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A series of different initial adsorption configurations were constructed for eight model components (*n*-butanol, acetic acid, methyl acetate, *n*-hexanal, toluene, catechol, guaiacol, and 3-methyl-1,2-cyclopentanone) in bio-oil to determine their exact orientation on the Ni(111) surface and preferential binding site. To explore the difference between single-molecule adsorption and multi-molecule adsorption, we determined the competitive adsorption behavior of the multi-molecule system and the origin of the surface potential polarization effect through the reactive molecular dynamics adsorption model. The selection of model compounds needs to cover all categories of bio-oil components as much as possible. The multi-molecule competitive adsorption model between oxygenated species uses acetic acid with the lowest thermodynamic adsorption energy and guaiacol with the highest adsorption energy as key components. We present a comprehensive molecular-level investigation of the competitive adsorption process of oxygenated compounds. This work would bridge the gap between first principles and molecular dynamic theoretical predictions and experimental observations in the field of biomass catalytic upgrading.

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1. Introduction

Biomass pyrolysis has been proven to be an effective method for treating biomass and achieving sustainable production of liquid fuels and other chemicals.^{1–3} In this respect, biofuels are currently the only sustainable source of liquid fuels.^{4–6} However, the resulting bio-oil from biomass pyrolysis is a complex mixture of over 700 organic compounds, including phenols (such as phenol, catechol, eugenol, and guaiacol), oxygenates (alcohols, acids, esters, aldehydes, and ketones), hydrocarbons (aromatics and olefins), sugars, polymeric compounds (lignin-derived oligomers, lignin, hemicellulose, and cellulose), and water (about 35 wt%).⁷ The main goal of

Adsorption variations on the Ni(111) surface: electron density diversity from oxygen-containing functional groups[†]

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In the catalytic hydrodeoxygenation (HDO) upgrading process of biomass pyrolysis, adsorption behavior plays a crucial role in subsequent reaction processes. A comprehensive understanding of the interfacial behavior is essential for advancing novel biomaterials and commercial bio-oil. We initially establish their precise orientation on the Ni(111) surface and identify the preferential binding site by calculating the binding energy of eight model components (*n*-butanol, acetic acid, methyl acetate, *n*-hexanal, toluene, catechol, guaiacol, and 3-methyl-1,2-cyclopentanone). Differences in the electrostatic potential of functional groups and their interactions with the surface lead to surface electrostatic potential distributions, with compounds containing aldehyde functionality demonstrating increased reactivity. To account for competitive adsorption behavior among multiple molecules, ReaxFF-MD simulations were conducted to investigate the adsorption of guaiacol molecules. The inclusion of acetic acid enhances the polarization effect and non-uniformity, indicating competitive adsorption between guaiacol and acetic acid molecules. The chair conformation of acetic acid was demonstrated to be more reasonable from a kinetic perspective, leading to a stronger surface charge induction effect compared to guaiacol. Additionally, this non-uniform distribution is closely correlated with the characteristic bond activations of adsorbed active molecules, serving as a driving force to enhance further hydrogenation and deoxygenation activities of the molecules.



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the hydrodeoxygenation (HDO) process is to maximize the reduction of oxygen-containing functional groups (such as acids, esters, aldehydes, and phenols) in the bio-oil,^{8,9} and a comprehensive understanding of the adsorption and interfacial behavior exhibited by biomass oil pyrolysis liquid is crucial for the advancement of novel biomaterials and commercial bio-oil.

In recent years, there has been an increasing focus on exploring the kinetics and thermodynamics involved in utilizing biomass processes. Of particular interest is the study of the mechanism of each component involved in the HDO process. Through extensive experimentation, including isotope labeling, intermediate species analysis, and observation of products under process conditions, the HDO mechanism of various components of bio-oil on various catalysts and non-metal) can (metal be roughly understood.¹⁰⁻¹² For example, Michelle S. Hofman et al. studied acetic acid (HAc) adsorption and reactions at multiple surface coverage values by combining TPD and infrared reflection absorption spectroscopy (IRAS) measurements.¹³ However, the composition of bio-oil is extremely complex, making it very difficult to identify the complete reaction mechanism from experimental data. Therefore, the atomic-molecular mechanism of oxygencontaining compounds on the catalyst surface during the HDO process is still unclear.

According to relevant reports, employing density functional theory (DFT) to elucidate the HDO mechanism of bio-oil on the catalyst surface has become one of the main research methods. Non-noble metal nickel is attractive due to its ability to activate C-O bonds and its economic viability.14,15 Based on previous reports, the study of the adsorption configuration of reactants and intermediates in the HDO process is crucial to understanding the reaction mechanism. Chen et al.¹⁶ studied the geometric structures of furfural adsorbed on the Ni and Ni/Fe surfaces and their influence on the reaction pathway, with results that were consistent with experiments. Mushrif and colleagues¹⁷ accurately predicted the most stable adsorption configuration of aldose and glucose on Pd and Pt, respectively, using modified PBE. The above computational studies have been conducted at the low coverage limit. Medlin et al. reviewed the effects of adsorbate-adsorbate interactions in other reaction systems, such as the hydrogenation of olefins with other carbonaceous adsorbates, to improve selectivity.¹⁸ Wang and co-workers also found that the effect of adsorbateadsorbate interactions on furfural adsorption and furfural hydrogenation to furfuryl alcohol and decarbonylation to furan using DFT calculations.¹⁹ Nevertheless, only a few authors elaborate on the HDO of mixtures of compounds with different oxygen functionalities,^{20,21} and few comprehensive reports have compared and summarized the single adsorption or competitive adsorption behavior of diverse bio-oil components with different functional groups on transition metal surfaces. Simultaneously, numerous researchers have investigated the catalytic performance and

stability of Ni-based catalysts on various crystal facets.^{22–24} On one hand, among different types of nickel surfaces, the Ni(111) surface is considered the most stable and possesses the highest catalytic activity among low-index surfaces.²⁵ On the other hand, due to its high symmetry and to the fact that is a well-understood system, Ni(111) represents a convenient model substrate. The surface science approach from model catalysts is useful for understanding mechanistic aspects of the reactions.

Our research systematically investigates the adsorption mechanisms of eight different functional groups of highcontent primary bio-oil components on the surface of Ni catalysts, as shown in Table 1. The (111) surface was chosen because it is the lowest energy facet and usually dominates the metal nanoparticle surface.²⁶ Therefor, we investigate the adsorption energy, charge transfer, and orbital contributions of each component of bio-oil on the Ni(111) interface. On this basis, we selected two key oxygen-containing monomers, guaiacol and acetic acid, and explained the correlation between the competitive adsorption behavior of multimolecule systems and the non-uniformity of surface charge polarization through ReaxFF-MD simulation. Furthermore, we observed the activating processes of the key bonds (C=O and π - π bonds) and the initial reaction process of adsorbed molecules. Particularly the effect of the presence of a carboxylic acid functionality in the mixtures sheds light upon the interactions between different compounds and their subsequent conversion in catalytic HDO of complex feedstocks.²⁷ In this way, the crucial pyrolysis mechanisms related to the interplay of different functionalities that cannot be observed during single-model compound HDO could be further demonstrated.

2. Computational methods

2.1. DFT calculation of adsorption energy

DFT calculations were performed with the Vienna *ab initio* simulation package (VASP).²⁸ Optimized adsorption behaviors of all isolated monomers on the Ni(111) were calculated utilizing the function of Perdew–Burke–Ernzerhof (PBE)²⁹ which belongs to the generalized gradient approximation method (GGA).³⁰ Furthermore, a well-known disadvantage of GGA functionals, including hybrids, which often replace part

Table	1	Representative	primary	bio-oil	component	of	7	different
functio	onal	groups						

	Category	Model compound
Long chain	Alcohol	<i>N</i> -Butanol
compounds	Acid	Acetic acid
	Ester	Methyl acetate
	Aldehyde	<i>N</i> -Hexanal
Cyclic compounds	Aromatic hydrocarbon	Toluene
	Phenol	Catechol
		Guaiacol
	Ketone	3-Methyl-1,2-cyclopentanone

of the local by a nonlocal Hartree–Fock exchange, is that they cannot describe long-range electron correlations that are responsible for vdW (dispersive) forces. As is the case in the present work, the inclusion of the dispersion correction is desirable when considering large atoms and/or molecule interactions. Therefore, the semiempirical long-range dispersion correction approach DFT-D3 scheme developed by Grimme *et al.*,³¹ was used to acquire dispersion corrections.

Based on our convergence test, the plane wave energy cutoff was set to 450 eV, and convergence criteria for energy and forces were set to 10^{-5} eV and 0.05 eV Å⁻¹. To model the Ni(111) surface, a 19.7 Å × 19.7 Å surface of a square supercell was constructed, which consists of trilayer nickel atoms. Furthermore, an 18 Å vacuum layer was utilized to avoid possible interactions between adjacent supercells.

The adsorption energy (E_{ads}) of all studied molecules on the Ni(111) slab was defined as follows

$$E_{\rm ads} = E_{\rm system} - E_{\rm surface} - E_{\rm M} \tag{1}$$

where E_{system} is the total energy of the optimized substrateadsorbate system; E_{M} and E_{surface} are the total energies of the molecules and the nickel surface slab, respectively.

To evaluate charge transfer induced by electronic hybridization between the orbitals of adsorbates and Ni slab, the electron density difference (EDD) was analyzed as follows:

$$\Delta \rho(r) = \rho_{\text{system}}(r) - \rho_{\text{surface}}(r) - \rho_{\text{M}}(r)$$
(2)

Here, $\rho_{\text{system}}(r)$ is the total density of the whole system; $\rho_{\text{surface}}(r)$ and $\rho_{\text{M}}(r)$ are the electronic density of the Ni surface and the studied model molecules, respectively.

2.2. Reactive molecular dynamics (RMD) simulations

The ReaxFF method, a reactive molecular dynamics potential, has demonstrated its ability to accurately simulate the dynamic behavior of diverse molecular systems.^{32–35} ReaxFF/ LAMMPS is an engine for modeling complex catalytic and non-catalytic environments based on the reactive force field developed by Adri van Duin and coworkers.^{36,37} The overall system energy (E_{system}) defined as a function of bond order,³² which is determined by the inter-atomic distance, is partitioned into contributions from several partial energy terms according to eqn (3).

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{lp}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}} + E_{\text{coa}} + E_{\text{conj}} + E_{\text{tors}} + E_{\text{H-bond}} + E_{\text{vdW}} + E_{\text{Coulomb}}$$
(3)

where the bond energy (E_{bond}) , lone pair energy (E_{lp}) , overcoordination energy (E_{over}) , under-coordination energy (E_{under}) , valence angle terms (including E_{val} , E_{pen} , and E_{coa}), conjugation energy (E_{conj}) , and torsion angle (E_{tors}) describe the valence forces. The hydrogen bond interactions $(E_{\text{H-bond}})$ describe the bond-order dependent hydrogen bond term. The non-bond terms that are independent of bond order handle the vdW (E_{vdW}) and Coulomb ($E_{Coulomb}$) interactions. For the connectivity-dependent interactions (*i.e.* valence and torsion angles, H-bond), the core of bond-order-dependent is expected to ensure that their energy contributions disappear upon bond dissociation. ReaxFF uses the EEM method, a geometry-dependent charge calculation scheme, for the Coulomb interaction, to account for polarization effects. For the van der Waals pair interactions, which are calculated between every atom pair, the Reaxff method adopts a shield pattern to avoid excessive close-range nonbonded interactions.

In this work, the simulations of competitive adsorption of HAc and guaiacol were first performed on a trial basis on an eight-layer $p(3 \times 3)$ slab, and two-dimensional periodic boundary conditions were applied to the system on the X-Y plane parallel to the surface due to the bottom four layers of the slab were immobilized. A vacuum space of 3 times the slab thickness (45 Å) was created perpendicular to the surface with a random distribution of 15 HAc and 15 guaiacol molecules, as shown in Fig. 1(c). To prevent particles from interacting with the fixed bottom plate of the Ni slab and affecting the analysis of surface adsorption, we employed a reflective wall at the top of the vacuum space that reflects particles in the substrate group when they attempt to traverse it. The Ni/C/H/O ReaxFF force field^{38,39} is used for RMD simulations and the previous Ni/C/H force field has been successfully used to investigate the methane dissociative adsorption on Ni(111).40

We use separate temperature baths for gas and Ni slab to investigate the polarization and interactions of AcOH with the Ni slab surface. During the initialization, the flexible molecule and adsorption surface were held at 298.15 K for 20 ps before being rapidly heated to 600 K within 10 ps. Finally, the system was equilibrated at the target temperature of 600 K for 1 ns, because during the HDO experimental process,^{7,9,41} carboxylic acids, phenolic ethers, and phenols undergo reactions involving catalytic hydrogenation as well as thermal dehydration in the temperature range of 573 to 623 K and the deformation of Ni(111) surface was within the acceptable limits. For pure component adsorption systems, we placed 30 HAc or guaiacol molecules separately in vacuum layers, as shown in Fig. 1(a and b). All the simulation parameters are configured following the mixed component system. ReaxFF describes dynamic charge transfer between atoms based on the charge equilibration (QEq) method,^{42,43} which minimizes the electrostatic energy based on the electronegativity and the stiffness parameters. The atoms' position, bonds, and velocity were collected every 25 fs.

3. Results and discussion

3.1. Adsorption sites on the Ni slab surface

To investigate the most stable adsorption configurations of four linear compounds, namely *n*-butanol, HAc, methyl acetate, and *n*-hexanal, on the Ni(111) surface, we constructed six different initial adsorption configurations for each



Fig. 1 Initial adsorption structure for ReaxFF molecule dynamics simulations. (a) Pure HAc/Ni(111) system, (b) pure guaiacol/Ni(111) system; (c) mix HAc/guaiacol/Ni(111) system.

component which was generated by placing the molecule in different orientations and positions. Due to the anisotropy of the Ni(111) surface, it exhibits distinct properties along the parallel and perpendicular Ni–Ni directions. The alkyl chains were arranged in chair and zigzag configurations, denoted by letters A and Z, respectively. Moreover, we considered two different orientations of the alkyl chains, *i.e.*, horizontal and vertical. Specifically, for the vertical orientation, there were two possible arrangements due to the proximity of the oxygen functional group to the surface, which we labeled as 1 for the configuration with the oxygen atom furthest from the surface and 2 for the one closest to the surface. The horizontal configuration was labeled as 3. The endpoint carbon atom of the alkyl chain was placed on the hollow site (H, above the triangular center of the Ni atoms), as illustrated in Fig. 2.



Fig. 2 Possible adsorption sites were labeled on the Ni(111) surfaces. The atoms in the first, second, and third layers were presented in green, yellow, and violet balls, respectively. T, H, and B represent the possible orientations of the aromatic ring at the three high symmetry sites of the Ni(111) surface.

The adsorption characteristics of four cyclic compounds, including toluene, catechol, guaiacol, and 3-methyl-1,2cyclopentanedione, on the Ni surface were also investigated. We adopt three different active sites: the top site (T), the hollow site (H), and the bridge site (B). To obtain the most stable adsorption configurations, specifically, the aromatic ring was positioned parallel to the Ni surface, with two directions (horizontal and vertical) on the plane labeled Hz and Vt. The center of the aromatic ring was fixed on the T, B, and H sites, while the numbers 1 and 2 represented the possible positions of other functional groups on the Ni surface. For the aliphatic compound 3-methyl-1,2-cyclopentanedione, 13 adsorption configurations were constructed, and the center of the five-membered heterocycle was arranged at the T, B, and H sites. Then the C atom of the five-membered heterocycle was located at the T site, while the C-C bond opposite to this C atom was placed parallel to the Ni-Ni bond, which was labeled as 1-5 according to different types. It is worth mentioning that the initial geometries have no physical meaning and therefore they were not further detailed. All initial configurations and optimized structure files can be viewed in Fig. S1 and S3-S9 in the ESI.†

The ESP map provides an intuitive visualization of the electron distribution on individual molecule surfaces, as illustrated in Fig. 3a. As we observed that the local vdW surfaces surrounding O atoms exhibit negative ESP, such as acetic acid, methyl acetate, *n*-hexanal, and 3-methyl-1,2-cyclopentanedione. Especially for carboxylic groups, the acyl site registers a negative electrostatic potential of -40.61 kcal mol⁻¹, while hydroxyl (OH) groups exhibit a positive electrostatic potential of 60.28 kcal mol⁻¹, signifying the significant polarity of acetic acid. Additionally, we observed a notably negative electrostatic potential near the aromatic



Fig. 3 (a) ESP mapped the vdW surface (the electrostatic potential on a surface with an electron density of 0.001 a.u.). The minima and maxima of the ESP are drawn as cyan and orange spheres on the vdW surface, respectively. All values are expressed in kcal mol⁻¹. (b)–(i) The most stable configurations of eight compounds adsorbed on the Ni(111) surface.

ring, indicating the presence of a rich π -cloud.^{44,45} In the case of the central region of the five-membered ring in the 3-methyl-1,2-cyclopentanedione, compound а global maximum ESP value is generated (29.24 kcal mol⁻¹), significantly higher than other positions. This is primarily attributed to the presence of two connected acyl oxygen atoms, which attract a substantial number of electrons from the adjacent carbon atoms. Especially, the distribution range of ESP in toluene (as an aromatic compound used as a control in comparison to oxygenated aromatic hydrocarbons) is -18.26-+0.95 kcal mol⁻¹, which is narrow and uniform, indicating that the polarity of toluene is weak. Notably, for compounds containing hydroxyl groups, like N-butanol, guaiacol, and catechol, the surface minima are consistently found at the oxygen atoms, while the surface maxima are observed at the hydrogen atoms.

Fig. 3(b-i) shows the most stable geometries of the adsorbed molecules, and the values of adsorption energies

Table 2 Adsorption energy of the optimized geometries of four chain compounds ($\Delta E,$ eV)

Sites _{ads}	HAc	Methyl acetate	<i>N</i> -Butanol	<i>N</i> -Hexanal
A1	-0.344	-0.486	-0.702	-0.818
Z1	-0.343	-0.485	-0.699	-1.166
A2	-0.675	-0.798	-0.744	-1.268
Z2	-0.448	-0.839	-0.950	-1.321
A3	-0.630	-0.845	-0.785	-1.329
Z3	-0.770	-0.837	-0.811	-1.275

Table 3 Adsorption energies of the optimized geometries of four cyclic compounds (ΔE , eV)

Sites _{ads}	Guaiacol	Toluene	Catechol	Sites _{ads}	Cyclopentanedione
THz	-2.388	-1.075	-2.297	T1	-2.376
TVt	-2.250	-2.226	-2.281	T2	-2.374
BHz1	-2.323	-2.431	-2.238	T3	-2.213
BHz2	-2.345	-2.396	-2.306	B1	-2.235
BVt1	-2.314	-2.297	-2.045	B2	-2.331
BVt2	-2.373	-2.295	-2.108	B3	-2.191
HHz1	-2.244	-2.300	-2.093	B4	-2.235
HHz2	-2.345	-2.298	-2.122	B5	-2.327
HVt	-2.110	-2.345	-2.288	H1	-2.345
				H2	-2.097
				H3	-2.300
				H4	-2.209
				H5	-2.251

for all possible adsorption sites are listed in Table 2 and Table 3. All four linear oxygen-containing compounds tend to adopt a chair-like arrangement (Fig. 3(b-e)), obtaining the most stable adsorption configurations. Although the carboxyl functional group in acetic acid has the highest local polarity (Fig. 3b), the optimal adsorption configuration has the lowest adsorption energy (-0.770 eV). In contrast, N-hexanal has the lowest polarization, yet the highest adsorption energy (-1.329 eV), which may be due to a larger contribution of dispersive interactions between more CH_x (x = 1, 2, 3) groups and the Ni slab for the adsorption energy. The acetic acid, guaiacol, and catechol adsorption energy on Ni(111) is stronger than previously reported⁴⁶⁻⁴⁸ because of the different molecular coverage and different GGA pseudo potentials used as shown in Table S1.† Additionally, due to the more local negative ESP values, the acyl oxygen all point toward the Ni surface, and the lone pair electrons on O form bonds with the unpaired d-electrons of Ni. Furthermore, we found that the adsorption energies of aromatic hydrocarbons are much higher than those of linear compounds. By comparing the adsorption energies at different adsorption sites, it can be seen that guaiacol tends to adsorb at the hollow site (the center of the benzene ring is in the hollow site) (Fig. 3f), while toluene and catechol compounds tend to adsorb at the bridge site (Fig. 3(g and h)), and cyclohexanone tends to adsorb at the top site (Fig. 3i). Although the five-membered ring in cyclic compounds leads to significant repulsion on the surface, the three Ni-O single bonds formed by two keto oxygens have shorter average bond lengths (approximately 1.96 Å), resulting in higher adsorption energy (-2.376 eV) (Fig. 3i).

Simultaneously, due to the extensive positive electrostatic potential (ESP) distribution in the vicinity of the methoxy and hydroxyl groups in guaiacol, a significant upward rotation of the methoxy group is observed. This results in the C atom moving away from the Ni surface, as indicated by the lower RDF peak relative to toluene and catechol at 2.04 Å (Fig. S2†). For catechol, it seems that having two hydroxyl substituents located at the T position and the H position is more advantageous in terms of energy. Furthermore, due to the weak overall polarization of toluene with the weakly donating CH₃, the ESP on the benzene ring is more uniform. The slight distortion of the benzene ring induced by the upward rotation of the CH₃ group leads to the formation of more C–Ni bonds (defined as a distance less than or equal to the average carbon-metal bond length of 2.14 Å), resulting in the highest adsorption energy (approximately 2.431 eV).

Interestingly, the variation in the adsorption behavior of the benzene ring on different positions of the Ni surface is quite substantial. When the toluene adsorbs at the T position with the CH₃ group at the H position with no significant distortion of the benzene ring (Fig. S3[†]), the adsorption energy at this point is only -1.075 eV which primarily reflects dispersive interactions. In contrast, for guaiacol and catechol, top-site adsorption of the benzene ring is nearly impossible regardless of the initial placement (Fig. S1[†]). Especially for catechol compounds, the orientation of the benzene ring on the Ni surface also has a significant impact on the adsorption energy. For instance, regarding adsorption at position B, the first scenario with horizontal orientation exhibits the highest adsorption energy, approximately -2.306 eV, and the second scenario with vertical orientation yields adsorption energies of only -2.045 eV and -2.108 eV (corresponding to different orientations of the hydroxyl group), as depicted in Fig. S4.† This fact suggests a substantial weakening of π -d conjugation interactions in the second scenario and the phenomenon is presented for the first time in this paper. One can also note that for the same position over the surface, the energy can be slightly different depending on the substituent group location in the ring. In addition, the density of states (DOS) and projected density of states (PDOS) of the adsorbate adsorbed on Ni(111) represent significant overlaps between the s, p orbitals of O atoms or aromatic-C atoms and d states of Ni as shown in Fig. S10 and S11,† corresponding to significant changes in electron density occur between Ni atoms and C/O atoms indicated from the electron density difference (EDD) and Bader charge.

3.2. Revealing interactions between the compounds and the slab

The sign $(\lambda_2)\rho$ colored δg^{inter} isosurface maps are given in Fig. 4. In the IGMH map, the interaction regions of different strengths are exhibited by the isosurface of δg function with different values, and sign $(\lambda_2)\rho(r)$ is also employed as the mapped function to visually distinguish interaction types. The above analysis of the electron wave function was carried out using the Multiwfn49 program and visualized by the VMD software.50 From the blue isosurface observed between the molecule and the substrate in the IGMH map, it becomes evident that the IGMH analysis accurately represents the true nature of chemical adsorption, *i.e.*, the carbonyl oxygen in acetic acid, methyl acetate, n-hexanal, and cyclohexane interacts significantly with the Ni atom through nonnegligible covalent interactions (blue isosurfaces in Fig. 4(a, b, d and h)). This is further supported by the presence of a peak in the δg^{inter} vs. $\operatorname{sign}(\lambda_2)\rho(r)$ scatter plot at approximately



Fig. 4 $sign(\lambda_2)\rho$ colored IGMH $\delta g^{inter} = 0.01$ a.u. isosurfaces for representing the physical adsorption of chain and cyclic compounds on Ni(111) surface. (a) Acetic acid, (b) methyl acetate, (c) *n*-butanol, (d) *n*-hexanal, (e) guaiacol, (f) toluene, (g) catechol, and (h) 3-methyl-1,2-cyclopentanone. In IGMH analyses, the compounds and the slab are respectively defined as the two fragments.

-0.08 a.u. (Fig. 5). However, it is worth noting that these regions are characterized by a relatively sparse distribution despite their higher electron density. In contrast, alcohols like *N*-butanol show no significant peaks after -0.06 a.u. (Fig. 5c), suggesting that these points correspond to regions of chemical bonding. This observation is in line with the bonding assessments presented in Fig. 3. It is noteworthy that *n*-hexanal exhibits a combination of repulsive forces, dispersion interactions, and covalent interactions with the Ni surface (as indicated by extensive blue and red regions in Fig. 4d). This corresponds to regions of higher density

appearing in the IGMH scatter plots at both strongly negative and strongly positive positions (Fig. 5d). Additionally, a relatively strong interaction akin to hydrogen bonding is observed between CH_2 and the Ni atom. This significant contrast primarily arises from *n*-hexanal's horizontal adsorption on the Ni surface, which brings the molecule closer to the Ni surface and may induce surface coking on the Ni surface. Moreover, this proximity results in a pronounced steric hindrance effect between the C–C bonds and the Ni surface. Compared to nonaromatic molecules, the π -d conjugate adsorption between aromatic rings and Ni



Fig. 5 IGMH scatter plots for chain and cyclic compounds. (a) Acetic acid, (b) methyl acetate, (c) *n*-butanol, (d) *n*-hexanal, (e) guaiacol, (f) toluene, (g) catechol, and (h) 3-methyl-1,2-cyclopentanone.

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atoms is a crucial factor for the strong adsorption of aromatic compounds. As shown in Fig. 5(e–h), there is a significant electron density at -0.08 a.u., indicating the formation of

covalent interactions between the aromatic ring and Ni to confirm chemical adsorption. Maintaining the parallel adsorption of the benzene ring on the Ni(111) surface is



Fig. 6 Relative frequency of number density for the molecular mass center and particular atoms (such C and O atoms) of (a) pure guaiacols, (b) pure HAc, (c) guaiacol in mixed system ($N_{Guaiacol}: N_{HAc} = 1:1$), and (d) HAc in mixed system ($N_{Guaiacol}: N_{HAc} = 1:1$) in the *z* direction at 600 K, respectively. The first adsorption layer configuration of (e) acetic acid and (f) guaiacol on Ni(111) surface. γ , δ , and α represent the angles between the C=O bond, C-O bond, and C-C bond in acetic acid molecules and the plane containing the first adsorption layer C(α); θ , σ , and ζ represent the angles between the C(p)-H bond, C(p)-O(α) bond, C(p)-C(β) bond in guaiacol and the plane containing the center of the first adsorption layer benzene ring. The charge distribution on the Ni(111) slab surface corresponds to induced charge by (g) guaiacol molecules (i) HAc molecules, and (k) mixed system, respectively. Corresponding induced electric field on the Ni(111) slab surface by (h) guaiacol, (j) HAc, and (l) mixed HAc and guaiacol molecules, respectively. A delta value of 0.0015 in reduced units means there will be 667 layers (0.1 Å for the real length of the layer) from 0 to 1.0.

advantageous for the hydrogenation of benzene rings and the removal of active oxygen substitution groups through hydrogenation. Compared to the physical adsorption of benzene on an Ag surface,⁵¹ it is evident that Ni exhibits significant activation of the benzene ring. Additionally, in the case of 3-methyl-1,2-cyclopentadione (Fig. 5h), the steric hindrance of the five-membered ring is much smaller than that of the aromatic ring, which is attributed to the upward rotation of the five-membered ring away from the Ni surface. These IGMH findings align with the structural characteristics of the investigated adsorption systems.

3.3. Competitive adsorption of guaiacol with acetic acid

multi-molecule adsorption systems, the dynamic In adsorption behaviors of different species merit further investigation due to the presence of competitive adsorption. It is reported that carboxylic acids have the strongest impact on the adsorption of aldehydes and aromatic oxygenates, thereby inhibiting their conversion by HDO and shifting it to higher temperature.²⁷ Therefore, we selected two typical oxygen-containing components, namely, guaiacol with the highest adsorption energy, and acetic acid with the lowest adsorption energy, as model compounds to conduct reaction kinetics adsorption simulations. First, we considered the average density distribution of different types of atoms on the HAc and guaiacol molecules from the surface, as shown in Fig. 6(a-d) For single guaiacol component (Fig. 6a), the adsorption peak of the atom (Cp) on the benzene ring is about 2.19 Å, and the first adsorption peak of $C(\beta)$, Cp, $O(\alpha)$, $O(\beta)$ and the overall mass center of the molecule are slightly shifted to the right, which reflects that guaiacol tends to adsorb horizontally, with its substituent hydroxyl and methoxy groups pointing away from the Ni surface. The angle formed with the surface is approximately $\sigma \cong \xi = \pi/6$ rad (Fig. 6f), and the methyl group is farther away from the surface. The $O(\alpha)$ atoms in guaiacol formed a small covalent interaction (1.84 Å) with Ni atoms, which may be caused by vertical adsorption. For the single acetic acid component, Fig. 6e illustrates the dynamic adsorption configuration of acetic acid. Compared to the thermodynamically optimal adsorption behavior, the C–C bond of acetic acid forms a δ angle of approximately $\pi/6$ rad with the surface. The carbonyl oxygen sinks upon adsorption, while the hydroxyl oxygen points upward, resulting in a stable chair-like molecular configuration. As shown in Fig. 6b, there is a sharp peak for $O(\alpha)$ at a position of 1.68 Å (with an average Ni–O bond length of 2.01 Å), significantly lower than the spike for $O(\alpha)$ at 2.18 Å. This observation indicates the formation of covalent interactions between $O(\alpha)$ and Ni atoms during the kinetic adsorption process. However, when mixed with guaiacol, the $O(\alpha)$ peak shifted from 1.68 Å to 1.99 Å (Fig. 6d), indicating that there was a certain interaction force (steric hindrance, hydrogen bonding, etc.) between guaiacol and acetic acid, which made acetic acid molecules away from the Ni surface. For guaiacol in the mixed components

(Fig. 6c), the relative adsorption in the second layer is significantly higher than that in the pure guaiacol component. This indicates that acetic acid occupies more active sites, leading to a significant reduction in the relative adsorption of the first layer of guaiacol. Furthermore, the peak of the number density of the center of mass, not only in guaiacol (Fig. 6c, blue dashed line) but also in acetic acid (Fig. 6d, blue dashed line), is far from the surface origin, which further confirms the existence of competitive adsorption between acetic acid and guaiacol.

To characterize dynamic electrostatic polarization of the Ni surface due to the HAc or the guaiacol adsorption, the Ni surface's image charges are monitored by using an electrostatic contour, and the charge density $\rho(z)$ is calculated by histogramming the charges of the atoms as a function of position in z and averaging over time as shown in Fig. 6(g-l). As depicted in the charge distribution on the Ni(111) slab surface (Fig. 6), the surface charge of the Ni in all three systems is essentially around 0 at 0 ps. However, after 250 ps, a significant number of molecules are adsorbed on the surface. In the guaiacol system, the surface charge ranges from 0 to 0.06e, while in the acetic acid system and the mixed system, the Ni slab surface charge exhibits a more positive range (range from 0 to 0.15e).⁵² This may be attributed to the adsorption of Ni slab by HAc molecules, which introduces more polarizable atoms, such as oxygen, and more unsaturated bonds (C=O) located adjacent to the Ni surface. Despite acetic acid exhibiting weaker adsorption energy thermodynamically, these neighboring unsaturated bonds and polarizable atoms introduce a more pronounced electrostatic potential on the Ni surfaces during the dynamic adsorption process, compared to the Ni slab adsorbed by guaiacol molecules. This results in a significant competitive adsorption behavior of acetic acid for guaiacol. Another important observation is that the charge distribution above the first layer of the Ni slab is inhomogeneous, *i.e.*, there are local sites on the surface with charges close to 0 in Fig. 6i, which was due to the steric and competitive adsorption effects in the adsorption process between multiple molecules. Similar to the above DFT simulations, the ReaxFF simulations show that the surface of the Ni slab has a positive charge distribution (a positive charge density peak is observed at z = 0.22 in Fig. 6(h, j and l)), whereas the second Ni layer displays negative charges (a negative charge density peak is observed at z = 0.25 in Fig. 6(h, j and l)). As the simulation time progresses, the charge density distribution curve of the system tends to align with the adsorption of guaiacol after 125 ps. Additionally, two charge density peaks appear at z = 0.283 and z = 0.29 in the first adsorption layer (Fig. 6h), corresponding to the adsorption positions of the aromatic ring (Cp) and $O(\alpha)$, respectively (Fig. 6a). In contrast, the charge density curve of the system with acetic acid molecules stabilizes after 250 ps, with a sharp negative charge density peak at z = 0.275 (Fig. 6j) and a sharp positive charge density peak at z = 0.282 (Fig. 6j). This indicates the strong polarity of acetic acid molecules. The charge density

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distribution in the mixed system is consistent with that of the pure acetic acid system (Fig. 6l), suggesting that the polarization of the surface during the adsorption process is predominantly driven by the acetic acid component.

3.4. Chemical bond analysis and initial reaction pathway of guaiacol and HAc

Firstly, the Mayer bond orders acetic acid and guaiacol are calculated at the B3LYP/6-31G** calculation level as shown in Tables 4 and 5, respectively. After adsorption, the bond order of acetic acid decreases from 1.959 to 1.732, indicating the activation of the unsaturated C=O bond on the Ni surface. Meanwhile, the bond orders of C-O (5), C-C (1), and O-H (7) bonds increase, indicating electron transfer during adsorption. In comparison to the activation of the C=O bond, the activation of the aromatic ring is more complex. As shown in Table 5, before adsorpted, the Mayer bond order of Cp-Cp bond orders in guaiacol ranged from 1.296 to 1.468, but all six Cp-Cp Mayer bond orders decreased after adsorpted. This is attributed to the presence of Ni breaking the conjugated π bonds of the benzene ring, and the bond connected to the hydroxyl group (bond number 5) can be considered almost as a single bond (a Mayer bond order reduced to 1.084), which facilitates the subsequent hydrogenation and deoxygenation of the benzene ring.

To validate the reliability of the dynamic adsorption of acetic acid and guaiacol, we statistically tracked the distribution of C=O bond and C-C bond orders on the benzene ring over the simulation time based on ReaxFF parameters, as shown in Fig. 7(a and b). Instantaneous bond orders (BO_{*ij*}), including contributions from sigma, pi, and double-pi bonds are calculated from the interatomic distances, using eqn (4)

$$BO'_{ij} = BO^{\sigma}_{ij} + BO^{\pi}_{ij} + BO^{\pi\pi}_{ij} = \exp\left[p_{b01} \cdot \left(\frac{r_{ij}}{r_o^{\sigma}}\right)^{p_{b02}}\right]$$
(4)
+
$$\exp\left[p_{ba3} \cdot \left(\frac{r_{ij}}{r_o^{\sigma}}\right)^{p_{b01}}\right] + \exp\left[p_{b05} \cdot \left(\frac{r_{ij}}{r_o^{\sigma}}\right)^{p_{b06}}\right]$$

where BO_{ij} is the bond order between atoms *i* and *j*, r_{ij} is interatomic distance, r_0 terms are equilibrium bond lengths, and p_{b0} terms are empirical parameters. From Fig. 7a, the bond orders of the $C(\alpha)=O(\alpha)$ bonds in acetic acid molecules range from 1.5 to 2.0 (approximately 1.66) at the initial moment, indicating that they are not purely single or double

 Table 4
 Comparison of Mayer bond orders of acetic acid before and after adsorption

Bond index	Bond order (before)	Bond order (after)
1	0.963	1.109
2	0.953	0.940
3	0.945	0.962
4	0.945	0.967
5	1.038	1.365
6	1.959	1.732
7	0.862	0.961

 Table 5
 Comparison of Mayer bond orders of guaiacol before and after adsorption

Bond index	Bond order (before)	Bond order (after)
1	1.408	1.209
2	1.399	1.131
3	1.468	1.158
4	1.414	1.134
5	1.443	1.084
6	1.296	1.191
7	0.861	1.266
8	0.861	0.963
9	0.962	1.137

bonds. This is attributed to the strong polarity of acetic acid. After the simulation progresses to 100 ps, a significant number of $C(\alpha) = O(\alpha)$ bonds become activated, with bond orders decreasing to a range between 0.9 and 1.3 which are attributed to the induction of electron delocalization by the Ni atom. This is consistent with the changes observed in the Mayer bond orders. For guaiacol, the activation of the aromatic ring appears to be slower. In the initial stages, the bond orders of the Cp-Cp bonds in the aromatic ring are approximately 1.4, almost consistent with the Mayer bond orders. When the simulation progresses to around 200 ps, a decrease in bond orders begins, but the subsequent activation level is quite low. This is largely attributed to the significant steric hindrance between guaiacol molecules and a shortage of active sites (as shown in Fig. 7b). Compared to Mayer bond orders, the dynamic bond order distribution based on ReaxFF seems to provide a more accurate reflection of the overall trend in the activation of C=O bonds and the aromatic ring because chemical adsorption is a dynamic process. Furthermore, during the adsorption process, the activation of C=O double bonds ultimately leads to the formation of new covalent interactions, such as Ni–O(α) bonds, Ni–C(α) bonds, and others, as shown in Fig. 7c. The period from 0 to 200 ps represents the initial stages of adsorption. During this time, the number of Ni–O(α) bonds linearly increases, while $C(\alpha) = O(\alpha)$ bonds linearly decrease, accompanied by the appearance of $C(\alpha)$ -O(α) bonds. The appearance of Ni-O(B) bonds indicates the O-H bond in acetic acid breaks to form bridge-bonded bidentate acetate, as depicted in Fig. 7e, which is consistent with the characterization results reported by Hofman et al. based on reflection absorption spectroscopy (IRAS).¹³ infrared Additionally, the period from 200 ps to 700 ps represents the equilibrium stage of adsorption, during which the first-layer adsorption structures are mostly stable. After 700 ps, the main dehydrogenation reaction stage ensues, during which Ni–O(β) bonds rapidly increase.¹³ Regarding guaiacol adsorption, Ni-Cp bonds undergo multiple plateaus and eventually reach equilibrium in the first adsorption layer around 400 ps. This may be attributed to the intense competitive adsorption among guaiacol molecules. Moreover, Ni–O(β) bonds rapidly increase at 500 ps (Fig. 7d, red line), possibly due to the vertical adsorption of guaiacol on the Ni



Fig. 7 (a) Bond order (BO_{ij}) distribution of the unsaturated C==O bond in the HAc molecule. (b) Bond order (BO_{ij}) distribution of the C-C bonds in the phenyl ring of guaiacol molecule. (c) Evolution of Ni–O(α), Ni–O(β), Ni–C(α), C(α)==O(α), and C(α)–O(α) bonds during the adsorption process of pure HAc with respect to simulation time. (d) Evolution of Ni–Cp and Ni–O(β) bond over time in the pure guaiacol system. (e) Snapshot of the simulation depicting the dehydrogenation of HAc molecule on the surface. (f) Simulation snapshot of the dehydrogenation process of guaiacol.

surface. This results in dynamic covalent interactions with methoxy groups near the surface, leading to the dissociation of C–O bonds and the formation of Ni–O bonds, as depicted in Fig. 7f. This adsorption configuration tends to activate the $C(\beta)$ –O(α) bond, leading to its breaking and the occurrence of methoxy deoxygenation reactions.^{6,53}

4. Conclusion

In the study of single-molecule adsorption behavior, DFT method for static energy calculations allows us to determine the adsorption orientations and sites for various species. It was found that the more negative the ESP position, the more favorable it is for molecules to approach the surface. Specifically, linear hydrocarbons tend to undergo chair-like adsorption, while aromatic compounds preferentially adsorb parallel to the surface. Moreover, we measure the differences in the adsorption behavior of eight molecules using IGMH and EDD methods. To take the competitive adsorption behavior between multiple molecules into consideration, the RMD simulations were performed to investigate the adsorption of guaiacol molecules on the Ni(111) surface. Shorter-chain carboxylic acids, e.g., acetic acid, adsorb less strongly in thermodynamics, yet still non-negligible competitive

adsorption effect. The inclusion of acetic acid increases the polarization effect and non-uniformity. Additionally, the chair conformation of acetic acid on Ni, more kinetically reasonable, induces a stronger surface charge compared to guaiacol Furthermore, we found that this non-uniform distribution is highly correlated with the characteristic bond activations of adsorbed active molecules, serving as a driving force for promoting further hydrogenation and deoxygenation activities of the aforementioned molecules.

Conflicts of interest

There are no conflicts to declare.

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