Theoretical Study of the Mechanism of Furfural Conversion on the NiCuCu(111) Surface

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**ABSTRACT:** The full potential energy surface for the hydrodeoxygenation of furfural to furan and other ring-opening products has been systematically investigated using periodic density functional theory including dispersion corrections (PBE-D3) on the bimetallic NiCuCu(111) surface. For furan formation, the most favorable first step is the dehydrogenation of furfural into furoyl (F-CHO + H = F-CO + 2H), the successive step is decarbonylation of furoyl into furanyl (F-CO + H = F + CO + 2H), and the third step of furan formation from the hydrogenation of furanyl (F + CO + 2H = FA + CO + H) is the rate-determining step. In addition, on the basis of the most stably adsorbed furan and H, the ring opening of furan was found to be more favorable for producing many chemicals such as propane, butanal, butanol, and butene. In summary, furan is the main product of furfural conversion on the NiCuCu(111) surface. Since results have been obtained only for the NiCuCu(111) surface constructed by replacing the topmost Cu atoms by Ni atoms, the entire experimentally observed reactivity and selectivity of bimetallic CuNi catalysts for different construction methods cannot be fully rationalized. Nevertheless, the results provide the basis for investigating the intrinsic activity of CuNi catalysts in the hydrodeoxygenation of oxygenates involved in the refining of biomass-derived oils.

1. INTRODUCTION

The furfural molecule contains a carbonyl group and furan ring, which contains two C=C double bonds and one cyclic ether bond. The furfural molecule, therefore, is highly reactive and can be converted into many useful chemicals such as furan, tetrahydrofuran, furfuryl alcohol, tetrahydrofurfuryl alcohol, and 2-methylfuran through decarbonylation, hydrogenation, and hydrodeoxygenation. It is a multiply oxygenated compound usually found in bio-oils and is considered as a key molecule in biomass conversion, which has been widely studied by researchers.

Experimentally, furfural can be converted to different products using a variety of catalysts. Reactions involving the use of this molecule have been extensively studied employing single-metal catalysts such as Cu, Ni, Pd, Pt, and Ru. For example, Sitthisa et al. found that at a low temperature, furfural is hydrogenated mainly to furfuryl alcohol and a small amount of 2-methylfuran, and the production of 2-methylfuran increases at high temperatures (>200 °C) upon using a Cu-based catalyst. Using a Pd-based catalyst, a 99.5% production of furan can be achieved in the decarbonylation of furfural.

Recently, it has been found that after a metal is doped with another metal to form a bimetallic catalyst, its activity changes significantly due to the structural or electronic effects, possibly affording a new catalyst with higher catalytic performance and broad application prospects in catalysis. Non-noble-metal bimetallic CuNi catalysts have received widespread attention because of their low cost. Lukes et al. found as early as in 1951 that furan is the main product in furfural conversion using bimetallic CuNi (Cu/Ni = 1:1) catalysts at temperatures of more than 200 °C. Merat’s research team and Liu’s group found that furfural hydrogenation mainly produced tetrahydrofurfuryl alcohol with a yield of >90% employing the bimetallic catalyst using a Cu/Ni molar ratio of 1/1. Results obtained by Yang et al. showed that the main product of the furfural reaction catalyzed by a CuNi bimetallic catalyst in an aqueous solvent is cyclopentanone. Recently, it has been determined that the properties of CuNi bimetallic catalysts in the liquid-phase hydrogenation of furfural are significantly affected by the chemical composition of the catalyst as well as the method and solvent used in the reaction. For example, the optimized CuNi (Cu/Ni = 1/1) catalyst showed high activity and selectivity for furfural conversion to tetrahydrofurfuryl alcohol in ethanol, whereas the main product converted to furfuryl alcohol in methanol.

These experimental studies have shown that even for the same catalyst, the selectivities and activities of the catalyst are different under different experimental conditions. This needs to be rationalized on the basis of the theoretically determined reaction mechanisms. However, few theoretical studies have been undertaken to investigate the reaction mechanism of furfural conversion on bimetallic catalysts. Xiong et al. studied only the adsorption configuration of furfural on CuNi bimetallic catalysts and speculated the possible reaction mechanism according to the adsorption configuration, but the specific reaction mechanism has not been clarified.
In this work, the dispersion-corrected PBE-D3 method was used to explore the mechanism of furfural conversion to furan as well as the reaction of furan on the bimetallic NiCuCu(111) surface. On the basis of the computed kinetic and thermodynamic results, the minimum reaction path and rate-determining step were identified. In agreement with the experimental data, the results provide insights into the bimetallic CuNi-catalyzed selective furfural conversion and broaden the fundamental understanding of the selective deoxygenation reactions of biomass-derived oxygenates.

2. RESULTS AND DISCUSSION

2.1. Adsorption of Intermediates. The top and side views of the NiCuCu(111) surface are shown in Figure 1. There are four potential exposed sites for adsorption, i.e., the top (t), bridge (b), 3-fold hollow face-centered cubic (fcc) site over the third layer of atoms, and 3-fold hexagonal close-packed (hcp) site over the second layer of atoms.

2.1.1. Adsorption of Furfural, Furan, Propene, Propane, Butanal, Butanol, Butene, and Butane on the NiCuCu(111) Surface. The adsorptions of the trans and cis configurations of furfural (F-CHO, F = 2-furanyl) as well as furan (FA), propene (CH3CHCH2), propane (CH3CH2CH3), butanal (R-CHO, R= CH3CH2CH2), butene (R-CH=CH2, R′ = CH3CH2), and butane (R-CH3) were computed on the NiCuCu(111) surface. The adsorption configurations and their structural properties are shown in Figure 1 and Table 1, respectively.

For the adsorptions of cis- and trans-furfural, it was found that all C and O atoms interacted with the surface Ni atoms, and the entire molecule was parallel to the surface. As shown in Figure 1, F-CHO showed an obvious η2(C=O) surface bonding mode, as the C=O bonds were elongated by 0.087 and 0.097 Å, compared with the corresponding bonds in the gas phase. The computed adsorption energies of cis- and trans-F-CHO were −1.78 and −1.88 eV, respectively, significantly

| configuration | E_{ads} (eV) | d_{Ni-C} (Å) | d_{Ni-O} (Å) | d_{Ni-H} (Å) |
|---------------|--------------|--------------|--------------|--------------|
| cis-furfural  | −1.78        | 2.223, 1.987, 2.414, 2.097, 2.067, 1.995 | 2.391 | 1.910 |
| trans-furfural| −1.88        | 2.065, 2.026, 2.060, 2.452, 2.105, 1.984 | 2.235 | 1.910 |
| furan         | −1.42        | 1.979, 2.074, 2.477, 2.083, 1.976 | 2.190 | 1.976 |
| propene       | −1.95        | 2.147, 2.147, 2.136, 1.970 | 1.885, 1.904 |
| propane       | −0.54        | 1.967 | 1.980, 2.000 | 1.916 |
| butanal       | −1.08        | 1.967 | 1.980, 2.000 | 1.916 |
| butanol       | −1.03        | 2.034 | 1.895, 1.872 |
| butene        | −1.48        | 2.143, 2.130, 2.154, 1.975 | 1.895, 1.872 |
| butane        | −0.73        | 1.587, 1.589 |
| H$_2$         | −0.61        | 1.686, 1.689, 1.689, 1.685, 1.689 | 1.689, 1.691 |
| 2H            | −1.66        | 1.587, 1.589 | 1.686, 1.689, 1.689, 1.685, 1.689, 1.691 |
larger than those on the Cu(111) surface (−0.88 and −0.91 eV),\textsuperscript{31} for which F-CHO showed a $\eta^1$(O) surface bonding mode. In addition, the values were lower than those obtained on the Mo2C(101) surface (−2.68 and −2.50 eV),\textsuperscript{32} for which F-CHO showed the same $\eta^1$(C==O) surface bonding mode.

Furthermore, the adsorptions of furan (FA), propene (CH3CHCH2), propane (CH3CH2CH3), butanal (R-CHO), butanol (R-CH2OH), butene (R-CH==CH2), and butane (R-CH4) were computed. For FA, a similar adsorption configuration as that of F-CHO was observed and the computed adsorption energy was −1.42 eV. For propene and butene, the molecule interacted with the surface mainly through the C==C bond with one C atom at the fcc site and one C at the top site, and the adsorption energies were −1.95 and −1.48 eV, respectively. For propane and butane, the molecules were above the surface with all C atoms over the top sites without direct bonding interactions, and the adsorption energies were −0.54 and −0.73 eV, respectively. For R-CHO, the molecules contacted the surface mainly through the C==O bond, and the Ni–O distances were 1.980 and 2.000 Å, the Ni–C distance was 1.967 Å. This shows that R-CHO exhibited a $\eta^1$(C==O) surface bonding mode, where the C==O distance was elongated by 0.152 Å compared with that in the gas phase, and the computed adsorption energy was −1.08 eV. The most stable adsorption of R-CH2OH contacted with the surface via the O atom and two H atoms, in which the Ni–O and two Ni–H distances were 2.034, and 1.895 and 1.872 Å, respectively. The adsorption energy was −1.03 eV, which was slightly lower than that of R-CHO.

2.1.2. $\text{H}_2$ Dissociative Adsorption. As $\text{H}_2$ is used in furfural conversion, $\text{H}_2$ dissociative adsorption on the NiCuCu(111) surface was computed for direct comparison with that on the Cu(111) surface.\textsuperscript{31} The adsorption configurations and structural properties are shown in Figure 2. $\text{H}_2$ was adsorbed at the top site, parallel to the surface, and the Ni–H distances were 1.587 and 1.589 Å, which were much shorter than those (2.960 and 3.022 Å) on the Cu(111) surface, indicating stronger adsorption of $\text{H}_2$ in this case than on the Cu(111) surface. In effect, the adsorption energy was −0.61 eV, much higher than that (−0.08 eV) on the Cu(111) surface.

Starting from the molecularly adsorbed $\text{H}_2$ at the top site, the dissociative adsorption of two H atoms showed a barrier of only 0.08 eV and was highly exothermic by 1.05 eV, indicating a thermodynamically and kinetically favorable process. Compared with the results obtained for the Cu(111) surface,\textsuperscript{31} it was concluded that $\text{H}_2$ dissociative adsorption on the NiCuCu(111) surface was significantly more favored both kinetically (0.08 vs 0.59 eV) and thermodynamically (−1.05 vs −0.55 eV). In the transition state TS($\text{H}_2$−H), both H atoms were at the top sites with a H–H distance of 1.156 Å, and the Ni–H distances were 1.490 and 1.508 Å. For the most stable co-adsorption of two H atoms, one H atom was at the fcc site and the other was at the hcp site, and they shared one surface Ni atom, wherein the distance between the two H atoms was 2.961 Å and the corresponding Ni–H distances were 1.686, 1.689, and 1.689 Å as well as 1.685, 1.689, and 1.691 Å.

Furthermore, $\text{H}$ diffusion from one hcp site to the neighboring fcc site was computed, which had a barrier of only 0.13 eV and was neutral in terms of reaction energy, indicating the high mobility of surface $\text{H}$ atoms. This result was in close agreement with that observed for the Cu(111) surface.\textsuperscript{31} In the transition state TS($\text{H}_{\text{hcp}}$−H$_{\text{fcc}}$), a H atom bridged the Ni–Ni bond with a Ni–H distance of 1.608 Å. In addition, the co-adsorption of two H atoms at two remote fcc sites was less stable by 0.02 eV than that where both H atoms at two neighboring fcc sites shared one Ni atom. For the adsorption of one H atom, the computed adsorption energy at the fcc site was slightly higher than that at the hcp site (the values were −3.25 and −3.23 eV, respectively).

2.2. Mechanisms of Furfural Conversion. Using the most stably adsorbed trans-F-CHO in the parallel configuration, the full potential energy surface (PES) for furfural selective conversion was computed, for which the energy barrier and reaction energy were computed on the basis of the stable species without direct co-adsorption interactions. As the adsorption energies of the H atom on the fcc and hcp sites were very close in value and the H atom showed high diffusion mobility, a H atom was placed on either the fcc site or the hcp site for computation, which was close to the substrates, for finding the transition states. The selected structural parameters of the IS, TS, and FS, as well as the computed energy barrier and reaction energy, are included in the Supporting Information (Tables S1 and S2).

2.2.1. −CH==O Hydrogenation against Dissociation. For the first reaction route of furfural, five possible reaction pathways were considered: selective hydrogenation of the −CH==O group, i.e., (a) a hydrogenation of the C atom of the C==O group (R1, F-CHO + H = F-CH2O) and (b) hydrogenation of the O atom of the C==O group (R2, F-CHO + H = F-COHOH), and the parallel and competitive −CH==O dissociation reactions, i.e., (c) direct C−H dissociation (R3, F-CHO + H = F-CO + 2H), (d) direct C==O dissociation (R4, F-CHO + H = F-CH + O + H), and (e) direct −CHO dissociation (R5, F-CHO + H = F + CHO + H). The optimized structures of the adsorbed intermediates are shown in the Supporting Information (Figure S1). The full PES was plotted on the basis of a step-by-step comparison (Figure 3), i.e., searching all possible pathways for a given adsorbed species gained from the previous step and continuing with only the reaction pathways with the lowest reaction barriers while abandoning those with clear high barriers.

In the reaction step R1, a H atom was added to the C atom of the C==O group, leading to a F-CH2O intermediate. In the co-adsorbed structure (IS1), the H atom was located at the hcp site in the vicinity of the −CH==O group with Ni–H distances of 1.665, 1.673, and 1.711 Å. In the transition state (TS1), the H atom moved to the top site and the forming C6−
H distance observed was 1.551 Å. In the final state (FS1), the adsorption of the C6 atom occurred away from the surface and the O7 was at the bridge site with Ni−O distances of 1.934 and 1.929 Å. The computed energy barrier was 0.89 eV, and the reaction was exothermic by 0.40 eV. The alternative reaction route to R1 was the H addition to the O atom of the C=O group, resulting in a F-CHOH intermediate. In the transition state (TS2), the forming O7−H distance was 1.378 Å and the H atom was at the bridge site away from the original hcp site. The energy barrier was 0.85 eV, and the reaction was endothermic by 0.42 eV. This indicated that F-CH2O and F-CHOH formations were parallel and were both kinetically (0.89 vs 0.85) and thermodynamically (0.40 vs 0.42 eV) competitive.

The parallel and competitive reactions of −HC=O hydrogenation are direct C−H, C=O, and CHO dissociations. In the R3 step (F-CHO + H = F-CO + 2H), F-CHO dissociated into F-CO and H. In the transition state (TS3), the C6−H breaking distance was 1.690 Å and H moved to the top site with a Ni−H distance of 1.512 Å. The energy barrier was 0.42 eV, and the reaction energy was −0.13 eV. For F-CHO dissociation into F-CH and O (R4), the transition state (TS4) and the final state (FS4) were computed. In TS4, the O atom moved from the top site to the bridge site, and the C6−O7 breaking distance was 1.822 Å. The energy barrier was 1.32 eV, and the reaction energy was −0.42 eV. For direct CHO dissociation (R5, F-CHO + H = F + CHO + H), the energy barrier was 1.11 eV and the reaction energy was 0.50 eV. As shown in Figure 3, all of these results clearly demonstrate that direct C−H dissociation involves the lowest energy barrier and is most kinetically favorable. Therefore, the co-adsorption of surface F-CO and H was used to discuss the furan formation.

2.2.2. Furan Formation. Starting from the most stable co-adsorption of F-CO and H, CO dissociation (R6, F-CO + 2H = F + CO + 2H) was first computed. In the transition state TS6, the C−C breaking distance was 1.876 Å and the O atom of the CO group was away from the surface. In the final state (FS6), the CO molecule formed was almost perpendicular to the surface with the C atom located at the fcc site, and the Ni−C distances were 1.921, 1.925, and 1.918 Å. The computed energy barrier was 0.63 eV, and the reaction was exothermic by 0.70 eV. Second, on the basis of the most stable co-adsorbed F−CO+2H, furan formation was computed (R7, F + CO + 2H = FA + CO + H). The forming C−H distance determined was 1.763 Å for TS7. In FS7, furan and CO were as far away from each other as possible without direct co-adsorption. The energy barrier was 0.76 eV, and the reaction energy was −0.33 eV. As shown in Figure 3, on the NiCuCu(111) surface, furan formation was both kinetically and thermodynamically facile. In the following sections, the hydrogenation and ring opening of furan will be discussed.

2.2.3. Propene and Propane Formation. On the basis of the co-adsorption of furan and H, the hydrogenation and ring opening of the furan ring were computed. The optimized structures of the adsorbed intermediates are shown in the Supporting Information (Figure S2), and the potential energy surface is shown in Figure 4. For the hydrogenation reaction, there are two possible reaction routes: a H atom is added either to the C2 atom (R8, FA + H = FA-C2H) or to the C3 atom (R9, FA + H = FA-C3H), as C5 and C4 atoms are equivalent to C2 and C3 atoms, respectively. The computed results show that the energy barriers of R8 and R9 are very close (0.93 and 0.95 eV, respectively), and the reaction energies are 0.57 and 0.73 eV, respectively. This result implies that hydrogenation of the C2 atom is slightly more favored than that of the C3 atom kinetically (0.93 vs 0.95 eV) and thermodynamically (0.57 vs 0.73 eV) and therefore the steps should be competitive.
In addition, starting from the most stable adsorption of furan and H as the initial state (IS10), the ring opening of furan (R10, FA + H = C3H4O + H) was computed. In the transition state (TS10), the C5−O1 breaking distance was 1.839 Å. The computed energy barrier was only 0.41 eV, and the reaction was exothermic by 0.59 eV. Compared with the hydrogenation of the furan ring, the C−O breaking was much more kinetically (0.41 vs 0.93 and 0.95 eV) and thermodynamically (∼0.59 vs 0.57 and 0.73 eV) favored. Therefore, surface C3H4O + H was used for the subsequent reaction.

First, on the basis of the most stable adsorption of C3H4O + H, the dissociation of CHO into C3H3 + CHO + H (R11, C4H5O + H = C3H3 + CHO + H) was computed. In the transition state (TS11), the C−C breaking distance was 1.961 Å. In FS11, the dissociated CHO group was at the fcc site owing to the interaction between Ni and C as well as that between Ni and O. The energy barrier was 0.67 eV, and the reaction was endothermic by 0.19 eV. Second, starting from the co-adsorbed C3H3 + CHO + H, the hydrogenation of C3H3 and dehydrogenation of CHO were calculated separately. The computed results indicated no transition state in the dehydrogenation of CHO into CO + H (C3H4 + CHO + H = C3H3 + CHO + 2H) as the structure with a reasonable C−H distance showed a lower energy than that of the initial state. This implied that CHO dissociation into CO + H was spontaneous and highly exothermic by 1.41 eV. With respect to the hydrogenation of C3H3, there are two competitive and parallel pathways: H addition to the C1 atom leading to CH2CHCH (R12, C3H3 + 2H + CO = CH2CHCH + H + CO) and H addition to the C2 atom resulting in CH2CHCH (R13, C3H3 + 2H + CO = CH2CHCH + H + CO), as the C3 atom is the same as the C1 atom. As shown in Figures 5 and S3, CH2CHCH formation involved a lower barrier (0.60 vs 1.20 eV) and reaction energy (0.16 vs 0.59 eV) than CH2CHCH formation. It was concluded that as the reaction energy increases, the energy barrier increases. Therefore, only the step showing the lowest reaction energy was considered in the subsequent hydrogenation of CH2CHCH.

Following the hydrogenation of the C1 atom leading to CH2CHCH, the H addition to the C3 atom leading to CH2CHCH (R14, CH2CHCH + H + CO = CH2CHCH + CO) was computed as it had a lower reaction energy than that of hydrogenation of C1 (CH2CHCH + H + CO = CH2CHCH + CO) and C2 (CH2CHCH + H + CO = CH2CHCH + CO) atoms (0.06 vs 0.46 and 0.68 eV). The computed results indicated that hydrogenation of the C3 atom had the lowest barrier (0.49 vs 1.00 and 1.04 eV, Figure S7).

On the basis of the most stable adsorption of CH3CH2 + CO, the co-adsorption of one H atom as the initial state (IS15) was computed and two parallel and competitive pathways were considered: the hydrogenation of C1 leading to propene (R15, CH2CHCH + H + CO = CH3CHCH + CO) and the C2 atom resulting in the CH2CHCH intermediate (CH2CHCH + H + CO = CH2CHCH + CO). It was found that the reaction energy of propene formation was lower than that of CH2CHCH formation (0.44 vs 0.68 eV, Figure S7), therefore, the transition state of propene formation (TS15) was located where H moved to the top site from the original fcc site and the forming C−H distance was 1.510 Å, and the computed barrier was 0.95 eV. Subsequently, the adsorption energies of CH3CHCHs owing to H addition to the C2 atom (R16, CH3CHCH + H + CO = CH3CHCH + CO) and HCHCH3s owing to H addition to the C3 atom (CH2CHCH + H + CO = CH2CHCH + CO) were computed, and it was determined that the formation of CH3CHCHs required a lower energy (0.25 vs 0.60 eV, Figure S7) than that of CH3CHCHs. The computed energy barrier of CH3CHCH formation was only 0.29 eV, indicating that it was the kinetically favorable step. The last step of propene formation was the hydrogenation of the C2 atom (R17, CH3CHCH + H + CO = CH3CHCH + CO), which showed a barrier of 1.00 eV, and the reaction was endothermic by 0.12 eV.

2.2.4. Butanal Formation. The alternative way to CHO dissociation is the hydrogenation of C4H4O. On the basis of the most stable adsorbed C4H4O, the co-adsorption of one H atom in the initial state (C4H4O + H) was computed for the following parallel and competitive pathways: the hydrogenation of the O atom or the four other C atoms leading to C4H4-OH (R18, C4H4O + H = C4H4-OH) or C4H4O (R19, C4H4O + H = C4H4-OH + H) and the formation of CH4H4 (R20, C4H4O + H = C4H4-OH + C2H2; R21, C4H4O + H = C4H4-OH + C2H2) or C4H4O-C3H2 (R22, C4H4O + H = C4H4O-C3H2), respectively. The optimized structures are given in the Supporting Information (Figure S4), and the potential energy surface is also shown in Figure 4. Starting from the co-adsorbed C4H4O and H, the C4H4-OH intermediate was computed. In TS18, the forming O−H distance was 1.441 Å, the energy barrier was 0.96 eV, and the reaction energy was 0.58 eV. For the hydrogenation of four C atoms, the energy barrier was found to be 1.02, 1.05, 0.94, and 0.79 eV, and the reaction energies were 0.84, 0.84, 0.78, and 0.34 eV for the formation of C4H4-O-C2H2, C4H4-O-C3H2, C4H4-O-C4H2, and C4H4-O-C5H2, respectively. As expected, the hydrogenation of the C5 atom was the most favored, both kinetically (0.79 vs 1.02, 1.05, 0.94, and 0.96 eV) and
thermodynamically (0.34 vs 0.84, 0.84, 0.78, and 0.58 eV). Under hydrogenation-rich conditions, it can be assumed that hydrogenation of the C5 atom and CHO dissociation should be competitive, although CHO dissociation is slightly more favored kinetically (0.67 vs 0.79 eV) and thermodynamically (0.19 vs 0.34 eV). In addition, the result showed that the most favored hydrogenation of the C3H4O intermediate occurred at the C atom, which was the farthest away from the −CHO group. Therefore, the hydrogenation of the C atom distant from the −CHO group was considered stepwise. The optimized structures are also given in the Supporting Information (Figure S4), and the potential energy surface is given in Figure 6.

![Figure 6. Potential energy surfaces (in eV) for the reaction routes of R23–R25 on the NiCuCu(111) surface.](image)

First, the second H addition to the C5 atom leading to the formation of the C5HbO-C5H3 intermediate (R23, C5HbO-C5H3 + H = C5HbO-C5H3) was computed; the energy barrier was found to be 0.83 eV, and the reaction was endothermic by 0.44 eV. As shown in the SI (Figure S7), the hydrogenation of the other three C atoms and the O atom was neither kinetically (0.83 vs 0.91, 1.10, 0.95, and 1.06 eV, respectively) nor thermodynamically (0.44 vs 0.69, 0.80, 0.77, and 0.51 eV, respectively) favored when compared with the hydrogenation of the C5 atom.

Second, starting from the co-adsorption of C5HbO-C5H3 and the H atom, the hydrogenation of the C4 atom was computed (R24, C5HbO-C5H3 + H = CH4CH2CHCHCHO). The energy barrier and reaction energy were 0.59 and 0.54 eV, respectively. Finally, butanal (R-CHO) was formed by the hydrogenation of the C3 atom (R25, CH4CH2CHCHCHO + H = R-CHO), with an energy barrier of 0.59 eV and a reaction energy of 0.21 eV.

2.2.5. Butanal and Butene Formation. On the basis of the most stable adsorption configuration of butanal and one H atom, the hydrogenation and dissociation of the CHO group according to the following pathways were considered: (a) the hydrogenation of the C atom of the C==O group (R26, R-CHO + H = R-CH2O), (b) the hydrogenation of the O atom of the C==O group (R27, R-CHO + H = R-CH2OH), and (c) direct −CHO dissociation (R28, R-CHO + H = R + CHO + H). The optimized structures are shown in the Supporting Information (Figure S5), and the energy profile is given in Figure 7.

On the basis of the co-adsorbed R-CHO + H, the hydrogenation of C and O atom of the CHO group was calculated. H addition to the C atom leading to the R-CH3O intermediate was much more kinetically (0.59 vs 0.81 eV) and thermodynamically (−0.10 vs 0.46 eV) favored than R-CHOH formation. In addition, direct CHO dissociation was less favored kinetically (1.10 vs 0.59 eV) than R-CH2O formation. As shown in Figure 7, the hydrogenation of the C atom resulting in R-CH3O was the most favorable for the first reaction step of butanal. Therefore, the surface R-CH2O was used for the formation of butanal (R-CH2OH).

Starting from the most stable adsorbed R-CH2O, the co-adsorption structure of one H atom was computed, and two competitive pathways were considered: the hydrogenation of O atom (R29, R-CH2O + H = R-CH2OH) and direct C−O dissociation (R30, R-CH2O + H = R-CH2 + O + H). The computed results show that R-CH2OH formation was slightly more favored kinetically (1.13 vs 1.23 eV) than C−O direct dissociation into R-CH2 + O. Therefore, the most stable surface species was R-CH2OH, which was used for the subsequent reaction.

On the basis of the most stable adsorption of R-CH2OH, the direct OH dissociation was computed (R31, R-CH2OH = R-CH2 + OH). In TS31, the C−O breaking distance was 2.320 Å, and the OH group was at the bridge site with Ni−O distances of 1.891 and 2.330 Å. The computed energy barrier was 1.57 eV, and the reaction was exothermic by 0.45 eV. Starting from the co-adsorbed R-CH2 + OH + H as the initial state, the parallel and competitive reaction pathways of butane formation (R32, R-CH2 + OH + H = R-CH3 + H2O), H2O formation (R33, R-CH2 + OH + H = R-CH2 + H2O), and butene formation (R34, R-CH2 + OH + H = R-CH=CH2 + 2H + OH) were computed. As shown in Figures 8 and S6, the formation of butene from β-H elimination was much more favored, both kinetically (0.07 vs 0.87 and 1.10 eV) and thermodynamically (−0.44 vs 0.12 and 0.50 eV), than butane and H2O formation. Therefore, the main product should be butene rather than butane. Nevertheless, butane formation is also possible under hydrogenation-rich conditions as it has a relatively low barrier of 0.87 eV and is slightly endothermic by 0.12 eV.

Finally, the formation of H2O (R35, R-′-CH=CH2 + 2H + OH = R-′-CH=CH2 + H2O) was computed on the NiCuCu(111) surface after the formation and desorption of butene. The computed energy barrier was 1.09 eV, and the reaction was endothermic by 0.51 eV.

![Figure 7. Potential energy surfaces (in eV) for the reaction routes of R26–R30 on the NiCuCu(111) surface.](image)
of Furan Formation on the NiCuCu(111) Surface

The computed energy barrier and reaction energy as well as the rate constant for furan formation are included in Table 2.

| reaction                  | $E_a$ (eV) | $E_r$ (eV) | $k$ (473 K) | $k$ (493 K) | $k$ (523 K) | $k$ (553 K) | $k$ (573 K) |
|---------------------------|------------|------------|-------------|-------------|-------------|-------------|-------------|
| F-CHO + H = F-CHOH        | 0.85       | 0.42       | 8.94 × 10^{-6} | 2.17 × 10^{-6} | 7.26 × 10^{-6} | 2.13 × 10^{-6} | 4.12 × 10^{-6} |
| F-CHO + H = F-CO + 2H     | 0.42       | -0.13      | 2.71 × 10^{-3} | 4.29 × 10^{-3} | 8.03 × 10^{-3} | 1.41 × 10^{-3} | 1.98 × 10^{-3} |
| F-CHO + H = F-CHO + O + H | 1.32       | -0.42      | 4.65 × 10^{-8} | 1.80 × 10^{-8} | 1.13 × 10^{-8} | 5.86 × 10^{-8} | 1.60 × 10^{-8} |
| F-CHO + H = F + CHO + H   | 1.11       | 0.50       | 2.30 × 10^{-1} | 7.22 × 10^{-1} | 3.43 × 10^{-1} | 1.38 × 10^{-1} | 3.22 × 10^{-1} |
| F-CO + 2H = F + CO + 2H   | 0.63       | -0.70      | 1.86 × 10^{-8} | 3.63 × 10^{-8} | 9.01 × 10^{-8} | 2.03 × 10^{-8} | 3.34 × 10^{-8} |
| F + CO + 2H = FA + CO + H | 0.76       | -0.33      | 1.59 × 10^{-8} | 3.53 × 10^{-8} | 1.04 × 10^{-8} | 2.76 × 10^{-8} | 4.98 × 10^{-8} |

2.2.6 Potential Energy Surface. On the basis of the above results and the full potential energy surfaces (Figures 3, 4, 5, 6, 7, and 8), the formation of the intermediates and the rate-determining step for the overall reaction would be interesting to investigate. In addition, to explain the selective conversion of furfural, the rate constants ($k$) were computed on the basis of the transition-state theory, \(^{33,34}\) which was used in my previous work.\(^{35}\) The computed energy barrier and reaction energy as well as the rate constant for furan formation are included in Table 2.

As shown in Figure 3, for the first step of the F-CHO reaction, C-H direct dissociation was the most favorable pathway as it had a lower barrier than that of the hydrogenation of C and O atoms as well as direct C==O and CHO dissociations (0.42 vs 0.89, 0.85, 1.32, and 1.11 eV, respectively). In addition, the computed rate constants also revealed that F-CHO dissociation into F-CO + H was the fastest, and the rate constant at 473 K was as high as 2.71 × 10^6, which was much higher than that of the other four reaction pathways (2.71 × 10^6 vs 2.44 × 10^3, 8.94 × 10^3, 4.63 × 10^{-5}, and 2.30 × 10^{-1}). In the subsequent reaction of FA formation starting from the surface F-CO + H, CO dissociation had a barrier of 0.63 eV, and the last step of FA formation with the highest energy barrier (0.76 eV) was the rate-determining step. As shown in Table 2, the computed rate constants were consistent with the energy barriers, wherein the formation of FA showed a lower rate constant than that of C-H and CO dissociations (1.59 × 10^8 vs 2.71 × 10^8 and 1.86 × 10^9, respectively). In addition, the rate constants of higher temperatures were also computed. As shown in Table 2, the results are in good agreement with those at 473 K, further confirming the predominance of the main product of furan for the studied reaction pathway.

Figure 3. Potential energy surfaces (in eV) for the reaction routes of R31–R35 on the NiCuCu(111) surface.

Figure 8. Potential energy surfaces (in eV) for the reaction routes of R31–R35 on the NiCuCu(111) surface.
On the basis of the above discussion, it could be concluded that furan was the main product of furfural conversion on the NiCuCu(111) surface as furan formation was highly exothermic by 1.16 eV, indicating a thermodynamically favorable process (Figure 3). This was in agreement with the experimental study, in which Lukes et al. found that furan was the main product with a yield of 46% upon using a 1:1 Ni–Cu catalyst above 200 °C. In addition, they did not observe the reduction of furan to tetrahydrofuran, which was consistent with my theoretical results, i.e., the ring opening of furan was much more favorable than the hydrogenation of furan (Figure 4). Based on the complete PES, the main product, furan, can also be converted into propane as well as butanal, butanol, and butene. This result also agrees with the experimental findings regarding butanal formation.

Furthermore, it is interesting to compare the results obtained in this study with those computed on the pure metallic Cu(111) surface. On the Cu(111) surface, F-CHO showed a tilted π*(O) surface bonding mode in which furfural interacted with the surface only via the O7 atom. On the bimetallic NiCuCu(111) surface, not only the −HC≡O group but also the furan ring was in contact with the surface and the molecule was nearly parallel to the surface. The adsorption energies of cis- and trans-F-CHO on the NiCuCu(111) surface (−1.78 and −1.88 eV, respectively) were much higher than those on the Cu(111) surface (−0.88 and −0.91 eV, respectively). As expected, the adsorption configurations of F-CHO were different on the two surfaces as the d-band of Cu was filled whereas that of Ni was unfilled, and this facilitated the electron transfer to the substrate.

Due to different adsorption configurations, different reaction mechanisms were possible on the two surfaces. On Cu(111), the most favorable process for the first step was the hydrogenation of the C atom of the C≡O group, leading to a F-CH2O intermediate. In the subsequent reaction, both F-CH2O hydrogenation into F-CH2OH and F-CH2O dissociation into F-CH2 were kinetically competitive and, in addition, the final product was F-CHO, resulting from F-CH2OH dissociation and hydrogenation as well as the hydrogenation of F-CH2. On NiCuCu(111), the F-CHO dehydrogenation into F-CO + H was much more kinetically and thermodynamically favored than F-CHO hydrogenation into F-CH2O, leading to the main product, furan. On the basis of the principal reaction of furan formation, formation of other products, such as propane, butanal, butanol, and butene, was considered possible. From the entire PES, CO constituted the remaining surface species, with a high adsorption energy of −2.30 eV. Therefore, it was inferred that CO may have accumulated on the surface and blocked the available surface sites, resulting in catalyst deactivation. This highlights the need to find ways to eliminate CO during experimental investigations.

3. CONCLUSIONS

In this study, the full potential energy surface of furfural conversion into furan and other ring-opening products on the NiCuCu(111) surface was investigated using periodic density functional theory computations including the latest correction of long-range dispersion interaction (PBE-D3). The goal was to clarify the full reaction mechanism by explaining the experimentally observed selectivity of furan as well as other byproducts in selective furfural conversion. All results obtained will contribute toward the fundamental understanding of the hydrodeoxygenation reactions of oxygenates obtained from biomass materials. Comparison of NiCuCu(111) and Cu(111) for furfural hydrodeoxygenation revealed their intrinsic differences in selectivity mainly owing to the different adsorption configurations of furfural.

On the basis of the detailed comparisons, F-CHO dissociation into F-CO + H (F-CHO + H = F-CO + 2H) could be considered as the most favorable reaction for the first step of furfural conversion, the subsequent step was the decarbonylation of F-CO into furanyl (F-CO + 2H = F + CO + 2H), and the last step of furan formation from the hydrogenation of furanyl (F + CO + 2H = FA + CO + H) was the rate-determining step. This implies that furan is the principal product of furfural conversion.

Starting from the most stable adsorption of furan and one H atom, the computed results showed that the ring opening was much more kinetically and thermodynamically favored than the hydrogenation of furan, indicating that there was no possibility of the reduction of furan to tetrahydrofuran. It was determined that the ring opening of furan could form a series of products, such as propane, butanal, butanol, and butene. Notably, the significant surface CO accumulation could occur due to the strong adsorption of CO and favorable decarbonylation of F-CO; therefore, researchers should consider eliminating the dissociated CO experimentally.

Finally, it should be noted that the computed results will not always show good agreement with all experimental observations using bimetallic Cu–Ni catalysts. This is because there are many factors that affect the activity of the catalyst in experiments, such as the composition, preparation method, morphology, and support of the catalyst. Especially, the reaction kinetics and products also depend on the changes of the reaction conditions, such as the realistic experimental temperatures and hydrogen pressures. In addition, there are different methods for constructing monolayer bimetallic surfaces; in this study, only one of them was selected to investigate the furfural conversion. In the future, it would be interesting to explore other methods to construct Cu–Ni bimetallic surfaces to study furfural hydrodeoxygenation.

4. COMPUTATIONAL METHODS AND MODELS

4.1. Methods. All calculations were performed using the plane-wave-based periodic density functional theory (DFT) method implemented in Vienna ab initio simulation package (VASP, version 5.3.5), wherein the ionic cores were described by the projector-augmented wave (PAW) method. The exchange and correlation energies were computed using the Perdew, Burke, and Ernzerhof functional together with the latest dispersion correction for counting van de Waals interactions (PBE-D3). To ensure accurate energies with errors of less than 1 meV per atom, a cutoff energy of 400 eV and the Gaussian electron smearing method with σ = 0.10 eV were used. Geometry optimization was performed until the forces acting on atoms were lower than 0.02 eV Å⁻¹, whereas the energy threshold-defining self-consistency of the electron density was set at 10⁻⁴ eV. All transition-state structures were located using the climbing image nudged elastic band (CI-NEB) method. For each optimized stationary point, vibrational analysis was carried out at the same level of theory to determine its characteristic as the minimum or saddle point, and it was ensured that each transition state had only one imaginary frequency along the reaction coordinate. In my previous work, it was demonstrated that the zero-point
energy correction had a slight effect on the calculated kinetic and thermodynamic results; therefore, it was not included in this study. For bulk optimization, the lattice parameter of the face-centered cubic (fcc) Cu unit cell was determined by minimizing the total energy using a conjugated gradient algorithm to relax the ions, and a $15 \times 15 \times 15$ Monkhorst-Pack k-point grid was used for sampling the Brillouin zone. The computed lattice parameter of 3.561 Å was in good agreement with the experimental value (3.614 Å) and results of other DFT calculations.

4.2. Models. Chen et al. found that depending on the deposition temperature and reaction environment, the bimetallic surface can be in one of the three structures: occupying the topmost surface sites to produce the surface monolayer, diffusing into the subsurface region to form the subsurface monolayer, and alloying with the surface to produce intermixed bimetallic surfaces. In a previous work by Myint, the Fe/Ni(111) and Cu/Ni(111) surfaces were modified by replacing all Ni atoms in the top layer with Fe or Cu atoms. In addition, Xiong et al. modeled the Ni/Cu(111) surface by replacing all Cu atoms in the first layer of Cu(111) with Ni atoms. In my previous study, a three-layer model of the most stable Cu(111) surface was chosen to investigate the selective hydrodeoxygenation of furfural, where the first layer was allowed to relax, whereas the bottom two layers were fixed as bulk positions by maintaining their optimized lattice constants. In this study, the NiCuCu(111) surface was constructed by replacing all Cu atoms of the first layer with Ni atoms, in agreement with the previous reports.

The surface structural relaxation and total energy calculations were performed with $3 \times 3 \times 3$ Monkhorst-Pack k-point sampling. For relevant gas phase species, a cubic box with a side of 15 Å was used to determine the structures and total energies.

The adsorption energy ($E_{\text{ads}}$) was calculated according to the equation $E_{\text{ads}} = E_{X/slab} - E_{X} - E_{\text{slab}}$, where $E_{X/slab}$ is the total energy of the slab with the adsorbate in its equilibrium structure, $E_{X}$ is the total energy of the slab without the adsorbate, and $E_{\text{slab}}$ is the total energy of the free adsorbate in the gas phase. According to this relationship, the more negative the $E_{\text{ads}}$ the stronger the adsorption. The energy barrier ($E_{\text{b}}$) and reaction energy ($E_{\text{r}}$) were calculated according to the equations $E_{\text{b}} = E_{\text{TS}} - E_{\text{IS}}$ and $E_{\text{r}} = E_{\text{FS}} - E_{\text{TS}} + E_{\text{ads}}$, where $E_{\text{IS}}, E_{\text{TS}}, E_{\text{FS}}$, and $E_{\text{ads}}$ are the total energies of the initial state (IS), transition state (TS), and the final state (FS), respectively.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02237.

Bond distances (Å) of the IS, TS, and FS for furfural hydrodeoxygenation on the NiCuCu(111) surface (Table S1); energy barrier $E_{\text{b}}$ (eV) and reaction energy $E_{\text{r}}$ (eV) of furfural hydrodeoxygenation on the NiCuCu(111) surface (Table S2); top and side views of the optimized geometries for the reaction routes of R1–R7, R8–R11, R12–R17, R18–R25, R26–R30, R31–R35, and R36–R43 on the NiCuCu(111) surface (Figures S1–S7) (PDF)

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