Exploring the Reaction Mechanisms of Furfural Hydrodeoxygenation on a CuNiCu(111) Bimetallic Catalyst Surface from Computation

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ABSTRACT: In this study, the selectively catalytic hydrodeoxygenation of furfural (F−CHO) to 2-methylfuran (F−CH3) on the CuNiCu(111) bimetallic catalyst surface was systematically investigated based on the periodic density functional theory, including dispersion correction. The formation of furfuryl alcohol (F−CH2OH) involved two steps: the preferred first step was the hydrogenation of the branched C atom, forming the alkoxyl intermediate (F−CHO + H = F−CH2O), and the second step was H addition to the alkoxyl group, resulting in furfuryl alcohol (F−CH2O + H = F−CH2OH), which was the rate-controlling step. In contrast, in the formation of 2-methylfuran, the first step was the dehydroxylation of furfuryl alcohol, resulting in alkyl (F−CH2) and OH (F−CH2OH = F−CH2 + OH) groups, the second step was the hydrogenation of F−CH2 (F−CH2 + OH+H=F−CH3 + OH), and the rate-controlling step was the hydrogenation of OH to H2O (OH + H = H2O). Based on the comparison results of the NiCuCu(111), Cu(111), and CuNiCu(111) surfaces, it was concluded that the catalytic performance of the catalyst was closely related to the adsorption structure of furfural. These results provide a basis for studying the intrinsic activity of NiCu catalysts during the hydrodeoxygenation of refined oxygenated compounds involving biomass-derived oils.

1. INTRODUCTION

Owing to the increasing number of problems and challenges posed by environmental pollution, population growth, and exhaustion of fossil fuels, the effective use of renewable biomass as an alternative source to chemicals and fuels has attracted extensive attention in science and technology.1−5 Furfural, one of the most important biomass-derived chemicals, can be selectively catalyzed into several highly valued derivatives, such as furfuryl alcohol, furan, and 2-methylfuran, through hydrogenation, decarbonylation, and hydrodeoxygenation.6−10 For instance, 2-methylfuran, the half-hydrogenation product of furfural, has been considered as a better additive to gasoline. Therefore, the selective conversion of furfural to 2-methylfuran has become the subject of intensive scientific research.

Experimentally, furfural can be selectively converted into 2-methylfuran using both metal catalysts and transition-metal carbide catalysts. The metal catalysts that can catalyze the conversion of furfural to 2-methylfuran are mainly copper-based11−17 and ruthenium-based18−22 catalysts. Dong et al.15 prepared an AE-Cu/SiO2 catalyst for furfural conversion and obtained a yield of 95.5% for 2-methylfuran. Wang et al. employed an Ru/NiFe2O4 catalyst to convert furfural into 2-methylfuran at 453 K and an N2 pressure of 2.1 MPa, and the results demonstrated a 2-methylfuran yield of 83%.18 Apart from metal catalysts, transition-metal carbides, such as Mo2C,23−25 can also convert furfural into 2-methylfuran. Both Xiong et al.25 and Lee et al.23 investigated the hydrodeoxygenation of furfural using a Mo2C catalyst. They found that 2-methylfuran was the main product, with a selectivity of approximately 60%. In recent years, considerable research has been conducted on the conversion reaction of furfural over bimetallic catalysts owing to their high catalytic performance. NiCu catalysts,26 one of the non-noble bimetallic catalysts, have received considerable attention owing to their low cost. Lukes and Wilson26 studied furfural conversion using bimetallic NiCu (Ni/Cu = 4:1) catalysts at 110 °C and found that 2-methylfuran exhibited a selectivity of up to 97%. Merat et al.27 found that tetrahydrofurfuryl alcohol was the main product formed over the NiCu bimetallic catalyst (Ni/Cu = 1:1). Quite recently, Zhang et al.31 investigated the furfural hydrodeoxygenation using a CuNi2Al catalyst and found that 2-methylfuran was the principal product.

Considerable research has been conducted on the catalytic conversion of furfural using different metal catalysts and transition-metal carbides in experiments; however, there are
extremely few systematic studies on the mechanisms of furfural conversion in theory,33−35 particularly on bimetals.36,37 Ren et al.34 investigated the complete reaction mechanisms of furfural conversion to furan, tetrahydrofuran, furfuryl alcohol, tetrahydrofurfuryl alcohol, and 2-methylfuran and provided the optimal reaction path. In our previous study on Cu(111) surfaces,33 the mechanisms of hydrodeoxygenation of furfural to 2-methylfuran was reported in detail, and the theoretical calculations perfectly explained the selective conversion of furfural to furfuryl alcohol and the equilibrium of furfural/furfuryl alcohol under hydrogen-rich conditions in the experiment. Quite recently, I investigated the detailed mechanism of decarboxylation of furfural mainly to furan on the NiCuCu(111) bimetallic surface,36 and my results rationalized some experimental observations. In addition, Dong et al.37 conducted hydrodeoxygenation and hydrogenation of furfural on an Re/Pt catalyst and found that the Re/Pt system exhibited a better catalytic performance during the hydrodeoxygenation than that of the monometallic Pt.

In this study, the PBE-D3 method including dispersion correction was used to investigate the reaction mechanism of selective hydrodeoxygenation of furfural to 2-methylfuran on the CuNiCu(111) bimetallic surface. Based on the calculated thermodynamic and kinetic results, the optimal reaction route and rate-controlling step were determined. These results provide a basis for studying the intrinsic catalytic activity of NiCu catalysts during the hydrodeoxygenation of refined oxygenated compounds involving biomass-derived oils.

2. RESULTS AND DISCUSSION

2.1. Adsorption of Intermediates. As illustrated in Figure 1, there are four possible adsorption sites on the CuNiCu(111) surface: one top (T), one bridge (B), and two threefold (3F1 and 3F2) sites.

2.1.1. Adsorption of Furfural, Furfuryl Alcohol, and 2-Methylfuran on the CuNiCu(111) Surface. The most stable adsorption configurations of furfural (F=CHO; F = 2-furanyl), including trans and cis configurations, furfuryl alcohol (F=CH2OH), and 2-methylfuran (F=CH3) on the CuNiCu(111) bimetallic surface were determined. The adsorption configurations are depicted in Figure 1, and the structural properties are listed in Table 1.

In the most stable adsorption structures of furfural, the O atom of the −CHO group was connected to the surface Cu atom, and the Cu−O distances in trans- and cis-furfural configurations were 2.163 and 2.210 Å, respectively. From Figure 1, it is evident that the adsorption configuration of furfural is in the η1(O) surface bonding mode. The adsorption energies of trans- and cis-furfural were −0.79 and −0.76 eV, respectively, which were slightly lower than those (−0.91 and −0.88 eV) obtained on the Cu(111) surface,33 where furfural revealed the same η1(O) surface species. In addition, these results were significantly lower than those obtained on the NiCuCu(111) bimetallic surface (−1.88 and −1.78 eV),31 where furfural exhibited bicoordinated η2(C==O) surface species.

Furthermore, the most stable adsorption configurations of furfuryl alcohol and 2-methylfuran were determined. It was observed that furfuryl alcohol was connected to the top site of the surface Cu atom via the O atom of the OH group, and the Cu−O distance was 2.370 Å. As shown in Figure 1, the entire ring of furan was approximately parallel to and above the surface. The adsorption energy of furfuryl alcohol was −0.87 eV, which was slightly lower than that (−0.97 eV) obtained on the Cu(111) surface.33 In 2-methylfuran, it was observed that the entire molecule did not interact directly with the surface, and the calculated adsorption energy was −0.79 eV, which was slightly lower than that (−0.92 eV) obtained on the Cu(111) surface.33 Thus, the calculated results indicated that the adsorption energy of furfuryl alcohol was slightly higher than those of furfural and 2-methylfuran.

2.1.2. H2 Dissociative Adsorption. Because H2 was used in the hydrodeoxygenation of furfural, the dissociative adsorption of H2 on the CuNiCu(111) surface was calculated to directly compare the obtained data with those obtained on the Cu(111)33,38,39 and NiCuCu(111)36 surfaces. The adsorption configurations of H2 are depicted in Figure 2, and its structural properties are listed in Table 2.

The H2 molecule was adsorbed at the top site without any direct interaction with the surface, and the Cu−H distances were 3.069 and 3.018 Å, which were slightly higher than those (3.022 and 2.960 Å) obtained on the Cu(111) surface. The calculated adsorption energy was only −0.05 eV, which was approximately the same as that (−0.08 eV) obtained on the Cu(111) surface, whereas it was much lower than that (−0.61 eV) obtained on the NiCuCu(111) surface, where the H2 molecule interacted...
The calculated energy barrier and reaction energy were 1.39 and 0.61 eV, respectively, indicating that the H2 dissociation is slightly more favored as compared to that on the Cu(111) surface. However, as presented in Table 2, the H2 dissociation in the most stable adsorption configuration of H2O parallel to the surface Ni atom was slightly higher than that of the H atom adsorbed at the 3F2 site with Cu−H distances of 1.735 Å and 1.739 Å, and the other was located at the 3F2 site with Cu−H distances of 1.731, 1.733, and 1.735 Å. The calculated energy barrier and reaction energy were 0.47 and −0.61 eV, respectively, indicating that the H2 dissociation is favored thermodynamically. It was observed that the H2 dissociative adsorption on the CuNiCu(111) surface was slightly more favored than that where both H atoms are located at neighboring 3F1 sites and share a single Cu atom. As shown in Table 3, the adsorption energy (related to the gas H atom) of the H atom located at the 3F1 site was slightly higher than that of the H atom located at the 3F2 site (−2.43 vs −2.41 eV), and these results were lower than those reported on Cu(111)33,39 and NiCuCu(111)36 surfaces.

2.1.2. H2O Dissociative Adsorption. Because H2O is the main product of furfural hydrodeoxygenation, dissociative adsorption of H2O on the CuNiCu(111) surface was calculated to directly compare the obtained data with those reported for the Cu(111) surface.33 The adsorption configurations and their structural properties are provided in Figure 3 and Table 4, respectively.

In the most stable adsorption configuration of H2O parallel to the surface, the O atom was located at the top site with a Cu−O distance of 2.181 Å. The calculated adsorption energy was −0.19 eV, which was slightly lower than that (−0.32 eV) obtained on the Cu(111) surface.33 Starting from H2O molecular adsorption, its dissociation into OH and H was determined. The energy barrier and reaction energy were 1.39 and −0.03 eV, respectively. In the TS(HO−H), the OH group was located at the original top site with a Cu−O distance of 2.181 Å. The calculated adsorption energy was only −0.19 eV, which was slightly lower than that (−0.32 eV) obtained on the Cu(111) surface.33 Starting from H2O molecular adsorption, its dissociation into OH and H was determined. The energy barrier and reaction energy were 1.39 and −0.03 eV, respectively.
Dissociation Energies (lower than that obtained on the Cu(111) surface, indicating coadsorption of OH and H was less stable than the remote H2O and OH than that of the Cu(111) surface. The CuNiCu(111) surface had a better ability to dissociate (Å) in the TS remote coadsorption by 0.16 eV.

As shown in Table 4, the dissociation energy barrier of H2O and H dissociation was determined. It exhibited an energy barrier of 1.58 eV, and the reaction was endothermic by 0.51 eV. This result indicated that the OH dissociation is not favored thermodynamically or kinetically. In TS(O−H), the dissociating H atom shifted to the neighboring bridge site with Cu−H distances of 1.672 and 1.769 Å, and the O−H breaking distance was 1.551 Å. In the FS of O and H dissociation, both H and O atoms were located at the neighboring 3F1 sites sharing a single surface Cu atom. Such coadsorption of OH and H was less stable than the remote coadsorption by 0.11 eV, as shown in Figure 3.

Based on the most stable remote coadsorption of OH and H, OH dissociation was determined. It exhibited an energy barrier of 1.58 eV, and the reaction was endothermic by 0.51 eV. This result indicated that the OH dissociation is not favored thermodynamically or kinetically. In TS(O−H), the dissociating H atom shifted to the neighboring bridge site with Cu−H distances of 1.672 and 1.769 Å, and the O−H breaking distance was 1.551 Å. In the FS of O and H dissociation, both H and O atoms were located at the neighboring 3F1 sites sharing a single surface Cu atom. Such coadsorption was less stable than the remote coadsorption by 0.16 eV.

As shown in Table 4, the dissociation energy barrier of H2O and OH obtained on the CuNiCu(111) surface was slightly lower than that obtained on the Cu(111) surface, indicating that the CuNiCu(111) surface had a better ability to dissociate H2O and OH than that of the Cu(111) surface.

2.2. Mechanisms of Furfural Hydrodeoxygenation.

Using the most stable adsorption structure of trans-F−CHO, the full potential energy surface (PES) of the hydrodeoxygenation of furfural into furfuryl alcohol and 2-methylfuran was determined; the reaction energy and energy barrier were calculated based on the stable species without any direct coadsorption interactions.

2.2.1. −CH==O Hydrogenation Against Dissociation. Based on the coadsorbed configuration of furfural and one H atom, five possible reaction routes could be considered: the selective hydrogenation of the −CH==O group, that is, (a) the H atom is added to the C atom of C==O (R1, F−CHO + H = F−CH2O), (b) the H atom is added to the O atom of C==O (R2, F−CHO + H = F−CHOH) and the parallel and competitive dissociation of the −CH==O group, that is, (c) direct dissociation of C==O (R3, F−CHO + H = F−CH + O + H), (d) direct dissociation of C−H (R4, F−CHO + H = F−CO+2H), and (e) direct dissociation of −CHO (R5, F−CHO + H = F + CHO + H). The optimized geometries of the IS, TS, and FS and the calculated Ea and Er are provided in Figure 4.

In R1, the intermediate, F−CH2O, was formed by the hydrogenation of the branched C atom of F−CHO. In the coadsorbed furfural and H (IS1), furfural was connected to the surface via the O atom of C==O with a C−O distance of 2.115 Å, and the H atom was located at the 3F1 site with Cu−H distances of 1.733, 1.750, and 1.726 Å. In TS1, the H atom shifted to the top site, and the Cu−H distance and C−H forming distance were 1.622 and 1.717 Å, respectively. In FS1, the F−CH2O intermediate was connected to the surface through the branched O atom located at the 3F1 site, and the Cu−O distance was 1.946 Å and 1.964 Å, respectively. The calculated energy barrier and reaction energy were 0.83 and −0.34 eV, respectively. In R2, the intermediate, F−CHOH, was formed by the hydrogenation of the O atom of C==O. In TS2, the H atom shifted to the bridge site from the original 3F1 site; the Cu−H distances were 1.861 and 1.889 Å, and the O−H forming distance was 1.345 Å. In FS2, the branched H atom was located at the top site with a Cu−C distance of 2.117 Å. The calculated energy barrier was 0.92 eV, and the reaction was endothermic by 0.18 eV. These results indicated that the formation of F−CH2O was more favorable than that of F−CHOH both thermodynamically (−0.34 vs 0.18 eV) and kinetically (0.82 vs 0.92 eV).

The competitively parallel reactions of −HC==O hydrodeoxygenation are C==O, C−H, and −CHO dissociations. In R3, TS of C==O direct dissociation was determined; here, the C−O breaking distance was 1.949 Å, and the O atom shifted to the neighboring 3F1 site with Cu−O distances of 2.539, 2.085, and 1.961 Å. The energy barrier was as high as 2.08 eV, and the reaction energy was 0.67 eV. In R4, the dissociation of F−CHO into F−CO and H was examined. In TS4, the dissociating H atom contacted the surface Cu atom, and the Cu−H distance and C−H breaking distance were 1.589 and 1.612 Å, respectively. The energy barrier and reaction energy were 1.28
and 0.54 eV, respectively. However, the calculated energy barrier of –CHO direct dissociation was up to 2.10 eV, and the reaction energy was 1.12 eV. Thus, it was evident that the formation of F−–CH2O from the hydrogenation of C of the C=O group exhibited the lowest barrier and was most favored in kinetics, as shown in Figure 4. Therefore, the coadsorbed configuration of F−–CH2O and H was used to discuss the formation of furfuryl alcohol.

### 2.2.2. Furfuryl Alcohol Formation

Based on the coadsorbed structure of F−–CH2O and H, two parallel and competitive reaction routes could be considered: the hydrogenation of F−–CH2O, resulting in F−–CH2OH (R6, F−–CH2O + H = F−–CH2OH), and the dissociation of F−–CH2O, resulting in F−–CH2 and O (R7, F−–CH2O + H = F−–CH2 + O + H). The optimized structures of the adsorbed intermediates are shown in Figure 5.

Based on the most stable adsorbed configuration of F−–CH2O, the coadsorption of F−–CH2O and H was determined; here, the H atom was located at the 3F1 site with Cu−H distances of 1.673, 1.733, and 1.800 Å. In TS6, both the H and O atoms shifted to the bridge sites away from their original 3F1 sites, and the O−H forming distance was 1.428 Å. The calculated energy barrier was 1.14 eV, and the reaction was slightly exothermic by 0.08 eV. Based on the coadsorption of F−–CH2O and H, TS7 and FS7 of the decomposition of F−–CH2O to F−–CH2 and O were determined. In TS7, the calculated C−O breaking distance was 2.116 Å. In FS7, the dissociated O atom was located at the 3F1 site, and the Cu−O distances were 1.903, 1.898, and 1.909 Å. The F−–CH2 group was connected to the surface though the branched C atom with a Cu−C distance of 2.085 Å. The energy barrier and reaction energy were 1.24 and 0.29 eV, respectively. This indicated that the hydrogenation of F−–CH2O was more favorable than the dissociation of F−–CH2O both kinetically (1.14 vs 1.24 eV) and thermodynamically (−0.08 vs 0.29 eV).

### 2.2.3. 2-Methylfuran Formation

Based on the most stable adsorbed configuration of F−–CH2OH, its dehydroxylation reaction (R8, F−–CH2OH = F−–CH2 + OH) was determined. In TS8, the dissociating OH group bridged the Cu−Cu bond with Cu−O distances of 2.045 and 2.087 Å, and the C−O breaking distance was 2.112 Å. In FS8, the dissociated OH group was located vertically at the 3F1 site with Cu−O distances of 2.055, 2.012, and 2.049 Å, and the F−–CH2 group was located at the top site with a Cu−C distance of 2.085 Å. The dehydroxylation of F−–CH2OH exhibited an energy barrier of 1.13 eV, and this reaction was exothermic by 0.13 eV.

Based on the coadsorption of F−–CH2, OH, and H, two competitively parallel reaction routes were determined: (a) the hydrogenation of F−–CH2, resulting in F−–CH3 (R9, F−–CH2 + OH + H = F−–CH3 + OH) and (b) the hydrogenation of OH, resulting in H2O (R10, F−–CH2 + OH + H = F−–CH2 + H2O). In TS9, the H atom shifted to the bridge site from the original 3F1.
site, and the Cu−H distances were 1.871 and 1.643 Å. The calculated C−H forming distance was 1.767 Å. The energy barrier was 0.74 eV, and the reaction was exothermic by 0.55 eV. In the competitive pathway (R10), an H atom was added to the OH group, resulting in the formation of H2O. In TS10, the OH group and H atom were located at the top and bridge sites, respectively, and the calculated O−H forming distance was 1.642 Å. The formation of H2O exhibited an energy barrier of 1.27 eV, and the reaction was exothermic by 0.12 eV. The H2O formation was unfavorable as compared to the F−CH3 formation both thermodynamically (−0.55 vs −0.12 eV) and kinetically (0.74 vs 1.27 eV). The last step of the entire reaction was the formation of H2O (R11, F−CH3 + OH + H = F−CH3 + H2O) from the coadsorbed structure of F−CH3, OH, and H. In TS11, the O−H forming distance was 1.635 Å. The formation of H2O exhibited an energy barrier of 1.22 eV, and the reaction was exothermic by 0.18 eV. These results are close to the data (1.42 and 0.03 eV) obtained on a clean CuNiCu(111) surface, as shown in Figure 3, and it was concluded that the formation of F−CH3 was more favorable than that of H2O both thermodynamically and kinetically.

2.2.4. Potential Energy Surface. According to the aforementioned discussion, the full PES of selective hydrodeoxygenation of furfural on the CuNiCu(111) surface was plotted, as
Methylfuran Formation on the CuNiCu(111) Surface

Generally, the hydrogenation of furfural to 2-methylfuran is formed from the surface OH species; this reaction exhibited an exothermicity of 2.47 eV. Moreover, as shown in Figure 6, the hydrogenation of furfural to 2-methylfuran is exothermic by 0.08 eV. In the first step, the formation of F−CH2OH from the coadsorbed configuration of F−CH2O and H exhibited an energy barrier of 1.13 eV, and the reaction was slightly exothermic by 0.08 eV. In the second step, F−CH2OH was first decomposed into F−CH2 and OH, and then, F−CH2 was hydrogenated to form F−CH2OH. The energy barriers of the dehydroxylation of F−CH2OH and the hydrogenation of F−CH2 were 1.13 and 0.74 eV, respectively, and their reaction energies were −0.13 and −0.55 eV, respectively. In the final step of the entire reaction, H2O was formed from the surface OH species; this reaction exhibited an energy barrier of 1.22 eV, and it was exothermic by 0.18 eV. Generally, the hydrogenation of furfural to 2-methylfuran is exothermic by 2.47 eV. Moreover, as shown in Figure 6, the thermodynamic (−0.08 vs −0.13 eV) and kinetic (1.14 vs 1.13 eV) parameters of formation and dehydroxylation of F−CH2OH were comparable, and it could be inferred that the yield of F−CH2OH and 2-methylfuran would be approximately equal; however, the final product was 2-methylfuran.

Based on the aforementioned results, the rate constant was calculated and the rate-controlling step in the entire reaction was discussed. The rate constants (k) were calculated according to eq 1 based on the TS theory,^{40,41} which was used in our previous reports.\(^{36,42}\) In eq 1, \(k_\text{th}\), \(T\), \(h\), and \(E_0\) represent the Boltzmann constant, temperature of the reaction in Kelvin, Planck constant, and activation energy, respectively; \(q_\text{TS,vib}\) and \(q_\text{IS,vib}\) are the harmonic vibrational partition functions of the TS and IS, respectively; \(q_\text{th}\) is calculated according to eq 2, where \(\nu_i\) is the vibrational frequency of each vibrational mode of the adsorbed intermediate calculated using the density functional theory (DFT). The calculated reaction energy, energy barrier, and the rate constant of 2-methylfuran formation are listed in Table 5.

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k = \frac{k_\text{th} T q_\text{TS,vib}}{h} e^{-E_0/k_\text{th} T}
\]

Table 5. Energy Barrier (\(E_i\); eV), Reaction Energy (\(E_f\); eV), and Rate Constant (k) at 383, 403, 423, 483, and 503 K of 2-Methylfuran Formation on the CuNiCu(111) Surface

For the formation of F−CH2OH resulting from the hydrogenation of the C atom first (F−CHO + H = F−CH2O) and then the O atom (F−CH2O + H = F−CH2OH), the hydrogenation of F−CH2OH in F−CH2OH with a higher energy barrier (1.14 eV), was the rate-controlling step, and the calculated rate constants were in agreement with the calculated barriers; the rate constant of F−CH2O formation was 1.13 × 10^3 times that of F−CH2OH formation (2.03 × 10^3 vs 1.80 × 10^3 at 483 K). For the formation of F−CH2OH from the dehydroxylation of F−CH2OH and hydrogenation of F−CH2, the F−CH2OH dehydroxylation with a higher energy barrier (1.13 vs 0.74 eV) determined the reaction rate. The rate constants of decomposition of F−CH2OH to F−CH2 and OH and addition of H atom to F−CH2 resulting in the formation of F−CH3 were 1.37 × 10^3 and 2.43 × 10^3, respectively, at 483 K, and the F−CH2OH dissociation was 1.77 × 10^5 times slower than the F−CH2 hydrogation. Considering the entire reaction, as shown in Figure 6, it was concluded that the H2O formation exhibited the highest energy barrier (1.22 eV) and should be the rate-controlling step. As shown in Table 5, the rate constant of H2O formation at 483 K was the lowest (1.65 × 10^9 vs 2.03 × 10^9, 1.80 × 10^10, 1.37 × 10^11, and 2.43 × 10^11 in the entire reaction of conversion of furfural to 2-methylfuran). In addition, Table 5 lists the rate constants obtained at other temperatures, and the results are consistent with those obtained at 483 K, further confirming the rate-controlling step of the studied reaction pathway of 2-methylfuran formation. As shown in Table 5, the reaction rate increases with the increasing temperature.

Because the formation of H2O from OH and H with the highest energy barrier was the rate-controlling step, the possible OH disproportionation (2OH = H2O + O) was investigated (Figure 7), as studied in our previous study.\(^{33}\) Based on the coadsorbed structure of two OH groups located at adjacent 3F\(_i\) sites, TS(OH−OH) and FS(H2O + O) were determined. In TS(OH−OH), one OH group was still located at the 3F\(_i\) site and the other OH group shifted to the top site with a Cu−O distance of 1.939 Å; the O−H breaking and forming distances were 1.053 and 1.492 Å, respectively. In the FS of H2O and O, the formed H2O was adsorbed at the top site and the O atom was located at the original 3F\(_i\) site. The calculated energy barrier and reaction energy of OH disproportionation were 0.29 and 0.01 eV, respectively. Therefore, based on the extremely low energy barrier of OH disproportionation, it could be concluded that the reaction is not thermodynamically favored.
accumulation of OH on the CuNiCu(111) surface was unlikely; this is the same as that on the Cu(111) surface.33

Furthermore, it is quite interesting to compare my results with those obtained on the Cu(111)33 and NiCuCu(111) bimetallic surfaces.36 On Cu(111) and CuNiCu(111) surfaces, furfural exhibited a weak η1(O) surface bonding, where furfural was connected to the surface Cu atom via the branched oxygen atom. On the NiCuCu(111) bimetallic surface, furfural exhibited a η1(C═O) surface bonding, where furfural was connected to the surface via both the branched C═O group and the furan ring, and the entire molecule was approximately parallel to the surface. The calculated adsorption energies of trans- and cis-FCHO obtained on the CuNiCu(111) surface are close to those (−0.79 and −0.76 vs −0.91 and −0.88 eV, respectively) obtained on the Cu(111) surface and much lower than those (−0.79 and −0.76 vs −1.88 and −1.78 eV, respectively) obtained on the NiCuCu(111) surface. As expected, the adsorption configuration of furfural on Cu(111) and NiCuCu(111) surfaces was different from that on the NiCuCu(111) surface because the d-band of Cu was filled, whereas that of Ni was unfilled, and this facilitated the transfer of electrons from Cu to Ni.

Different reaction mechanisms could be observed on these surfaces owing to different adsorption structures. On Cu(111) and CuNiCu(111) surfaces, the hydrogenation of furfural into an F−CH2O intermediate was the most favorable step for the first reaction route, and subsequently, F−CH2O was hydrogenated to form F−CH2OH. In the subsequent reaction, F−CH2OH was decomposed into F−CH2 first, and then, F−CH2 was hydrogenated, resulting in the formation of F−CH3. On the NiCuCu(111) surface, the most favorable step for the first reaction route was dehydrogenation of F−CHO, resulting in F−CHO; the subsequent reaction was the decarbonylation of F−CO, and ultimately, the main product, furan, was formed from the hydrogenation of furan-free radical.

Based on the aforementioned discussion, it can be concluded that 2-methylfuran was the final product of furfural hydrodeoxygenation on the CuNiCu(111) surface, as shown in Figure 6. The formation of 2-methylfuran was exothermic by up to 2.47 eV, suggesting that this process is favorable thermodynamically. The calculated result was consistent with the experimental research,36 where Zhang et al. found that the principal product of furfural hydrodeoxygenation was 2-methylfuran using the CuNi2Al catalyst. In my previous study on NiCuCu(111),36 furan was the principal product of furfural decarbonylation; this agreed well with the experimental observation. All these results further confirmed that the activity and selectivity of the same catalyst are different under different experimental conditions.

3. CONCLUSIONS

In this study, the full PES of hydrodeoxygenation of furfural to 2-methylfuran on the CuNiCu(111) surface was investigated using periodic DFT, including the latest dispersion correction (PBE-D3). My goal was to elucidate the complete reaction mechanism of furfural hydrodeoxygenation using different methods employed for constructing monolayer bimetallic surfaces. The results provide a basis for studying the intrinsic activity of NiCu catalysts during the hydrodeoxygenation of refined oxygenated compounds involving biomass-derived oils. Based on the comparison of the reaction mechanism of furfural conversion on the Cu(111), NiCuCu(111), and CuNiCu(111) surfaces, it can be concluded that the inherent difference in catalyst selectivity is mainly due to the different adsorption structures of furfural.

Based on the detailed comparisons, it was found that the formation of the F−CH2O intermediate resulting from the addition of hydrogen to the C atom of the C═O group (F−CHO + H = F−CH2O) was the most kinetically favored process for the first reaction route of furfural hydrodeoxygenation, and the hydrogenation of F−CH2O, resulting in the formation of furfuryl alcohol (F−CH2O + H = F−CH3OH), was the rate-controlling step. For the formation of 2-methylfuran from the furfuryl alcohol dehydration (F−CH2OH = F−CH2 + OH) and subsequent hydrogenation (F−CH2 + OH + H = F−CH3 + OH), the formation of H2O from the surface OH group and H atom (OH + H = H2O) was the rate-controlling step. For the entire reaction of 2-methylfuran formation, the hydrogenation of OH, resulting in H2O, was determined as the rate-controlling step. In addition, the calculated rate constants confirmed the rate-controlling step of the studied reaction pathway of 2-methylfuran formation.

Finally, it is worth noting that the calculated results may not always agree well with all the experimental results, where NiCu bimetallic catalysts are employed. This is because there are several factors that can affect the selectivity and activity of catalysts in experiments: the composition, structure, preparation method, promoter, and support of the catalyst. In particular, changes in realistic reaction conditions, such as the hydrogen pressures and experimental temperatures, can also lead to different reaction kinetics and products. In addition, there are several other methods of constructing monolayer bimetallic surfaces; in this study and that on NiCuCu(111), only two of the methods were selected to study the hydrodeoxygenation of furfural. Therefore, it would be quite interesting to investigate other methods of constructing NiCu bimetallic surfaces to investigate furfural conversion reactions.

4. COMPUTATIONAL METHOD AND MODEL

4.1. Method. All the periodic DFT calculations were performed using the Vienna Ab Initio Simulation Package (VASP, version 5.3.5),43,44 where the ionic cores were described by the projector augmented wave method.45,46 The exchange–correlation energies were calculated using the Perdew, Burke, and Ernzerhof functional along with the latest long-range dispersion correction (PBE-D3).47–49 To ensure accurate energies with errors less than 1 meV per atom, a cutoff energy of 400 eV and the Gaussian electron smearing method with $\sigma = $
0.10 eV were used. Geometry optimization was converged when the changes in the forces were lower than 0.02 eV/Å, and the energy threshold defining the self-consistency of the electron density was set to 10^{-4} eV. The calculations were performed using spin polarization. The climbing image nudged elastic band method\textsuperscript{50} was used to locate all the TS structures. For each optimized stationary point, vibrational frequencies were evaluated at the same level of theory to determine the minimum and transition states (TSs). For the bulk optimization of the face-centered cubic Cu unit cell, the lattice parameter was determined using a 15 × 15 × 15 Monkhorst-Pack k-point grid\textsuperscript{31} for sampling the Brillouin zone. The calculated lattice parameter of the Cu unit cell was 3.561 Å, which agreed well with the experimental result (3.614 Å)\textsuperscript{12} and other theoretical data.\textsuperscript{33,34}

### 4.2. Model

It was found that, depending on the deposition temperature and reaction condition, the bimetallic surface can possess one of the three following structures: a surface monolayer formed by the occupation of the uppermost surface sites, an underground monolayer formed as a result of the diffusion into the underground area, and intermixed bimetallic surfaces formed as a result of alloying with the surface.\textsuperscript{31} In a previous study, Jiang et al.\textsuperscript{55} developed the PtCo/Pt(111) bimetallic surface by replacing all the Pt atoms in the second layer of Pt(111) to study the furfural conversion. In our previous study,\textsuperscript{35} the most stable Cu(111) surface, with a p(5 × 5)-3L supercell, where the first layer was relaxed and the bottom two layers were fixed, was selected to investigate the selective hydrogenation of furfural to 2-methylfurfural. Quite recently, the bimetallic NiCuCu(111) was modeled by replacing all the uppermost atoms of the Cu(111) surface to investigate the conversion of furfural to furan.\textsuperscript{36} In this study, the CuNiCu(111) bimetallic surface was modified by replacing all the Cu atoms in the second layer with Ni atoms; this is in good agreement with the previous investigation.\textsuperscript{36}

The Monkhorst-Pack k-point mesh of 3 × 3 × 1 was applied to perform the surface structural relaxation and calculate the total surface energy. The structures and total energies of the related gas-phase species were calculated using a cubic box with a side length of 15 Å.

The adsorption energy ($E_{\text{ads}}$) was calculated by subtracting the energies of the gas-phase species (X) and the clean surface (slab) from the total energy of the adsorbed system: \textsuperscript{51} $E_{\text{ads}} = E_{\text{X/\text{slab}}} - E_{\text{slab}} - E_{\text{X}}$; a more negative $E_{\text{ads}}$ indicates a stronger and more stable adsorption. The activation energy barrier ($E_a$) and heat of reaction ($E_r$) were defined using the following equations: $E_a = E_{\text{TS}} - E_{\text{IS}}$ and $E_r = E_{\text{FS}} - E_{\text{IS}}$, where $E_{\text{IS}}$, $E_{\text{TS}}$, and $E_{\text{FS}}$ are the energies of IS, TS, and FS, respectively.

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### REFERENCES

1. Liu, W.-J.; Li, W.-W.; Jiang, H.; Yu, H.-Q. Fates of chemical elements in biomass during its pyrolysis. Chem. Rev. 2017, 117, 6367–6398.

2. Besson, M.; Gallozet, P.; Pinel, C. Conversion of biomass into chemicals over metal catalysts. Chem. Rev. 2014, 114, 1827–1870.

3. Sun, D.; Sato, S.; Ueda, W.; Primo, A.; Garcia, H.; Corman, A. Production of C4 and C5 alcohols from biomass-derived materials. Green Chem. 2016, 18, 2579–2597.

4. Nakagawa, Y.; Tamura, M.; Tomishige, K. Catalytic reduction of biomass-derived furanic compounds with hydrogen. ACS Catal. 2013, 3, 2655–2668.

5. Zhang, X.; Wilson, K.; Lee, A. F. Heterogeneously catalyzed hydrothermal processing of C6-C8 sugars. Chem. Rev. 2016, 116, 12323–12368.

6. Zhang, Z.; Song, J.; Han, B. Catalytic transformation of lignocellulose into chemicals and fuel products in ionic liquids. Chem. Rev. 2017, 117, 6834–6880.

7. Li, X.; Jia, P.; Wang, T. Furfural: a promising platform compound for sustainable production of C4 and C5 chemicals. ACS Catal. 2016, 6, 7621–7640.

8. Deng, Y.; Gao, R.; Lin, L.; Liu, T.; Wen, X.-D.; Wang, S.; Ma, D. Solvent Tunes the Selectivity of Hydrogenation Reaction over α-MoC Catalyst. J. Am. Chem. Soc. 2018, 140, 14481–14489.

9. Burnett, L. W.; Johns, I. B.; Holdren, R. F.; Hixon, R. M. Production of 2-methylfurfural by vapor-phase hydrogenation of furfural. Ind. Eng. Chem. Res. 1948, 40, 502–505.

10. Srivastava, S.; Jadhav, G. C.; Parikh, J. A versatile bi-metallic copper-cobalt catalyst for liquid phase hydrogenation of furfural to 2-methylfurfural. RSC Adv. 2016, 6, 1649–1658.

11. Sittisita, S.; Sooknai, T.; Ma, Y.; Balbuena, P. B.; Resasco, D. E. Kinetics and mechanism of hydrogenation of furfural on Cu/SiO2 catalysts. J. Catal. 2011, 277, 1–13.

12. Jung, S.; Karaiskakis, A. N.; Biddinger, E. J. Enhanced activity for electrochemical hydrogenation and hydrogenolysis of furfural to biofuel using electrodeposited Cu catalysts. Catal. Today 2019, 323, 26–34.

13. Zheng, H.-Y.; Zhu, Y.-L.; Bai, Z.-Q.; Huang, L.; Xiang, H.-W.; Li, Y.-W. An environmentally benign process for the efficient synthesis of cyclohexanone and 2-methylfuran. Green Chem. 2006, 8, 107–109.

14. Cui, J.; Tan, J.; Cui, X.; Zhu, Y.; Deng, T.; Ding, G.; Li, Y. Conversion of xylose to furfuryl alcohol and 2-methylfuran in a continuous fixed-bed reactor. ChemSusChem 2016, 9, 1259–1262.

15. Dong, F.; Ding, G.; Zheng, H.; Xiang, X.; Chen, L.; Zhu, Y.; Li, Y. Highly dispersed Cu nanoparticles as an efficient catalyst for the synthesis of the biofuel 2-methylfurfural. Catal. Sci. Technol. 2016, 6, 767–779.

16. Ren, G.; Wang, G.; Mei, H.; Xu, Y.; Huang, L. Reaction mechanism investigation of furfural conversion to 2-methylfuran on Cu(111) surface. Chem. Phys. Lett. 2018, 703, 1–7.

17. Park, S.; Kannapu, H. P. R.; Jeong, C.; Kim, J.; Suh, Y. H. Highly active mesoporous Cu–Al2O3 catalyst for the hydrodeoxygenation of furfural to 2-methylfuran. ChemCatChem 2012, 10, 105–111.

18. Wang, B.; Li, C.; He, B.; Qj, J.; Liang, C. Highly stable and selective Ru/NiFeO3 catalysts for transformation of biomass-derived furfural to 2-methylfuran. J. Energy Chem. 2017, 26, 799–807.

19. Panagiotopoulou, P.; Martin, N.; Vlachos, D. G. Effect of hydrogen donor on liquid phase catalytic transfer hydrogenation of furfural over a Ru/RuO2/C catalyst. J. Mol. Catal. A: Chem. 2014, 392, 223–228.

20. Gilkey, M. J.; Panagiotopoulou, P.; Mironenko, A. V.; Jenness, G. R.; Vlachos, D. G.; Xu, B. Mechanistic insights into metal Lewis acid-
mediated catalytic transfer hydrogenation of furfural to 2-methylfuran. *ACS Catal.* **2015**, *5*, 3988–3994.

(21) Panagiotopoulou, P.; Martin, N.; Vlachos, D. G. Liquid-phase catalytic transfer hydrogenation of furfural over homogeneous lewis acid-Ru/C catalysts. *ChemSusChem* **2015**, *8*, 2046–2054.

(22) Dunndell, L. J.; Zou, G.; Shangguan, W.; Lee, A. F.; Wilson, K. Structure-Reactivity Relations in Ruthenium Catalysed Furfural Hydrogenation. *ChemCatChem* **2019**, *11*, 3927–3932.

(23) Lee, W.-S.; Wang, Z.; Zheng, W.; Vlachos, D. G.; Bhan, A. Vapor phase hydrodeoxygenation of furfural to 2-methylfuran on molybdenum carbide catalysts. *Catal. Sci. Technol.* **2014**, *4*, 2340–2352.

(24) McManus, J. B.; Vohs, J. M. Deoxygenation of glycoaldehyde and furfural on Mo,C/Mo(100). *Surf. Sci.* **2014**, *630*, 16–21.

(25) Xiong, K.; Lee, W.-S.; Bhan, A.; Chen, J. G. Molybdenum carbide as a highly selective deoxygenation catalyst for converting furfural to 2-methylfuran. *ChemSusChem* **2014**, *7*, 2146–2149.

(26) Lukes, R. M.; Wilson, C. L. Reactions of Furan Compounds. XI. Side Chain Reactions of Furfural and Furfuryl Alcohol over Nickel-Copper and Iron-Copper Catalysts. *J. Am. Chem. Soc.* **1951**, *73*, 4790–4794.

(27) Merat, N.; Godawa, C.; Gaset, A. High selective production of tetrahydrofurfuryl alcohol. *J. Chem. Technol. Biotechnol.* **2007**, *78*, 145–159.

(28) Liu, L.; Lou, H.; Chen, M. Selective hydrogenation of furfural to tetrahydrofurfuryl alcohol on Ni/CNTs and bimetallic Cu/CNTs catalysts. *Int. J. Hydrogen Energy* **2016**, *41*, 14721–14731.

(29) Yang, Y.; Du, Z.; Huang, Y.; Lu, F.; Wang, F.; Gao, J.; Xu, J. Conversion of furfural into cyclopentanone over Ni-Cu bimetallic catalysts. *Green Chem.* **2013**, *15*, 1932–1940.

(30) Wu, J.; Gao, G.; Li, J.; Sun, P.; Long, X.; Li, F. Efficient and versatile CuNi alloy nanocatalysts for the highly selective hydrogenation of furfural. *Appl. Catal., B* **2017**, *203*, 227–236.

(31) Zhang, Z.; Pei, Z.; Chen, H.; Chen, K.; Hou, Z.; Lu, X.; Ouyang, P.; Fu, J. Catalytic in-situ Hydrogenation of Furfural over Bimetallic Cu-Ni Alloy Catalysts in Isopropanol. *Ind. Eng. Chem. Res.* **2018**, *57*, 4225–4230.

(32) Sánchez, V.; Salagre, P.; González, M. D.; Llorca, J.; Cesteros, Y. Effect of the formation of NiCu alloy and use of biomass-derived furfural on the catalytic hydrogenation of furfural to THFA. *Mol. Catal.* **2020**, *490*, 110956.

(33) Shi, Y.; Zhu, Y.; Yang, Y.; Li, Y.-W.; Jiao, H. Exploring furfural catalytic conversion on Cu(111) from computation. *ACS Catal.* **2015**, *5*, 4020–4032.

(34) Ren, G.; Wang, G.; Mei, H.; Xu, Y.; Huang, L. A theoretical insight into furfural conversion catalyzed on the Ni(111) surface. *Phys. Chem. Chem. Phys.* **2019**, *21*, 23685–23696.

(35) Dong, H.; Zheng, Y.; Hu, P. A DFT study of direct furfural conversion to 2-methylfuran on the Ru/Co,O₃ surface. *Phys. Chem. Chem. Phys.* **2019**, *21*, 1597–1605.

(36) Shi, Y. Theoretical study of the mechanism of furfural conversion on the NiCu(111) surface. *ACS Omega* **2019**, *4*, 17447–17456.

(37) Dong, H.; Zheng, Y.; Hu, P. DFT study of furfural conversion on a Pt/Ni bimetallic surface: synergistic effect on the promotion of hydrodeoxygenation. *Phys. Chem. Chem. Phys.* **2019**, *21*, 8384–8393.

(38) Kratzer, P.; Hammer, B.; Norskov, J. K. Geometric and electronic factors determining the differences in reactivity of H₂ on Cu(100) and Cu(111). *Surf. Sci.* **1996**, *359*, 45–53.

(39) Gokhale, A. A.; Dumesc, J. A.; Mavrakiakis, M. On the mechanism of low-temperature water gas shift reaction on copper. *J. Am. Chem. Soc.* **2008**, *130*, 1402–1414.

(40) Eyring, H. The activated complex in chemical reactions. *J. Chem. Phys.* **1935**, *3*, 107–115.

(41) Lu, J.; Bellem, S.; Faheem, M.; Heyden, A. Microkinetic modeling of the decarboxylation and decarbonylation of propanoic acid over Pd(111) model surfaces based on parameters obtained from first principles. *J. Catal.* **2013**, *305*, 56–66.

(42) Shi, Y.; Yang, Y.; Li, Y.-W.; Jiao, H. Mechanisms of Mo,C(101)-catalyzed furfural selective hydrodeoxygenation to 2-methylfuran from computation. *ACS Catal.* **2016**, *6*, 6790–6803.