

Effect of Cu addition to carbon-supported Ru catalysts on hydrogenation of alginic acid into sugar alcohols

Chunghyeon Ban, Seungdo Yang, Hyungjoo Kim, Do Heui Kim*

School of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University, 1, Gwanak-ro, Gwanak-gu, Seoul, Republic of Korea

ARTICLE INFO

Keywords:

Biomass
Alginic acid
Heterogeneous catalysis
Hydrogenation
Sugar alcohol
RuCu bimetallic catalyst

ABSTRACT

The objective of this study was to investigate the effect of Cu addition to carbon supported Ru catalysts on the hydrogenation of macroalgae-derived alginic acid into sugar alcohols, mainly sorbitol and mannitol. Both geometric and electronic effects were determined based on results of H₂-TPR, H₂- or CO-chemisorption, and XPS analyses after Cu was added to Ru. The addition of Cu to Ru caused blocking of active Ru surface and electron transfer between Ru and Cu. The intimate interaction between Ru and Cu formed RuCu bimetallic clusters which expedited hydrogen spillover from Ru to Cu. The highest yield of target sugar alcohols of 47.4% was obtained when 5 wt% of Ru and 1 wt% of Cu supported on nitric acid-treated activated carbon reacted at 180 °C for 2 h. The RuCu bimetallic catalyst exhibited deactivation upon repeated reactions due to the carbon deposition on the catalyst.

1. Introduction

Development of renewable energy sources is of great importance due to depletion of fossil fuel reservoirs and fossil fuel-related environmental pollutions. In view of production of sustainable fuels and chemicals to replace petroleum-based fuels and chemicals, biomass is considered as one of promising sources of organic carbons among various renewable resources such as wind, tidal, and solar power [1]. Biomass captures atmospheric CO₂ by means of photosynthesis achieving a net zero carbon footprint (carbon neutral). Despite the difficulty in processing biomass feedstock due to high oxygen contents, it would lead to versatile products with diversified functionality. Sustainable production of green chemicals from biomass can be realized by using catalyst. Commercial production of sugar alcohols as value-added renewable platform chemicals occurs by hydrogenation of sugars such as glucose and fructose over Raney nickel catalysts, where sugars are being derived from components of terrestrial biomass such as starch and sucrose. [2,3] However, the use of nickel suffers from leaching which causes problems in catalyst deactivation and purification of end-products [2]. Therefore, other catalysts such as Ru, Pd, and Pt are being investigated for hydrogenation of sugars and cellulose. [4,5]

To enhance a catalytic activity, various bimetallic catalysts have been studied. Among them, RuCu bimetallic catalysts have exhibited superior catalytic activities compared to Ru and Cu alone in numerous fields of reactions. [6,7] It has been suggested that the interfacial

interaction between Ru and Cu is the reason for such unique catalytic properties of RuCu bimetallic catalysts, although these two metals are completely immiscible in bulk. [8] Addition of Cu to Ru catalysts has both geometric and electronic effects. It has been previously reported that the addition of Cu to Ru-based catalysts caused the formation of a thin layer of Cu on the Ru kernel as well as electron transfer between Ru and Cu [9,10]. Due to above features and enhanced ability of hydrogen spillover, RuCu bimetallic catalysts were applied to various reactions such as selective hydrogenation of glucose, citral, and cinnamaldehyde [6,7].

Catalytic valorization of algal biomass, also known as the third generation biomass, could benefit from advantageous features such as inedibility, rapid growth, and lignin-free structure, compared to its former generations such as agricultural crops and wood. [11,12] The potential of alginic acid, a major constituent of brown algae, as a surrogate for cellulose to produce valuable platform chemicals has been suggested by several researches. [13–19] Specifically, it has been recently reported that sugar alcohols such as sorbitol and mannitol could also be produced over Ru-based catalysts from alginic acid, a major constituent of brown algae. [20] Production of C6 sugar alcohols from alginic acid involves several reactions such as hydrolysis of ether bonds in alginic acid and hydrogenation of aldehyde and carboxyl groups in uronic acid, aldonic acid, and aldose as depicted in Scheme 1. However, no studies have used RuCu bimetallic catalysts to produce sugar alcohols from macroalgae-derived alginic acid. Thus, the objective of the

* Corresponding author.

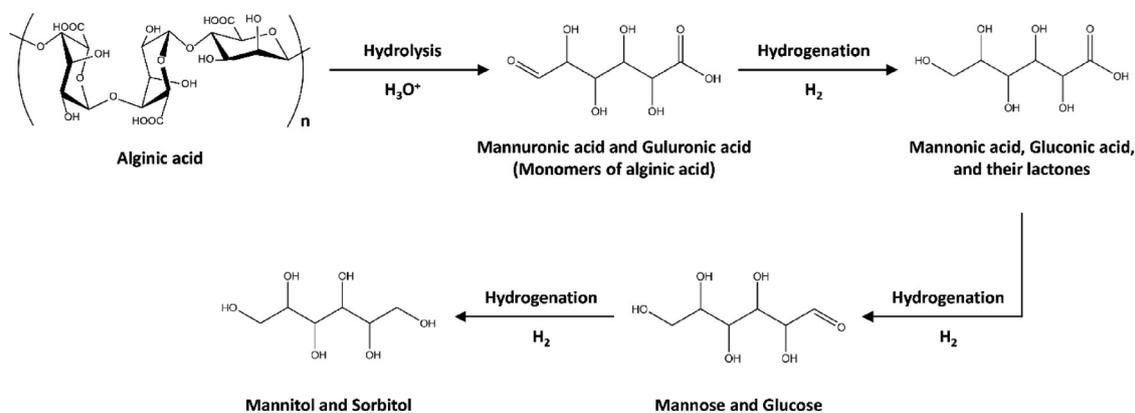
E-mail address: dohkim@snu.ac.kr (D.H. Kim).

<https://doi.org/10.1016/j.apcata.2019.04.003>

Received 23 January 2019; Received in revised form 23 March 2019; Accepted 4 April 2019

Available online 05 April 2019

0926-860X/ © 2019 Elsevier B.V. All rights reserved.



Scheme 1. A reaction scheme of hydrogenation of alginic acid.

present study was to investigate the effect of Cu addition to carbon-supported Ru catalysts on hydrogenation of macroalgae-derived alginic acid into sugar alcohols, mainly sorbitol and mannitol. Electronic and geometric effects resulting from the addition of Cu and the role of Cu in the hydrogenation reaction were elucidated by using various characterization techniques.

2. Experimental

2.1. Materials

Activated carbon was purchased from Sigma-Aldrich. Nitric acid was supplied from Samchun Chemical Co., Ltd. Various metal precursors of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$, and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ were bought from Sigma-Aldrich except $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ from Alfa Aesar. Alginic acid, a reactant, was obtained from Sigma-Aldrich. Sugar alcohols (sorbitol, mannitol, galactitol, arabitol, ribitol, and xylitol), polyols (glycerol and propylene glycol), sugars (glucose and mannose), and glucono-1,5-lactone were purchased from Alfa Aesar. Mannono-1,4-lactone was supplied from TCI Chemicals. All chemicals were used without further purification.

2.2. Catalyst preparation

Ru-based bimetallic catalysts or monometallic catalyst were synthesized via traditional wet impregnation method using aqueous solutions of metal precursors. Activated carbon was oxidized with 13 N of nitric acid to impart acidity according to the method reported elsewhere (AC-N-13) [16]. Loading amount of Ru was maintained at 5 wt% while those of other promoters (Sn, Fe, Co, Ni, Mo and Cu) were kept at 1 wt%. Loading amount was varied only for Cu (1, 3, 5, and 10 wt%). Wet-impregnated catalysts were dried in an oven at 100 °C overnight followed by reduction at 300 °C for 3 h under 10% H_2 stream (100 ccm). Reduced catalysts were passivated under 5% O_2/N_2 (100 ccm) to prevent sudden oxidation upon exposure to air. Resultant bimetallic catalysts are denoted as Ru(5)M(x)/AC-N-13, where M and x stand for a bimetal used and weight percent of the metal, respectively. Ru or Cu monometallic catalysts were synthesized as described above except using a precursor of each metal at a time. Resultant monometallic catalysts are denoted as Ru(5)/AC-N-13 and Cu(y)/AC-N-13, where y stand for weight percent of the metal.

2.3. Catalyst characterization

N_2 adsorption-desorption analysis was performed on a BELSORP-mini II (BEL Japan Inc.). Catalysts were evacuated at 200 °C for at least 3 h before analysis. An X-ray diffractometer (Rigaku, $\text{CuK}\alpha$ radiation with 40 kV and 30 mA) was used to analyze diffraction patterns of

catalysts. To investigate acid densities of catalysts, back titration was performed using NaOH (0.01 M) and HCl (0.02 M) according to a previously reported method. [16] To determine the amounts of Ru and Cu loaded on catalysts and amounts of metals leached, inductively coupled plasma atomic emission spectroscopy (ICP-AES) was conducted on an Optima-4300DV (PerkinElmer). H_2 or CO Chemisorption analysis was performed on a BELCat (BEL Japan Inc.). Before pulse chemisorption, a catalyst was reduced at 300 °C for 2 h under 5% H_2/Ar flow (50 ccm). After cooling down to 50 °C, pulses of H_2 or CO were injected with loop volume of 0.8570 mL. Temperature programmed reduction (H_2 -TPR) of the catalyst was then executed on a BEL-CAT BASIC (BEL Japan Inc.). Prior to the detection of hydrogen uptake by a thermal conductivity detector, a catalyst was pretreated at 150 °C for 2 h under Ar stream (50 ccm). After cooling down to 40 °C, the sample was heated to 900 °C with a ramping rate of 10 °C/min under 5% H_2/Ar flow (50 ccm). X-ray absorption spectroscopy (XAS) was carried out on the 7D beamline of Pohang Light Source (PLS-II) with SR E-beam energy of 2.5 GeV and SR current of 360 mA using Si(111) crystal as a monochromator. X-ray photoelectron spectroscopy (XPS) was conducted on K-alpha (Thermo Scientific) equipped with Al K α μ -focused monochromatic source (1486.6 eV). C 1 s peaks for all catalysts were calibrated to 284.5 eV.

2.4. Catalytic hydrogenation reaction

Hydrolytic hydrogenation of alginic acid was carried out in an autoclave (100 mL, Parr Instrument Company). Alginic acid (0.3 g), distilled water (30 mL), and a catalyst (0.1 g) were charged into the autoclave. The vessel was heated to 150 °C or 180 °C under 50 bar of H_2 after purging with 50 bar of H_2 three times to remove air inside. After a desired reaction time, the reactor was quickly quenched in an ice-cold bath to avoid side reactions. The liquid mixture inside the vessel was agitated with an impeller at 1000 rpm during heating of the reactor and reaction at the designated temperature. Recyclability experiment was performed using a multi-batch process according to a previously reported method to compensate weight loss of the catalyst during a catalyst recovery step [16].

2.5. Product analysis

Gas chromatography (GC, Agilent 6890) equipped with a DB-5 column and an autosampler was utilized to analyze liquid products. Before injection to GC, liquid products were filtered and freeze-dried followed by silylation with BSTFA (N,O-Bis trimethylsilyl trifluoroacetamide) [21]. Carbon yield was calculated as follows: Carbon yield (%) = $100 \times (\text{number of carbons in an organic compound}/6) \times (\text{moles of an organic compound in the product mixture}/\text{moles of a repeating unit in alginic acid of 0.3 g})$. Total organic carbon (TOC) was measured by injecting the filtered liquid product into Sievers 5310C (GE). Gel permeation chromatography (GPC) was performed on Dionex

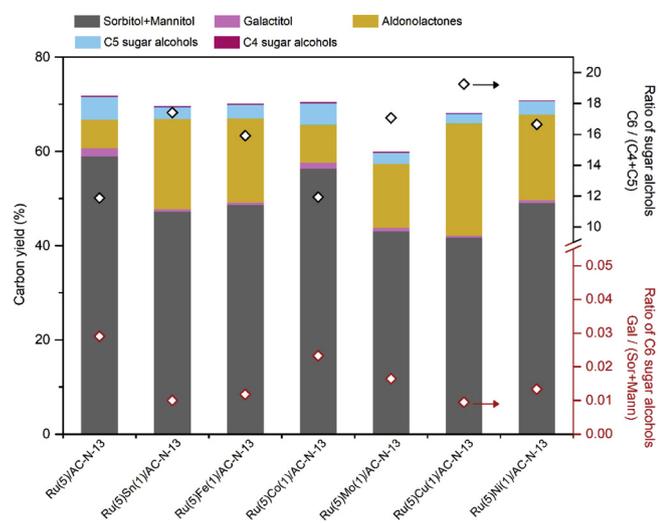


Fig. 1. Product distribution over various bimetallic carbon catalysts at 150 °C for 3 h under 50 bar of H₂. C6 sugar alcohols: sorbitol (Sor), mannitol (Mann), and galactitol (Gal); C5 sugar alcohols: xylitol, arabitol, and ribitol; C4 sugar alcohols: threitol and erythritol; Aldonolactones: glucono-1,5-lactone and mannono-1,4-lactone.

Ultimate 3000 calibrated with Pullulan (molecular weight, 342–80500).

3. Results and discussion

Various Ru-based bimetallic catalysts were synthesized and applied to hydrolytic hydrogenation of alginic acid for the production of sugar alcohols, mainly sorbitol and mannitol. The support material used was nitric acid-treated activated carbon to facilitate the hydrolysis of glycosidic bonds in alginic acid since the acidity of activated carbon could be enhanced by oxidation of carbon materials with nitric acid [22]. It has been previously reported that the acid density of various carbon materials is increased when the concentration of nitric acid is increased, resulting in improved hydrolysis of sodium alginate into uronic acids [16]. As shown in Fig. 1, a screening experiment was carried out at 150 °C for 3 h. It was found that Cu-promoted catalyst exhibited the highest sugar alcohol ratio of C6/(C4 + C5) and the lowest galactitol formation. The formation of byproducts such as C4–C5 sugar alcohols and galactitol, would decrease the selectivity to desired products, namely sorbitol and mannitol. Thus, Cu was chosen for further studies shown below. Since the cleavage of C–C bonds and the isomerization of sugar alcohols could be expedited under harsher reaction condition, the reaction temperature was further elevated to 180 °C to better understand a synergistic effect of Cu addition on Ru catalyst [23,24].

To investigate the effect of Cu addition, catalysts were applied to the reaction after various amounts of Cu were loaded to 5 wt% Ru. Conversion of alginic acid over the catalysts was indirectly measured by GPC due to difficulty in separating unreacted alginic acid from the reaction mixture [16,20]. As shown in GPC chromatograms (Fig. 2), the reactant was fully converted to smaller molecules over bimetallic catalysts in all cases. However, a peak corresponding to a compound having molecular weight higher than a C6 sugar alcohol was also observed. For comparison, a sugar alcohol with 12 carbon atoms, namely maltitol, was analyzed. The general trend of the increase in the intensity of such higher MW compound was in line with the increase in Cu content. It has been previously suggested that, under pressurized H₂ atmosphere, spilled-over hydrogens by a metallic site can result in the formation of protonic acid sites that are able to catalyze the hydrolysis of cellulose [25]. Similarly, the ability of Ru to catalyze the hydrolysis of C–C bonds in cellobiose into glucose has been also reported [26]. Thus, the above result implies that the addition of Cu could partly cover

the active surface of Ru for hydrogen spillover, resulting in lowered hydrolysis activity and unconverted oligomeric compounds when the amount of Cu was increased. As summarized in Table 1, acid densities of catalysts measured by back titration under atmospheric condition exhibited an inverse correlation with the amount of Cu loaded. This might arise partly from the deposition of Cu on surface acidic oxygenates formed after oxidation of activated carbon with nitric acid. It has been previously reported that surface oxygenates of an oxidized carbon material could act as anchoring sites for a metal which eventually affects its dispersion [27].

As shown in Fig. 3, Ru catalysts added with varied amounts of Cu exhibited different activities. The yield of target C6 sugar alcohols, sorbitol and mannitol, was greatly improved from 33.3% to 47.4% when 1 wt% of Cu was added. However, further increase of Cu content to 3 wt% and 5 wt% reduced yields of the target product to 15.2% and 5.0%, respectively. Surprisingly, the yield was partially recovered to 18.0% when the loading amount of Cu was increased to 10 wt%. In addition, it was found that pure Cu itself, Cu(10)/AC-N-13, was inactive in the hydrogenation of alginic acid. To investigate such unusual catalytic behavior with the addition of Cu, physicochemical properties of these catalysts were analyzed as follows.

As shown in Fig. S1, all ruthenium-based catalysts displayed type IV isotherm with H4 hysteresis, a representative of micro-mesoporous carbons [28]. As summarized in Table 1, when the amount of Cu was increased, surface area and pore volume of catalysts were decreased from 642.4 to 510.6 m²/g and from 0.46 to 0.39 cm³/g, respectively, indicating partial pore blocking of the support.

As shown in Fig. 4, diffraction lines for Cu metal were observed for samples loaded with Cu at 5 wt% or higher. It was worth noting that Cu existed mainly in the metallic form in bimetallic catalysts in the bulk state while Cu₂O crystallite and metallic Cu co-existed in pure Cu catalyst. This suggests that the noble metal, Ru, can inhibit metallic Cu from being oxidized upon exposure to air during passivation [29]. On the other hand, in all samples, no diffraction lines for Ru was detected. This might suggest that Ru was well dispersed with average particle size below the detection limit of the instrument (< 5 nm). This might also suggest the formation of amorphous RuO₂·xH₂O upon exposure to the air after the reduction of catalysts [30]. As shown in Fig. 5, this oxidized Ru species was further evidenced by positive shifts of binding energy of Ru 3p_{3/2} compared to metallic Ru (ca. 461 eV) [30,31].

Surface oxidation states of Ru and Cu on the activated carbon was further investigated by XPS. As shown in Fig. 5, a positive shift (ca. 0.4 eV) for Cu⁺ (932.5 eV) in Cu 2p spectra was observed along with a negative shift (ca. 0.8 eV) for oxidized Ru species (462.8 eV) in Ru 3p spectra when the loading amount of Cu was increased compared to each monometallic catalyst. This result is inconsistent with previous studies concerning a direction of electron transfer between Ru and Cu. Previous XPS studies have proposed that an electron transfer from Ru to Cu can occur for silica supported RuCu bimetallic catalysts [32,33]. However, electron transfer from Cu to Ru has also been suggested based on infrared spectroscopy of CO adsorbed on RuCu supported on silica [34]. The result obtained in the present study indicates electron transfer is more likely to occur from Cu to Ru. Since the formation of galactitol, C4 epimer of sorbitol, was well-reported to be catalyzed by metallic sites under pressurized H₂, [35]. Hence, the suppression of galactitol formation, as shown in Fig. 3, might be due to non-zero valent Ru species formed by the electronic effect caused by Cu addition. Copper in its oxidation state of Cu²⁺ was also observed, which could be characterized by broad satellite peaks (939–946 eV and 960–965 eV) on the side of main peaks partially screened by large Cu⁺ peak [36]. Unfortunately, the oxidation state of Cu⁺ could not be characterized since photoelectron peaks for Cu⁺ overlapped with those of Cu⁺. The effect of Cu addition was further investigated by chemisorption analysis as follows.

Results of H₂- and CO-chemisorption are summarized in Table 2. As indicated in the last row of Table 2, Cu was unable to chemisorb H₂ or CO under the condition studied [37]. This corresponds well to the

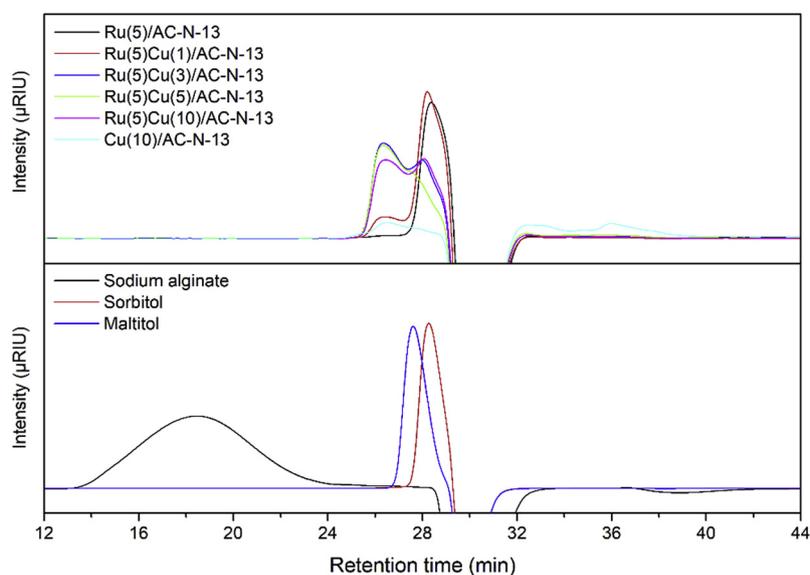


Fig. 2. GPC chromatograms of liquid products obtained over monometallic and bimetallic catalysts at 180 °C for 2 h under 50 bar of H₂.

Table 1

Textural properties of monometallic and bimetallic catalysts.

Catalyst	Specific surface area ^a (m ² /g catalyst)	Total pore volume ^a (cm ³ /g catalyst)	Acid density ^b (mmol/g catalyst)
Ru(5)/AC-N-13	642.4	0.46	1.54
Ru(5)Cu(1)/AC-N-13	670.9	0.51	1.28
Ru(5)Cu(3)/AC-N-13	637.9	0.49	1.15
Ru(5)Cu(5)/AC-N-13	588.0	0.45	1.01
Ru(5)Cu(10)/AC-N-13	510.6	0.39	0.91
Cu(10)/AC-N-13	483.7	0.38	0.84

^a Measured by N₂ adsorption-desorption.

^b Measured by back titration.

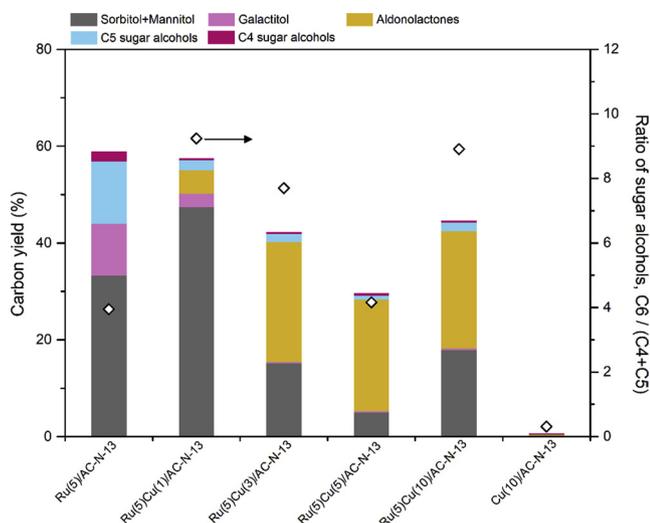


Fig. 3. Product distribution over bimetallic and monometallic carbon catalysts at 180 °C for 2 h under 50 bar of H₂. C₆ sugar alcohols: sorbitol, mannitol, and galactitol; C₅ sugar alcohols: xylitol, arabinol, and ribitol; C₄ sugar alcohols: threitol and erythritol; Aldonolactones: glucono-1,5-lactone and mannono-1,4-lactone.

inactive nature of Cu in hydrogenation of alginic acid as already shown in Fig. 3. A general trend of decrease in the amount of CO adsorbed was observed with the addition of Cu with the exception of Ru(5)Cu(10)/AC-N-13. This result implies that the number of active Ru exposed is decreased due to partial coverage of Ru surface by Cu. [7,34]. The

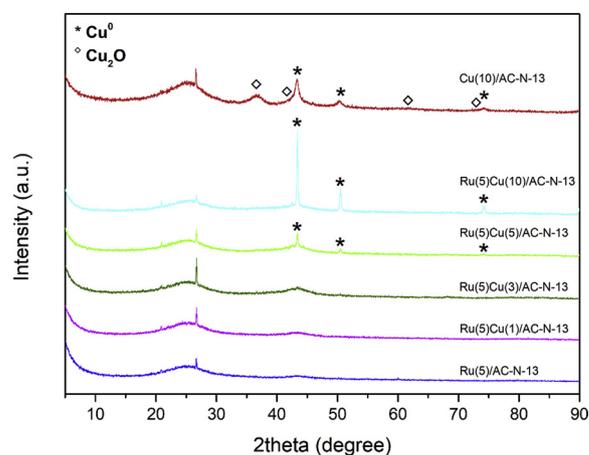


Fig. 4. XRD diffractograms of monometallic and bimetallic catalysts.

decrease in the yield of sorbitol and mannitol correlated well with the decrease in the active Ru sites measured by CO chemisorption. Similarly, with the exception of Ru(5)Cu(1)/ and Ru(5)Cu(10)/AC-N-13, the amount of hydrogen adsorbed exhibited a decreasing trend with increasing Cu content. The higher amount of hydrogen adsorption for Ru(5)Cu(1)/AC-N-13 than for Ru/AC-N-13 implies facile hydrogen spillover from Ru to Cu due to their intimate contact. [7,38,39] Thus, Ru(5)Cu(1)/AC-N-13 could retain its ability of hydrogen activation and hydrogenation, although Ru surface was partially screened by Cu. Increases in amounts of hydrogen and CO adsorption were also observed for Ru(5)Cu(10)/AC-N-13. Such increases might indicate separation of

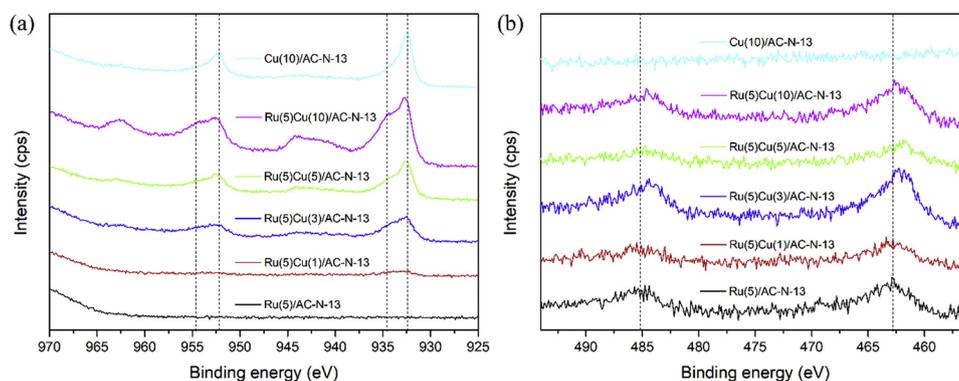


Fig. 5. XPS spectra of (a) Cu 2p and (b) Ru 3p of bimetallic and monometallic catalysts.

Cu from Ru surface at high Cu loading [6,38]. In this regard, restoration of the hydrogenation activity to some extent for Ru(5)Cu(10)/AC-N-13 could be explained by the recovery of active Ru surface. Similar behavior was further evidenced by H₂-TPR as shown below.

Reducible behavior of each catalyst was then investigated by H₂-TPR. Results are shown in Fig. 6. Monometallic Ru(5)/AC-N-13 exhibited one reduction peak at ca. 130 °C which could be assigned to the reduction of Ru species [40,41] while Cu(10)/AC-N-13 exhibited two reduction peaks: one at 192 °C and the other broader one at 261 °C that could be assigned to the reduction of Cu²⁺ to Cu⁺ and Cu⁺ to Cu⁰, respectively [42]. Interestingly, reduction peak of Ru species shifted to higher temperature by 7 °C for bimetallic Ru(5)Cu(1)/AC-N-13 compared to monometallic Ru(5)/AC-N-13. This result might indicate the presence of a strong interaction between Ru and Cu, forming bimetallic clusters [34,43]. When Cu loading amount was more than 1 wt%, the reduction peak of Ru species shifted back to ca. 130 °C and the reduction peak of CuO_x appeared. These above results further support the separation of Cu from Ru surface when Cu content was increased to more than 1 wt%. Compared to monometallic Cu catalyst which exhibited two reduction peaks, the reduction peak of Cu⁺ shifted to lower temperature for all bimetallic catalysts except Ru(5)Cu(1)/AC-N-13, resulting in one broad reduction peak near 205 °C. This might indicate the intimate contact between Cu and Ru which could give rise to facile reduction of Cu oxides with the aid of Ru by means of hydrogen spillover, thus overlapping two CuO_x reduction peaks. [44,45]

To further investigate the bimetallic interaction, XAS was conducted. Fig. 7(b) shows k²-weighted Fourier-transformed EXAFS spectra for these catalysts. For the case of Ru(5)Cu(1)/ and Ru(5)Cu(3)/AC-N-13, a backscattering peak with interatomic distance of ca. 2.55 Å was observed. This could be attributed to multiple interatomic interactions longer than Cu-O and Cu-Cu, implying RuCu bimetallic entities and a strong interaction between Cu and Ru as discussed in the H₂-TPR result [7,46]. Although the above result was similar to previous researches, the extent of the interatomic interaction between Ru and Cu was

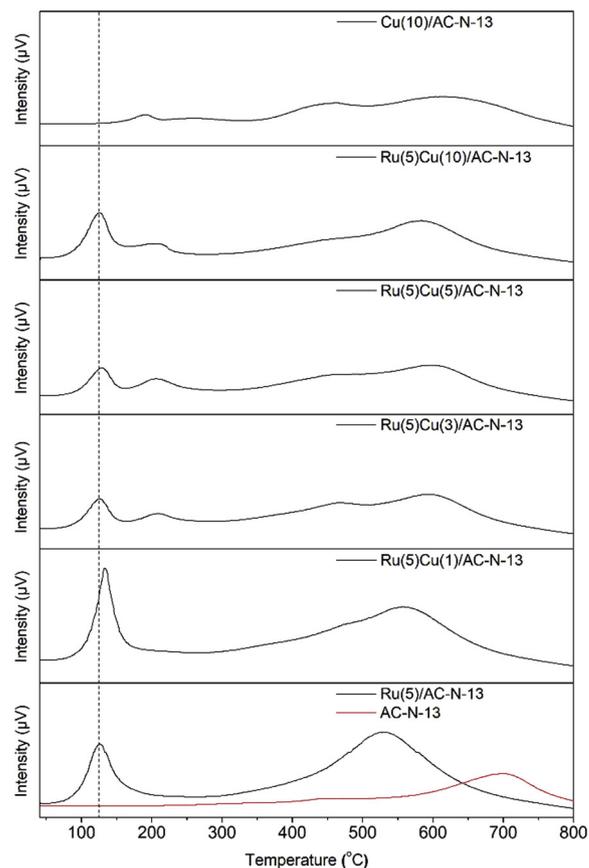


Fig. 6. H₂-TPR profiles of the support, monometallic and bimetallic catalysts.

Table 2

Metal contents of catalysts and results of H₂- and CO-Chemisorption of catalysts.

Catalyst	Actual metal contents ^a		Relative adsorbed amount of H ₂ /Ru ^b	Relative adsorbed amount of CO/Ru ^b
	Ru (%)	Cu (%)		
Ru(5)/AC-N-13	4.8	–	1.00	1.00
Ru(5)Cu(1)/AC-N-13	4.2	1.1	1.73	0.93
Ru(5)Cu(3)/AC-N-13	3.5	3.0	0.55	0.50
Ru(5)Cu(5)/AC-N-13	4.0	5.2	0.11	0.22
Ru(5)Cu(10)/AC-N-13	4.6	10.6	0.31	0.53
Cu(10)/AC-N-13	–	12.1	– ^c	0.01

^a Actual metal contents were measured by ICP-AES.

^b The values were normalized by the adsorbed amount of each adsorbate on Ru(5)/AC-N-13.

^c Slightly negative value was observed.

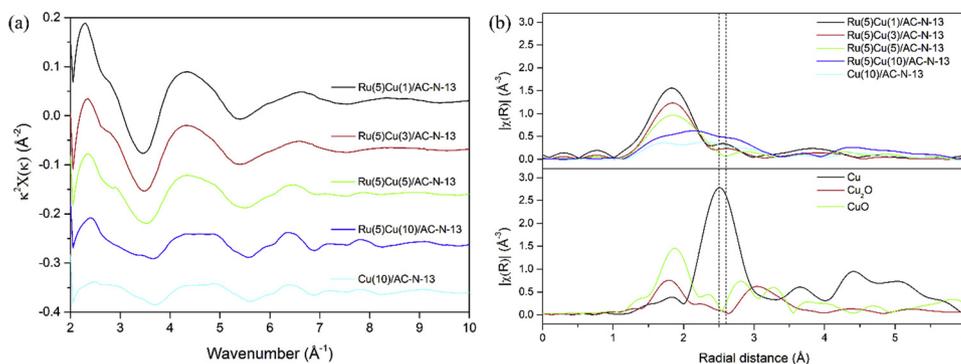


Fig. 7. (a) k^2 -weighted Cu K-edge EXAFS spectra for the catalysts and their (b) Fourier-transforms. The spectra were taken over the wave vector range of $2.1 \leq k \leq 8.9 \text{ \AA}^{-1}$.

relatively low compared to that in previous studies. There have been contradictory opinions regarding the presence of RuCu bimetallic entities. The subject of controversy includes the formation of bimetallic clusters as evidenced by EXAFS and a simple masking of active Ru surface as evidenced by H_2 -chemisorption [6]. In addition, different extent for the formation of RuCu bimetallic clusters on various supports has been previously discussed. It has been suggested that a stronger metal-support interaction can result in a lower degree of the formation of RuCu bimetallic aggregates [47]. Thus, a lower degree of the formation of RuCu bimetallic clusters in the present study compared to previous researches might be explained by a strong metal-support interaction induced by surface oxygenates of AC-N-13.

Long-term stability of a catalyst is crucial for practical application of catalysts. To investigate the durability of Cu-promoted Ru catalyst, the catalyst was subjected to repeated reactions. As shown in Fig. S2, the catalyst deactivated after each reaction. ICP result of liquid product after recycle runs indicated the leaching of Ru and Cu was negligible (less than 3%). To investigate the cause for the catalyst deactivation, N_2 adsorption-desorption was performed for spent catalysts. As summarized in Table S1, the result exhibited a general trend of decrease in specific surface area. This might indicate that carbon byproducts have been formed on the support. Hence, carbon deposition on the catalyst could be the reason for the catalyst deactivation. The above result left us a further study to design a more stable Cu-promoted bimetallic catalyst.

4. Conclusion

In conclusion, RuCu bimetallic carbon catalysts were successfully hydrogenated macroalgae-derived alginic acid into sugar alcohols, mainly sorbitol and mannitol. The addition of Cu resulted in coverage of active Ru surface and electron transfer between Ru and Cu. Furthermore, the addition of a proper amount of Cu, namely 1 wt% Cu, resulted in a strong interaction between Ru and Cu and formation of RuCu bimetallic aggregates as evidenced by H_2 -TPR and XAS. Such intimate interaction between metals facilitated hydrogen spillover from Ru to Cu, which enabled Ru to maintain its hydrogenation activity in spite of a decrease in active Ru exposed. The highest yield of target sugar alcohols was 47.4% when alginic acid was hydrogenated at 180°C for 2 h over Ru(5)Cu(1)/AC-N-13. Such RuCu bimetallic catalyst deactivated over repeated reactions owing to carbonaceous byproduct deposition on the catalyst.

Acknowledgement

This research was supported by a grant (2018R1A2B2005168) of the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcata.2019.04.003>.

References

- [1] G.W. Huber, S. Iborra, A. Corma, *Chem. Rev.* 106 (2006) 4044–4098.
- [2] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* 107 (2007) 2411–2502.
- [3] M. Makkee, A.P.G. Kieboom, H. van Bekkum, *Starch - Stärke* 37 (1985) 136–141.
- [4] C. Chatterjee, F. Pong, A. Sen, *Green Chem.* 17 (2015) 40–71.
- [5] H. Kobayashi, T. Komanoya, S.K. Guha, K. Hara, A. Fukuoka, *Appl. Catal. A Gen.* 409–410 (2011) 13–20.
- [6] E. Asedegbega-Nieto, B. Bachiller-Baeza, A. Guerrero-Ruiz, I. Rodríguez-Ramos, *Appl. Catal. A Gen.* 300 (2006) 120–129.
- [7] J. Liu, L.L. Zhang, J. Zhang, T. Liu, X.S. Zhao, *Nanoscale* 5 (2013) 11044–11050.
- [8] J.H. Sinfelt, *J. Catal.* 29 (1973) 308–315.
- [9] A.J. Rouco, G.L. Haller, J.A. Oliver, C. Kemball, *J. Catal.* 84 (1983) 297–307.
- [10] S. Bhatia, X. Wu, D.K. Sanders, B.C. Gerstein, M. Pruski, T.S. King, *Catal. Today* 12 (1992) 165–175.
- [11] S. Behera, R. Singh, R. Arora, N.K. Sharma, M. Shukla, S. Kumar, *Front. Bioeng. Biotechnol.* 2 (2015).
- [12] F. Alam, S. Mobin, H. Chowdhury, *Procedia Eng.* 105 (2015) 763–768.
- [13] W. Jeon, C. Ban, G. Park, J.E. Kim, H.C. Woo, D.H. Kim, *Catal. Surv. From Asia* 20 (2016) 195–209.
- [14] W. Jeon, C. Ban, G. Park, T.-K. Yu, J.-Y. Suh, H.C. Woo, D.H. Kim, *J. Mol. Catal. A Chem.* 399 (2015) 106–113.
- [15] G. Park, W. Jeon, C. Ban, H.C. Woo, D.H. Kim, *Energy Convers. Manage.* 118 (2016) 135–141.
- [16] C. Ban, W. Jeon, G. Park, H.C. Woo, D.H. Kim, *ChemCatChem* 9 (2017) 329–337.
- [17] W. Jeon, C. Ban, G. Park, H.C. Woo, D.H. Kim, *Catal. Today* 265 (2016) 154–162.
- [18] W. Jeon, C. Ban, G. Park, H.C. Woo, D.H. Kim, *Catal. Sci. Technol.* 6 (2016) 1146–1156.
- [19] W. Jeon, C. Ban, J.E. Kim, H.C. Woo, D.H. Kim, *J. Mol. Catal. A Chem.* 423 (2016) 264–269.
- [20] C. Ban, W. Jeon, H.C. Woo, D.H. Kim, *ChemSusChem* 10 (2017) 4891–4898.
- [21] L. Yang, J. Su, S. Carl, J.G. Lynan, X. Yang, H. Lin, *Appl. Catal. B: Environ.* 162 (2015) 149–157.
- [22] F. Rodríguez-reinoso, *Carbon* 36 (1998) 159–175.
- [23] L. Chen, Y. Zhu, H. Zheng, C. Zhang, B. Zhang, Y. Li, *J. Mol. Catal. A Chem.* 351 (2011) 217–227.
- [24] X. Zhang, L.J. Durdell, M.A. Isaacs, C.M.A. Parlett, A.F. Lee, K. Wilson, *ACS Catal.* 6 (2016) 7409–7417.
- [25] A. Fukuoka, P.L. Dhepe, *Angew. Chem. Int. Ed.* 45 (2006) 5161–5163.
- [26] H. Kobayashi, T. Komanoya, K. Hara, A. Fukuoka, *ChemSusChem* 3 (2010) 440–443.
- [27] J.L. Figueiredo, *Chem. A* 1 (2013) 9351–9364.
- [28] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, F. Rodríguez-Reinoso, J. Rouquerol, K.S. Sing, *Pure Appl. Chem.* 87 (2015) 1051–1069.
- [29] S. Chen, H. Zhang, L. Wu, Y. Zhao, C. Huang, M. Ge, Z. Liu, *J. Mater. Chem.* 22 (2012) 9117–9122.
- [30] T. Komanoya, H. Kobayashi, K. Hara, W.-J. Chun, A. Fukuoka, *Appl. Catal. A Gen.* 407 (2011) 188–194.
- [31] D.J. Morgan, *Surf. Interface Anal.* 47 (2015) 1072–1079.
- [32] M.C. Schoenmaker-Stolk, J.W. Verwijs, J.J.F. Scholten, *Appl. Catal.* 30 (1987) 339–352.
- [33] T. Jiang, Y. Zhou, S. Liang, H. Liu, B. Han, *Green Chem.* 11 (2009) 1000–1006.
- [34] R. Liu, B. Tesche, H. Knözinger, *J. Catal.* 129 (1991) 402–413.
- [35] P.J.C. Hausoul, L. Negahdar, K. Schute, R. Palkovits, *ChemSusChem* 8 (2015) 3323–3330.
- [36] J.P. Espinós, J. Morales, A. Barranco, A. Caballero, J.P. Holgado, A.R. González-Elipe, *J. Phys. Chem. B* 106 (2002) 6921–6929.
- [37] D.W. Goodman, C.H.F. Peden, *J. Catal.* 95 (1985) 321–324.
- [38] X. Wu, B.C. Gerstein, T.S. King, *J. Catal.* 121 (1990) 271–293.
- [39] Z. Wu, Y. Mao, X. Wang, M. Zhang, *Green Chem.* 13 (2011) 1311–1316.

- [40] J. Jae, W. Zheng, R.F. Lobo, D.G. Vlachos, *ChemSusChem* 6 (2013) 1158–1162.
- [41] H. Kobayashi, H. Matsuhashi, T. Komanoya, K. Hara, A. Fukuoka, *Chem. Commun. (Camb.)* 47 (2011) 2366–2368.
- [42] G. Zhang, Z. Li, H. Zheng, T. Fu, Y. Ju, Y. Wang, *Appl. Catal. B: Environ.* 179 (2015) 95–105.
- [43] J. Álvarez-Rodríguez, A. Guerrero-Ruiz, I. Rodríguez-Ramos, A. Arcoya-Martín, *Microporous Mesoporous Mater.* 97 (2006) 122–131.
- [44] S. Galvagno, C. Crisafulli, R. Maggiore, A. Giannetto, J. Schwank, *J. Therm. Anal.* 32 (1987) 471–483.
- [45] E.S. Vasiliadou, A.A. Lemonidou, *Appl. Catal. A Gen.* 396 (2011) 177–185.
- [46] D. Chakraborty, C.D. Damsgaard, H. Silva, C. Conradsen, J.L. Olsen, H.W.P. Carvalho, B. Mutz, T. Bligaard, M.J. Hoffmann, J.-D. Grunwaldt, F. Studt, I. Chorkendorff, *Angew. Chem. Int. Ed.* 56 (2017) 8711–8715.
- [47] C. Crisafulli, S. Galvagno, R. Maggiore, S. Scirè, A. Saeli, *Catal. Lett.* 6 (1990) 77–83.