Conversion of Succinic Acid to 1,4-Butanediol via Dimethyl Succinate Over Rhenium Nano-Catalyst Supported on Copper-Containing Mesoporous Carbon

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Copper-containing mesoporous carbons (XCu-MC) with different copper content ($X = 8.0$, 12.7, 15.9, 23.3, and 26.8 wt%) were prepared by a single-step surfactant-templating method. Rhenium nano-catalysts supported on copper-containing mesoporous carbons (Re/XCu-MC) were then prepared by an incipient wetness method. Re/XCu-MC ($X = 8.0$, 12.7, 15.9, 23.3, and 26.8 wt%) catalysts were characterized by nitrogen adsorption-desorption isotherm, HR-TEM, FT-IR, and H_2-TPR analyses. Liquid-phase hydrogenation of succinic acid to 1,4-butanediol (BDO) via dimethyl succinate (DMS) was carried out over Re/XCu-MC catalysts in a batch reactor. The effect of copper content on the physicochemical properties and catalytic activities of Re/XCu-MC catalysts in the hydrogenation of succinic acid to BDO was investigated. Re/XCu-MC catalysts retained different physicochemical properties depending on copper content. In the hydrogenation of succinic acid to BDO, yield for BDO showed a volcano-shaped trend with respect to copper content. Thus, an optimal copper content was required to achieve maximum catalytic performance of Re/XCu-MC. It was also observed that yield for BDO increased with increasing the amount of hydrogen consumption by copper in the Re/XCu-MC catalysts.

Keywords: Mesoporous Carbon, Succinic Acid, 1,4-Butanediol, Copper Catalyst, Rhenium Nano-Catalyst.

1. INTRODUCTION

1,4-Butanediol (BDO) is used as a desirable solvent in plastic and elastic fiber industries.[1,2] BDO is currently produced from several feedstocks, such as maleic anhydride, acetylene, and propylene oxide.[3–5] However, these petrochemical-based feedstocks have economical and environmental problems.[6] Therefore, demand for finding a cheap and clean feedstock for the production of BDO has continuously increased.

Recently, succinic acid (SA) has attracted much attention as a cheap and bio-derived chemical that can be converted into BDO.[7,8] It has been reported that hydrogenation of dicarboxylic acid with alcohol can yield diol via alkyl oxalate.[9] In the same manner, SA can react with methanol to produce BDO via dimethyl succinate (DMS) (Fig. 1). It is known that rhenium-based catalysts are efficient for methylation of SA to DMS.[10] However, strong

activity for demethylation of DMS to BDO is also required for efficient production of BDO from SA. Therefore, it is important to find a suitable catalyst that has both methylation activity (SA → DMS) and demethylation activity (DMS → BDO) in the BDO production from SA. It has also been reported that copper-based catalysts are efficient for demethylation of DMS to BDO.[11–13] Thus, a rhenium-copper bimetal catalyst can be a potential candidate for the production of BDO from SA.

Mesoporous carbon has found successful applications as a support due to its well-developed porosity and hydrophobic property.[14] It has been reported that metal-containing mesoporous carbon prepared by a single-step surfactant-templating method can produce finely dispersed metal particles on the carbon surface.[15] Therefore, it is expected that copper-containing mesoporous carbon prepared by a single-step surfactant-templating method can serve as a catalyst and as a supporting material for rhenium at the same time.

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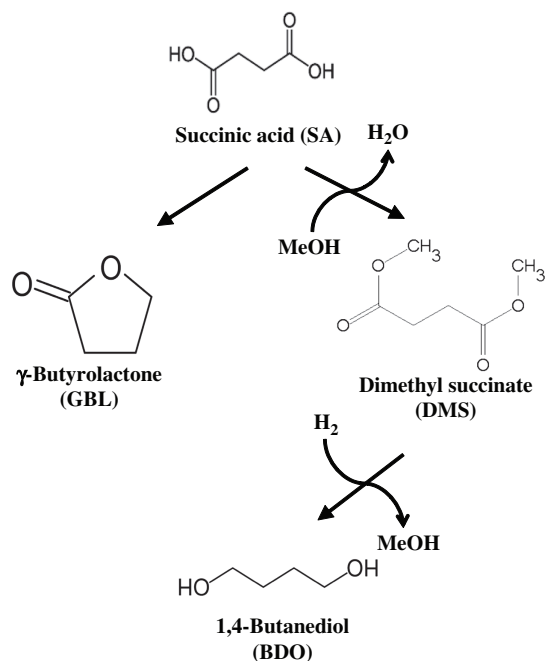
Figure 1. Reaction pathways for the conversion of succinic acid (SA) to 1,4-butanediol (BDO) via dimethyl succinate (DMS).

In this work, copper-containing mesoporous carbons (XCu-MC) with different copper content ($X = 8.0$, 12.7, 15.9, 23.3, and 26.8 wt%) were prepared by a single-step surfactant-templating method. Rhenium nano-catalysts supported on copper-containing mesoporous carbons (Re/XCu-MC) were then prepared by an incipient wetness method. Re/XCu-MC catalysts were characterized by nitrogen adsorption-desorption isotherm, HR-TEM, FT-IR, and H_2-TPR analyses. Liquid-phase hydrogenation of succinic acid (SA) to 1,4-butanediol (BDO) was carried out over Re/XCu-MC catalysts in a batch reactor. The effect of copper content on the physicochemical properties and catalytic activities of Re/XCu-MC catalysts was investigated.

2. EXPERIMENTAL DETAILS
2.1. Preparation of Supported Rhenium Catalysts (Re/XCu-MC)
Sucrose (Aldrich, 0.8 g), P123 (Aldrich, 1.6 g), and copper nitrate (Aldrich, 0.1, 0.2, 0.3, 0.4, and 0.5 g) were dissolved in 4 M HCl solution (30 ml) at 40 °C for 4 h under stirring. After a silica precursor (TEOS, 3.6 ml, Aldrich) was slowly added into the solution, the resultant was dried overnight at 100 °C. After filtering and washing the resulting precipitate with de-ionized water, it was dried at 80 °C to obtain a sucrose/copper/surfactant/silica composite. The 2 g of composite was treated with 40 ml of 0.4 M H_2SO_4 solution for 12 h. After drying the mixture at 160 °C for 8 h, the obtained brown solid was carbonized at 800 °C for 4 h at a heating rate of 5 °C/min in a nitrogen stream (100 ml/min). The solid product was further treated with

5 wt% HF solution to remove silica template. The resulting copper-containing mesoporous carbon was denoted as XCu-MC ($X = 8.0$, 12.7, 15.9, 23.3, and 26.8), where X represented weight percentage of copper determined by ICP-AES analysis. Rhenium nano-catalyst supported on copper-containing mesoporous carbon (Re/XCu-MC) was prepared by an incipient wetness impregnation method using an acetone solution of rhenium chloride ($ReCl_5$, Aldrich). Rhenium loading was fixed at 5 wt% in all the catalysts. The supported catalyst was calcined at 600 °C, and it was reduced with a mixed stream of hydrogen (2.5 ml/min) and nitrogen (47.5 ml/min) at 600 °C for 4 h prior to characterization and catalytic reaction.

2.2. Characterization
Surface areas and pore volumes of supported rhenium catalysts (Re/XCu-MC, $X = 8.0$, 12.7, 15.9, 23.3, and 26.8) were calculated using the BET equation and the BJH model, respectively, from nitrogen adsorption-desorption measurements (ASAP2010, Micromeritics). Surface morphologies of Re/XCu-MC catalysts were examined by HR-TEM (Jeol, JEM-3000F) analysis. FT-IR spectra of Re/XCu-MC catalysts were obtained with a Thermo Nicolet 6700 spectrometer. The amount of hydrogen consumption and reduction peak temperature of Re/XCu-MC catalysts were examined by H_2-TPR (temperature-programmed reduction) experiments using a conventional flow system equipped with a TCD (thermal conductivity detector) at temperatures ranging from 25 to 900 °C with a ramping rate of 5 °C/min. For the TPR measurements, a mixed stream of H_2 (2 ml/min) and N_2 (20 ml/min) was employed for 0.05 g of catalyst sample.

2.3. Hydrogenation of Succinic Acid
Liquid-phase hydrogenation of succinic acid (SA) to 1,4-butanediol (BDO) was carried out over Re/XCu-MC catalysts ($X = 8.0$, 12.7, 15.9, 23.3, and 26.8) in a batch reactor at 200 °C and 80 bar (H_2). Succinic acid (0.5 g), methanol (25 ml), and a reduced catalyst (0.2 g) were charged into an autoclave (150 ml). 1,4-Dioxane (25 ml) was used as a solvent for the reaction. The reactor was purged with nitrogen to remove air, and it was then pressurized up to 40 bar using hydrogen. After heating the reactor to reaction temperature (200 °C), hydrogen pressure was raised up to 80 bar. The catalytic reaction was carried out for 20 h. The reaction mixture was stirred at 700 rpm in order to avoid mass transfer limitation. Reaction products were analyzed using a gas chromatograph (Younglin, ACME-6100) equipped with a FID (flame ionization detector).

3. RESULTS AND DISCUSSION
### 3.1. Morphology and FT-IR Studies of Supported Rhenium Catalysts (Re/XCu-MC)
HR-TEM images of Re/XCu-MC catalysts ($X = 8.0$, 12.7, 15.9, 23.3, and 26.8) reduced at 600 °C are shown in
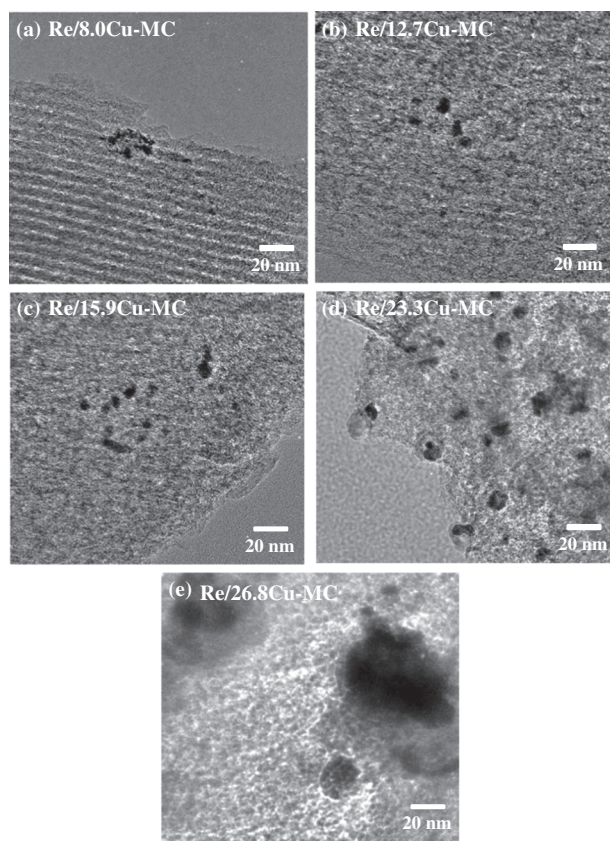
Figure 2. HR-TEM images of supported rhenium catalysts (Re/XCu-MC) reduced at 600 °C.

Figure 2. Re/XCu-MC (X = 8.0, 12.7, and 15.9) catalysts retained a 2-dimensional ordered carbon nanorod array, while Re/XCu-MC (X = 23.3 and 26.8) catalysts had a collapsed carbon structure. As a consequence, Re/XCu-MC (X = 8.0, 12.7, and 15.9) catalysts retained finely dispersed small metal particles (less than 10 nm), while Re/XCu-MC (X = 23.3 and 26.8) catalysts had large metal aggregates (more than 15 nm).

Figure 3 shows the FT-IR spectra of Re/XCu-MC catalysts reduced at 600 °C. Re/XCu-MC (X = 8.0, 12.7, and 15.9) showed three characteristic IR bands at 967 cm^{-1} (C—O—C), 1352 cm^{-1} (–OH), and 1639 cm^{-1} (C=O), while Re/XCu-MC (X = 23.3 and 26.8) catalysts showed only two characteristic IR bands at 1352 cm^{-1} (–OH) and 1639 cm^{-1} (C=O). Because copper nanoparticles tend to aggregate, it is important to form an interaction between copper and carbon for fine dispersion of copper in the copper-carbon composite material. It is believed that C—O—C bond on the surface of carbon nanorods played an important role in overcoming Van der Waal's force between carbons,[16] leading to a strong interaction between copper precursor and carbon atoms during the preparation step. In other words, the presence of C—O—C bond gives rise to the well incorporation of copper into carbon framework in the Cu-MC support. Therefore, Re/XCu-MC
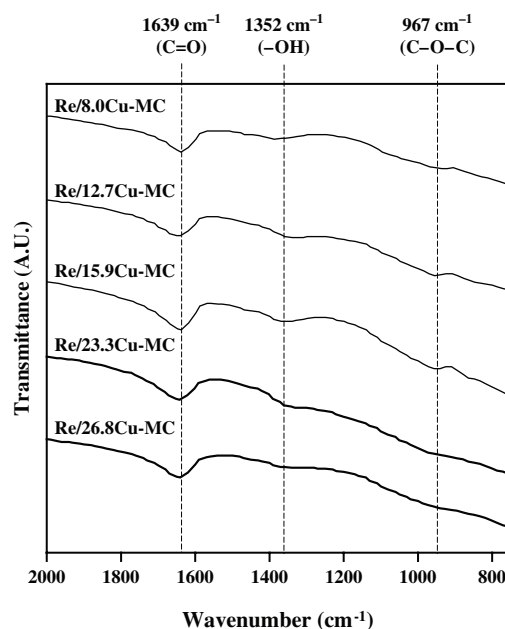

Figure 3. FT-IR spectra of supported rhenium catalysts (Re/XCu-MC) reduced at 600 °C.

(X = 8.0, 12.7, and 15.9) catalysts containing C—O—C bond retained an ordered pore structure and fine metal dispersion. However, an excess amount of copper in the Re/23.3Cu-MC and Re/26.8Cu-MC prohibited the formation of C—O—C bond and suppressed the formation of ordered copper-carbon structure, leading to large metal aggregation and pore blocking. Thus, TEM and FT-IR results revealed that an optimal copper content was required to obtain ordered mesoporous structure and fine metal dispersion of the catalysts.

3.2. Physicochemical Properties of Supported Rhenium Catalysts (Re/XCu-MC)

Nitrogen adsorption–desorption isotherms and textural properties of Re/XCu-MC catalysts (X = 8.0, 12.7, 15.9,
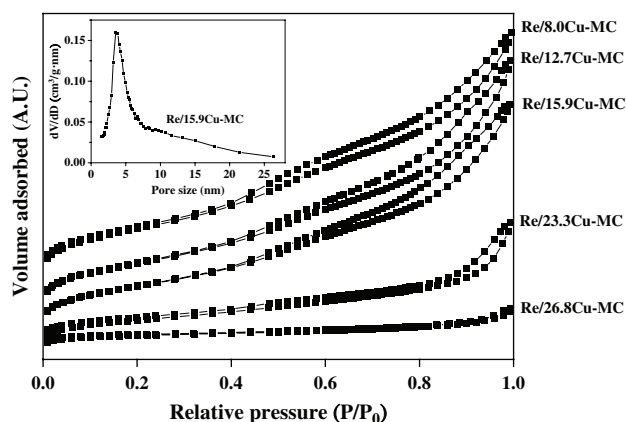
Figure 4. Nitrogen adsorption-desorption isotherms of supported rhenium catalysts (Re/XCu-MC) reduced at 600 °C.

Table I. Physicochemical properties of Re/XCu-MC catalysts.

|	Surface area $(m^2/g\text{-cat.})$	Pore volume $(cm^3/g\text{-cat.})$	Average pore size (nm)	Amount of hydrogen consumption by rhenium (mmol/g-cat.)	Amount of hydrogen consumption by copper (mmol/g-cat.)
Re/8.0Cu-MC	865	1.26	5.5	7.9	5.4
Re/12.7Cu-MC	840	1.30	5.5	7.4	16.8
Re/15.9Cu-MC	771	1.17	5.5	7.0	25.1
Re/23.3Cu-MC	412	0.61	5.2	6.2	4.2
Re/26.8Cu-MC	339	0.33	3.9	4.1	2.3

23.3, and 26.8) are presented in Figure 4 and Table I, respectively. All the Re/XCu-MC catalysts exhibited type-IV isotherms. With decreasing copper content, more apparent type-H3 hysteresis loop indicating the existence of mesopores was developed.[17] Surface area of Re/XCu-MC catalysts decreased with increasing copper content. Average pore size of Re/XCu-MC catalysts was in the mesopore range (3.9–5.5 nm). Re/XCu-MC ($X = 8.0$, 12.7, and 15.9) catalysts retained high surface area (865, 840, and 771 m^2/g, respectively) and large pore volume (1.26, 1.30, and 1.17 cm^3/g, respectively), while Re/XCu-MC ($X = 23.3$ and 26.8) catalysts had low surface area (412 and 339 m^2/g, respectively) and small pore volume (0.61 and 0.33 cm^3/g, respectively). These results indicate that copper in the Re/XCu-MC ($X = 8.0$, 12.7, and 15.9) catalysts was well incorporated into carbon framework, resulting in high surface area and large pore volume. As described earlier, however, an excess amount of copper in the Re/XCu-MC ($X = 23.3$ and 26.8) catalysts did not cause a strong interaction between copper and carbon framework during the preparation step, leading to the pore blocking by copper aggregation.

TPR results of Re/XCu-MC ($X = 8.0$, 12.7, 15.9, 23.3, and 26.8) catalysts are presented in Figure 5 and Table I. TPR profiles of Re/XCu-MC ($X = 8.0$, 12.7, 15.9, 23.3, and 26.8) catalysts revealed that there were two hydrogen consumption peaks (reduction peaks) appearing at 270–310 °C and 450–600 °C, which were attributed to the reduction of rhenium and copper species, respectively. Reduction peak temperature of rhenium in the Re/XCu-MC ($X = 8.0$, 12.7, 15.9, 23.3, and 26.8) catalysts showed a slight difference. However, reduction temperature of copper in the Re/XCu-MC ($X = 8.0$, 12.7, and 15.9) catalysts significantly increased with increasing copper content. It has been reported that single-step self assembly synthesis of binary materials caused a strong interaction during the preparation step.[18] Therefore, it is believed that the interaction between copper species and carbon framework in the XCu-MC ($X = 8.0$, 12.7, and 15.9) increased with increasing copper content, leading to an increased reduction temperature of copper with increasing copper content. On the other hand, although large amount of copper included, Re/XCu-MC ($X = 23.3$ and 26.8) showed low reduction temperature of copper (498 °C and 452 °C, respectively) due to a weak interaction between carbon species and copper aggregation. As listed in Table I, the

amount of hydrogen consumption by rhenium (calculated from TPR peak area) in the Re/XCu-MC ($X = 8.0$, 12.7, 15.9, 23.3, and 26.8) catalysts decreased with increasing copper content due to the decrease of metal dispersion. It was observed that the amount of hydrogen consumption by copper increased with increasing copper content in the Re/XCu-MC ($X = 8.0$, 12.7, and 15.9) catalysts. However, the amount of hydrogen consumption by copper in the Re/XCu-MC ($X = 23.3$ and 26.8) was much smaller than that in the Re/XCu-MC ($X = 8.0$, 12.7, and 15.9) due to the copper aggregation. From Table I, it should be noted that the amount of hydrogen consumption by copper in the Re/XCu-MC ($X = 8.0$, 12.7, 15.9, 23.3, and 26.8) showed a volcano-shaped trend with respect to copper content. The above results indicate that physicochemical properties could be controlled by changing the amount of copper content in the Re/XCu-MC catalysts.

### 3.3. Hydrogenation of Succinic Acid to 1,4-Butanediol (BDO) Over Supported Rhenium Nano-Catalysts (Re/XCu-MC)

Catalytic activities of Re/XCu-MC catalysts ($X = 8.0$, 12.7, 15.9, 23.3, and 26.8) in the liquid-phase hydrogenation of succinic acid (SA) are summarized in Table II. 1,4-Butanediol (BDO) was produced as a target product and dimethyl succinate (DMS) was produced as
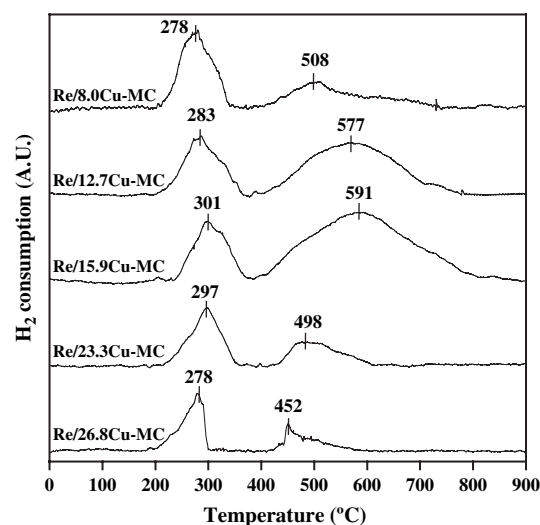
Figure 5. TPR profiles of supported rhenium catalysts (Re/XCu-MC) calcined at 600 °C.

Table II. Catalytic performance of Re/XCu-MC catalysts in the liquid-phase hydrogenation of succinic acid (reaction temperature = 200 °C, reaction pressure = 80 bar, reaction time = 20 h).

	Conversion of SA (%)	Yield (%)		
		BDO	DMS	GBL
Re/8.0Cu-MC	100	6.2	83.6	10.2
Re/12.7Cu-MC	100	7.7	79.8	12.5
Re/15.9Cu-MC	100	11.3	65.4	23.3
Re/23.3Cu-MC	100	5.7	86.3	8.0
Re/26.8Cu-MC	100	4.2	91.1	4.6

an intermediate via methylation of SA with methanol. Cyclization of SA and DMS by rhenium component of the catalysts produced γ-butyrolactone (GBL) as a by-product as shown in Figure 1. All the catalysts exhibited a complete conversion (100%) of SA. This means that the catalytic function of rhenium was sufficient in the liquid-phase hydrogenation of SA to DMS over Re/XCu-MC catalysts. However, yield for BDO showed a volcano-shaped trend with respect to copper content. This means that an optimal copper content was required for maximum catalytic performance. Among the catalyst tested, Re/15.9Cu-MC catalyst showed the highest yield for BDO (11.3%). The enhanced catalytic performance of Re/15.9Cu-MC might be due to the largest amount of hydrogen consumption by copper. It has been reported that hydrogen consumption by metal for reduction plays an important role in determining the catalytic performance in the liquid-phase hydrogenation of succinic acid.[18] It has also been reported that dealkylation of alkyl oxalate is a rate-determining step in the hydrogenation of dicarboxylic acid with alcohol.[19] Therefore, it is believed that the excellent catalytic performance of Re/15.9Cu-MC catalyst was due to the largest amount of hydrogen consumption by copper and the enhanced demethylation activity of copper from DMS to BDO.
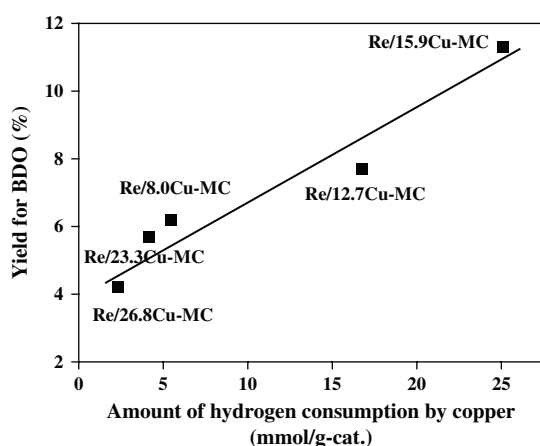
Figure 6. A correlation between the amount of hydrogen consumption by copper and catalytic activity of Re/XCu-MC catalysts in the hydrogenation of SA to BDO.

In order to investigate the effect of hydrogen consumption by copper in the Re/XCu-MC (X = 8.0, 12.7, 15.9, 23.3, and 26.8) catalysts on the catalytic activity in the hydrogenation of SA, a correlation between the amount of hydrogen consumption by copper in the Re/XCu-MC catalysts and yield for BDO was established. Figure 6 shows the correlation between the amount of hydrogen consumption by copper and yield for BDO in the hydrogenation of SA. The correlation clearly shows that yield for BDO increased with increasing the amount of hydrogen consumption by copper. This result strongly supports that the capacity of hydrogen consumption by copper served as a key factor determining the catalytic activity in the hydrogenation of SA to BDO over Re/XCu-MC catalysts.

4. CONCLUSIONS

Copper-containing mesoporous carbons (XCu-MC) with different copper content (X = 8.0, 12.7, 15.9, 23.3, and 26.8 wt%) were prepared by a single-step surfactant-templating method. Rhenium nano-catalysts supported on copper-containing mesoporous carbons (Re/XCu-MC, X = 8.0, 12.7, 15.9, 23.3, and 26.8) were then prepared by an incipient wetness method. Physicochemical properties of Re/XCu-MC (X = 8.0, 12.7, 15.9, 23.3, and 26.8 wt%) were affected by copper content. The amount of hydrogen consumption by copper in the Re/XCu-MC (X = 8.0, 12.7, 15.9, 23.3, and 26.8) showed a volcano-shaped trend with respect to copper content. In the liquid-phase hydrogenation of SA to BDO, yield for BDO also showed a volcano-shaped trend with respect to copper content. Yield for BDO increased with increasing the amount of hydrogen consumption by copper in the Re/XCu-MC catalysts. It is concluded that an optimal copper content was required to achieve maximum catalytic performance of Re/XCu-MC catalysts in the hydrogenation of SA to BDO.

References and Notes

1. H. Haitao, Y. Zhao, C. Gao, Y. Wang, Z. Sun, and X. Liang, *Chem. Eng. J.* 181–182, 501 (**2012**).
2. R. Marín, A. Alla, A. M. de Ilarduya, and S. Muñoz-Guerra, *J. Appl. Polym. Sci.* 123, 986 (**2012**).
3. C. I. Meyer, A. J. Marchi, A. Monzon, and T. F. Garetto, *Appl. Catal. A-Gen.* 367, 122 (**2009**).
4. L.-F. Chen, P.-J. Guo, L.-J. Zhu, M.-H. Qiao, W. Shen, H.-L. Xu, and K.-N. Fan, *Appl. Catal. A-Gen.* 356, 129 (**2009**).
5. J. Xu and B.-H. Guo, *Biotechnol. J.* 5, 1149 (**2010**).
6. U. G. Hong, S. Hwang, J. G. Seo, J. Yi, and I. K. Song, *Catal. Lett.* 138, 28 (**2010**).
7. R. Luque, J. H. Clark, K. Yoshida, and P. L. Gai, *Chem. Commun.* 5305 (**2009**).
8. P. Gallezot, *Chem. Soc. Rev.* 41, 1538 (**2012**).
9. L. Rosi, M. Frediani, and P. Frediani, *J. Org. Chem.* 695, 1314 (**2010**).

10. J. R. Budge, T. G. Attig, and R. A. Dubbert, U. S. Patent No. 5,969,164 **(1999)**.

11. C. Ohlinger and B. Kraushaar-Czarnetzki, *Chem. Eng. Sci.* 58, 1453 **(2003)**.

12. G. Ding, Y. Zhu, H. Zheng, H. Chen, and Y. Li, *J. Chem. Technol. Biot.* 86, 231 **(2011)**.

13. J. H. Schlander and T. Turek, *Ind. Eng. Chem. Res.* 38, 1264 **(1999)**.

14. U. G. Hong, D. R. Park, S. Park, J. G. Seo, Y. Bang, S. Hwang, M. H. Youn, and I. K. Song, *Catal. Lett.* 132, 377 **(2009)**.

15. X. Song, Y. Ding, W. Chen, W. Dong, Y. Pei, and J. Zang, *Catal. Commun.* 19, 100 **(2012)**.

16. S. K. Singhal, M. Lal, I. Sharma, and R. B. Mathur, *J. Compos. Mater.* 0, 1 **(2012)**.

17. K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquérol, and T. Siemieniewska, *Pure Appl. Chem.* 57, 602 **(1985)**.

18. U. G. Hong, H. W. Park, J. Lee, S. Hwang, J. Yi, and I. K. Song, *Appl. Catal. A-Gen.* 415–416, 141 **(2012)**.

19. M. C. van Engelen, H. T. Teunissen, J. G. de Vries, and C. J. Elsvier, *J. Mol. Catal. A-Chem.* 206, 185 **(2003)**.