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Hydrodeoxygenation of m-cresol over bimetallic NiFe alloys: Kinetics and thermodynamics insight into reaction mechanism

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ABSTRACT

Developing mechanistic insights into the reaction network of hydrodeoxygenation (HDO) of lignin-derived compounds is key to rational design of high-performance catalysts for bio-oils upgrading. Herein, we present a comprehensive theoretical study on HDO of m-cresol, a model compound of phenolics, on Ni(1 1 1) and NiFe(1 1 1) surfaces using periodic density functional theory calculations and microkinetic modeling techniques, with a focus on the several competing reaction pathways including enol-keto tautomerization, hydrogenation, and dehydroxylation. Our results show that the activation of the C—OH bond of m-cresol and phenolic intermediates can be greatly promoted on oxophilic NiFe (1 1 1), evidenced by the elongated C—OH bond length and the enhanced dehydroxylation activity with respect to Ni(1 1 1). It is found that m-cresol HDO on NiFe(1 1 1) shares certain common features with that on Ni(1 1 1), but exhibits important differences that result in dramatic changes in selectivity. We show that the C—OH bond length of adsorbed phenolic intermediates can be used as a good descriptor for prediction on the C—OH bond scission reaction in HDO. Finally, microkinetic modeling augmented by degree of rate control analysis is applied to rationalize the experimentally-observed differences in product distributions over Ni and NiFe catalysts when kinetic factors still dominate.

1. Introduction

To address issues caused by fossil fuel consumption, the conversion of biomass to biofuels has become a promising approach for realizing CO_2-neutral energy and for mitigating adverse environmental impacts. Lignocellulose is the most abundant component in biomass, which typically includes various plants, grass, straw, and residues of agricultural crops. It consists of three main components: cellulose, hemicellulose, and lignin. Lignin has the highest energy density [1–3], and in particular, pyrolysis of lignin can produce up to approximately 30 wt% of phenolic compounds, such as phenols, cresol, guaiacols, and syringols [3]. Unfortunately, the liquid product (bio-oil) generated via thermal breakdown of lignocellulose contains highly oxygenated species and therefore cannot be used as a transportation fuel without reducing its oxygen content by catalytic upgrading.

Significant experimental efforts have been directed to the development of effective catalysts for hydrodeoxygenation (HDO) of lignin-derived phenolic compounds [1–20] that can remove oxygen-containing functional groups under ambient or high pressure of H_2 [4]. Supported noble metals, such as Pt [3,21–30], Pd [3,24,27,31,32], Ru [3,5,22,24,29], and bimetallic PtPd [31,33], Pt-Ni, Pt-Zn and Pt-Cu [30] have been reported to be more active and effective than traditional catalysts (e.g., CoMo [16,34]) towards HDO. The supports, particularly those providing acidic sites, may also be actively involved in promoting HDO. The distributions of the main products can vary, depending upon the metals and supports employed. For example, Zhu et al. have investigated the catalytic conversion of anisole (methoxybenzene) to gasoline-range molecules over a bifunctional Pt/HBeta catalyst at 400 °C and atmospheric pressure [25]. They found that the acidic function (HBeta) catalyzes the methyl transfer reaction (transalkylation) from methoxyl to the phenolic ring, yielding phenol, cresols, and xylenols as the major products. The metal catalyzes the demethylation, hydrodeoxygenation, and hydrogenation in sequence, resulting in phenol, benzene, and cyclohexane. Foster et al. [28] have reported that Pt catalysts supported on γ-Al_2O_3 and SiO_2 are effective for the conversion of m-cresol (3-methylphenol) to toluene and methylcyclohexane at 533 K and 0.5 atm of H_2. Previous combined experimental/theoretical studies on the conversion of m-cresol over Pt/SiO_2 and Ru/SiO_2 catalysts have shown that

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3-methyl-cyclohexanone is the dominant product without ring-opening by-products over Pt/SiO_2 at low conversions, while toluene is the dominant product along with ring-opening by-products over a Ru(0 0 0 1) surface [22].

Despite the high effectiveness of noble metals as HDO catalysts, their high cost has limited their applications. As a consequence, more efforts have been focused on searching for alternative catalysts of base-metals, such as Fe [24,29,35,36], Co [37], Ni [4,27,37–42], Cu [24] and Ga [43,44]. However, these monometallic catalysts possess lower activity and selectivity towards HDO. Alternatively, bimetallic alloy catalysts have attracted much attention for their improved HDO activity due to the new catalytic functionality (e.g., C—OH bond breaking) introduced by the secondary metals [45–47], which normally possess oxophilicity (e.g., Fe in NiFe [36] and PdFe [24]), which is beneficial for HDO. For example, Zhao et al. [48] have investigated HDO of phenols over RANEY Ni and $Nafion/SiO_2$ catalysts. They found that RANEY Ni acts as the hydrogenation catalyst, resulting in cyclohexane/alkylcylcohexane being the dominant products formed from full hydrogenation of the aromatic ring, while $Nafion/SiO_2$ acts as the Brønsted solid acid for hydrolysis and dehydration. Sun et al. compared HDO of guaiacol over several carbon-supported metal catalysts (Cu/C, Fe/C, Pd/C, Pt/C, PdFe/C, and Ru/C) [24]. They found that over the precious metal catalysts, saturation of the aromatic ring to form cyclohexanone and cyclohexanol is the major reaction pathway, followed by ring opening to form gaseous by-products. In comparison, the base metal catalysts exhibit lower activity than the precious metals, but they can selectively form benzene along with small amounts of toluene, trimethylbenzene, and cresol without forming ring-saturated or ring-opening products. With respect to Fe/C and Pd/C, bimetallic PdFe/C exhibits a substantially enhanced activity while maintaining the high selectivity to HDO products without ring saturation or ring opening. Nie et al. [36] investigated the selective conversion of m-cresol on SiO_2-supported Ni, Fe, and bimetallic NiFe catalysts at 300 °C and atmospheric pressure, and they found that the dominant product is toluene over Fe and Ni–Fe bimetallic catalysts, whereas 3-methyl-cyclohexanone is generated over Ni. In particular, NiFe with a 1:1 M ratio is the best catalyst for HDO of m-cresol, confirming the beneficial effects of the secondary metal Fe. Other bimetallic $Ni_{85}M_{15}$ (M = Ru, Rh, and Pd) catalysts have also been investigated for their HDO efficiency, and among these $Ni_{85}Ru_{15}$ stands out for its high activity in the hydrogenolysis of lignin model compounds under low temperature (100 °C) and low H_2 pressure (1 bar) as a result of the oxophilic ability of Ru [49].

Density functional theory (DFT) calculations can provide an instructive and clear understanding of the mechanistic details involved in the reaction network and can play an important role in interpreting the experimental results and in providing fundamental understanding of the HDO of lignin-derived phenolic compounds [5,18,22,24,26,29,36,50–58]. For example, Vlachos et al. [51] have performed first-principles microkinetic calculations of p-cresol HDO on a Pt(1 1 1) surface. They showed that single metal functionality is sufficient to selectively carry out the HDO chemistry via partial ring activation, and moreover, the complete hydrogenation of the phenyl ring is neither necessary nor kinetically preferred. Instead, the conversion of p-cresol to toluene follows a complex energy landscape, where methylcyclohexanol and methylcyclohexane are not intermediates to toluene, but rather, share a common pool of intermediates with the hydrocarbons. Griffin et al. have investigated the deoxygenation of m-cresol over Pt/C and Pt/TiO_2 catalysts using an experimental/computational approach [26]. They found that over Pt/C, the hydrogenation of the C-ring to 3-methylcyclohexanone and 3-methylcyclohexanol was the most energetically favorable pathway, while over Pt/TiO_2(1 0 1), enol-keto tautomerization and direct deoxygenation to toluene were additionally identified as energetically favorable routes. Hensley et al. have comparatively studied the deoxygenation of phenol on the Fe(1 1 0) and Pd(1 1 1) surfaces and found that the most energetically and kinetically favorable reaction mechanism occurs via the direct cleavage of the C—OH bond over the Fe(1 1 0) surface [56]. Recently, Robinson et al. who also employed an experimental/computational approach have reported that PtMo can catalyze m-cresol deoxygenation via a pathway involving an initial tautomerization step [55]. Although a lot has been learned, based mostly on model catalyst of precious metals, studies of HDO on base metals are critically needed, considering their relevance to realistic applications in bio-oils upgrading. Furthermore, there still exist some uncertainties regarding the following questions:

a. What is the first step for hydrogenation and hydrodeoxygenation of phenolic compounds? For example, Ge et al. proposed (based on DFT calculations and microkinetic analysis) that direct hydrogenation of the aromatic ring is the first step of phenol hydrogenation on Pt, in contrast to the dissociation of phenol to phenoxy on Pd [58]. In comparison, Nie et al. have proposed that enol-keto tautomerization of m-cresol to 3-methyl-3,5-cyclohexadienone (KetCO) is the first step for HDO [36]. They later reported that the direct dehydroxylation of m-cresol as the first step is more favorable on the more oxophilic Ru(0 0 0 1) surface than tautomerization on the less oxophilic Pt(1 1 1) surface [22].
b. What are the key elementary steps for hydrodeoxygenation of phenolic compounds (sequential hydrogenation to saturate the aromatic ring or enol-keto tautomerization to form the keto-tautomer intermediate)? For example, Lercher and co-workers concluded that phenol can be hydrogenated all the way to cyclohexanol over the Pt and Ni catalysts without the tautomerization step in a vapor phase reaction. However, for phenol hydrogenation in a water solvent, there is an energetic preference for forming ketones as a result of tautomerization of surface-bound enol intermediates [53]. Recently, de Souza et al. have tested the HDO reaction of phenol over Pd catalysts supported on SiO_2, Al_2O_3, and ZrO_2, and their DRIFTS experiments revealed that a key elementary step is the enol-keto tautomerization of phenol, forming a 2,4-cyclohexadienone intermediate [32]. This can be further hydrogenated along two different pathways: On Pd/SiO_2 or Pd/Al_2O_3, the phenyl ring is hydrogenated to form cyclohexanone and cyclohexanol as the main products, whereas on Pd/ZrO_2, the carbonyl C═O is hydrogenated followed by rapid dehydration of the unstable cyclohexadienol intermediate to primarily form benzene. Their results demonstrate that the selectivity for HDO of phenol can be controlled by using supports of varying oxophilicity, i.e., the stronger oxophilicity of ZrO_2 than SiO_2 or Al_2O_3.
c. Can we identify an effective 'descriptor' from DFT calculations for a specific elementary reaction involving multi-functional groups of complex molecules (e.g., selective cleavage of the C—OH bond)? Will the Brønsted-Evans-Polanyi (BEP) relation [59–62] still be applicable to a complex reaction such as phenolic-HDO? For example, Hensley et al. [56] has reported the BEP relationships for the elementary C—O cleavage steps and the C—H formation steps, which are represented by the binding energies of the initial, final, and transition states, respectively. Vlachos and co-workers demonstrated the BEP relations and transition-state scaling (TSS) relations for various homologous series of p-cresol on Pt(1 1 1), such as C—H, O—H and C—OH bond scission reactions [51], which demonstrated that the structural similarity in reactants and transition states is a prerequisite for improved BEP relations of C—O and C—C scission [63].