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1 **Mechanism of hydrodeoxygenation (HDO) in anisole**
2 **decomposition over metal loaded Brønsted acid sites:**
3 **Density Functional Theory (DFT) study**

4 Jiajun Zhang^{a, b, c}, Beatriz Fidalgo^c, Dekui Shen^{a,*}, Xiaolei Zhang^{b,*}, Sai Gu^d

5 * Corresponding author: D.S., e-mail address: 101011398@seu.edu.cn

6 X.Z., email address: xiaolei.zhang@qub.ac.uk

7 ^a Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education,
8 Southeast University, Nanjing, China

9 ^b School of Mechanical and Aerospace Engineering, Queen's University Belfast,
10 Belfast, United Kingdom

11 ^c School of Water, Energy and Environment, Cranfield University, Cranfield, United
12 Kingdom

13 ^d Faculty of Engineering and Physical Sciences, University of Surrey, Surrey, United
14 Kingdom

15 **Abstract:**

16 In this work, the mechanism and intrinsic reaction energy barriers of hydro-
17 deoxygenation (HDO) of anisole, as key stage of the catalytic decomposition over
18 metal-loaded acid support catalysts (bi-functional catalysts), were investigated by
19 Density Functional Theory (DFT). Common transition metals were compared in terms
20 of their adsorption energy when adsorbing anisole molecule for the selection of loading
21 metals. The roles of metal and acid sites in the HDO of phenolic compounds (Phs) over

bi-functional catalyst were investigated¹, and a novel HDO mechanism was proposed by combining Fukui index and bond orders of phenol molecule analyses. HDO reactions of Phs over sole acid sites and the bi-functional catalysts were modelled. The modelling results revealed that, for anisole adsorption, Co, Mo, Ni and Cu showed higher adsorption energy than other transition metals. Molecule analysis results showed that HDO over bi-functional catalysts was dominated by the protonation of the hydroxyl group on Phs. Reaction modelling exhibited that active metals had significant effects in lowering energy barriers of the reactions for all the Phs; the metal active sites facilitated the protonation by developing strong interaction with the adsorbed reactant, and they also aid the hydrogen molecule dissociation. Ni and Mo showed the best catalytic effect on the HDO for most Phs. The effect of side chain methyl substitutes on the HDO reactions for various Phs intermediates during anisole decomposition was also investigated by reaction modelling. [Modelling results in this study were found in good agreement with experimental data.](#)

Key words: anisole; catalytic decomposition; hydrodeoxygenation; DFT modelling; bi-functional catalysts

1. Introduction

Increasing concern about climate change and unsustainable fossil fuel resources are attracting more and more attention to renewable clean energy [1]. Biomass is regarded as an ideal carbon resource for the production biofuels without hazardous effects to the environment [2]. Lignin is one of the three main components in lignocellulosic biomass (constituting 15-35 wt.% of dry biomass) and the most abundant aromatic-rich bioresource [3]. Fast pyrolysis is accepted as a feasible and viable route to convert lignin into value added aromatic hydrocarbons (AHs) in fuel application [4–6]. However,

¹ Abbreviations: Phs, phenolic compounds; AHs, aromatic hydrocarbons; Brøn, Brønsted acid sites

the primary lignin derived bio-oil cannot be directly used in fuel applications because of its inadequate properties, including acidity, low calorific value, and low stability, which are a consequence of its high oxygen content in composition. Methoxyl group is an oxygen containing functional group which abundantly exists in the components present in the primary bio-oil obtained from the fast pyrolysis of lignin, such as anisole, guaiacol, syringol and their derivatives [7]. Deoxygenation reaction was identified as the key stage of the thermal decomposition of methoxyl group, leading to the prominent production of mono AHs, such as benzene, toluene and xylene (BTX). Understanding the deoxygenation during the decomposition of methoxyl group is therefore important to properly tailor the catalytic reforming process towards the desired lignin-derived AHs.

Anisole (or methoxybenzene) is a prototype model compound to investigate the reactivity of methoxyl-based lignin-derived compounds [8]. The decomposition of anisole proceeds by a first stage of transmethylation and a second stage of deoxygenation reactions. Phenolic compounds (Phs) are the main products from transmethylation and are the precursors for AHs resulted from the deoxygenation reactions [9]. Our previous work [10,11] demonstrated that ortho- and para-cresols are the predominant phenolics produced by the transmethylation of anisole. Most investigations consider the addition of hydrogen to the reaction media to favour the occurrence of hydrogenation or hydrogenolysis along with deoxygenation, termed as hydrodeoxygenation (HDO) [12–17]. Metal-based solid catalysts are widely used in the HDO reactions to produce AHs. Transition metals have been observed to be highly active for the reaction; and various supports have been studied, including inert solids (i.e. SiO_2 , Al_2O_3 , Silicalite) and acid zeolites (i.e. HBeta, HZSM-5) [15,18–21].

The nature of the catalyst is considered to determine the reaction pathway [22–29]. Two main parallel pathways have been reported for the HDO of Phs in the decomposition of anisole, leading to different products: (1) direct HDO giving rise to the

formation of AHs and water; and (2) hydrogenation of the phenolic ring followed by deoxygenation to form cyclohexane and its derivatives, as well as water [23]. HDO over metal-supported inert solid catalysts has been proved to more likely undergo ring saturation and produce cyclohexanols before deoxygenation [15–17,20,23,30,31]. The addition of acid supports has been argued to effectively inhibit ring saturation during the HDO [15,31]. This hypothesis has been confirmed by the experimental investigation with ^{13}C labelled anisole decomposition over sole acid catalyst [32]. It was observed that the benzene ring remained intact throughout HDO reactions.

Even though metal loaded acid catalysts show good performance in AHs production, the mechanism for HDO over the bi-functional (metal sites and acid sites) catalysts is still not clear. Specifically, detailed interactions between reactants and catalyst surface, and the role of both metal and acid catalytic sites on the HDO mechanism have not been reported in the literature. The aim of this work is to establish by means of DFT modelling the mechanism of HDO (the second stage) in the catalytic decomposition of anisole over bi-functional catalysts, and to identify the effect of different metal loadings and acid sites on the reaction. HDO of phenol, xlenols, and tri-methyl Phs is investigated.

2. Computational method

The first-principle density functional theory plus dispersion (DFT-D) calculations were implemented in the DMol³ module available in Materials Studio 2016 from BIOVIA [33,34]. The double numerical plus polarization (DNP) basis set was used to calculate the valence orbital of all the atoms, including a polarization p-function on all hydrogen atoms. The numerical basis sets in Dmol³ minimize or even eliminate basis set superposition error (BSSE), in contrast to Gaussian basis sets, in which BSSE can be a serious problem [35,36]. Calculations used the generalized gradient corrected approximation (GGA) [37] treated by the Perdew–Burke–Ernzerhof (PBE) exchange-

correlation potential with long-range dispersion correction via Grimme's scheme [38]. The self-consistent field (SCF) procedure was used with a convergence threshold of 10^{-6} au on the energy and electron density. Geometry optimizations were performed with a convergence threshold of 0.002 Ha/Å on the gradient, 0.005 Å on displacements, and 10^{-5} Ha on the energy. The real-space global cut-off radius was set to 5 Å. In this study, no symmetry constraints were used for any cluster models. The transition state was completely determined by the LST/QST method, and confirmed by the unique imaginary frequency as shown in S1 of the Supplementary Material and the intrinsic reaction coordinate (IRC) calculation. Free energy of each transition state at 600°C² was determined as shown in S2 of the Supplementary Material. Mulliken charges were assigned to each bond to address the bond order, and Hirshfeld charges were assigned to each atom for the function selected as the Fukui field [39]. All the adsorbent models were based on single metal loaded Brønsted acid sites (see Figure S3). The adsorption energy E_{ad} was determined by Eq.1, where $E_{catalyst}$, $E_{adsorbate}$ and $E_{adsorbate/catalyst}$ are the total energies of clean metal loaded catalyst, free adsorbate molecule and catalysts with molecule respectively. The initial configuration of the 8T model to simulate the Brøn was adopted from the MFI structure [40,41]. One metal atom was loaded on the Brøn to simulate ideally dispersed metal site in bi-functional catalyst. All the models of bi-functional catalysts, adsorbate, and reactants were optimized to find their most stable structures before adsorption and reaction modelling. The energy barriers of reactions $E_{barrier}$ were determined by the difference between the transition state and reactant energies, as shown in Eq.2, where $E_{transition\ state}$ and $E_{reactant}$ are the total energies of the transition state and reactant of a reaction. All the energies were calculated at 0K in this DFT investigation.

$$E_{ad} = E_{catalyst} + E_{adsorbate} - E_{adsorbate/catalyst} \quad Eq.1$$

² Hydrodeoxygenation of anisole derived phenolic compounds was found in experimental investigation to be dominating reaction around 600°C over pure HZSM-5 catalyst [10].

123

$$E_{\text{barrier}} = E_{\text{transition state}} - E_{\text{reactant}}$$

Eq.2

124 3. Results and discussion

125 3.1. Anisole adsorption on the surfaces of transition metals

126 Adsorption happens as the first step of catalytic reactions and consists of the link
127 between the reactants and the catalyst active sites [42–44]. It has been reported that
128 adsorption plays an important role in determining the selectivity to desired products, i.e.
129 BTX, during the HDO in anisole decomposition [17]. The adsorption energy of the
130 reactant onto metal loadings was evaluated to predict the performance of metals as
131 active sites, and aid the selection of the preferred metal catalysts. Thus, cluster models
132 with eleven transition metals, i.e. Mn, Fe, Co, Ni, Cu, Zn, Mo, Ru, Rh, Pd, and Pt, were
133 built and compared in terms of their performance in the adsorption of molecular anisole,
134 used as model of molecules existing in real HDO reactions. Fig. 1 shows the calculated
135 values of the adsorption energy of anisole onto the metal/Brøn.

136 In the perspective of thermodynamic, high adsorption energy implies strong binding
137 between the anisole molecule and the metal surfaces. It can be seen that Co, Mo, Ni
138 and Cu exhibited the highest adsorption energy values. On the contrary, Mn, Fe and Zn
139 showed the lowest adsorption energy, corresponding to weak binding between the
140 catalytic site and the adsorbates. Based on these results, Ni, Mo, Cu and Co were
141 further considered as metal sites used of the bi-functional catalysts for the modelling
142 investigation of the HDO reaction.

Fig. 1 Adsorption energy of anisole onto metal/Brøn

3.2. Mechanism of HDO of Phs in catalytic anisole decomposition

The Phs produced from transmethylation stage in the anisole catalytic decomposition are the main reactants for the catalytic deoxygenation stage [10]. Although there is no agreement on the mechanism for HDO [8,18,31,32,45,46], it is accepted that the occurrence of a straightforward hydrogenolysis reaction in the HDO of Phs is unlikely because the $C_{sp^2}-O$ bond strength is reinforced by the $\pi-p$ conjugation compared to aliphatic hydroxyl [15]. Besides, many studies confirmed that the Brøn play an important role in enhancing the HDO reaction [15,32], implying that the HDO reactions of Phs are likely to commence through the electrophilic attack by protons (protonation). Therefore, using a phenol molecule as representative of Phs compounds, a Fukui analysis was performed to evaluate the reactivity of each atom to an electrophilic attack. As shown in Fig. 2, the oxygen, para-carbon (C2), ortho-carbon (C4, C6), and the carbon linked to oxygen (C5) were identified as the most vulnerable sites to

electrophilic attack on the phenol molecule. These results are in line with the electrophilic substitution priority observed in experiments [10]. Two possible electrophilic attack mechanisms for the HDO reaction of Phs were proposed based on the protonation of carbon or oxygen atoms respectively. The “carbon protonation mechanism” considers that the reaction is initiated through an electrophilic attack by a proton to one of the ring carbons (Fig. 3), while the “hydroxyl protonation mechanism” considers the electrophilic attack to the hydroxyl group (Fig. 4).

Atom	Fukui (-) index
	O7	0.152
	C2	0.136
	C4	0.089
	C5	0.089
	C6	0.083
	C1	0.073
	C3	0.068
	H9	0.061
	H13	0.055
	H11	0.050
	H8	0.049
	H10	0.048
	H12	0.048

Fig. 2 Fukui indices for electrophilic attack on phenol molecule (Fukui (-)). Atoms are coloured as follows: carbon atom (grey), hydrogen atom (white) and oxygen atom (red)

168

Fig. 3 Carbon protonation mechanism for HDO of phenol

169

170

Fig. 4 Hydroxyl protonation mechanism for HDO of phenol

171 Since the oxygen atom exhibits the highest Fukui index (i.e. 0.152), it was inferred that
 172 the HDO reaction is more likely to be initiated by the electrophilic attack to the oxygen
 173 by a proton. To confirm this hypothesis, the possible cations formed under carbon and
 174 hydroxyl protonation of the carbon and oxygen atoms that exhibit high Fukui index
 175 were compared, and the bond orders of $C_{sp^2}-O$ were assessed accordingly (Fig. 5). Fig.
 176 5 shows that the proton attack to different positions gave rise to significant change of
 177 the $C_{sp^2}-O$ bond order. The bond orders of $C_{sp^2}-O$ were 0.781 and 0.668 when the
 178 proton attacked C6 (Fig. 5(a)) and C5 (Fig. 5(b)), respectively. The electrophilic attack
 179 to the C2 atom resulted in the $C_{sp^2}-O$ bond order of 0.783 (Fig. 5(d)), and it was 0.397
 180 when both oxygen and C4 are under electrophilic attack (Fig. 5(e)). The lowest $C_{sp^2}-O$
 181 bond order of 0.332 was attributed to the oxygen atom under electrophilic attack (Fig.
 182 5(c)). This result reveals that the $C_{sp^2}-O$ bond strength is significantly weakened when
 183 the proton attacks the phenol molecule at oxygen atom, and confirms the hypothesis of
 184 the HDO reaction being most likely to commence following the hydroxyl protonation in
 185 the presence of the Brøn.

(a)

(b)

(c)

(d)

(e)

Fig. 5. C_{sp^2} -O bond orders of possible cations under protonation of: (a) ortho-carbon (C6); (b) carbon linked to oxygen (C5); (c) oxygen; (d) para-carbon (C2); and (e) both oxygen and ortho-carbon (C4). Atoms are coloured as follows: carbon atom (grey), hydrogen atom (light grey), oxygen atom (red), and proton (yellow).

Based on this analysis, it is considered that the most likely mechanism of the HDO reaction of Phs in the anisole catalytic decomposition is the “hydroxyl protonation mechanism”. As depicted in Fig. 4, this reaction pathway consists of the electrophilic attack reaction, followed by a reduction reaction and a substitution reaction. The proton from Brøn attacks the oxygen atom and enables the formation of an aromatic cation. The cation is then reduced by one of the hydrogen atoms from hydrogen molecule and substituted by another hydrogen atom to produce a molecule of water and an AH compound (represented by a benzene molecule in Fig. 4). Meanwhile, the oxidised hydrogen atom becomes a new proton, and the acid site is recovered. Overall, there are two hydrogen atoms engaging in the reaction.

3.3. Modelling of the HDO reaction of Phs in catalytic anisole decomposition over bi-functional catalyst

The HDO reactions of phenol, cresols, xylenols and trimethyl phenols over metal-supported Brøn were modelled as second stage of the catalytic decomposition of anisole. Ni, Co, Mo and Cu were evaluated as active metal sites loaded on the Brøn, and phenol, o-cresol, p-cresol, 2,4-xyleneol, 2,6-xyleneol, 3,5-xyleneol, 2,4,6-trimethylphenol, 2,3,6-trimethylphenol and 3,4,5-trimethylphenol were modelled as reactants. These phenolic compounds are intermediates of the process obtained from the transmethylation of anisole [10,47–49]. Catalytic HDO reactions over sole Brøn (no metal loaded) were also modelled for comparison. Both Brøn and metal/Brøn catalytic HDO models were built by locating equidistantly the reactant molecule (within 3Å) over the acid site before the geometry optimization to minimize any possible position-related

errors. In both cases, the catalytic HDO reaction was modelled based on the hydroxyl protonation mechanism shown in Fig. 4. The HDO reaction of phenol over Brøn and over Ni/Brøn are shown in Fig. 6 (a) and (b), respectively, as examples of the catalytic HDO reactions of Phs. The transition state was the one with the highest energy throughout both reactions (over sole Brøn and Ni/Brøn). It worth noting that in the reaction over Ni/Brøn; a ligand centred on the metal that connected the reactant molecule and the support was formed, and the hydrogen molecule was also bound to the metal atom and dissociated into two atoms. [Examples for the reactions of Phs over other metal/Brøn catalysts are shown in S4 of the Supplementary Material.](#)

(a)

(b)

Fig. 6. Modelling of the HDO reactions of phenol molecule over (a) sole Brøn catalyst; and, (b) Ni/Brøn catalyst. Atoms are coloured as follows: carbon atom (grey), hydrogen atom (light grey), oxygen atom (red), silica atom (yellow), aluminium atom (pink) and nickel atom (blue).

The intrinsic energy barriers for the HDO reactions of the Phs over respective Brøn and metal/Brøn catalysts were calculated and are summarized in Table1. In the case of non-metal Brøn catalytic reactions, the energy barriers of HDO changed by as much as 25.4 kcal/mol depending on the reactant molecules. This is related to the fact that the number and position of methyl groups in the reactant molecule affect the inner electron distribution of the aromatic rings [50]. Thus, the HDO of phenol presented an energy barrier of 93.4 kcal/mol, while the HDO of o-cresol and p-cresol exhibited lower energy barriers of 74.2 kcal/mol and 89.0 kcal/mol respectively. This result implies the positive effect of the presence of a single methyl group in the Phs molecule on the Csp²-O bond activation, especially when the methyl group was at 2-ortho position (o-cresol). The evaluation of HDO of multi-methyl Phs gave rise to a broad range of energy barrier values. An energy barrier of 77.1 kcal/mol was obtained in the case of the reaction of 2,4-xlenol, which confirms the positive effect of the presence of methyl groups on ortho and para positions on the HDO reaction. In the case of HDO of 2,6-xlenol, 2,3,6-trimethyl phenol and 2,4,6-trimethyl phenol, energy values higher than that observed for the HDO of phenol were observed. This result implies that the presence of methyl groups on both ortho positions decreases the molecule reactivity in the HDO reactions because of the steric hindrance effect caused by multi-methyl group close to the hydroxyl [51].

Table1. Energy barriers of the HDO reactions for various phenolic compounds over Brøn and metal/Brøn catalysts as the second stage of the catalytic decomposition of anisole. Metal active sites: Ni, Co, Mo, and Cu.

Phs (reactants)	Energy barrier (kcal/mol)								
	Brøn	Ni/Brøn	Decline by (%)	Co/Brøn	Decline by (%)	Mo/Brøn	Decline by (%)	Cu/Brøn	Decline by (%)
phenol	93.4	18.9	79.8	32.7	65.0	14.3	84.6	13.5	85.6
o-cresol	74.2	38.0	48.7	18.1	75.5	30.0	59.6	23.9	67.9
p-cresol	89.0	27.9	68.7	31.2	64.9	37.1	58.3	54.7	38.6
2,4-xyleneol	77.1	13.3	82.8	15.7	79.6	12.5	83.8	56.0	27.4
2,6-xyleneol	99.6	15.1	84.8	55.3	44.5	16.0	83.9	79.9	19.8
3,5-xyleneol	81.8	58.7	28.2	26.1	68.1	14.0	82.9	26.1	68.1
2,4,6-tri-ph	95.7	43.8	54.2	39.3	59.0	26.5	72.3	30.5	68.1
2,3,6-tri-ph	97.0	13.5	86.1	34.4	64.5	33.9	65.1	63.8	34.3
3,4,5-tri-ph	86.5	20.0	76.9	10.5	87.8	26.9	68.9	70.3	18.7

The results obtained from the HDO reactions over metal/Brøn catalyst showed notable decreases in the energy barrier values for the reactions of all the phenolic compounds and confirmed that the presence of these four metals that lead to larger binding energy may significantly facilitate the HDO reaction [17,52]. In the case with Ni/Brøn catalyst, all the energy barriers were below 60 kcal/mol, and the energy barriers for HDO of phenol, 2,4-xyleneol, 2,6-xyleneol, 2,3,6-trimethylphenol and 3,4,5-trimethylphenol decreased more significantly to be lower than 20kcal/mol. This result points that the presence of the metal site compensated the steric hindrance effect observed in HDO of phenolics with methyls on both ortho positions over sole Brøn catalyst. In the case with Co/Brøn catalyst, the highest energy barrier was 55.3 kcal/mol for the HDO of 2,6-xyleneol, and the energy barriers for o-cresol, 2,4-xyleneol and 3,4,5-trimethylphenol were lower than 20 kcal/mol. Regarding Mo/Brøn catalyst, all energy barrier values were found to be lower than 40 kcal/mol, and those for phenol, 2,4-xyleneol, 2,6-xyleneol and 3,5-xyleneol were lower than 20 kcal/mol. Cu/Brøn catalyst also showed a positive effect in decreasing the energy barrier values. For example, in the case of the HDO of phenol, the energy barrier was 13.5 kcal/mol. Nevertheless, it is worth noting that the

effect of Cu on the decrease of the HDO energy barriers was much more moderate than that from Ni, Co, and Mo. This may be related with the lower adsorption energy (i.e. less strong binding between reactant and metal surface) that Cu presents.

Reductions in the energy barrier values due to the presence of the metals larger than 70% are highlighted in red in Table1. It is observed that Ni/Brøn and Mo/Brøn achieved the highest number and average reduction in the HDO reaction energy barrier values among the four tested metals, indicating the most effective metals for the HDO reaction of Phs are Ni and Mo. This can be due to the intermediate adsorption energy shown by Ni and Mo among the four metals; they adsorb the reactants strongly enough to hold and activate them compared to Cu, but moderately compared to Co, which allows the desorption of the products [53]. It is also observed that Mo/Brøn catalyst is more effective on lowering the energy barrier for the most abundant intermediate Phs compounds in the anisole decomposition system, such as phenol and xylenols. Ni/Brøn exhibits excellent effect on the HDO reactions for phenol, xylenols and trimethylphenols. Large drops in the energy barrier values confirm that the presence of metal active sites may promote the catalytic effect of the Brøn present in the solid support by enhancing the reactivity of Phs for protonation (change the inner electron density of the adsorbed molecules) and by dissociating dihydrogen molecules [54–56]. Furthermore, as explained above, both Ni and Mo are found to compensate the steric hindrance and promote the HDO of Phs with methyl groups on both ortho positions.

3.4. Comparison of modelling results with experimental data

Experiments of anisole decomposition were carried out in previous work of our group, and the BTX yield and selectivity over pure HZSM-5 zeolite (Si/Al=25, HZ(25)) and single metal (Co, Mo, Ni and Cu) loaded HZSM-5 catalysts are shown in Table 2 [9]. As a typical Brønsted acid catalyst, the experimental data with HZSM-5 zeolite are compared with the modelling results based on Brønsted acid sites in this study.

Table 2. BTX yield and selectivity of anisole deoxygenation over the metal loaded HZSM-5 zeolites at 500°C [9]

Catalyst	HZ(25)	1%Ni/HZ(25)	1%Co/HZ(25)	1%Mo/HZ(25)	1%Cu/HZ(25)
BTX yield (wt.% reactant)	23.6	25.6	25.9	30.0	28.3
BTX selectivity (wt.% liquid fraction)	57.1	81.9	68.8	77.4	69.3

Experimental investigation revealed all the four metals are effective in promoting the deoxygenation reaction, leading to both higher yield and selectivity of BTX in anisole decomposition. This could be sufficiently explained in microscale by the contribution of metal loading on Brøn in promoting HDO reactions by dramatically decreasing the energy barriers.

Based on the experiments data, Ni and Mo exhibited the best effects in deoxygenation of anisole decomposition among the four metals; Ni loading led to the highest BTX selectivity by converting more Phs to monocyclic AHs, while Mo loading presented the best catalytic activity towards the highest overall AHs yield. The outstanding deoxygenation performance of Ni/HZ(25) and Mo/HZ(25) in anisole decomposition are in good line with the superior property of Ni/Brøn and Mo/Brøn in lowering energy barriers observed in this study.

4. Conclusion

In this work a mechanism for the HDO of phenolic compounds over bi-functional (metal and acid sites) catalysts was established by means of DFT modeling results. Ni, Co, Mo and Cu were selected as active metals after the modelling of anisole adsorption on transition metal surfaces revealed that the four metals exhibited the highest adsorption energy values. Results confirmed that catalytic HDO of Phs, which are intermediate compounds in the catalytic decomposition of anisole, was initiated from hydroxyl protonation and that the presence of metals on the catalysts promoted both the

reaction and the dissociation of the hydrogen molecule. Thus, the presence of active metals, particularly Ni and Mo, led to significant decrease in the energy barriers for the HDO reactions of various Phs. Modelling of the HDO reaction over non-metal acid catalyst showed that a single methyl group on the ortho-position of the phenolic compound enhanced the Csp²-O bond and promoted the reactivity. The presence of methyl groups on the two ortho-positions pointed to an inhibition of the reaction due to steric hindrance effect when using non-metal acid catalyst. However, the addition of a metal site was found to compensate this effect and promote the HDO of these phenolic compounds. [The excellent activity of metal/Brøn sites were found in line with the HDO performance of corresponding catalysts in experiments.](#)

Author information

Corresponding Authors

D.S.: 101011398@seu.edu.cn

X.Z.: xiaolei.zhang@qub.ac.uk

Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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