Chirality, Rigidity, and Conjugation: A First-Principles Study of the Key Molecular Aspects of Lignin Depolymerization on Ni-Based Catalysts

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S Supporting Information

ABSTRACT: Efficient lignin depolymerization is crucial for achieving a positive economical return in biorefineries. However, because of the complex cross-polymerized network formed by the aromatic lignols, catalysts that can work at low temperatures perform insufficiently in terms of both activity and selectivity. Recently, Ni-based catalysts have been reported to exhibit a superior catalytic behavior in lignin valorization, but the mechanism of the depolymerization remains unclear. In this study, we employed density functional theory to investigate lignin decomposition on pure and Ru-doped Ni(111) surfaces to unravel the key issues that limit performance. The reaction network was screened by using complex coniferyl dimer models containing different stereocenters to simulate the most abundant β -O-4 linkages in lignin, thus presenting a better representation of the complexity of the parent compound. Our results show that on nickel, both adsorption geometries and the preferred reaction paths are different depending on the chirality of the dimer reactants. In addition, the rigidity of the β -O-4 link is also responsible for the reactivity found. Finally, the presence of small amounts of Ru on the surface simplifies the reaction as they act as preferential points for β -O-4 bond cleavage via the weakened C–O bond that is induced by increasing metal–O bond strength.

KEYWORDS: lignin, DFT, β -O-4, chirality, rigidity, conjugation, Ni, Ru

1. INTRODUCTION

Lignin is a complex cross-linked phenolic polymer that widely exists in the cell walls and supports plants via its strength and rigidity. It is one of the main components in lignocellulosic biomass resources, accounts for 15–30% of the weight, and stores 40% of the energy.¹ However, because of its high stability, efficient depolymerization methods are lacking,^{2–4} and 98% of the lignin produced by the paper and pulp industry was considered a low-value material and burned for heating at the beginning of the 21st Century.⁵

In the near future, because of the depletion of oil reserves, lignin will be seen as a new source of the major aromatic compounds (such as the BTX fraction of benzene, toluene, and the three xylene isomers)⁶ or will directly provide some synthetic intermediates that are used in the industry. Altogether, the derived platform chemicals could be used as renewable materials in the polymer industry with great potential in food and medical applications and as carbon fibers to name just a few.^{7,8} However, the optimal processing of lignin

is far from being realized. Hence, developing catalysts with high efficiency and selectivity for depolymerization is the key to allowing application in high value-added chemicals and improving the economics of the biorefinery process.^{9–11}

One of the added difficulties in the chemical treatment of lignin is its variable composition when different raw materials, such as hardwood, softwood, and grass, are fed in the bioconfinery process.³ The proportions of the monomeric units and linkages depend on the origin of lignin.³ The most common monolignols (see Figure 1) from the depolymerization are *p*-coumaryl (H), coniferyl (G), and sinapyl alcohols (S)¹² and different linkage topologies connecting these monomers have been identified: β -O-4, β -5, α -O-4, β - β , 5-5, 4-O-5, β -1, and others (see Figure S1). The most representative linkage is β -O-4, which accounts for 43–50% in softwood and

Figure 1. Structures of three lignin monomers.

50–65% in hardwood and happens to be the most labile. Therefore, breaking the β -O-4 bond is the highest priority in catalytic depolymerization and valorization processes.

Some compounds have been proposed as homogeneous depolymerization catalysts, but heterogeneous catalytic lignin transformation has advantages in flow processing,^{13,14} production separation, and catalyst recycle ability and is suitable for large industry scale processes. Comprehensive reviews of the advances in the area were presented by Calvo-Flores,⁷ Zakzeski,² Zhang,³ and Behling et al.,⁴ focusing on: (i) the basic lignin compositions, (ii) various lignin valorization approaches in both heterogeneous and homogeneous systems, and (iii) wide potential uses of its products in chemicals, fuels, and materials. A majority of catalysts investigated are transition metal-based, including those based on Mn, Co, Ni, Ru, Pd, and Pt. Multicomponent catalysts like transition metal (Ti, Mo, Nb, and W) nitrides have been applied by Chen et al.,¹⁵ and Ti–N was identified as a promising catalyst for partial lignin depolymerization. The titanium–nitride–nickel catalyst (TiN–Ni) has also been used under mild reaction conditions by Molinari et al.¹⁶ and exhibited a performance comparable to that of the Raney Ni catalyst, which is a well-known catalyst for hydrogenation processes.

Among the transition metal catalysts, Ni exhibits superior activity in aryl–alkyl bond activations in lignin hydrogenolysis, as the aromatic moieties are kept intact in both homogeneous¹⁴ and heterogeneous¹⁷ processes. Still, Ni-based catalysts exhibit poor activity below 120 °C,¹⁸ and thus, improvements in performance to reduce working temperatures are desirable. By combining Pd and Ni into a bimetallic nanoparticle catalyst, Zhang et al.¹⁹ observed a remarkable catalytic enhancement compared with the results with only Ni and Pd. A previous study by Yan et al.¹⁸ showed that a Ni–Ru bimetallic catalyst exhibits excellent behavior in aqueous lignin hydrogenolysis, compared with that of Ni–Rh and Ni–Pd catalysts. Both studies show the synergistic effects of two metals.

Density functional theory (DFT) approaches to understanding the reaction network for depolymerization are rather scarce. By combining DFT calculations and experiments, Wang et al.²⁰ investigated the β -O-4 bond scission on Pd(111). In this study, the lignin model was represented by 2-phenoxy-1-phenylethanol and its β -O-4 bond cleavage was studied. Recently, adsorption structures of the same simple model on Ni(111) and a MoS₂ surface have been optimized.²¹ In addition, Hamou et al.²² studied the adsorption and decomposition mechanism of lignin on Pt(111) by using 2-phenoxyethanol. The use of surrogates has proven to be interesting for small molecules;²³ however, lignin models employed in theoretical and experimental studies are exceedingly too simple to fully represent and describe the real lignin adsorption configurations.⁴ For example, numerous lignin linkages with stereocenters are formed between monolignols,²⁴

and the steric effect of methoxy or other groups in the *meta* and *para* aromatic substitution positions would also have an impact on the interactions between molecules and the surface and further affect the reaction network.²⁵

Besides, to improve the catalyst design, a further understanding of the reaction process at the atomic level is needed. Knowledge of the depolymerization mechanisms of lignin on the Ni-based catalysts is lacking. This is due to several factors, including: (i) the large size of lignin that has prompted the use of small surrogates⁴ that does not account for key aspects like the chirality of the linkers, the rigidity of the molecules, and the conjugation of intermediates, (ii) the complex reaction networks that involve various products, and (iii) the variety of metal catalysts and the complexity of advanced materials like TiN–Ni.¹⁶ In view of these fundamental complexities, we have employed DFT calculations on slab models representing the simplest of these materials (Ni and Ru-doped Ni) but considered large molecular surrogates that have stereocenters [dimers (C₁₇H₂₀O₆) of the most abundant monolignols coniferyl alcohol (G)] and an extensive reaction network that accounts for many of the potential transformations taking place. Our results first reveal the effects of the stereocenters on the decomposition mechanism and the synergistic effects on the Ru-doped Ni catalyst, thus providing guidelines for the design of the incoming catalysts.

2. COMPUTATIONAL DETAILS

In this work, slab model calculations were performed by using the Vienna Ab-initio Simulation Package (VASP).^{26,27} The exchange and correlation energies were obtained via the PBE functional.²⁸ We also included van der Waals (vdW) corrections by applying the Grimme’s DFT-D2 method,^{29,30} with the C₆ reparametrized by our group.³¹ The inner electrons were represented by projector augmented wave (PAW) pseudopotentials with cutoff energies of 450 eV.^{32,33} The Brillouin zone was sampled by a Γ -centered k-point mesh generated through the Monkhorst–Pack method.³⁴ The calculated Ni and Ru lattice parameters of 3.517 and 2.712 Å, respectively ($c/a = 1.581$), agree well with previous experimental results of 3.524 and 2.706 Å, respectively ($c/a = 1.582$).³⁵

For small species such as ethylene glycol (EG), H₂O, H, CO, O, and OH, adsorptions were optimized on a p -(3 × 3) supercell with four layers and Γ -centered 5 × 5 × 1 k-point sampling was used. The energies are listed in Table S1. In larger slab optimizations, the Ni(111) and Ru(0001) surfaces were modeled by a four-layer slab with p -(7 × 4) supercells, the two uppermost layers were fully relaxed, and the remaining bottom atoms were fixed to the bulk distances. Then, the atoms in the last bottom layer were removed and the three remaining layers were fixed and used for adsorption and transition state calculations. As the adsorption was performed on one side of the slab, a 15 Å thick vacuum region was set between each slab to prevent their interaction, and dipole correction along the z direction³⁶ was also applied to eliminate the spurious contributions arising from the system’s asymmetry. To reduce the computational burden, we used Γ -point sampling to obtain the adsorption and transition state structures first. Then, they were taken as the initial inputs for reoptimization via the denser k-point mesh of 2 × 3 × 1. Because of the large sizes of slabs and adsorbates, the level of accuracy in our model has been tested by comparing the adsorption and reaction energies on a three-layer slab Ni(111) surface with those on the four-layer

Figure 2. Adsorptions of four β -O-4 bond isomers, two structures from the A isomer after rotation of the C_α - C_β bond and using the other face on the Ni(111) surface. Ar_{Ru} and O_{Ru} are two surface A isomer structures on the Ru-Ni(111) surface. Ni, Ru, C, H, and O atoms are colored blue, yellow, gray, white, and red, respectively.

Scheme 1. Reaction Network of Isomer A Depolymerization and Hydrogenation on the Ni(111) Surface^a

^aBlue and red pathways are preferred reactions from α -C and β -C sides, respectively.

slab. The tested results are listed in Tables S2 and S3. The adsorption energy differences of four β -O-4 models and 10 depolymerization products are in the range of 0.14–0.23 eV, which is within the traditional accuracy of the GGA-PBE level we used.³⁷ Eight reactions on two slabs were tested, and their reaction energy differences are from 0.00 to 0.05 eV, demonstrating the reliability and accuracy by using a three-layer slab to describe the surface reactions.

We employed the climbing image nudged elastic band method (CI-NEB),³⁸ the improved dimer method (IDM),³⁹ and the quasi-Newton algorithm to locate and optimize the transition states in the potential surfaces. The thresholds were 10^{-5} eV and 0.03 eV/Å for electronic and ionic relaxations, respectively. The saddle point nature of the transition states was assessed by the calculation of the numeric Hessian with a

step of 0.02 Å and its diagonalization that rendered a single imaginary frequency.

All molecules in the gas phase were relaxed in a box with dimensions of $20 \times 20 \times 20$ Å³. Four coniferyl alcohol dimers with different chiralities [named A (α -S, β -S), B (α -R, β -S), C (α -R, β -R), and D (α -S, β -R)] were used as the lignin β -O-4 model in this study, as shown in Figure 2 and Figure S2. The aliphatic side chain on the right aromatic moiety was removed to reduce the length of the molecule and also the model surface length along the y direction. Solvation effects have been considered by calculating solvation energies of those closed-shell molecules both in ethylene glycol and in water via the MGCM methodology (multigradient continuum model).^{40,41}

To study the Ru doping effects, the system stability was investigated first via a few aspects following the procedures as in

Scheme 2. Reaction Network of Isomer B Depolymerization and Hydrogenation on the Ni(111) Surface^a

^aBlue and red pathways are preferred reactions from α -C and β -C sides, respectively.

Table 1. Adsorption Energies (E_{ads} in electronvolts) of Closed-Shell Species and Small Molecules on the Ni(111), Ru(0001), and Ru–Ni(111) Surfaces and Their Solvation Energies in EG ($E_{\text{sol}}^{\text{EG}}$) and Water ($E_{\text{sol}}^{\text{H}_2\text{O}}$)^a

species	Ni(111)	Ru(0001)	Ru–Ni(111)	$E_{\text{sol}}^{\text{EG}}$	$E_{\text{sol}}^{\text{H}_2\text{O}}$	N_{covered}	$E_{\text{ads}}(\text{EG})$
A	−2.28	−3.59	−2.28	−0.60	−1.00	20	−0.21
B	−2.29	−3.42	−2.35	−0.60	−1.02	20	−0.23
C	−1.76	−3.12	−1.83	−0.60	−1.02	20	0.31
D	−1.86	−3.16	−1.97	−0.62	−1.04	20	0.20
E	−2.33	−3.43	−2.39	−0.56	−0.59	20	−0.25
G0	−1.24	−1.96	−1.18	−0.32	−0.47	12	−0.04
G1	−2.34	−3.38	−2.58	−0.49	−0.75	13	−0.90
G2	−2.07	−3.28	−2.24	−0.39	−0.61	13	−0.80
G3	−1.78	−3.07	−2.30	−0.45	−0.73	13	−0.33
G4	−1.96	−2.99	−2.23	−0.36	−0.73	13	−0.62
G5	−1.62	−2.47	−1.78	−0.49	−0.79	13	−0.22
G6	−1.57	−2.29	−1.76	−0.44	−0.69	13	−0.26
G7	−1.44	−2.30	−1.58	−0.35	−0.60	13	0.01
G8	−1.20	−2.02	−1.31	−0.48	−0.49	13	0.19
G9	−1.29	−1.97	−1.43	−0.35	−0.60	13	0.01
G10	−1.53	−2.17	−1.53	−0.26	−0.26	13	−0.32

^a N_{covered} stands for the surface metal atoms covered by the adsorbates. $E_{\text{ads}}(\text{EG})$ is the solvation effect-corrected adsorption energy of a species on the Ni(111) surface in ethylene glycol.

ref 42. The solubility was calculated in a bulk model containing 32 Ni atoms. Segregation and near surface energies were obtained via a p -(2×2) slab with six layers, and the top four layers were optimized. The island formation energy was calculated on a p -(3×3) slab with four layers, and the top two layers were relaxed. As listed in Table S5, the energy of dissolving one Ru atom into the Ni bulk is 0.53 eV, implying a relative instability in forming the alloy. However, the endothermic energy would be compensated by the entropic contributions as Ru can replace Ni atoms from three directions with higher disorder, which corresponds to the higher entropy and therefore reduces the dissolving energy.^{42,43} A small exothermic segregation energy (−0.05 eV) implies that penetration of Ru into the bulk is slightly preferable and can occur both on the surface and in the bulk. From the positive island formation energy (0.12 eV), it is safe to derive that Ru dispersion on the surface is preferred. According to this analysis, Ru effects have been investigated by substituting the Ni atom under the breaking bonds with Ru on the top layer. In other words, the active site Ni atoms for a variety of types of bond breakages as well as adsorption structures have been

replaced by the Ru atoms specifically, depending on the reaction types.

All energies presented in the schemes and diagrams were obtained from the gas phase and slab calculations without solvent or zero-point energy contributions except as indicated otherwise. All coordinates of these structure geometries as well as the related transition states in this work are listed in the Supporting Information by using VASP POSCAR's format. In addition, the data are also freely accessible from the ioChem-BD database,^{44,45} and the instructions to use this platform have also been described in the Supporting Information.

3. RESULTS AND DISCUSSION

3.1. Adsorption. Adsorption energies of reactants (A–D) and products (G0–G10 in Schemes 1 and 2) on Ni(111), Ru(0001), and Ru-doped Ni(111) surfaces and their solvation energies in water and EG are listed in Table 1. Adsorption geometries of these four lignin β -O-4 models are shown in Figure 2. Isomers A and B with β -S carbons bind to the surface at least 0.40 eV stronger than β -R configurations do (C and D), because of the chirality difference at β -C caused by changing

the relative positions of the H and CH₂OH groups. On the contrary, the chirality at α -C has little effect on the adsorption energies. For instance, isomers A and B adsorb to the surface with similar exothermic energies of -2.28 and -2.29 eV, respectively, on Ni(111).

To ensure the stabilities of A and B isomers, we also tried two geometries derived from the A isomer by rotating the C $_{\alpha}$ –C $_{\beta}$ bond and using the other face to adsorb, see Figure 2. For these alternative structures, the molecule adsorbs on the surface with only one aromatic unit connecting to the β -O-4 bond, leaving the other aromatic unit intact. When A adsorbs to the surface by using the other face, the aryl–surface interactions are blocked for both sides by the γ -CH₂OH group and A adsorbs on the surface in a tilted way. As the aryl–surface interactions make the main contributions to the adsorption energy, these two geometries with only one aryl–surface interaction and without any aryl–surface interactions have small adsorption energies of -1.08 and -0.69 eV, respectively, showing the stereoeffects in the adsorption energies.

There are two important aspects to consider about the adsorption of very large molecules from the liquid phase. For molecules like the lignin A model, a sergeant-and-soldier principle can be applied to understand adsorption.⁴⁶ The largest driving force is the adsorption of the aryl groups that act as directing groups for adsorption; this fact coupled to the rigidity of the Ar–C $_{\alpha}$ –C $_{\beta}$ –O $_4$ –Ar structure implies that C $_{\beta}$ stands relatively far from the surface, and this will prevent an easy activation. This can be seen from the fact that molecular adsorption for the configurations with two rings on the surface is double that of only one ring interacting with the catalyst. In addition, the large adsorption energy arising from the large molecule sizes of the β -O-4 model would also lead to a large energy span in the reaction profile. However, adsorption occupies a large number of sites, and thus, the adsorption energy per area is more meaningful for assessing the real strength of the binding at the interface. For instance, hydrogen has been reported to affect co-adsorption;⁴⁷ however, in our case, the reactions are performed in solvent (EG), and thus, a competition among hydrogen, solvent, and lignin for the active sites will appear. The corresponding adsorptions are -0.60 eV/H atom, -0.71 eV for EG, and around -2.28 eV for A, but the corresponding adsorption energy densities (divided by the number of metal atoms in the ensembles, N_{covered} in Table 1) are quite similar. In addition, the reactions are performed in solvent. Solvent contributions are difficult to assess⁴⁸ and would require extensive first-principles molecular dynamics sampling,⁴⁹ which are not possible for the lignin dimers presented here. Instead, we have followed two methods to report the contributions: (i) adsorption/desorption events calculated in the gas phase (rendering large values, around 2 eV for the model A lignin) and (ii) introduction of the replacement energy that implies removal of some solvent from the surface and desolvation of the reactants from our continuum model (see the Born–Haber cycle in section S3.2). The discussion in terms of only the competition between the solvent and lignin model A is sufficient to identify potential bottlenecks.

On the Ru(0001) surface, our results show that adsorptions for all species are much stronger than those on Ni(111). Therefore, the adsorption of intermediate species on a Ru-decorated Ni(111) surface would be between those on pure Ni(111) and Ru(0001) surfaces. This has been confirmed by the calculated adsorption energies on the Ru–Ni(111) surface. When A and B approach the Ru–Ni(111) surface, the

adsorption energies depend on their motifs above the Ru atom. Two A structures with an aromatic part and O (from β -O-4) above the Ru atom, denoted as Ar_{Ru} and O_{Ru}, respectively, were optimized, and their adsorption energies are -2.28 and -2.13 eV, respectively. The local surface environment and lignin rigidity would account for the weaker O_{Ru} adsorptions. The Ni atoms surrounding Ru have been increased by 0.02 Å, and Ru is 0.06 Å above the surface. The local surface roughness pushes the adsorbate up in the z direction slightly, compared to the flat Ni(111) surface. For example, the carbon atoms from the benzene ring connecting the O atom shift upward slightly with a range from 0.003 to 0.098 Å, weakening the aryl–metal interaction. In addition, the aryl far from the O atom nearly keeps its structure unaltered, and this rigidity might bring out the intramolecule strain, further reducing its adsorption strength.

3.2. Reaction Network. Because of their lower adsorption energies, C and D were not further considered in the depolymerization and hydrogenation network. For A and B conversions on the Ni(111) surface, as reported experimental results show that aromatic parts are undisturbed during the catalytic process by using an activated carbon-supported Ni (Ni/AC) catalyst,¹⁷ only reactions related to α - and β -C were considered, and the full decomposition pathways are outlined in Schemes 1 and 2 and Figure S3 and S4. Two C–C bonds, C $_{\alpha}$ –C_{aromatic} and C $_{\alpha}$ –C $_{\beta}$, were assumed to require high barriers to proceed because of interactions lacking between these bonds and the surface metals. The reactants can be treated as EG with its H atoms being replaced by aromatic moieties and CH₂OH; a previous study of EG dehydrogenation shows that the C–C bond breaks in the late reaction steps.⁵⁰ In addition, in the previous experimental studies over the Ni catalyst,¹⁷ C_{aromatic}–O, C $_{\alpha}$ –C_{aromatic}, and C $_{\alpha}$ –C $_{\beta}$ bond scissions were not observed and the C $_{\beta}$ –C $_{\gamma}$ bond breaking product accounts for only 1% of the product distribution. Therefore, aromatic hydrogenation and C_{aromatic}–O and C–C bond breaking are not further considered. Calculated reaction barriers and energies from A and B isomers are also shown in Schemes 1 and 2, and the energy diagrams and geometries are plotted in Figures 3 and 4. To describe the complex reaction network more clearly, all

Figure 3. Reaction profile and intermediates' structures of isomer A conversion on the Ni(111) surface. For smaller molecules on a p -(7 × 4) Ni(111) surface, some of the surface metal atoms are not shown in the figures. Same color code as in Figure 2.

Figure 4. Reaction profile and intermediate structures of isomer B conversion on the Ni(111) surface. Same color code as Figure 2.

steps in the schemes are labeled with notations such as A01, A11, etc. Here, A01 stands for the first possible elementary reaction in the first reaction stage from the A isomer. Because of the different chirality of A and B isomers, the reactions that take place at the same α - or β -C positions at the same stage in two isomer conversions are labeled with the same number even though the bond breaking types are different. For instance, A01 and B01 are C–OH and C–H bond breakings, respectively. C–OH from the B isomer is not labeled as B01 because this bond is not activated in the adsorbed B isomer.

3.2.1. Reactions Starting from Isomer A. The reaction network and the energy profile starting from isomer A are shown in Scheme 1 and Figure 3. For reactions from the α -C side of this isomer, there are two competing reactions, C–OH (A01) and O–H (A03) bond ruptures. The barriers (reaction energies) for them are 0.87 (–0.36) and 1.00 (0.38) eV, respectively. After the A03 step, α -C–O breaking (A12) proceeds with lowest barriers of 0.38 eV in three possible steps (A12–A14), and this step is highly exothermic with an energy of –1.04 eV. As a result, a common intermediate appears from the A01 step or the combined A03 and A12 steps. Then, it is interesting to find that the β -O-4 bond is very easy to break (A11) both kinetically and thermodynamically with energies of 0.39 (–0.82) eV. Such a lower barrier for β -O-4 bond rupture is attributed to the formation of a highly conjugated coniferyl alcohol (G1). After A01, another α -C hydrogenation step (A22) to produce E has been calculated, and this step has an activation barrier of 0.85 eV and is nearly thermoneutral by 0.06 eV. The inverse reaction of A01 is difficult because of its higher barrier of 1.23 eV. Hence, once the C–OH bond breaks, both the hydrogenation step (A22) and the reverse reaction of A01 cannot compete with β -O-4 bond breakings. Another product of the β -O-4 bond cleavage is 2-methoxy-phenolate, which requires 0.82 eV (A21) to be hydrogenated into 2-methoxy-phenol (G0). The desorption energies for G0 and G1 are 1.24 and 2.34 eV, respectively. When solvation effects are considered, their desorption energies decrease to 0.04 and 0.90 eV, respectively, in the EG solvent. Compared to the higher barrier to desorb for G1, two hydrogenation steps at the C=C bond (A33 and A43) would take place, and the hydrogenation product is G6. In the last step, G6 would desorb in the gas phase (EG solvent) with a lower barrier of 1.57 (0.26) eV.

For reactions starting from the β -C side, β -C–H (A02) and direct β -O-4 bond breaking (A04), were first investigated. Our results show that the A02 step is blocked by its high barrier and endothermic energy of 1.92 and 1.49 eV, respectively, because of the rigidity of the lignin structure arising from the strong interactions between two aromatic units that prevents the rotation of the C $_{\alpha}$ –C $_{\beta}$ bond. Hence, the possible reactions after the β -C–H step have not been considered in the next step. For direct β -O-4 bond breaking (A04), this step needs a relatively low barrier of 1.07 eV and is exothermic by –0.66 eV. Therefore, this step would compete with the C–OH and O–H bond breakings from the α -C side. One of its products, 2-methoxy-phenolate, would be hydrogenated to G0 and then desorb. For the other product, there are three possible reactions that can proceed; one is the direct hydrogenation step (A17) that takes place with a comparable energy of 0.82 (–0.05) eV, while its product G5 requires 1.62 (0.22) eV to desorb in the gas phase (or EG solvent). The other two are C–OH bond breakings from α -C (A15) and β -C (A16) sides with energies of 0.86 (–0.45) and 0.76 (–0.23) eV, respectively. Among them, step A16 with the lowest barrier is the most kinetically favorable. The A15 step produces the coniferyl alcohol (G1), and the A16 step produces another unsaturated intermediate (G2) that needs a high energy of 2.07 (0.80) eV to desorb in the gas phase (or EG solvent). From G2, two hydrogenation steps proceed on the β -C (A34) and γ -C (A44) sides and the product G7 needs 1.44 (0.01) eV to desorb.

For the analysis presented above, we noticed that C–OH and β -O-4 scissions can affect each other when they proceed in a different sequence order. For example, C–OH bond breaking in A01 facilitates the subsequent β -O-4 bond rupture (A11) by forming the conjugated structures. On the other hand, direct β -O-4 bond cleavage (A04) facilitates C–OH bond ruptures (A15 and A16) by ~ 0.10 eV, compared with the A01 step.

3.2.2. Reactions Starting from Isomer B. The B isomer can be regarded as the product of changing the H and OH group positions (epimers) at α -C in the A isomer, and the reaction network and profile for its conversion are outlined in Scheme 2 and Figure 4. For reactions starting at the α -C side, only the C–H bond interacts with the surface; thus, the α -C–H bond breaking proceeds first with a barrier of 0.67 eV, and this step is almost thermodynamically neutral, –0.06 eV. Then, β -O-4 bond scission (B11) is greatly promoted with energies of 0.15 (–0.78) eV. This indicates that conjugation again plays a significant role in reducing the barrier to breaking the β -O-4 bond. In addition, the barrier in B11 is 0.24 eV lower than that in the A11 step (0.39 eV). The differences between initial structures of A11 and B11 are the H and OH groups at the α -C side. As oxygen has a higher electron affinity, more electrons would be transferred from the β -O-4 bond to the α -C–OH bond and the β -O-4 bond in B11 is more activated than that in A11, resulting in a lower barrier. 2-Methoxy-phenolate and G3 are the products in this step. From G3, two sequential C hydrogenation steps (B33 and B43) proceed with barriers of 0.85 (0.55) and 1.14 (–0.03) eV, respectively, and G8 is the product that needs less energy (1.20 eV) to desorb. The solvent-corrected adsorption energy of G8 is 0.19 eV; this means that it will desorb once it is formed.

For reactions from the β -C side, similar to those from A, β -C–H bond rupture (B02) again requires the highest barrier among all reactions, showing that the change in chirality from that of α -C has little effect on reducing the structure's rigidity. Thus, reactions after the B02 step are no longer considered. For

direct β -O-4 bond breaking (B04), the activation barrier (1.15 eV) is 0.08 eV higher than that in the A04 step. One product is 2-methoxy-phenolate, and the other one would undergo three possible reactions, α -C-H (B15) and γ -C-OH bond breakings (B16) and β -C hydrogenation (B17), the products being G3, G4, and G8, respectively. The energies in the B15-B17 steps are 0.89 (−0.33), 0.90 (−0.42), and 0.77 (0.15) eV, respectively. From G3, two hydrogenation steps would proceed, and the final product is G8 as stated before. From G4, both β -C (B34) and γ -C (B35) hydrogenations take place with energies of 0.84 (0.40) and 0.72 (0.24) eV, respectively. In the next steps, the energies are 0.88 (−0.34) and 0.71 (−0.18) eV for the B44 and B45 steps, respectively. The hydrogenation product G9 needs 1.29 (0.01) eV to desorb in the gas phase (or EG solvent). Considering the energies in the three initial steps (B01–B03), it is safe to infer that the reaction proceeds via α -C–H scission first, followed by the β -O-4 bond cleavage and hydrogenation steps. The products should be G0 and G8.

3.2.3. Comparison of the Reactivity for A and B Isomers. As described above, the most preferred reaction pathways for A and B isomers on the Ni(111) surface have been selected and the energy diagrams are shown in Figure 5. G0, G6, G7, etc., in

Figure 5. Comparison between the reaction energy profiles for A and B conversions on the Ni(111) surface.

the profiles stand for their desorption steps. For isomer A, the pathway starting from the α -C side is A01–A11–A21–A33–A43–G6–G0, with sequential reaction barriers of 0.87, 0.39, 0.82, 0.82, 0.87, 1.57, and 1.24 eV. Similarly, for the other path starting from the β -C side, the sequential barriers (A04–A16–A21–A34–A44–G7–G0) are 1.07, 0.76, 0.82, 0.84, 0.99, 1.44, and 1.24 eV. In the last two steps, product desorptions require more energy. However, when solvation effects are considered, the desorption barriers are diminished. For instance, in the EG solvent, the barriers of G6 and G7 desorptions decrease from 1.57 and 1.44 eV to 0.24 and 0.20 eV, respectively. For the B isomer, the barriers in the pathway starting from the α -C side (B01–B11–A21–B33–B43–G8–G0) are 0.67, 0.15, 0.82, 0.85, 1.14, 1.20, and 1.24 eV, respectively. The barriers in the pathway starting from the β -C side (B04–B16–A21–B35–B45–G9–G0) are 1.15, 0.90, 0.82, 0.72, 0.71, 1.29, and 1.24 eV. Thus, the reactions starting from the α -C side are kinetically preferred. For elementary reactions in two pathways starting from the α -C side for A and B isomers, entropy and zero-point energy corrections to their activation barriers have

been considered by analyzing the vibration modes under 473 K, which is the experiment temperature from ref 17. As shown in Table S7, entropy contributions are very small for the surface reactions, and this has also been shown in previous studies by Hamou et al.²² For reactions related to the A isomer, A01, A33, and B43 have very close barriers, and it is difficult to tell which one is the rate-limiting step. However, for reactions related to the B isomer, B43 has the highest barrier of 1.03 eV. This again implies the chirality effects in the reaction pathways.

3.2.4. Reactions on the Ru-Doped Ni(111) Surface. A previous experimental study by Yan et al.¹⁸ demonstrated that bimetallic Ru–Ni exhibits superior activity during the hydrogenolysis of lignin in water. By combination of XPS and X-ray absorption spectroscopy methods, it was found that the catalyst is surfaced-enriched with Ni. In the study presented here, the Ru effects were studied via a simple model by replacing one surface Ni with a Ru atom (impurity model), and then the adsorption properties and transition states were optimized. Reaction barriers and energies on Ni(111) and Ru–Ni(111) surfaces are listed in Table 2, and effects of Ru on the energy profiles for the selected pathways are plotted in Figure S8.

Table 2. Comparison of Activation Barriers, E_a , and Reaction Energies, ΔE (both in electronvolts), on Pure Ni(111) and Ru-Doped Ni(111) Surfaces

label	type	Ni(111)		Ru–Ni(111)	
		E_a	ΔE	E_a	ΔE
A01	α -C–OH	0.87	−0.36	0.78	−0.12
A04	β -O-4	1.07	−0.66	0.77	−0.39
A11	β -O-4	0.39	−0.82	0.29	−1.20
A15	α -C–OH	0.86	−0.45	1.01	−0.39
A16	β -C–OH	0.76	−0.23	0.72	−0.04
A21	O4+H	0.82	0.37	1.06	0.74
B01	α -C–H	0.67	−0.06	0.74	−0.09
B04	β -O-4	1.15	−0.40	0.96	−0.18
B11	β -O-4	0.15	−0.78	0.05	−1.18
B15	α -C–H	0.89	−0.33	0.56	−0.68
B16	γ -C–OH	0.90	−0.42	0.87	−0.20

When α -C–OH bond cleaves (A01) over the substituted Ru atom, the barrier decreases slightly by 0.09 eV, and the process is less exothermic by 0.24 eV. Large differences are observed in direct β -O-4 bond scission (A04) with the barrier decreasing from 1.07 to 0.77 eV, and the reaction is less exothermic by 0.28 eV. Ru has little effect on the barrier of β -O-4 in the second step (A11) but a strong effect on the reaction energy (from −0.82 to −1.20 eV). The α -C–OH breaking step (A15) after A04 needs 0.15 eV more energy to proceed on the Ru–Ni(111) surface, and the reaction energy decreases slightly by 0.06 eV. The barrier of another α -C–OH scission step (A16) changes slightly by 0.04 eV, and the process turns out to be thermoneutral. Furthermore, for hydrogenation of 2-methoxy-phenolate to G0 (A21), Ru also increases the barrier by 0.24 eV and the reaction becomes more endothermic from 0.37 to 0.74 eV.

For the reactions of B, Ru also decreases the barrier by 0.16 eV for direct β -O-4 bond scission (B01). A larger release of energy from the second β -O-4 bond (B04) has been observed again, in agreement with reaction from A. It is interesting to observe that for B15, the C–H bond breaking after the B04 step is also activated by 0.33 eV and is thermodynamically more favorable by −0.68 eV. However, A15 becomes more difficult

to reach as the energy requirement increases by 0.15 eV on the Ru–Ni(111) surface. Compared to those of A01 and A15, the lower barrier in the first C–H breaking step (B01) due to its chirality at α -C and the barrier lowered by the doped Ru in the second step (B15) demonstrate the synergistic effects of stereocenters and Ru on the promotion of lignin conversion. For the C–OH bond in B16, the barrier is slightly reduced from 0.90 to 0.87 eV and the reaction is less exothermic by 0.23 eV, which is similar to the A situation. Thus, for C–OH bond breaking, Ru has weak (for A16 and B16) or negative (for A15) effects on the reaction barriers and reactions become more endothermic by 0.20–0.30 eV. For β -O-4 bond breaking in the first steps (A04 and B04), doped Ru facilitates the reaction by reducing the barrier by ≤ 0.30 eV, with reactions becoming less exothermic by 0.20 eV. For β -O-4 bond breaking in the second steps (A11 and B11), Ru has little effect on the barriers but the reaction becomes more exothermic by 0.40 eV. In the final step, the introduced Ru increases the barrier and energy for phenolate hydrogenation into phenol by 0.27 and 0.35 eV, respectively. This can be attributed to the O affinity of Ru being stronger than that of Ni, which stabilizes the phenolate species. In spite of that, this step can be promoted by the high surface H concentration and H₂O via the formation of hydrogen bonds.

3.3. Discussion. **3.3.1. Chirality, Rigidity, and Conjugation Effects.** As stated above, three stereoeffects were found in this study: rigidity, chirality, and conjugation. First, the most stable adsorption geometries would be affected by the rigidity of the dimer molecules. For example, when the H and CH₂OH group positions are switched at the β -C side in A and B isomers, the products would bind to the surface more weakly by ~ 0.50 eV (see Table 1). In addition, when the C _{α} –C _{β} bond rotates, because of the increased strain in the structures, the adsorption energy decreases significantly (Figure 2). To further clarify the effects of rigidity on the adsorption energies, the aromatic units connecting to α -C were replaced by H atoms from A and D isomers to eliminate the rigidity (see Figure 6).

Figure 6. Adsorption of rigidity-eliminated isomers from A and D by substitution of the aromatic units bound to α -C with H atoms on the Ni(111) surface.

Calculated adsorption energies are -1.42 and -1.58 eV, respectively. It should be emphasized here that the adsorption energies of A and D on the Ni(111) surface are -2.28 and -1.86 eV, respectively. Thus, the replaced D isomer becomes more stable upon removal of the structural rigidity. The rigidity also has an impact on the reactions from α - and β -C sides. A previous study that used 2-phenoxyethanol as a surrogate²² showed that the α -C–H and β -C–H bond breakings have barriers of 1.21 and 1.14 eV, respectively, on Pt(111). However, these very similar barriers were not observed in the A and B

structures on the Ni(111) surface. In fact, the rigidity inhibits the β -C–H bond breakings as the A02 and B02 steps need to overcome extremely large barriers of 1.92 and 1.87 eV, respectively. The α -C–H bond breaking barrier in the B01 step is only 0.67 eV. As there are two faces of the isomers, we also tried to put the other face of the A isomer on the surface. However, because of the stereoeffects from the γ -C side, the interactions between aromatic rings and the surface are blocked, which results in the rather weak adsorption.

Second, for chirality effects, the differences from the α -C side on the adsorption energies are small, -2.25 and -2.27 eV for A and B, respectively. However, this is not the case for the reaction networks. From the reaction network discussed before, the reactions starting from α -C and β -C sides proceed differently for both A and B isomers, and the pathway starting at α -C is more preferable than those from the β -C side. As shown in the two reaction schemes, changing the chirality at the α -C side (from A to B) would also lead to different product distributions. For example, C–OH bond scission from the α -C side in the B isomer is unlikely because the lack of interaction of C–OH with the surface leads to the unactivated C–OH bond. Thus, the OH group on the α -C side of reactant B remains during the reaction network. It should be emphasized here that the various products from A and B cannot be observed when the simple β -O-4 surrogates are used in the study. From the comparison between reaction barriers of the A01 and B01 steps, it is clear that C–H bond breaking with a barrier of 0.66 eV proceeds easier than C–OH bond breaking, which has barrier of 0.86 eV. Because of the lower barriers in the first two steps (C–H and β -O-4 scissions), lignin decomposition from reactant B would proceed much faster than that from reactant A, demonstrating that stereocenters affect the relative rates.

Third, for both A and B conversions, the formation of conjugation structures would significantly reduce the reaction barriers for β -O-4 bond breaking. For example, direct bond breakings in A04 and B04 need barriers of 1.04 and 1.15 eV, respectively, and the barriers decreased to 0.39 and 0.11 eV for the A11 and B11 steps, respectively. This is an indication of a useful strategy for breaking the β -O-4 bond by breaking one bond on the α -C side ahead and allowing the formation of conjugation structures.

3.3.2. Solvation Effects. In the reaction profiles of A and B conversions (Figure 5), a large energy span from the lowest structures to the products exists (~ 3.0 eV). This is mainly due to the large size of the molecule when the gas phase and pure slab energies are used as reference energies. Under real reaction conditions, reactants and products are surrounded by the solvent molecules and solvation energies will decrease the initial energy level (gas phase and the pure slab surface) on a large scale. On one hand, by using the MGCM method,⁴⁰ the computed solvation energies of A and B are -0.60 eV in EG. This means their adsorption energy would approximately be reduced to -1.65 and -1.67 eV, respectively. On the other hand, the surface is also covered by the solvent molecules; if adsorption were to proceed, the surface solvent species would be pushed back into the solvent. Therefore, the energy to remove surface solvent molecules should be paid by the adsorption energy of these adsorbates. The energy for this whole replacement process can then be written as $E_{\text{ads}}(\text{EG})$.^{41,51} For example, for the adsorbed A isomer and EG on the Ni(111) surface, they roughly cover 20 and 4.5 Ni atoms, respectively. The monolayer-covered Ni(111) surface

was optimized by adding up to eight EG molecules on a p -(6 × 6) supercell (see Figure S7); 20/4.5 surface EG molecules would be substituted by only one A isomer. Thus, the replacement on the surface in the solvent goes as

where A^{solvated} and EG^{solvated} are species in the solvation and A^* and EG^* are surface-adsorbed species. The adsorption energy in this step can be obtained via a Born–Harber cycle as shown in Figure S6 and its corresponding eq S8. For all the reactants and products, their adsorption energies are reduced to a large degree when solvation effects are employed, and this also decreases the large energy span in the energy profiles. The A01–A11–A21–A33–A43–G6–G0 pathway on Ni(111) is taken as an example to illustrate solvation effects. As shown in Figure 7, when the solvation energy is corrected, the large energy span when taking the gas phase energies as references is reduced to more representative values.

Figure 7. Reaction profiles employing gas phase reference energies and the corrected solvation energy (replacement energy values) for the A01–A11–A21–A33–A43–G6–G0 path on the Ni(111) surface.

3.3.3. Ru Doping Effects. As stated in the adsorption section, on the Ru-doped Ni(111) surface, Ar_{Ru} binds to the surface more strongly (−2.28 eV) than O_{Ru} does (−2.15 eV). However, the β -O-4 bond breaking barrier of Ar_{Ru} is 0.13 eV higher than that of O_{Ru} . This implies that Ru participates in lowering the C–O bond breaking barriers. To confirm this assumption, the adsorptions of a single O atom atop Ni and Ru atoms in pure Ni(111) and Ru-doped Ni(111) surfaces were calculated. The Ni–O and Ru–O distances are 1.678 and 1.734 Å, respectively, with adsorption energies for the gas phase O_2 of −0.54 and −1.51 eV, respectively. The more negative O adsorption energy atop Ru indicates that the Ru–O bond is much stronger than the Ni–O bond. This shows that more electron density is localized between O and Ru, thus weakening the β -O-4 bond when A and B adsorb on the surface, in agreement with the earlier transition state C–O bond length of 2.103 Å on Ru–Ni(111), compared with the longer bond distance of 2.242 Å on Ni(111). Stronger Ru–O interaction can also be implied via comparison of the O adsorption energies on Ru(0001) and Ni(111) (−2.98 versus −2.45 eV). Therefore, the doped Ru strengthens the metal–O bond, which

in return weakens the β -O-4 linkage and promotes C–O bond cleavage.

In addition, adsorption energies are more exothermic on Ru(0001) than on the Ni(111) surface (Table 1). Thus, employing too much Ru on the surface would lead to surface poisoning by impeding the refreshing of the catalyst surface during the desorption step of the catalytic cycle. In addition, it has to be emphasized that Ru also has a strong ability to hydrogenate arenes.⁵² Therefore, a small percentage of Ru doped into the Ni catalyst would improve the catalytic process. The structure of this active site then recalls single atom catalysts. Our results are in excellent agreement with the experimental observations of Yan et al.,¹⁸ who found a volcano-like behavior exists upon variation of the Ru percentages in the Ni-based catalyst.

4. CONCLUSIONS

In this study, DFT calculations of complex lignin dimer β -O-4 bond models over Ni(111) and Ru-doped surfaces were performed. The reaction network accompanied by the stereoeffects and Ru doping effects has been investigated. Our results show that stereocenters have three effects: on the adsorption structures, on the reaction pathways in the network, and on product distributions. The chirality at the β -C side and the rigidity are important factors for the different adsorption energies of four reactant candidates and for the reactions from both α -C and β -C sides, thus determining the preferable reaction path from A and B isomers. For the favorable reactions from both A and B, it is chirality at the α -C side that leads to the different kinetic results and product distributions. Rigidity implies that adsorption becomes dominated by the large aryl rings, in the form of the sergeants-and-soldiers principle. In addition, it blocks the reactions from the β -C side at the beginning of the reaction networks. Computed barriers and energies imply that reactions from the B isomer should be faster than those from the A isomer. We also found that β -O-4 bond cleavage would be promoted or accelerated by the unsaturated α -C side (α -C–H and α -C–OH breaks ahead) because this would benefit the formation of conjugated products. Ru has both positive and negative effects on the catalytic behavior. It promotes direct β -O-4 bond scission by lowering the reaction barriers via the strengthened metal–O bond and makes it competitive with the first C–H or C–OH bond scissions. As Ru has a stronger adsorption toward reactants than Ni, too much Ru would lead to less active surface sites by covering the intermediates and impede catalysts. Our DFT study rationalizes the complex reaction network of the most abundant β -O-4 linkage in lignin, showing the role of stereocenters, rigidity, and conjugation in lignin depolymerization on nickel and Ru-doped nickel catalysts.

■ ASSOCIATED CONTENT

Supporting Information

Structures and their coordinates, decomposition networks, computed adsorption energies of closed-shell structures, reaction barriers, reaction energies, energy profiles, stability calculation details, and equations for solvation correction (PDF)

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Notes

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