are vague for CF@g-C$_3$N$_4$–Ru NPs, which likely indicates that the secondary pyrolysis destroyed the crystalline structure of g-C$_3$N$_4$. It is clear that heat treatment at 500 $^\circ$C not only accelerates the mobility of the reduced Ru species, but also provides another pathway to accelerate the aggregation to Ru NPs by the release of N-coordinated Ru species. By contrast, NaBH$_4$ reduction is not only beneficial to the synthesis of Ru SAs, but also helpful to remove the TiO$_2$ impurities.

Figure 2. XRD patterns of different samples.

N$_2$ adsorption/desorption reveals a mixed I and IV type isotherm with a distinct H$_4$ type hysteresis loop for CF@g-C$_3$N$_4$–Ru SAs (Figure 3a), indicative of hierarchical microand mesoporous materials with slit pores [22]. The mesopore size shows a mono distribution centered at ca. 3.7 nm, while the micropore size exhibits a bimodal distribution centered at 0.52 and 0.60 nm (Figure 3b). These hierarchical pores originate from the core–shell structured CF@g-C$_3$N$_4$ supporting matrix, which may facilitate the reactant/product transportation during the aqueous-phase reactions. Moreover, CF@g-C$_3$N$_4$–Ru SAs shows a BET surface area of 380 m$^2$ g$^{-1}$ and a total pore volume of 0.57 cm$^3$ g$^{-1}$ (Table S2). Meanwhile, CF@g-C$_3$N$_4$–Ru NPs exhibits a decreased surface area and pore volume due to the blocking of TiO$_2$. The mesoporosity, defined as $V_{meso}/V_p$, is determined to be 60.0%, which is lower than that for CF@g-C$_3$N$_4$–Ru SAs (71.9%). This may coincide with the removal of partial g-C$_3$N$_4$ upon the secondary pyrolysis that slightly erodes the hierarchical structure. On the other hand, CF–Ru is mesoporous, and gives an extremely high surface area of 587 m$^2$ g$^{-1}$, probably due to the removal of TiO$_2$, which acts as the template for micro-mesopores, while g-C$_3$N$_4$–Ru is determined to be microporous, showing an extremely low surface area of 16 m$^2$ g$^{-1}$ and a low pore volume of 0.09 cm$^3$ g$^{-1}$. These results demonstrate that CF is dominating in contributing to the porosity of CF@g-C$_3$N$_4$–Ru SAs.
In order to investigate the electronic structure and coordination configuration of the Ru species, an element-specific XAFS analysis was performed. As shown in Figure 4a, the absorption edge position of CF@g-C3N4–Ru SAs is between that of Ru and RuO2, suggesting that the Ru single atoms carry some positive charges [23]. These Ru single atoms may interact with the CF@g-C3N4 support by donating electrons to the surrounding N moieties. The derivative profile for CF@g-C3N4–Ru SAs exhibits the edge structure ranging from 22,126 to 22,131 eV. Additionally, the maximum slope is located at 22,130 eV, between that of RuCl3 and RuO2 (Figure 4b). Therefore, the valence state of the Ru species in CF@g-C3N4–Ru SAs is +3 to +4 [12]. On the contrary, the absorption edge and derivative profile for CF@g-C3N4–Ru NPs match well with those for Ru foil, demonstrating the formation of the metallic Ru species. In the corresponding k space, the \( k^2 \chi(k) \) oscillation curve of CF@g-C3N4–Ru SAs shows a reduction in the oscillation amplitude at a higher k region (k > 8 Å\(^{-1}\)) compared to that of Ru foil (Figure 4c), indicating the dominance of low Z backscatters, which would be N/C in our system [24]. As for CF@g-C3N4–Ru NPs, the strong oscillations at a high k region (k > 8 Å\(^{-1}\)) confirm the predominant Ru–Ru pairs (Figure 4c). Figure 4d shows the Fourier transformed (FT) \( k^2 \)-weighted extended X-ray absorption fine structure (EXAFS) spectra of CF@g-C3N4–Ru SAs and the reference Ru foil, RuO2 and RuCl3. There is only one prominent peak at 1.4 Å, which can be assigned to the Ru–N contribution [15], adjacent to the Ru–O scattering path at 1.5 Å as observed for RuO2 [8]. No peaks can be observed at ~2.6 and 1.8 Å corresponding to Ru–Ru and Ru–Cl pairs as shown for Ru foil and RuCl3, respectively [25]. This suggests the pristine Ru–Cl pair was broken to construct Ru–N coordination, forming atomically dispersed Ru species. Comparatively, the radical distribution of CF@g-C3N4–Ru NPs obtains a dominated Ru–Ru pair (2.6 Å) combined with Ru–N contribution (1.5 Å), implying that the metallic Ru is stabilized by the surrounding N moieties. In order to further explore the dispersion of the Ru species in CF@g-C3N4–Ru SAs, we performed wavelet transform (WT) of K-edge EXAFS. In Figure 2e, CF@g-C3N4–Ru SAs shows only one intensity maximum at 4.0 Å\(^{-1}\), ascribed to the Ru–N coordination. Additionally, no intensity maximum related to the Ru–Ru and Ru–O contributions can be found as compared to the WT plots of CF@g-C3N4–Ru NPs, Ru foil and RuO2 (Figure 2f–h). In order to further obtain the structure parameter of the Ru species, we conducted a least-squares EXAFS fitting. As illustrated in Figure S2 and Table 1, the coordination number of Ru–N for CF@g-C3N4–Ru SAs is approximately 5.3, and the mean bond length of Ru–N is 2.03 Å. This suggests that the Ru–N bonding in CF@g-C3N4–Ru SAs may adopt a square pyramidal configuration [26]. A coordination number for the Ru–N is 1.4 and the second shell Ru–Ru is 8.8 for CF@g-C3N4–Ru NPs, indicating that metallic Ru species are partially stabilized by N-coordination.
In order to further obtain the structure parameter of the Ru species, we conducted a least-squares EXAFS fitting. As illustrated in Figure S2 and Table 1, the coordination number of Ru–N for CF@g-C3N4–Ru SAs is approximately 5.3, and the mean bond length of Ru–N is 2.03 Å. This suggests that the Ru–N bonding in CF@g-C3N4–Ru SAs may adopt a square pyramidal configuration [26].

The surface composition and chemical state of different samples are investigated by X-ray photoelectron spectroscopy (XPS). The C, O, N and Ru elements can be found for both CF@g-C3N4–Ru SAs and CF@g-C3N4–Ru NPs (Figure S3). The high-resolution N 1s spectrum of CF@g-C3N4–Ru SAs can be deconvoluted into four peaks with binding energies of 398.8, 399.7, 400.4 and 401.2 eV (Figure 5a), corresponding to pyridinic-N, Ru–N, pyrrolic-N and graphitic-N, respectively [27]. Interestingly, the Ru–N signal for CF@g-C3N4–Ru SAs is negatively shifted by 0.1 eV compared to that for CF@g-C3N4–Ru NPs. This agrees with the positive Ru atoms that can denote more electrons to the surrounding N moieties, while the metallic Ru species shows a weak electron-denoting capability. The N moieties can be further confirmed by the asymmetric signals of C-N at 286.5 eV and N=C-N2 at 288.3 eV in

Figure 4. (a) Ru K-edge XANES, (b) the first derivative curves, (c) k²-weighted EXAFS spectra at k space, (d) the corresponding Fourier transformed EXAFS spectra, and (e–h) WT for the k²-weighted EXAFS signal of different Ru-containing samples.
the C 1s spectrum [28], as shown in Figure 5b. Three oxygen functionalities including O–C, O–H and Ru–O were found at the binding energies of ca. 532.8, 531.5 and 530.6 eV [29], respectively, as shown in Figure 5c. These results demonstrate that the carbon skeleton is decorated with some oxygen functionalities. Owing to the overlapping of C 1s and Ru 3d electrons, the binding energies at 280.9 and 282.1 eV can be ascribed to 3d5/2 of Ruδ+ (0 < δ < 4) and Ru4+ for CF@g-C3N4–Ru SAs, while those at 280.6, 281.4 and 284.4 eV correspond to 3d5/2 of Ru0 and Ruδ+, and 3d3/2 of Ru0 for CF@g-C3N4–Ru NPs [30,31]. Since the binding energy of Ru 3d3/2 (ca. 284.4 eV) is too close to C 1s (284.6 eV) to be distinguished, the electronic state of the surface Ru species was determined by the binding energy of Ru 3p. For CF@g-C3N4–Ru SAs, the binding energies at 463.7 and 485.9 eV correspond to Ru4+ (83%) of Ru 3p3/2 and Ru 3p1/2, while those at 462.4 and 484.5 eV can be ascribed to the positively charged Ruδ+ (17%, 0 < δ < 4) [11]. Comparatively, the de-convoluted Ru 3p spectrum of CF@g-C3N4–Ru NPs exhibits binding energies at 461.8 and 483.8 eV for Ru0 (15%) and those at 462.6 and 484.6 eV correspond to Ruδ+ (25%). An additional peak at 464.3 eV is present, due to the overlapping of Ru 3p and Ti 2p, which can be ascribed to 2p3/2 of Ti4+ [32]. These results demonstrate that the atomically dispersed Ru atoms are mainly surrounded by N moieties and are thus positively charged, showing a higher valence, while the Ru NPs possess both metallic and N-coordinated Ru species. Furthermore, the Ru content is determined to be 9.7 wt% by XPS analysis, which is much larger than that estimated by ICP-OES (Table S1), implying that the Ru species are mainly located outside, confirming the TEM observation.

Table 1. Fitting parameters for Ru-containing samples.

| Sample              | Absorber-Scatter Pair | Coordination Number | Bond Distance (Å) | [σ2] a | ∆E0 a (eV) | R Factor |
|---------------------|-----------------------|---------------------|-------------------|--------|------------|----------|
| CF@g-C3N4–Ru SAs   | Ru-N                  | 5.3                 | 2.03              | 0.0081 | 0.600      | 0.023    |
| CF@g-C3N4–Ru NPs   | Ru-N                  | 1.4                 | 1.95              | 0.0007 | –8.50      | 0.019    |
| RuO2                | Ru-Ru                 | 8.8                 | 2.68              | 0.0055 | –3.70      |          |
| RuO2                | Ru-O                  | 4.0                 | 1.98              | 0.0014 | 0.279      |          |
| RuCl3               | Ru-Ru                 | 2.0                 | 3.10              | 0.0030 | –8.075     | 0.029    |
| RuCl3               | Ru-Cl                 | 6.0                 | 2.36              | 0.0075 | –0.873     | 0.099    |
| Ru foil             | Ru-Ru                 | 2.0                 | 2.98              | 0.0130 | –9.249     |          |
| Ru foil             | Ru-Ru                 | 12.0                | 2.68              | 0.0048 | 3.663      | 0.007    |

a σ2 = Debye-Waller factor and ∆E0 = inner potential correction.

The hydrogenation of LA was performed under bath reactions in water to investigate the catalytic property of various Ru-containing catalysts. As listed in Table 2, similar to the blank reaction (entry 1), LA conversion can be ignored as CF@g-C3N4 was involved (entry 2), since no active Ru species are involved. Figure S4 shows the time-on-line concentration profiles for LA. As shown, all Ru-containing catalysts are active for LA hydrogenation, suggesting the importance of Ru species in LA hydrogenation reactions. Additionally, the LA conversion increased as the reaction time was prolonged, and then was nearly completed as the reaction time was extended to 1.3 h. GVL was found to be the main product over all Ru-containing catalysts, and trace 1,4-pentanediol (PD) and 2-methyltetrahydrofuran (MTHF) were also detected as consecutive hydrogenation reaction products. CF@g-C3N4–Ru NPs displays a higher catalytic activity under identical reaction conditions, delivering an LA conversion of 100% and a GVL yield of 99% for the duration of 2 h. This corresponds to a TOF value of 0.180 s⁻¹, which is higher than 0.062 s⁻¹ as CF@g-C3N4–Ru SAs was utilized. As previously reported, the TOF value as the single-atom Ru catalyst involved (0.17 s⁻¹) is also lower than that for the nanoparticle catalyst (0.82 s⁻¹) at 413 K and 10 bar H2 [14]. As demonstrated, H2 dissociation is a prerequisite for hydrogenation reactions, which is more important than C=O group activation. However, the H2 dissociation over single atoms (like Pd) was significantly retarded compared to that over nanoparticles [33]. The lower catalytic activity for CF@g-C3N4–Ru SAs as com-
pared to that for the Ru nanoparticle catalyst in this study agrees with the results in the literature [34,35]. Nevertheless, CF@g-C_{3}N_{4}–Ru SAs delivers a GVL yield of 99%, which is higher than that detected for g-C_{3}N_{4}–Ru (88%) and CF–Ru (92%), as LA was completely converted and some side products such as PD and MTHF were produced. The superior selectivity of GVL achieved by CF@g-C_{3}N_{4}–Ru SAs may correlate with the one-dimensional hierarchical supporting matrix, which provides well-defined pore arrays, facilitating the directional synthesis of GVL. This can also be confirmed by the high selectivity of 99%, as the nanoparticle catalyst CF@g-C_{3}N_{4}–Ru NPs was involved. A reaction scheme can be proposed as follows: when interacted with Ru single atoms, the active H^{+} is provided by the dissociation of molecular hydrogen (H_{2}). The C=O group in LA and H^{+} are separately adsorbed on N and Ru centers, and activated to form 4-hydroxypentanoic acid (4-HPA) as an intermediate product. The produced 4-HPA is unstable and can be easily converted into GVL via intramolecular lactonization, especially at a relatively high temperature or in acidic/basic reaction media.

![Figure 5](image-url)

**Figure 5.** High-resolution (a) N 1s, (b) C 1s, (c) O 1s and (d) Ru 3p spectra for CF@g-C_{3}N_{4}–Ru SAs and CF@g-C_{3}N_{4}–Ru NPs.

**Table 2.** Summary of the catalytic performance for different catalysts.

| Entry | Catalyst | LA Conversion a (%) | Selectivity to GVL (%) | Yield of GVL (%) | TOF (s⁻¹) c |
|-------|----------|---------------------|------------------------|-----------------|--------------|
| 1     | Blank    | 2                   | - b                    | -               | -            |
| 2     | CF@g-C_{3}N_{4} | 5                   | -                      | -               | -            |
| 3     | CF@g-C_{3}N_{4}–Ru NPs | 100                | 99                     | 99              | 0.180        |
| 4     | CF@g-C_{3}N_{4}–Ru SAs | 100                | 99                     | 99              | 0.062        |
| 5     | g-C_{3}N_{4}–Ru | 100                | 88                     | 88              | 0.025        |
| 6     | CF–Ru    | 100                 | 92                     | 92              | 0.040        |

a Reaction conditions: LA 0.12 g (1 mmol), catalyst 30 mg, H_{2} 4.5 MPa, water 40 mL, 2 h and 150 °C. b Not detected. c TOF = mol_{LA}/(mol_{Ru} × h) at a LA conversion of 10%.
The cycling stability of metal catalysts is important for their potential industry applications. To examine the stability of CF@g-C_3N_4–Ru SAs, cycling experiments were also carried out for other Ru-containing catalysts for comparison. As illustrated in Figure 6, CF@g-C_3N_4–Ru SAs was quite stable and could be used at least six times without a significant loss of GVL yield in water. The Ru concentration in the filtrate is 0.004 ppm estimated by ICP-OES (Table S1). The TEM observation for the spent CF@g-C_3N_4–Ru SAs demonstrates that the aggregation to Ru nanoparticles did not occur, and the hierarchical skeleton was almost intact after seven runs (Figure S5). These results are indicative of the highly stable CF@g-C_3N_4–Ru SAs toward the aqueous LA hydrogenation in acidic media (pH ≈ 1). For comparison, CF@g-C_3N_4–Ru NPs can be cycled twice and delivers a GVL yield of 99%, which is decreased by 35% at the third run. Additionally, the content of leached Ru is four times that of CF@g-C_3N_4–Ru SAs, as estimated by ICP-OES. Such a severe exfoliation is in accordance with the observation of excess leached Ru NPs as ultrasonic treatment is employed for CF@g-C_3N_4–Ru NPs. TEM observation for the spent CF@g-C_3N_4–Ru NPs reveals the aggregation of Ru NPs, though their hierarchical skeleton is almost intact (Figure S5). N_2 adsorption reveals that both spent CF@g-C_3N_4–Ru SAs and CF@g-C_3N_4–Ru NPs show a decreased mesopore size of 2.4 and 2.1 nm, respectively (Figure S6). Additionally, the microporous structure in fresh catalysts disappears upon cycling. Meanwhile, the specific surface area is decreased by 29.7 and 26.7% for spent CF@g-C_3N_4–Ru SAs and CF@g-C_3N_4–Ru NPs, respectively (Table S1). Therefore, the shielding effect of reagents retained after the reaction should be responsible for the degradation of the porous structure. More Ru^{3+} species (84.8%) are detected for spent CF@g-C_3N_4–Ru SAs, which is different from the dominated Ru^{4+} in the fresh catalyst (83.0%) (Figure S7). This implies that in the presence of H_2, most Ru^{4+} species evolve into Ru^{5+} after cycling. As for spent CF@g-C_3N_4–Ru NPs, the content of Ru^{5+} (43.3%) is similar to that of the fresh catalyst, while the atomic ratio of Ru^{6+} is increased by 14.5% (Figure S7). This leads to the rapid decrease in GVL yield, and confirms that Ru^{5+} is the actual active site and is dominated during the hydrogenation of LA. Based on these investigations, it can be inferred that the successive reduction in the Ru^{5+} species can be mainly responsible for the high stability of CF@g-C_3N_4–Ru SAs. On the other hand, it is also found that CF–Ru can be cycled twice, and only 54% of GVL yield is obtained at the third run. Owing to the absence of N-coordination, the anchored Ru species are easily leached, leading to a rapid decrease in activity. On the contrary, the g-C_3N_4–Ru catalyst exhibits a stepwise deactivation during cycling, with a drop in LA conversion from 100 to 70% as well as in GVL yield from 88 to 66% after four runs (Figure 6). A sharp decrease in GVL yield (32%) was observed for g-C_3N_4–Ru at the fifth run. Varma and his coworkers have reported a similar deactivation for the AgPd@g-C_3N_4 catalyst, which displays a steady decline in GVL yield from 42 to 34% after four cycles at 473 K in H_2 atmosphere (35 bar) [36]. The strong interaction between metal and g-C_3N_4 may slow down the deactivation. However, it is noteworthy that g-C_3N_4–Ru is less stable than CF@g-C_3N_4–Ru SAs in the aqueous and acidic media, suggesting that the hierarchical pore arrays can facilitate the mass transfer and thus retard the active site poisoning in the presence of impurities produced during reactions. Therefore, the unprecedented stability of CF@g-C_3N_4–Ru SAs can be ascribed to the following synergism: (1) The construction of N-isolated Ru atoms retards the Ru sintering, leaching and acid poisoning under harsh reaction conditions, and an over oxidation/reduction when exposed to air/H_2 is avoided and, thus active Ru^{5+} species are continuously created during reactions to retain a high activity. (2) The one-dimensional hierarchy CF@g-C_3N_4 combines the merits of mesoporous carbon and graphitic carbon nitride. Mesopores provide superior diffusion paths for LA/GVL diffusion, while N coordination sites not only stabilize Ru atoms, but also promote LA adsorption and thus promote its contact with active sites together with mesoporous carbon. Furthermore, the interaction with CF improves the dispersion of g-C_3N_4, which increases the Ru atom accessibility during reactions. The synergism between dynamically stable Ru atoms and a firm one-
dimensional hierarchy thereby improves the overall catalytic stability of CF@g-C$_3$N$_4$–Ru SAs under harsh reaction conditions.

Figure 6. Cycling tests for different Ru-containing catalysts.

4. Conclusions

In summary, we have successfully developed a stable LA hydrogenation catalyst with Ru single atoms anchored on a one-dimensional CF@g-C$_3$N$_4$ hierarchy. A deep investigation reveals that the durability of the obtained CF@g-C$_3$N$_4$–Ru SAs catalyst highly depends on single Ru atoms and the core–shell structured hierarchy, as well as their ensemble effect, verified by various characterization techniques and comparative catalytic tests. The elaborately fabricated CF@g-C$_3$N$_4$–Ru SAs catalyst demonstrates unprecedented catalytic stability for aqueous LA hydrogenation in acidic media. This is probably due to the fact that the N-coordinated Ru sites are isolated and are free from acid poisoning, and the hierarchical pore arrays facilitate the mass transfer and thereby retard the deactivation of active sites. The development of such an efficient CF@g-C$_3$N$_4$–Ru SAs catalyst successfully proves the concept of metal- and support-dependent durability, and also gives a strong indication of its generality in the fabrication of a variety of stable single-atom catalysts.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ma15217464/s1, Table S1. The atom percentage and elemental analysis for different Ru-containing catalysts, Table S2. Textural properties of various Ru-containing catalysts, Figure S1. TEM images for (a) CF@g-C$_3$N$_4$–Ru NPs and (b) filtrate obtained by ultrasonic treatment of CF@g-C$_3$N$_4$–Ru NPs in ethanol, with the corresponding particle size distribution histogram (inset), Figure S2. Curve fitting for (a) CF@g-C$_3$N$_4$–Ru SAs, (b) CF@g-C$_3$N$_4$–Ru NPs, (c) RuC$_3$, (d) RuO$_2$ and (e) Ru foil, Figure S3. XPS survey scan for (a) CF@g-C$_3$N$_4$–Ru SAs and (b) CF@g-C$_3$N$_4$–Ru NPs, Figure S4. Time profiles for catalytic conversion of LA in water using different Ru-containing catalysts, Figure S5. TEM images of (a,b) spent CF@g-C$_3$N$_4$–Ru SAs and (c,d) spent CF@g-C$_3$N$_4$–Ru NPs, Figure S6. N$_2$ adsorption/desorption isotherm and the corresponding pore size distribution curve (inset) for (a) spent CF@g-C$_3$N$_4$–Ru SAs and (b) CF@g-C$_3$N$_4$–Ru NPs, Figure S7. High-resolution Ru 3p spectra for (a) spent CF@g-C$_3$N$_4$–Ru SAs and (b) spent CF@g-C$_3$N$_4$–Ru NPs.
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