Submit to: Surface Science

Date: November 15th, 2015

Prepared for the Special Issue Honoring John Yates

Reaction Pathways of Furfural, Furfuryl Alcohol and 2-methylfuran on Cu(111) and NiCu Bimetallic Surfaces

Ke Xiong^[a], Weiming Wan^[b], Jingguang G. Chen^{*[b],[c]}

[a] Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE
19716, USA

[b] Department of Chemical Engineering, Columbia University, New York, NY 10027, USA

[c] Chemistry Department, Brookhaven National Laboratory, Upton, NY 11973, USA

Corresponding author: jgchen@columbia.edu

Abstract

Hydrodeoxygenation (HDO) is an important reaction for converting biomass-derived furfural to value-added 2-methylfuran, which is a promising fuel additive. In this work, the HDO of furfural to produce 2-methylfuran occurred on the NiCu bimetallic surfaces prepared on either Ni(111) or Cu(111). The reaction pathways of furfural were investigated on Cu(111) and Ni/Cu(111) surfaces using density functional theory (DFT) calculations, temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS) experiments. These studies provided mechanistic insights into the effects of bimetallic formation on enhancing the HDO activity. Specifically, furfural weakly adsorbed on Cu(111), while it strongly adsorbed on Ni/Cu(111) through an $\eta^2(\text{C},\text{O})$ configuration which led to the HDO of furfural on Ni/Cu(111). The ability to dissociate H_2 on Ni/Cu(111) is also an important factor for enhancing the HDO activity over Cu(111).

Keywords: Biomass; Furfural; Hydrodeoxygenation; NiCu bimetallic; 2-methylfuran

1. Introduction

Biomass represents sustainable alternative carbon sources for producing fuels and chemicals instead of from the traditional petroleum feedstock.[1-3] One of the difficulties in processing biomass for fuel applications is related to its high oxygen content[4, 5] with oxygen being present in the functional groups such as carbonyl and/or carboxyl groups. Hydrodeoxygenation (HDO) is a promising way to remove the extra oxygen in biomass-derived oxygenate molecules because an ideal HDO process selectively cleaves the C-O/C=O bonds of the oxygenates while keeping the C-C/C=C bonds intact, which is particularly important for fuel applications.[6] The obstacle for an efficient HDO process remains to be the discovery of efficient, low-cost and environmental-friendly HDO catalysts.

In recent years, converting biomass via several important platform chemicals appears to be a promising strategy because it allows fundamental studies of several types of well-defined model compounds. This also allows the utilization of electronic structure theory to guide catalyst design for processing biomass to value-added fuels and chemicals.[2, 3] Furfural is one of the important platform chemicals.[7] Furfural is produced in large scale in industry through the hydrolysis and dehydration of the hemicellulose components of raw biomass such as corncob, oat hull, etc. However, furfural has a tendency to polymerize under common storage conditions and is thus not a good fuel candidate. Several recent publications reported the possibility of converting furfural to 2-methylfuran, which is a promising biofuel due to its high energy density and high blending research octane number.[2, 7]

The conversion of furfural to 2-methylfuran requires a selective HDO catalyst which would selectively cleave the C=O bond in the aldehyde group of furfural while keeping the C-O bond inside the furan ring intact. Copper chromite was reported to be an efficient catalyst for this chemistry.[8] However, due to the possible leach of chromium, this catalyst could be highly toxic and is thus less desirable. Other reported active catalysts included FeCu[9], Cu/SiO₂[10, 11], Ni/SiO₂[11, 12] etc. Recently molybdenum carbide (Mo₂C) was discovered to be a highly selective catalyst for converting furfural to 2-methylfuran.[13-15] However, due to the existence of acidic sites on the catalysts,[16] the polymerization of furfural appeared to be accelerated,[17] which led to stability issues for the HDO reaction of furfural on Mo₂C.

Non-precious metal based bimetallic materials constitute potentially desirable catalysts for the HDO chemistry due to their low-cost. Recently, Sitthisa et al. reported that the addition of Fe

to Ni/SiO₂ could significantly improve the HDO activity of furfural to produce 2-methylfuran.[12, 18] Yu et al. continued the investigation and attributed the enhanced HDO activity of FeNi/SiO₂ to a change in the adsorption geometry of the furan ring.[19] NiCu could be another effective catalyst for the HDO chemistry. Dickinson et al. reported that NiCu was active for the aqueous phase HDO of o-cresol to produce liquid hydrocarbons.[20, 21] In this work, we report that the NiCu model surfaces, prepared on either the Cu(111) or Ni(111) substrate, are active for the HDO of furfural to produce 2-methylfuran. Density functional theory (DFT) calculations, temperature programmed desorption (TPD) and high resolution electron energy loss spectroscopy (HREELS) were employed to explore how the formation of the bimetallic NiCu surface enhances the HDO of furfural.

2. Experimental and Theoretical Methods

2.1 Density functional theory calculations

DFT calculations were utilized to obtain the binding energies and optimized adsorption configurations of furfural on Cu(111) and Ni/Cu(111). The calculations were performed using the Vienna *ab initio* Simulation Package (VASP) program.[22] A Cu(111) slab was modeled by a 3 x 3 unit cell with four atomic layers. The Ni/Cu(111) surface was modeled by replacing all the Cu atoms in first layer of Cu(111) with Ni atoms. The first two layers of both Cu(111) and Ni/Cu(111) were allowed to relax. The PW91 functional[23] and a cutoff energy of 396 eV were used for all calculations. The lattice constant of Cu is 0.3615 nm as reported in the literature.[24] The binding energy was calculated by subtracting the total energy of an adsorbed molecule on a slab from the sum of energies of the gas phase molecule and the slab. The utilization of a four-layer slab is commonly practiced by many research groups for DFT calculations of bimetallic surfaces [25], including the CuNi bimetallic surfaces[27].

2.2 Preparation of Ni/Cu(111) and Cu/Ni(111) surfaces

Single crystals of Ni(111) and Cu(111) were purchased from Princeton Scientific Corporation. The Ni(111) crystal has a purity of 99.999% , a diameter of 8 mm and a thickness of 1.5 mm. The Cu(111) crystal has a purity of 99.999%, a diameter of 10 mm and a thickness of 1.5 mm. The Ni(111) crystal was spot-welded onto two tantalum posts for resistive heating and liquid nitrogen cooling. The Cu(111) crystal was held by two tantalum wire which were spot-

welded to two tantalum posts. The temperature was measured by a K-type thermocouple at the back of the single crystals. The single crystal surfaces were cleaned by cycles of Ne^+ sputtering at 300 K and annealing at 1000 K and 900 K for Ni(111) and Cu(111), respectively. Residual carbon on the surface was removed by O_2 treatment.

The Ni/Cu(111) surface was prepared by thermal evaporation from a Ni source onto the Cu(111) surface held at 300 K. The typical set-up and experimental procedure were described previously.[25] After deposition, the Ni coverage was estimated to be one monolayer (ML) using the Auger electron spectroscopy (AES) standard overlay equation[26] based on the AES peak intensity of Ni (718 eV) and Cu (922 eV). The Cu/Ni(111) was prepared using a similar method by depositing Cu onto the Ni(111) surface at 300 K. After deposition, the Cu coverage was estimated to be 1 ML by AES. The growth of Cu on Ni(111) at 300 K was previously shown to follow a layer-by-layer growth mechanism.[27, 28]

2.3 TPD and HREELS measurements

The TPD and HREELS experiments on the Cu(111) and Ni/Cu(111) surfaces were performed in a three-level ultra-high vacuum (UHV) chamber with a base pressure in the range of 1×10^{-10} Torr. During TPD measurements, the surface with adsorbate was heated in a linear rate of 3 K/s and the products desorbing from the crystal surface were monitored by a quadrupole mass spectrometer. Each HREELS scan was taken after heating the surface with adsorbate to a certain temperature and cooling down to 120 K. The TPD experiments on the Ni(111) and Cu/Ni(111) surfaces were performed in a two-level UHV chamber with a base pressure in the range of 1×10^{-10} Torr. The chamber was also equipped with a similar quadrupole mass spectrometer and the TPD experiments were performed using the same procedures.

2.4 Chemicals

Liquid samples including furfural, furfuryl alcohol, 2-methylfuran and furan were purchased from Sigma-Aldrich with a purity of 99%. The samples were transferred into glass sample cylinders and purified using freeze-pump-thaw cycles. Gas samples including H_2 , O_2 , CO, ethylene and propylene were purchased from Airgas, Inc. and Ne was purchased from Keen Compressed Gas Co. All the gas samples were research purity and used without further

purification. The purities of all liquid and gas samples were checked using mass spectrometer before use.

3. Results and Discussion

3.1 DFT of furfural on Cu(111), Ni(111) and Ni/Cu(111) surfaces

The binding energies and bond lengths of adsorbed furfural on Cu(111), Ni(111) and Ni/Cu(111) are compared in Table 1, with the numbering system of carbon and oxygen atoms shown in scheme 1. The optimized configurations of furfural on these three surfaces were shown in Scheme 2. On Cu(111), furfural adsorbed through either an $\eta^1(\text{O})$ or $\eta^2(\text{C},\text{O})$ configuration. The $\eta^2(\text{C},\text{O})$ configuration was slightly more stable than the $\eta^1(\text{O})$ configuration with a 0.02 eV difference. The binding energy and bond lengths of the $\eta^2(\text{C},\text{O})$ configuration were given in Table 1. In contrast, on Ni/Cu(111), furfural adsorbed through an $\eta^2(\text{C},\text{O})$ configuration with the ring nearly parallel to the surface. The binding energy of furfural on Ni/Cu(111) was much larger than that on Cu(111). Compared to gas phase furfural, the C6-O7 bond and the bonds inside the ring of adsorbed furfural were lengthened to a larger degree on Ni/Cu(111) than those on Cu(111), indicating stronger interactions between the Ni/Cu(111) surface and the ring and the C6-O7 bond of adsorbed furfural. The bond lengths of furfural on Ni(111) were also investigated for comparison. Furfural adsorbed onto Ni(111) through an $\eta^2(\text{C},\text{O})$ configuration. The binding energy of furfural follows the trend of Ni/Cu(111) > Ni(111) > Cu(111).

It should be pointed out that the functional used in the current study, PW91, is not adequate to treat such weak interactions, such as the adsorption on the Cu(111) surface. The main purpose of the relatively simple DFT calculations in the current study is to compare the trend (not the absolute values) in the binding energy and bond length of furfural over Cu(111), Ni(111) and Ni/Cu(111) surfaces. Other functionals that more adequately address weaker interactions should be used for more quantitative comparisons over these surfaces.

3.2 TPD of furans on hydrogen pre-dosed Cu(111) and Ni/Cu(111) surfaces

3.2.1 TPD of furfural

Figure 1 displays the TPD spectra of 4 L furfural on hydrogen pre-dosed Cu(111) and Ni/Cu(111) surfaces. The coverage of the pre-dosed hydrogen on Ni/Cu(111) was determined to be 0.5 ML by a separate set of TPD experiments of H₂ on Ni/Cu(111) as a function of hydrogen

coverage. The Cu(111) surface did not dissociate H₂ based on the TPD experiment of H₂ on Cu(111). For fair comparison, the Cu(111) was exposed to the same amount of H₂ as Ni/Cu(111) before dosing furfural and the surface after exposing to H₂ was noted as H/Cu(111).

On both surfaces, the multilayer desorption of furfural was observed at around 222 K. On H/Cu(111), the monolayer desorption of furfural was detected at around 382 K; a decarbonylation pathway was indicated by the concurrent desorption of furan and CO at around 479 K. In contrast, the monolayer desorption of furfural was not observed on Ni/Cu(111); an unselective decomposition pathway was indicated by the desorption of H₂ and CO at around 379 K and a hydrodeoxygenation (HDO) pathway was revealed by the desorption of 2-methylfuran at around 310 K. The desorption of 2-methylfuran from H/Ni/Cu(111) was determined to be reaction-limited, namely 2-methylfuran desorbed from the surface immediately after formation, because a separate TPD experiment of 2-methylfuran on H/Ni/Cu(111) showed that it molecularly desorbed at lower temperatures (204 K and 262 K). The pathways of furfural reaction are summarized in equations (1-3) as follows:

Table 2 summarizes the TPD quantification results of furfural reaction on H/Cu(111) and H/Ni/Cu(111). The TPD quantification was accomplished by performing a combination of TPD and AES experiments of furan on Cu(111). A separate TPD experiment of furan on Cu(111) demonstrated that Cu(111) was not able to dissociate furan, consistent with reports by Sexton et al. that furan did not dissociate on Cu(100).[29] The sub-monolayer desorption of furan from the Cu(111) surface was detected at around 166 K and 193 K. The corresponding surface coverage for the sub-monolayer desorption peak area of furan was measured by AES before furan desorption. The concentrations of other gas-phase products (such as 2-methylfuran, H₂ and CO) were calculated by comparing the TPD peak area of each molecule with the sub-monolayer desorption peak area of furan and scaling by the ionization probability factors of furan and these molecules.

Based on the quantification results, decarbonylation to produce furan and CO was the dominant pathway of furfural reaction on H/Cu(111); unselective decomposition to produce syngas (H₂ and CO) and HDO to produce 2-methylfuran were the two major pathways of furfural reaction on H/Ni/Cu(111). The addition of Ni significantly changed the selectivity of furfural reaction on H/Cu(111) and introduced a new pathway to produce 2-methylfuran via HDO.

3.2.2 TPD of furfuryl alcohol and 2-methylfuran

TPD measurements of furfural alcohol and 2-methylfuran were also performed because furfuryl alcohol and 2-methylfuran could be the surface reaction intermediates from furfural. Figure 2 displays the TPD spectra of 4 L furfuryl alcohol on H/Cu(111) and H/Ni/Cu(111). The multilayer desorption of furfuryl alcohol was observed at 243 K from both surfaces. On H/Cu(111), H₂ and furfural were produced at around 350 K, indicating a dehydrogenation pathway of furfuryl alcohol. On H/Ni/Cu(111), a similar dehydrogenation pathway was observed as indicated by the desorption of furfural at around 382 K and of H₂ between 350 K and 550 K. In addition, the production of CO at around 323 K and 430 K indicated an unselective decomposition pathway while the production of 2-methylfuran at around 341 K revealed an HDO pathway. The desorption peak of 2-methylfuran from the reaction of furfuryl alcohol was broader than that from the reaction of furfural and appeared to include two peaks at 303 K and 341 K. The production of 2-methylfuran from the HDO of furfuryl alcohol was also reported on Pd(111)[30] at slightly higher temperatures (335 K and 370 K). The aforementioned pathways of furfuryl alcohol reaction are summarized in equations (4-6):

The TPD quantification results are summarized in Table 3 using a similar method as that described for furfural. On H/Cu(111), dehydrogenation to produce furfural was the dominant pathway. On H/Ni/Cu(111), the dehydrogenation pathway was suppressed while HDO to produce 2-methylfuran and unselective decomposition to produce CO and H₂ were observed as

two major pathways. The HDO pathway of furfuryl alcohol had a slightly larger activity compared to that of furfural.

Figure 3 displays the TPD spectra of 4 L 2-methylfuran on H/Ni/Cu(111). The multilayer desorption of 2-methylfuran was observed at around 150 K while the monolayer desorption of 2-methylfuran was detected at 204 K and 262 K. An unselective decomposition pathway was observed beyond 300 K, as indicated by the production of CO and H₂ between 300 K and 500 K. The TPD quantification results showed that the unselective decomposition activity of 2-methylfuran on H/Ni/Cu(111) was 0.03 molecules per metal atom, much larger than that of furfural (0.006) and furfuryl alcohol (0.008). This could partially explain the relatively low activity of the HDO pathway of furfural and furfuryl alcohol on H/Ni/Cu(111), because most of the produced 2-methylfuran surface intermediates from the HDO of furfural and furfuryl alcohol could further decompose to produce CO and H₂ instead of desorbing molecularly.

3.2.3 TPD of furfural on hydrogen pre-dosed Ni(111), Cu/Ni(111) surfaces

In order to investigate if the substrate would affect the reaction pathways on NiCu bimetallic surfaces, a Ni(111) single crystal was also used for preparing a NiCu bimetallic surface. Figure 4 displays the TPD spectra of 4 L furfural on H₂-predosed Ni(111) and Cu/Ni(111) surfaces. The coverage of the pre-dosed H was determined to be 0.5 ML by performing separate TPD experiments of H₂ on Ni(111). As shown in Figure 4a for Ni(111), after multilayer desorption of furfural, propylene was produced at 272 K and 321 K, indicating a ring opening pathway for propylene production. In addition, H₂ and CO were produced between 300 K and 500 K, revealing an unselective decomposition pathway. On the other hand, on Cu/Ni(111), an HDO pathway was observed by detecting 2-methylfuran production at around 309 K. The detection of ethylene at around 426 K suggested an ethylene production pathway from the decomposition of the furan ring. The propylene and ethylene production pathway are summarized in equations (7-8):

The TPD quantification of furfural reaction on H/Ni(111) and H/Cu/Ni(111) was accomplished by performing a separate TPD experiment of CO on Ni(111). The saturation

coverage of CO on Ni(111) was reported in the literature.[31] The coverage of the other products was calculated by comparing the peak areas of the products with the saturated peak area of CO on Ni(111) and by normalizing with the ionization probability factors. The quantification results are summarized in Table 2. The propylene production pathway on H/Ni(111) and the ethylene production pathway on H/Cu/Ni(111) were named hydrocarbon production pathway in the table. The results suggested that unselective decomposition to produce H₂ and CO was the dominant pathway of furfural reaction on H/Ni(111) while the ethylene production pathway was dominant on H/Cu/Ni(111). Noticeably, the HDO pathway is detected on both H/Cu/Ni(111) and H/Ni/Cu(111), suggesting that the bimetallic surfaces are active for the production of 2-methylfuran independent of whether NiCu is produced on Cu(111) or Ni(111).

3.3 HREELS of furans on hydrogen pre-dosed Cu(111) and Ni/Cu(111) surfaces

The adsorption configurations and reaction intermediates of furfural on H/Cu(111) and H/Ni/Cu(111) were investigated using HREELS as shown in Figure 5 and 6, respectively. Because furfural showed similar HDO pathway on H/Cu/Ni(111) and H/Ni/Cu(111), the latter surface was selected for further HREELS studies. HREELS measurements of furan and 2-methylfuran were also performed in order to help understand the reaction pathways of furfural. DFT frequency calculations of furfural were performed to confirm the adsorption configurations and help the vibrational mode assignments. The vibrational mode assignments of furfural are summarized in Table 4. On H/Cu(111), the generally similar peak positions between the 100 K spectrum and the Raman spectrum of liquid furfural[32] and IR spectrum of gas-phase furan[33] suggested that furfural and furan molecularly adsorbed onto the surface at 100 K. At 230 K, the intensity of all peaks for furfural decreased, consistent with the TPD results in Figure 1 showing that furfural molecularly desorbed at 222 K. The intense $\omega(\text{C-H})$ peak at around 765 cm⁻¹ and the broadening of the $\nu(\text{C=O})$ peak at 1644 cm⁻¹ compared with that at 100 K suggested the formation of a weakly bonded furfural at this temperature. Consistently, DFT frequency calculations of weakly bonded furfural on Cu(111) gave similar peak positions as shown in Table 4. At 300 K, the intensity of the 2866 cm⁻¹ mode (an aliphatic C-H stretch) increased for both furfural and furan, suggesting that the furan ring is undergoing either ring opening or partial decomposition.

On H/Ni/Cu(111), furfural and 2-methylfuran adsorbed molecularly at 100 K. At 230 K, the intensity of all peaks of furfural decreased, consistent with the TPD results in Figure 1 showing that furfural molecularly desorbed at around 228 K; the peak at 1664 cm^{-1} shifted to 1584 cm^{-1} , suggesting the formation of an $\eta^2(\text{C},\text{O})$ adsorbed furfural. Consistently, DFT frequency calculations of $\eta^2(\text{C},\text{O})$ adsorbed furfural on Ni/Cu(111) gave similar peak positions as shown in Table 4. The new peaks at 1832 cm^{-1} and 2034 cm^{-1} were assigned to CO from the UHV background which could adsorb onto the surface during the HREELS measurements. The peak at around 3600 cm^{-1} was assigned to H_2O adsorption from the UHV background during the HREELS scan. At 300 K, all peaks attenuated, consistent with the desorption of 2-methylfuran around this temperature as shown in Figure 1. The enhanced intensity of the peak at 2879 cm^{-1} suggested either ring opening or partial decomposition of the furan ring. The ring of 2-methylfuran underwent either opening or partial decomposition at 230 K as indicated by the increased peak intensity at 2879 cm^{-1} .

3.4 Reaction pathways on hydrogen pre-dosed Cu(111) and NiCu bimetallic surfaces

The combined DFT and HREELS results indicated that furfural weakly bonded onto H/Cu(111) through either an $\eta^1(\text{O})$ or $\eta^2(\text{C},\text{O})$ configuration. In comparison, furfural bonded more strongly onto H/Ni/Cu(111) through an $\eta^2(\text{C},\text{O})$ configuration. Based on the observation of the intense $\omega(\text{C}-\text{H})$ mode, at 765 cm^{-1} on Cu(111) (Figure 5) and at 772 cm^{-1} on Ni/Cu(111) (Figure 6), the furan ring of furfural is nearly parallel to the surfaces at 100 K, consistent with the DFT-predicted orientation shown in Scheme 2. The relative intensity of the $\omega(\text{C}-\text{H})$ peak is substantially reduced at 230 K on Ni/Cu(111), which could be attributed to the partial loss of the aromaticity of the furan ring, due to either a change in the orientation of the furan ring or a partial decomposition of the furan ring. The H/Ni/Cu(111) surface had a stronger interaction with the C6-O7 bond of furfural, as indicated by the shift of the $\nu(\text{C}=\text{O})$ peak from 1664 cm^{-1} to 1584 cm^{-1} at 230 K (Figure 6). Consistently, the DFT results in Table 1 indicated that the C6-O7 bond of furfural was lengthened to a larger degree on Ni/Cu(111) than on Cu(111). The TPD results suggested that the selective decarbonylation to produce furan occurred on H/Cu(111) while the HDO and unselective decomposition pathways occurred on H/Ni/Cu(111). A strong interaction with the C6-O7 bond of furfural is favorable for the HDO of furfural, consistent with previous results[13, 14, 34]. In addition, the ability to dissociate H_2 should also play a role in determining

the reaction pathways of furfural on these surfaces. As discussed in section 3.2.1, Cu(111) does not dissociate H₂ under UHV conditions while the HDO of furfural requires additional hydrogen to participate in the reaction. The lack of hydrogen on the surface could at least be partially responsible for the absence of the HDO pathway on Cu(111). On the other hand, the addition of Ni also introduced a significant unselective decomposition pathway to produce H₂ and CO while the same pathway was not observed on Cu(111). The emerging of the unselective decomposition could be associated with the enhanced interaction with the furan ring by the addition of Ni, as indicated by the DFT results in Tables 1.

The formation of the NiCu bimetallic surfaces, prepared on either Ni(111) or Cu(111), resulted in the onset of the HDO of furfural to produce 2-methylfuran (Table 2). The 2-methylfuran product desorbed at nearly the same temperature from these two NiCu bimetallic surfaces, indicating that the production of 2-methylfuran could be from a similar surface intermediate (e.g. $\eta^2(\text{C},\text{O})$ -bonded furfural) on both surfaces.

4. Conclusions

The reaction pathways of furfural on Cu(111), Ni(111) and NiCu bimetallic surfaces were investigated using a combination of DFT, TPD and HREELS. The onset of the HDO pathway of furfural on the NiCu bimetallic surfaces was explained by the increased degree of interaction with the carbonyl group of furfural compared with that on Cu(111). For example, Ni/Cu(111) had a stronger interaction with the carbonyl group of furfural which favored the HDO pathway. In addition, the enhanced dissociation of H₂ on Ni/Cu(111) over Cu(111) should also play a role in determining the reaction pathways. These studies provide important mechanistic insights into the effects of the bimetallic formation on the HDO of furfural.

Acknowledgements

We 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. 13-038.

Reference

- [1] B.H. Shanks, Conversion of Biorenewable Feedstocks: New Challenges in Heterogeneous Catalysis, *Ind.Eng.Chem.Res.*, 49 (2010) 10212-10217.
- [2] G.W. Huber, S. Iborra, A. Corma, Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering, *Chem. Rev.*, 106 (2006) 4044-4098.
- [3] A. Corma, S. Iborra, A. Velty, Chemical Routes for the Transformation of Biomass into Chemicals, *Chem. Rev.*, 107 (2007) 2411-2502.
- [4] H. Wang, J. Male, Y. Wang, Recent Advances in Hydrotreating of Pyrolysis Bio-Oil and Its Oxygen-Containing Model Compounds, *ACS Catal.*, 3 (2013) 1047-1070.
- [5] D. Vlachos, J. Chen, R. Gorte, G. Huber, M. Tsapatsis, Catalysis Center for Energy Innovation for Biomass Processing: Research Strategies and Goals, in: *Catal. Lett.*, Springer Netherlands, 2010, pp. 77-84.
- [6] H. Ren, W. Yu, M. Saliccioli, Y. Chen, Y. Huang, K. Xiong, D.G. Vlachos, J.G. Chen, Selective Hydrodeoxygenation of Biomass-Derived Oxygenates to Unsaturated Hydrocarbons using Molybdenum Carbide Catalysts, *ChemSusChem*, 6 (2013) 798-801.
- [7] J.-P. Lange, E.v.d. Heide, J.v. Buijtenen, R. Price, Furfural--A Promising Platform for Lignocellulosic Biofuels, *ChemSusChem*, 5 (2012) 150-166.
- [8] L.W. Burnett, I.B. Johns, R.F. Holdren, R.M. Hixon, Production of 2-Methylfuran by Vapor-Phase Hydrogenation of Furfural, *Industrial & Engineering Chemistry*, 40 (1948) 502-505.
- [9] R.M. Lukes, C.L. Wilson, Reactions of Furan Compounds. XI. Side Chain Reactions of Furfural and Furfuryl Alcohol over Nickel-Copper and Iron-Copper Catalysts¹, *J. Am. Chem. Soc.*, 73 (1951) 4790-4794.
- [10] S. Sitthisa, T. Sooknoi, Y.G. Ma, P.B. Balbuena, D.E. Resasco, Kinetics and mechanism of hydrogenation of furfural on Cu/SiO(2) catalysts, *J. Catal.*, 277 (2011) 1-13.
- [11] S. Sitthisa, D. Resasco, Hydrodeoxygenation of Furfural Over Supported Metal Catalysts: A Comparative Study of Cu, Pd and Ni, *Catal. Lett.*, 141 (2011) 784-791.
- [12] S. Sitthisa, W. An, D.E. Resasco, Selective conversion of furfural to methylfuran over silica-supported NiFe bimetallic catalysts, *J. Catal.*, 284 (2011) 90-101.
- [13] K. Xiong, W.-S. Lee, A. Bhan, J.G. Chen, Molybdenum Carbide as a Highly Selective Deoxygenation Catalyst for Converting Furfural to 2-Methylfuran, *ChemSusChem*, (2014) n/a-n/a.
- [14] K. Xiong, W. Yu, J.G. Chen, Selective deoxygenation of aldehydes and alcohols on molybdenum carbide (Mo₂C) surfaces, *Appl. Surf. Sci.*, 323 (2014) 88-95.
- [15] W.-S. Lee, Z. Wang, W. Zheng, D.G. Vlachos, A. Bhan, Vapor phase hydrodeoxygenation of furfural to 2-methylfuran on molybdenum carbide catalysts, *Catal. Sci. Technol.*, 4 (2014) 2340-2352.
- [16] S.K. Bej, C.A. Bennett, L.T. Thompson, Acid and base characteristics of molybdenum carbide catalysts, *Applied Catalysis A: General*, 250 (2003) 197-208.
- [17] Y. Nakagawa, M. Tamura, K. Tomishige, Catalytic Reduction of Biomass-Derived Furanic Compounds with Hydrogen, *ACS Catal.*, 3 (2013) 2655-2668.
- [18] K. Xiong, W. Yu, D.G. Vlachos, J.G. Chen, Reaction Pathways of Biomass-Derived Oxygenates over Metals and Carbides: From Model Surfaces to Supported Catalysts, *ChemCatChem*, 7 (2015) 1402-1421.
- [19] W. Yu, K. Xiong, N. Ji, M.D. Porosoff, J.G. Chen, Theoretical and experimental studies of the adsorption geometry and reaction pathways of furfural over FeNi bimetallic model surfaces and supported catalysts, *J. Catal.*, 317 (2014) 253-262.

- [20] J.G. Dickinson, P.E. Savage, Development of NiCu Catalysts for Aqueous-Phase Hydrodeoxygenation, *ACS Catal.*, 4 (2014) 2605-2615.
- [21] J.G. Dickinson, P.E. Savage, Stability and activity of Pt and Ni catalysts for hydrodeoxygenation in supercritical water, *Journal of Molecular Catalysis a-Chemical*, 388 (2014) 56-65.
- [22] G. Kresse, J. Furthmüller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Computational Materials Science*, 6 (1996) 15-50.
- [23] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Atoms, molecules, solids, and surfaces: Applications of the generalized gradient approximation for exchange and correlation, *Phys. Rev. B* J1 - PRB, 46 (1992) 6671 LP - 6687.
- [24] W.B. Pearson, A handbook of lattice spacings and structures of metals and alloys, 1967.
- [25] J.G. Chen, C.A. Menning, M.B. Zellner, Monolayer bimetallic surfaces: Experimental and theoretical studies of trends in electronic and chemical properties, *Surf. Sci. Rep.*, 63 (2008) 201-254.
- [26] P.J. Cumpson, M.P. Seah, Elastic Scattering Corrections in AES and XPS. II. Estimating Attenuation Lengths and Conditions Required for their Valid Use in Overlayer/Substrate Experiments, *Surf. Interface Anal.*, 25 (1997) 430-446.
- [27] M. Myint, Y. Yan, J.G. Chen, Reaction Pathways of Propanal and 1-Propanol on Fe/Ni(111) and Cu/Ni(111) Bimetallic Surfaces, *The Journal of Physical Chemistry C*, 118 (2014) 11340-11349.
- [28] H. Koschel, G. Held, H.P. Steinrück, The growth of thin Cu layers on Ni(111) studied by CO titration and photoelectron spectroscopy, *Surf. Sci.*, 453 (2000) 201-213.
- [29] B.A. Sexton, A vibrational and TDS study of the adsorption of pyrrole, furan and thiophene on Cu(100): Evidence for [pi]-bonded and inclined species, *Surf. Sci.*, 163 (1985) 99-113.
- [30] S.H. Pang, J.W. Medlin, Adsorption and Reaction of Furfural and Furfuryl Alcohol on Pd(111): Unique Reaction Pathways for Multifunctional Reagents, *ACS Catal.*, 1 (2011) 1272-1283.
- [31] F.P. Netzer, T.E. Madey, The structure of CO on Ni(111), *The Journal of Chemical Physics*, 76 (1982) 710-715.
- [32] T. Kim, R.S. Assary, L.A. Curtiss, C.L. Marshall, P.C. Stair, Vibrational properties of levulinic acid and furan derivatives: Raman spectroscopy and theoretical calculations, *Journal of Raman Spectroscopy*, 42 2069-2076.
- [33] W.W. Crew, R.J. Madix, Oxidative coupling and ring opening of furan on silver(110): formation of maleic anhydride, benzene, and bifuran, *J. Am. Chem. Soc.*, 115 (1993) 729-736.
- [34] D. Shi, J.M. Vohs, Deoxygenation of Biomass-Derived Oxygenates: Reaction of Furfural on Zn-Modified Pt(111), *ACS Catal.*, 5 (2015) 2177-2183.

Scheme 1. Labels of Furfural Schematic for Table 1

Scheme 2. (a) Optimized configuration of furfural on Cu(111); (b) Optimized configuration of furfural on Ni(111); (c) Optimized configuration of furfural on Ni/Cu(111). Mauve labels Ni atom, cyan labels Cu atom, gray labels C atom, red labels O atom and white labels H atom

Figure 1. TPD of 4 L furfural on H₂ pre-dosed (a) Cu(111) and (b) Ni/Cu(111) surfaces

Figure 2. TPD of 4 L furfuryl alcohol on H₂ pre-dosed (a) Cu(111) and (b) Ni/Cu(111) surfaces

Figure 3. TPD of 4 L 2-methylfuran on H₂ pre-dosed Ni/Cu(111) surface

Figure 4. TPD of 4 furfural on H_2 pre-dosed (a) Ni(111) and (b) Cu/Ni(111) surfaces

Figure 5. HREELS of 4 L furfural (red) and 4 L furan (black) on H₂ pre-dosed Cu(111)

Figure 6. HREELS of 4 L furfural (red) and 2-methylfuran (blue) on H₂ pre-dosed Ni/Cu(111)

Table 1. Bind Energies (BE/eV) and Bond Lengths (/Å) of Furfural from DFT calculations

Surface	BE	C2-O1	C5-O1	C2-C3	C3-C4	C4-C5	C2-C6	C6-O7
N/A ^[a]	--	1.38	1.36	1.38	1.42	1.37	1.45	1.23
Ni(111)	0.76	1.41	1.47	1.43	1.42	1.45	1.43	1.32
Cu(111)	0.22	1.38	1.36	1.38	1.41	1.37	1.44	1.24
Ni/Cu(111)	1.21	1.41	1.47	1.44	1.43	1.45	1.44	1.32

Note:[a] bond lengths of furfural in the gas phase

Table 2. TPD Quantification of Furfural Reactions

Surface	Activity (molecules per metal atom)				Total
	2-Methylfuran	Furan	Hydrocarbon	Unselective Decomposition	
H/Cu(111)	0	0.002	0	0	0.002
H/Ni/Cu(111)	0.001	0	0	0.031	0.032
H/Ni(111)	0	0	0.003	0.108	0.111
H/Cu/Ni(111)	0.003	0	0.044	0.009	0.056

Table 3. TPD Quantification of Furfuryl Alcohol Reactions

Surface	Activity (molecules per metal atom)			Total
	2-methylfuran	Furfural	Unselective Decomposition	
H/Cu(111)	0	0.006	0	0.006
H/Ni/Cu(111)	0.002	0.001	0.045	0.048

Table 4. Vibrational Mode Assignment of Furfural

Mode	Frequency (cm ⁻¹)					
	Raman ^[a]	Mo ₂ C ^[b]	H/Cu(111) ^[c]	Cu(111) ^[d]	H/Ni/Cu(111) ^[e]	Ni/Cu(111) ^[f]
τ (ring)		595	584	586, 625	577	653
ω (CH)		758	758	741, 770	745	713, 752, 754, 768
δ (ring)		866		828, 868, 889	873	803, 831
ν (CO)	930			905		921
χ (CH)	950			941		989
ν (CO)	1025	1028		1025, 1079	1027	1016
δ _b (O-C-H)	1157	1136		1145	1141	1122, 1164
ρ (CH)		1238		1207, 1263		1219, 1230
δ _b (O-C-H)	1370	1353	1356	1343	1336	1312
ν (CC)	1395			1387		1330
ν (C=C)	1466	1427		1443	1436	1415
ν (C=C)	1555, 1570	1536		1533	1578	
ν (C=O)	1684	1644	1624	1641		
ν (CH)		2882	2812	2857	2879	2973
ν (CH)	3153	3091	3081	3194	3087	3037

τ – torsion, ω - wagging, δ - deformation, ν – symmetric stretching,
 χ – scissoring, δ_b – bending, ρ - rocking

[a] Reference[32]

[b] Reference[13]

[c] Frequencies of furfural on H/Cu(111) at 230 K as shown in Figure 5

[d] Frequencies of furfural on Cu(111) from DFT calculations

[e] Frequencies of furfural on H/Ni/Cu(111) at 230 K as shown in Figure 6

[f] Frequencies of furfural on Ni/Cu(111) from DFT calculations

Graphical abstract