Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Z. Zhang, Q. Yang, H. Chen, K. Chen, X. Lu, O. Pingkai, J. Fu and J. G. Chen, *Green Chem.*, 2017, DOI: 10.1039/C7GC02774E.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/green-chem

Published on 13 October 2017. Downloaded by University of Newcastle on 13/10/2017 17:51:09.

In-situ Hydrogenation and Decarboxylation of Oleic Acid into Heptadecane over a Cu-Ni Alloy Catalyst using Methanol as **Hydrogen Carrier**

Zihao Zhang^a, Qiwei Yang^a, Hao Chen^a, Kequan Chen^d, Xiuyang Lu^a, Pingkai Ouyang^{a, d},

Jie Fu^{a, b, c}*, Jingguang G. Chen^{b, c}*

^a Kev Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China ^b Department of Chemical Engineering, Columbia University, New York 10027, USA ^c Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973,

USA

State Key Laboratory of Materials-Oriented Chemical Engineering, College of Biotechnology and Pharmaceutical Engineering, Nanjing Tech University, Nanjing 211816, China

* Corresponding author

Jie Fu, Tel: +86-571-87951065, E-mail address: jiefu@zju.edu.cn

Green Chemistry Accepted Manuscript

Jingguang Chen, Tel: +1-212-854-6166, Email address: jgchen@columbia.edu

Abstract: In this work, supported Cu-Ni bimetallic catalysts were synthesized and evaluated for the in-situ hydrogenation and decarboxylation of oleic acid using methanol as a hydrogen donor. The supported Cu-Ni alloy exhibited a significant improvement in both activity and selectivity towards the production of heptadecane in comparison to monometallic Cu and Ni based catalysts. The formation of Cu-Ni alloy is demonstrated dark-field high-angle annular scanning transmission electron microscopy by (HADDF-STEM), energy dispersive X-ray spectroscopy (EDS-mapping), X-ray diffraction (XRD) and temperature programmed reduction (TPR). A partially oxidized Cu in the Cu-Ni alloy is revealed by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) following CO adsorption and X-ray photoelectron spectroscopy (XPS). desorption Temperature programmed of ethylene and propane (ethylene/propane-TPD) suggested that the formation of the Cu-Ni alloy inhibited the cracking of C-C bonds compared to Ni, and remarkably increased the selectivity to heptadecane. Temperature programmed desorption of acetic acid (acetic acid-TPD)

Green Chemistry Accepted Manuscript

Published on 13 October 2017. Downloaded by University of Newcastle on 13/10/2017 17:51:09.

indicated that bimetallic Cu-Ni alloy and Ni catalysts had stronger adsorption of acetic acid than that of the Cu catalyst. The formation of the Cu-Ni alloy and a partially oxidized Cu facilitates the decarboxylation reaction and inhibits the cracking reaction of C-C bonds, leading to enhanced catalytic activity and selectivity.

Keyword: Oleic acid; Methanol; In-situ hydrogenation and decarboxylation; Heptadecane; Copper-Nickel alloy.

1. Introduction

Biodiesel, as an alternative for conventional fuel, has attracted considerable attention. The first generation of biodiesel was fatty acid (methyl) esters (FAME). However, the high cloud point and pour points of FAME as well as engine compatibility issues limit their applications in some geographical areas during cold weather.¹ The second generation biodiesel products consist of hydrocarbons. These products can successfully solve the cloud and pour point issues and also meet the requirements set by the European diesel fuel standard (EN590).² Therefore, the removal of oxygen is a vital step to produce the second

generation biodiesel and the hydrodeoxygenation (HDO) processes have been extensively

Page 4 of 31

Green Chemistry Accepted Manuscript

applied to achieve this goal.^{3, 4} However, HDO typically requires a considerable amount of molecular hydrogen because oxygen is removed in the form of H₂O, which potentially hinders its development and applications at a large scale.^{1,5} To solve this issue, Murzin et al.^{6, 7} firstly reported a direct decarboxylation of lipids to produce paraffin and a high conversion of fatty acid was achieved, but the conversion rate of fatty acid ester was still low. Afterwards, Fu et al. proposed consecutive steps of hydrolysis of fatty acid ester to fatty acid, followed by decarboxylation of fatty acid to corresponding n-alkanes. Up to the present, both precious and non-precious metal catalysts, such as Pt, Pd and Ni, showed good activity to produce corresponding alkanes from saturated fatty acids with no H₂ added.8-16

Compared to saturated fatty acids, the deoxygenation of unsaturated fatty acids that widely exist in the hydrolysate products of lipids is much more difficult to occur. For example, the selectivity of n-alkanes could be achieved to more than 90% from the corresponding saturated fatty acid (stearic, palmitic and lauric acid) over Pt/C, however,

View Article Online DOI: 10.1039/C7GC02774E

Green Chemistry Accepted Manuscript

the unsaturated fatty acids (oleic and linoleic acid) exhibited a low yield of 9.2% for the decarboxylation products.¹⁷ The deoxygenation of unsaturated acid involves the hydrogenation of double bonds, followed by the decarboxylation of saturated acid to produce hydrocarbons.^{8, 18, 19} The hydrogenation of double bonds still needs to consume a Vardon et al.²⁰ reported the in-situ hydrogenation and large amount of hydrogen. decarboxylation of oleic acid with glycerol as a hydrogen donor, but the activity was significantly influenced by the initial hydrogen pressure. As the initial hydrogen pressure increased, the yield of heptadecane increased from 7% (0 MPa initial H₂ pressure) to 83% $(5.17 \text{ Mpa initial H}_2 \text{ pressure})$. It is generally known that hydrogen has potential issues in safety, storage and transportation.²¹ Chang et.al reported that oleic acid could be completely converted at 400°C in 3 h over 5% Pt/C without using any hydrogen donor, and the selectivity to 8-heptadecene and heptadecane was around 72%.²² However. considering the cost and scarcity of precious metals, the development of non-precious metal catalysts becomes more and more important. Although a series of non-precious metals catalysts, such as Fe-MSN, Co_{0.5}Mo_{0.5}, SnAlMg-2 and MgO-Al₂O₃, were also tested for hydrogenation and decarboxylation of oleic acid without using hydrogen, the heptadecane selectivity was rather low (less than 12%).^{5, 23-25}

Herein, supported Cu-Ni bimetallic catalysts were synthesized and studied for the in-situ hydrogenation and decarboxylation of oleic acid using methanol as a hydrogen donor. The HADDF-STEM, EDS-mapping, XRD and TPR were utilized to probe the catalyst structure. CO-DRIFTS and XPS were used to determine electron transfer between Cu and Ni in bimetallic catalysts. Ethylene/propane-TPD was also employed to reveal the interaction between the C-C bonds on the catalyst surface. The catalytic activities of the Cu-Ni bimetallic catalysts were evaluated to identify the reaction pathway over Cu-Ni bimetallic catalysts and the synergistic effect of Cu and Ni on the in-situ hydrogenation and decarboxylation.

2. Experimental methods

2.1 Experimental procedures

Published on 13 October 2017. Downloaded by University of Newcastle on 13/10/2017 17:51:09.

All experiments were carried out in a micro batch reactor (1.67 mL), which was

Page 7 of 31

Green Chemistry

View Article Online DOI: 10.1039/C7GC02774E

Green Chemistry Accepted Manuscript

assembled from one 3/8-inch tube and two 3/8-inch caps purchased from Swagelok, USA. The micro batch reactor was charged with 50 mg of Oleic acid, 15 mg of catalyst and a specific amount of water and methanol. The sealed reactor was heated and maintained at the reaction temperature in a fluidized sand bath (Techne SBL-2). The reactor was soaking in cold water to quench the reaction after reaching the desired reaction time. Afterwards, the reaction mixture in the reactor was centrifuged to recover the solid catalyst and the liquid phase were rinsed, diluted in a 10 mL volumetric flask with acetone and then analyzed.

2.2 Analysis methods

Quantification of the liquid reaction products in acetone was performed using a gas chromatography (GC, Agilent 7890A) equipped with a 30 m \times 0.32 mm \times 0.25 µm HP-5 capillary column and an FID detector. The products were analyzed by a gas chromatography (GC, Agilent 7693) equipped with a CP-FFAP CB column and an FID detector in the low-temperature experiments. The carrier gas was nitrogen with a flow rate of 11 mL/min. The temperature of the injector and detector were 280 °C and

Green Chemistry Accepted Manuscript

300 °C, respectively. Quantitative analysis was performed using calibration curves for each compound in the mixture. Identification of the liquid reaction products was performed on a gas chromatography-mass spectrometry (Agilent 5977A MSD) system and then by matching gas chromatograph retention times with known standards.

Reactant mole conversions were defined as the number of moles of reactant consumed divided by the initial number of moles of reactant added into the reactor. Selectivities were displayed by the number of moles of product recovered divided by the number of moles of reactant reacted. Uncertainties reported were standard deviations determined by replicate experiments. Experiments at every reaction condition were repeated three times.

3. Results and discussion

3.1 Characterization

HADDF-STEM, EDS-mapping, XRD, CO-DRIFTS, TPR, XPS and

ethylene/propane-TPD were performed for the synthesized catalysts of 60wt% Cu/Al₂O₃

View Article Online DOI: 10.1039/C7GC02774E

Green Chemistry Accepted Manuscript

(CuAl), 40wt%Cu-20wt%Ni/Al₂O₃ (Cu₂NiAl), 30wt%Cu-30wt%Ni/Al₂O₃ (CuNiAl), 20wt%Cu-40wt%Ni/Al₂O₃ (CuNi₂Al) and 60wt% Ni/Al₂O₃ (NiAl). In Figures S1 and S2, TEM-mapping and line-scanning results of CuAl and NiAl indicated that monometallic Cu and Ni was observed and dispersed on the Al₂O₃ support. The high-resolution TEM (HRTEM) images of CuAl, Cu₂NiAl, CuNi₂Al and NiAl (Figure S3) exhibited the presence of metal grains containing different surface facets. The lattice spacing of these catalysts decreased from 2.13 Å to 1.99 Å with the percentage of Ni increased, suggesting that the alloying state existed in the samples of CuNi₂Al and Cu₂NiAl. Furthermore, as expected the Cu/Ni ratios of the CuNi alloy of CuNi₂Al and Cu₂NiAl were different. To further prove the existence of Cu-Ni alloy in bimetallic catalysts, the STEM dark field image and EDS mapping of Cu₂NiAl and CuNi₂Al were performed, as shown in Figure 1. The results indicated that Cu and Ni X-ray signals were uniformly mixed together, and Al and O also exhibited similar phenomenon. These results suggest the existence of Cu-Ni alloy in the samples of CuNi₂Al and Cu_2NiAl , which was in good accordance with the results of XRD and H_2 -TPR. The TEM

image of CuNi₂Al in Figure S4 displayed that Cu-Ni alloy particles were detected as

Green Chemistry Accepted Manuscript

relative darker spots, with an average size of 32.7 nm. Besides, CuNi₂Al showed a stronger signal of nickel than that of copper from line-scanning result in Figure 1b. Furthermore, the EDS results produced the trace spectrum of CuNi₂Al, and the weight ratio of Ni and Cu is about 1.6, similar to the value of 1.7 obtained from ICP-OES (Table S1). Cu₂NiAl exhibited a more intense signal of copper than that of nickel from line-scanning result in Figure 1b. The weight ratio of Cu and Ni from EDS is about 2.7, similar with the value of 2.6 obtained from ICP-OES (Table S1). These characterization results are consistent with the presence of uniform Cu-Ni alloy particles supported on Al₂O₃.

N₂ adsorption-desorption results in Table S3 show that the surface areas and pore size of NiAl were much larger than that of CuAl, consistent with the XRD results that Ni particles of NiAl were smaller than Cu particles of CuAl. The surface areas of Cu₂NiAl, CuNiAl and CuNi₂Al increased as the ratio of Cu/Ni decreased. With the decrease of Cu/Ni ratio, the pore volume of the corresponding catalysts increased firstly and then decreased. CuNi₂Al shows the highest pore volume of 0.576 cm³ g⁻¹.

XRD patterns of the reduced catalysts with different Cu/Ni mole ratios are shown in Figure 2. A strong diffraction of the metallic nickel phase (JCPDS #04-0850) was observed in the XRD pattern of NiAl at $2\theta = 44.5$, 51.8 and 76.4°, and a strong diffraction of the metallic copper phase (JCPDS #65-9743) was observed in the XRD pattern of CuAl at 2θ =43.4, 50.6 and 74.3°. The sharper diffraction peaks observed for metal Cu in CuAl relative to metal Ni in NiAl indicate that Cu particle was much larger than Ni particle. The location of diffraction peaks gradually shifted to larger 2θ degrees of metallic nickel phase when the Cu/Ni ratios increased from 1:2 to 2:1. These results further prove the existence of Cu-Ni alloy in Cu₂NiAl, CuNiAl and CuNi₂Al, and the Cu/Ni ratios was different in three bimetallic catalysts, consistent with the characterization results of STEM-EDS and H₂-TPR.

In Figure 3, TPR profile of NiAl shows a main peak at 635 °C and a small peak at 408 °C. The low temperature signal was attributed to the reduction of NiO to Ni, and the high temperature signal was ascribed to the reduction of Ni-Al spinel, since a strong **Green Chemistry Accepted Manuscript**

Green Chemistry Accepted Manuscript

interaction between Ni and aluminum matrix should lead to a higher reduction temperature.²⁶ For CuAl, only one reduction peak at 222 °C was detected, attributed to the reduction of CuO to Cu. For Cu₂NiAl, CuNiAl, and CuNi₂Al, only one main reduction peak was detected around 170 °C, which shifted to lower temperature compared to the peaks for CuAl and NiAl. Therefore, these results suggested that the Cu-Ni alloy oxides were more easily reduced than the monometallic oxides.

Figure 4 presents the XPS spectra of Cu $2p_{3/2}$, Ni $2p_{3/2}$ and Al 2p for CuAl, Cu₂NiAl, CuNi₂Al and NiAl. The XPS spectra of Cu $2p_{3/2}$ for CuAl was at 932.4 eV in Figure 4a, typical for XPS feature of Cu⁰. The binding energies in Cu₂NiAl and CuNi₂Al shifted to higher binding energies of 933.4 eV and 933.5 eV, respectively. The increase of Cu $2p_{3/2}$ binding energy should be ascribed to the partially oxidized Cu on the surface of the Cu-Ni alloy. The XPS spectra of Al 2p for the four catalysts did not show any difference in Figure 4b. In Figure 4c, the position of Ni $2p_{3/2}$ varies between 855.8 and 855.9 eV, which should be ascribed to the formation of NiO in air on the surface of Ni and Cu-Ni alloy particles during the test. For Ni $2p_{3/2}$, a satellite feature was detected at

View Article Online DOI: 10.1039/C7GC02774E

Green Chemistry Accepted Manuscript

higher binding energy values. There was no obvious shift of binding energy of Ni $2p_{3/2}$ in Cu₂NiAl, CuNi₂Al and NiAl, suggesting the presence of oxidized Ni on the surface of Cu-Ni alloy and Ni particles. The DRIFTS-IR spectra using adsorbed CO as probes of CuAl, Cu₂NiAl, CuNiAl, CuNi₂Al and NiAl were shown in Figure 5. CO bands on CuAl, Cu₂NiAl, CuNiAl, CuNi₂Al were observed, but not on NiAl. The band observed around 2100 cm⁻¹ could be assigned to CO adsorbed on Cu. No CO adsorbed on the Ni was found, probably because of the formation of NiO on the surface of Ni.²⁷ With the increase of Ni loading, a red shift on bimetallic Cu-Ni catalysts to lower vibrational frequencies was observed, suggesting an electron transfer phenomenon in Cu. Therefore, we deduced that the charge transfer on the surface of Cu occurred, contributing to the red shift.

Ethylene, propane and acetic acid-TPD were carried out for CuAl, CuNi₂Al and NiAl. The ethylene/propane-TPD results indicated all the catalysts showed the adsorption of ethylene and propane in Figures 6a and 6b. The adsorption amounts on CuNi₂Al and CuAl were very low, but that of NiAl was much higher. Intense

desorption peak of propane was only detected from NiAl in the temperature region

Green Chemistry Accepted Manuscript

between 330 and 350 °C, suggesting that the addition of Cu into Ni reduced the adsorption ability to C-C and C=C bonds. Therefore, the adsorption ability of C-C and C=C for NiAl is much higher than those for CuAl and CuNi₂Al. The acetic acid-TPD results in Figure 6c show that there were three peaks in the spectra of CuAl and NiAl, but only two peaks were observed in the spectrum of CuNi₂Al. The peaks in the range of 250~400°C should be associated with the chemisorption of acetic acid on the three catalysts. The temperatures of the main desorption peaks of CuNi₂Al (320 °C) and NiAl (283 °C) were higher than that of CuAl (246 °C), indicating that the adsorption strength of the carboxyl group on CuNi₂Al and NiAl was stronger than that on CuAl.

3.2 Catalytic activity of different catalysts for the conversion of oleic acid

As shown in Figure 7, Cu₂NiAl, CuNiAl and CuNi₂Al exhibited better activity towards heptadecane production at 330 °C after 1 h compared to Pt/C²⁸, CuAl and NiAl. The molar yield of heptadecane over CuNi₂Al achieved 92.7% at 330 °C after 1 h, meanwhile, stearic acid and octadecanol were not detected. To prove that stearic acid and

View Article Online DOI: 10.1039/C7GC02774E

Green Chemistry Accepted Manuscript

octadecanol were the intermediates on the conversion of oleic acid over CuNi₂Al, reaction time was shortened to identify the existence of these potential reaction intermediates. Figure 7b shows the GC-FID chromatograms for the variation of oleic acid conversion over CuNi₂Al as time elapsed, illustrating that stearic acid and octadecanol can be converted to heptadecane from 10 min to 60 min. During this reaction period, oleic acid was converted completely, and small amounts of octadecanol and stearic acid were also obtained at 10 min, which were further converted to heptadecane at longer reaction time. In Figure 7d, stearic acid, methyl stearate and octadecanol were converted to heptadecane at the same reaction condition, suggesting they were intermediates for the conversion of oleic acid. Table 1 showed the performance of the CuNi₂Al catalyst and a comparison with previous published work.^{5, 11,} 12, 17, 20, 22, 24, 28, 29, 30, 31 CuNi₂Al showed the best selectivity for heptadecane production from the conversion of oleic acid without hydrogen, even better than precious metal catalysts. Furthermore, CuNi₂Al also showed good performance for the deoxygenation of gutter oil hydrolysate according to the results before and after reaction in Figure S5.

To identify the specific reason why heptadecane could not be obtained over CuAl,

Green Chemistry Accepted Manuscript

the reaction time was prolonged in Figure 7c, and the main products were detected as octadecanol and stearic acid at the reaction time range of 1-2 h. Only 5.8% yield of heptadecane could be achieved at 2 h, suggesting that oleic acid was converted completely to stearic acid in a short time and stearic acid was easier to be hydrogenated to produce octadecanol than decarboxylated to produce heptadecane over CuAl. Therefore, it was difficult to cleave the C₁-C₂ bonds (Figure S7) in stearic acid and octadecanol over CuAl. However, octadecanol was not detected over NiAl in Figures 7d It has been reported that the addition of Cu into the CuNi alloy would weaken and S6a. the binding energy of hydrogen on Ni, and improve the hydrodeoxygenation activity³², which could explain that octadecanol was obtained over the Cu and Cu-Ni alloy catalysts, but not over the Ni catalyst. Figure 7c shows the product distribution over NiAl at the same reaction condition, and the yield of heptadecane increased firstly and then decreased with the decrease of the yield of stearic acid. At the same time the yield of cracked paraffins (C_{10-16} alkanes) slightly decreased with the reaction time, and alkanes

View Article Online DOI: 10.1039/C7GC02774E

with carbon number less than 10 were also detected. For CuAl, NiAl and CuNi₂Al, heptadecene was not detected, indicating that the decarboxylation of oleic acid was difficult to occur before the hydrogenation of the C=C double bond in this catalysis Fu et al.¹⁷ reported that the decarboxylation of unsaturated fatty acid was more system. difficult to occur compared to saturated fatty acid, however, hydrogen donors were not These results indicated that the hydrogenation of oleic acid to used to solve this issue. stearic acid was completed in a very short time followed by the decarboxylation of stearic acid to heptadecane with methanol. To further prove this hypothesis, oleic acid was reacted at 250 °C for 0.5 h over Pt/C and CuNi₂Al with/without methanol. As shown in Figure S6b, the GC/FID results indicated that oleic acid was much easier to be hydrogenated to produce stearic acid with methanol at 250 °C over Pt/C and CuNi₂Al. Immer et al.³³ also reported that the adsorption of the unsaturated fatty acids via the cis C-C double bond in the alkyl chain might inhibit the decarboxylation of oleic acid. In conclusion, hydrogen, achieved from the methanol steam reforming, can facilitate the hydrogenation of C=C in oleic acid. Methanol was converted to H₂, CO and CO₂, via

Published on 13 October 2017. Downloaded by University of Newcastle on 13/10/2017 17:51:09

the cleavage of C-H and O-H bonds in methanol to form H₂ and CO, followed by the water-gas shift reaction to form CO₂ and H₂.³⁴ In addition, the decarboxylation and decarbonylation reactions did not occur at low temperature. Therefore, heptadecene was not detected in this reaction system. For comparing the hydrogenation capacity of CuAl, CuNi₂Al and NiAl, the conversions of oleic acid over these three catalysts at 250°C for 0.5 h were shown in Figure S6c. The results indicated that the hydrogenation activity of the C=C bond in oleic acid increased in the order of Cu<CuNi₂<Ni.

3.3 Reaction pathways of oleic aicd conversion over CuNi₂Al

Published on 13 October 2017. Downloaded by University of Newcastle on 13/10/2017 17:51:09.

For NiAl, the main side reaction was short-chain hydrocarbon production from the cracking of C-C bonds, as shown in Figure 7c. Basem et.al ¹¹ also reported that NiWC/Al-SBA-15 possessed some cracking activity to form C_{11} - C_{16} hydrocarbons. For CuAl, the weak adsorption strength of the carboxyl group inhibited the decarboxylation reaction and then hindered the production of heptadecane. In Figure 6, CuAl, CuNi₂Al and NiAl exhibited a certain degree of adsorption ability of ethylene and propane, but the adsorption ability of NiAl was much higher than those of CuNi₂Al and CuAl. Strong

View Article Online DOI: 10.1039/C7GC02774E

Green Chemistry Accepted Manuscript

desorption peak of ethylene and propane can only be observed on Ni at the reaction temperature between 330 and 350 °C. Therefore, the adsorption ability of C-C and C=C for Ni is much stronger than that for Cu and CuNi₂. We deduced that cracking reaction of fatty acid proceed before decarboxylation owing to the stability of heptadecane. There are no cracking products from heptadecane at the same reaction condition, as shown in Figure S8. Therefore, the existence of the carboxyl group is necessary for the cracking of C-C bond. The formation of the Cu-Ni alloy inhibited the cracking of C-C bonds compared to Ni, and remarkably increased the decarboxylation ability to produce heptadecane. Overall, the CuNi₂Al appears to combine the advantages of CuAl for the in-situ hydrogenation and NiAl for the decarboxylation of unsaturated fatty acids.

4. Conclusions

In-situ hydrogenation and decarboxylation of oleic acid using methanol as hydrogen donor were studied on CuAl, Cu₂NiAl, CuNiAl, CuNi₂Al and NiAl. Cu-Ni bimetallic catalysts exhibited remarkably improved activities for in-situ hydrogenation and

Green Chemistry Accepted Manuscript

decarboxylation compared to monometallic catalysts. The results from experimental measurements and characterizations indicate that the enhanced activity of bimetallic catalysts can be attributed to the Cu-Ni alloy formation and a partially oxidized Cu. Ethylene, propane and acetic acid-TPD results suggest that the formation of the Cu-Ni alloy inhibits the cracking of C-C bonds compared to Ni, and enables stronger adsorption of the carboxyl group on CuNi₂Al compared to CuAl, leading to an increased selectivity to heptadecane. Furthermore, the CuNi₂ alloy also shows an equally promising performance for the in-situ hydrogenation and decarboxylation of mixed fatty acids from the hydrolysis of gutter oil.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (No.

21436007, 21676243), Zhejiang Provincial Natural Science Foundation of China (No. LR17B060002, LZ14B060002), and the China Scholarship Council. BNL researchers acknowledge support of this work under contract DE-AC02-98CH10886 with the U.S.

Department of Energy (DOE) and supported by the Brookhaven National Laboratory

Directed Research and Development (LDRD) Project No. 16-045.

References

- 1. E. Santillan-Jimenez and M. Crocker, J. Chem. Technol. Biot., 2012, 87, 1041-1050.
- 2. M. Snåre and D. Y. Murzin, Ind. Eng. Chem. Res., 2006, 45, 6875-6875.
- 3. A. Centeno, E. Laurent and B. Delmon, J. Catal., 1995, 154, 288-298.
- 4. G. W. Huber, P. O'Connor and A. Corma, Appl. Catal. A-Gen., 2007, 329, 120-129.
- J.-G. Na, B. E. Yi, J. N. Kim, K. B. Yi, S.-Y. Park, J.-H. Park, J.-N. Kim and C. H. Ko, *Catal. Today*, 2010, **156**, 44-48.
- I. Kubičková, M. Snåre, K. Eränen, P. Mäki-Arvela and D. Y. Murzin, *Catal. Today*, 2005, 106, 197-200.
- P. Mäki-Arvela, I. Kubickova, M. Snåre, K. Eränen and D. Y. Murzin, *Energy Fuels*, 2007, 21, 30-41.
- M. Snåre, I. Kubickova, P. Mäki-Arvela, K. Eränen and D. Y. Murzin, *Ind. Eng. Chem. Res.*, 2006, 45, 5708-5715.
- 9. J. Fu, X. Lu and P. E. Savage, Energy Environ. Sci., 2010, 3, 311-317.
- I. Simakova, B. Rozmysłowicz, O. Simakova, P. Mäki-Arvela, A. Simakov and D. Y. Murzin, *Top Catal.*, 2011, 54, 460-466.
- 11. B. Al Alwan, S. O. Salley and K. Y. S. Ng, Appl. Catal. A-Gen., 2015, 498, 32-40.
- 12. J. Fu, F. Shi, L. T. Thompson, X. Lu and P. E. Savage, ACS Catal., 2011, 1, 227-231.
- 13. J. Wu, J. Shi, J. Fu, J. A. Leidl, Z. Hou and X. Lu, Sci. Rep., 2016, 6.
- 14. C. Yang, R. Nie, J. Fu, Z. Hou and X. Lu, Bioresource technol., 2013, 146, 569-573.
- B. Rozmysłowicz, P. Mäki-Arvela, A. Tokarev, A.-R. Leino, K. Eränen and D. Y. Murzin, *Ind. Eng. Chem. Res.*, 2012, 51, 8922-8927.
- 16. E. Santillan-Jimenez, T. Morgan, J. Shoup, A. E. Harman-Ware and M. Crocker, Catal. Today,

2014, 237, 136-144.

Published on 13 October 2017. Downloaded by University of Newcastle on 13/10/2017 17:51:09

- 17. J. Fu, X. Lu and P. E. Savage, ChemSusChem, 2011, 4, 481-486.
- M. Snåre, I. Kubičková, P. Mäki-Arvela, D. Chichova, K. Eränen and D. Y. Murzin, *Fuel*, 2008, 87, 933-945.
- M. Ahmadi, A. Nambo, J. B. Jasinski, P. Ratnasamy and M. A. Carreon, *Catal. Sci. Technol.*, 2015, 5, 380-388.
- 20. D. R. Vardon, B. K. Sharma, H. Jaramillo, D. Kim, J. K. Choe, P. N. Ciesielski and T. J. Strathmann, *Green Chem.*, 2014, 16, 1507.
- A. Berenblyum, V. Y. Danyushevsky, E. Katsman, T. Podoplelova and V. Flid, *Petrol. Chem.*, 2010, 50, 305-311.
- 22. J.-G. Na, B. E. Yi, J. K. Han, Y.-K. Oh, J.-H. Park, T. S. Jung, S. S. Han, H. C. Yoon, J.-N. Kim, H. Lee and C. H. Ko, *Energy*, 2012, 47, 25-30.
- 23. K. Kandel, J. W. Anderegg, N. C. Nelson, U. Chaudhary and I. I. Slowing, *J. Catal.*, 2014, **314**, 142-148.
- 24. J.-O. Shim, D.-W. Jeong, W.-J. Jang, K.-W. Jeon, S.-H. Kim, B.-H. Jeon, H.-S. Roh, J.-G. Na, Y.-K. Oh, S. S. Han and C. H. Ko, *Catal. Commun.*, 2015, 67, 16-20.
- D. S. Tong, C. H. C. Zhou, Y. Lu, H. Yu, G. F. Zhang and W. H. Yu, *Appl. Clay Sci.*, 2010, 50, 427-431.
- 26. I. Obregon, I. Gandarias, N. Miletic, A. Ocio and P. L. Arias, ChemSusChem, 2015, 8, 3483-3488.
- 27. C.H. Bartholomew, R.B. Pannell, J. Catal. 1980, 65, 390.
- 28. J. Wu, T. Wang, J. Fu, Z. Hou and X. Lu, Energy Environ. Focus, 2016, 5, 163-168.
- 29. T. M. Yeh, R. L. Hockstad, S. Linic and P. E. Savage, Fuel, 2015, 156, 219-224.
- D. S. Tong, C. H. Zhou, M. Y. Li, W. H. Yu, J. Beltramini, C. X. Lin and Z. P. Xu, *Appl. Clay Sci*, 2010, 48, 569-574.
- H.-S. Roh, I.-H. Eum, D.-W. Jeong, B. E. Yi, J.-G. Na and C. H. Ko, *Catal. Today*, 2011, 164, 457-460.
- O. V. Cherstiouk, P. A. Simonov, A. G. Oshchepkov, V. I. Zaikovskii, T. Y. Kardash, A. Bonnefont,
 V. N. Parmon and E. R. Savinova, *J. Electroanal. Chem.*, 2016, 783, 146-151.
- 33. J. G. Immer, M. J. Kelly and H. H. Lamb, Appl. Catal. A-Gen., 2010, 375, 134-139.
- 34. S. Sá, H. Silva, L. Brandão, J. M. Sousa, A. Mendes, Appl. Catal. B-Environ. 2010, 99, 43-57.



Figure 1. (a) The dark filed TEM image of CuNi₂Al and its corresponding X-ray map of Ni, Cu, O and Al. (b) Line scanning of single particle and support of CuNi₂Al. (c) The dark filed TEM image of Cu₂NiAl and its corresponding X-ray map of Ni, Cu, O and Al. (d) Line scanning of single particle and support of Cu₂NiAl



Figure 2. XRD patterns of CuAl, Cu₂NiAl, CuNiAl, CuNi₂Al, and NiAl.

Published on 13 October 2017. Downloaded by University of Newcastle on 13/10/2017 17:51:09.



Figure 3. H₂-TPR profiles of calcined precursor of CuAl, Cu₂NiAl, CuNiAl, CuNi₂Al, and NiAl.



Published on 13 October 2017. Downloaded by University of Newcastle on 13/10/2017 17:51:09.

Figure 4. XPS spectra for (a) Cu $2p_{3/2}$ of three reduced samples; (b) Al 2p of four reduced samples; (c) Ni $2p_{3/2}$ of three reduced samples.



Figure 5. DRIFTS-IR spectra with CO probes showing reduced CuAl, Cu₂NiAl, CuNiAl, CuNi₂Al and NiAl.

Green Chemistry Accepted Manuscript









Figure 6. Temperature-programmed desorption (TPD) of (a) C_2H_4 , (b) C_3H_8 and (c) acetic acid on CuAl, CuNi₂Al and NiAl



Published on 13 October 2017. Downloaded by University of Newcastle on 13/10/2017 17:51:09.

Figure 7. (a) Mole yields of different products for the in-situ hydrogenation and decarboxylation of oleic acid over 5% Pt/C^{26} , CuAl, Cu₂NiAl, CuNiAl, CuNi₂Al, NiAl with the reaction time of 1 h. (b) GC/FID chromatograms over CuNi₂Al with reaction time. (c) The product distribution with reaction time over CuAl and NiAl. (d) Stearic acid, methyl stearate and octadecanol were chosen as the reactants. Reaction condition: T=330 °C, reactant loading=50 mg, catalyst loading=15 mg, methanol loading=10 mg, water =0.5 mL. Cracked paraffins stands for the total yield of docane, hendecane, dodecane, tridecane, tetradecane, pentadecane and hexadecane.

| Entry | Catalyst | Reaction | Hydrogen source | Conversion | Heptadecane | Heptadecane | ref |
|-------|---------------------------------------|----------------|--------------------------------|------------|-------------|-------------|----------|
| | | conditions | & Solvent | (%) | selectivity | yield (%) | |
| | | | | | (%) | | |
| 1 | 5% Pt/C | 350 °C, 3 h | no H ₂ , no solvent | 99 | 71 | 70.3 | 22 |
| 2 | Pt ₃ Sn/C | 350 °C, 3 h | no H ₂ , water | 100 | 60 | 60 | 29 |
| 3 | SnAlMg-2 | 300 °C, 6 h | no H ₂ , no solvent | 71.1 | 3.7 | 2.6 | 0 |
| 4 | Co _{0.5} Mo _{0.5} | 300 °C , 3 h | no H ₂ , no solvent | 88.1 | 6.1 | 5.4 | 24 |
| 5 | MgO-Al ₂ O ₃ | 400 °C, 3 h | no H ₂ , no solvent | 98 | 6.9 | 6.8 | 5 |
| 6 | NiWC/Al-SBA-15 | 400 °C, 4 h | no H ₂ , water | 97.3 | 5.2 | 5.1 | 11 |
| 7 | activity carbon | 370 °C, 3 h | no H ₂ , water | 80 | 7 | 5.6 | 12 |
| 8 | 5% Pt/C | 330 °C , 1.5 h | no H ₂ , water | 68.9 | 13.4 | 9.2 | 17 |
| 9 | Ni/MgO-Al ₂ O ₃ | 350 °C, 3 h | no H ₂ , water | 67.5 | 12.5 | 8.4 | 31 |
| 10 | 5% Pt/C | 330 °C, 1 h | methanol, water | 100 | 72.2 | 72.2 | 28 |
| 11 | Pt-Re/C | 300 °C, 3 h | glycerol, water | / | / | 7 | 20 |
| 12 | CuNi ₂ Al | 330°C , 1 h | methanol, water | 100 | 92.7 | 92.7 | Our work |

Table 1. The performance of CuNi2Al in this work and the comparison with previous published works