

## Article

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# Different Product Distributions and Mechanistic Aspects of the Hydrodeoxygenation of m-Cresol over Platinum and Ruthenium Catalysts

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#### Abstract

Experimental measurements of the conversion of m-cresol over Pt and  $Ru/SiO_2$ catalysts show very different product distributions, even when the reaction is conducted at similarly low conversions and the same operating conditions (300°C, 1 atm). That is, while ring hydrogenation to 3-methylcyclohexanone is dominant over Pt, deoxygenation to toluene and C-C cleavage to  $C_1$ - $C_5$  hydrocarbons prevail over Ru. To understand the differences in reaction mechanisms responsible for this contrasting behavior, the conversion of m-cresol over the Pt(111) and Ru(0001) surfaces has been analyzed using density functional theory (DFT) methods. The DFT results show that the direct dehydroxylation of m-cresol is unfavorable over the Pt(111) surface, with an energy barrier for the 242 kJ/mol. In turn, the calculations suggest that the reaction could proceed through a keto tautomer intermediate, which undergoes hydrogenation of the carbonyl group followed by dehydration to form toluene and water. At the same time, a low energy barrier for the ring hydrogenation path towards 3-methylcyclohexanone compared to the energy barrier for the deoxygenation path towards toluene over the Pt(111) surface is in agreement with the experimental observations, which show that 3methylcyclohexanone is the dominant product over Pt/SiO<sub>2</sub> at low conversions. By contrast, the direct dehydroxylation of m-cresol becomes more favorable than the tautomerization route over the more oxophilic Ru(0001) surface. In this case, the deoxygenation path exhibits an energy barrier lower than that for the ring hydrogenation, which is also in agreement with experimental results that show higher selectivity to the deoxygenation product, toluene. Finally, it is proposed that a partially unsaturated hydrocarbon surface species  $C_7H_7^*$  is formed during the direct dehydroxylation of mcresol over Ru(0001), becoming the crucial intermediate for the C-C bond breaking products,  $C_1$ - $C_5$  hydrocarbons, which are observed experimentally over the Ru/SiO<sub>2</sub> catalyst.

## **Keywords:**

Hydrodeoxygenation, m-cresol, hydrogenation, tautomerization, platinum, ruthenium, density functional theory

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# 1. Introduction

Biomass pyrolysis is a promising method being widely explored to displace petroleum-derived liquid fuels. Unfortunately, the liquid product generated via biomass pyrolysis (bio-oil) contains highly oxygenated species and could not be used as a transportation fuel without catalytic upgrading to reduce its oxygen content. Among the recalcitrant oxygenated species present in bio-oil, phenolic compounds formed from the thermal breakdown of lignin are major components. Significant research efforts have been directed to the development of catalysts for hydrodeoxygenation (HDO) of phenolic compounds such as phenol, cresol, and guaiacol.<sup>1-7</sup> Traditional hydrotreating catalysts composed of metal sulfides such as NiMoS or CoMoS have been tested.<sup>7-9</sup> However, they exhibit low HDO activity and require co-feeding of sulfur to prevent catalyst degradation. Supported metal catalysts that do not suffer from these limitations, including noble metals such as Pt, Pd, Rh and Ru as well as non-noble metals such as Ni and Fe, have become more attractive.<sup>2-4,10-13</sup> Several studies have shown that the composition of the metal catalyst can influence the activity and selectivity of HDO reactions of phenolic compounds. For instance, Mortensen et al.<sup>10</sup> investigated the phenol HDO on different carbon-supported catalysts and found that the order of activity for phenol HDO is Ru/C >Pd/C > Pt/C, which follows the trend of metal oxophilicity. Our recent study of m-cresol HDO shows that not only the activity, but also the product distribution greatly vary over SiO<sub>2</sub>-supported Ni, Fe, and Ni-Fe bimetallic catalysts.<sup>3</sup> That is, over Ni, the hydrogenation product 3-methylcyclohexanone is dominant, while the HDO product, toluene, appears in small amounts, even at high conversions. By contrast, over Fe and

Ni-Fe bimetallic catalysts, the dominant product is toluene while the hydrogenation products are practically negligible in the entire range of conversions. Significant effects of the support on activity and selectivity have also been reported. For example, reducible oxide supports such as  $ZrO_2$  and  $TiO_2$  can enhance the selectivity to toluene in the HDO of m-cresol over Pt and Ru catalysts compared to those supported on inert supports such as  $SiO_2$  or carbon. <sup>2,10</sup>

Even though a number of studies have reported differences in activity and HDO selectivity with varying metals and supports, the precise reaction mechanisms on the different catalysts and the exact influence of each metal and/or support on the reaction are still a matter of debate. In general, two types of mechanisms have been proposed for the HDO of phenolic compounds: (1) hydrogenation/deoxygenation (HYD) route <sup>5,14,15</sup> and (2) direct deoxygenation (DDO) route via C-O hydrogenolysis, <sup>8,16,17</sup> as shown in Figure 1 (*left*). The HYD route typically starts with hydrogenation of the aromatic ring of phenolic compounds to their corresponding saturated alcohols followed by the oxygen removal via dehydration. The HYD route has been proposed to occur over bi-functional catalysts such as Ni/HZSM-5 with the metal site providing hydrogenation activity to saturate the aromatic ring and the acid site catalyzing the dehydration path. The DDO route was proposed as the HDO pathway for the phenolic compounds on CoMo sulfide catalysts at high temperature and further extended to metal catalysts.<sup>10</sup>

Our group has recently investigated the HDO of m-cresol at relatively mild temperatures (300°C) on SiO<sub>2</sub>-supported Pt catalyst, which yield 3-methylcyclohexanone, 3-methycyclohexanol and toluene as the major products.<sup>2,10</sup> Importantly, when the ring-hydrogenated intermediate 3-methylcyclohexanol was fed over this catalyst at the same

reaction conditions, no toluene was observed. That is, neither the DDO mechanism nor the HYD mechanism can explain the behavior of this type of catalyst. The former mechanism is believed to require a high energy barrier which will be investigated in the following sections. Moreover, the absence of toluene production when feeding 3methylcyclohexanol contradicts the latter mechanism, which considers toluene as derived from the dehydration of 3-methycyclohexanol. When 3-methylcyclohexanol was reacted over the SiO<sub>2</sub> support alone, the conversion was extremely low, reflecting the low acidity of SiO<sub>2</sub>.<sup>2</sup> Thus, an alternative mechanism that starts with the tautomerization of m-cresol and forms an unstable ketone intermediate (3-methyl-3,5-cyclohexadienone) was proposed, as shown in Figure 1 (*right*)  $^{2,3}$ . This unstable ketone intermediate can be hydrogenated at either the ring C=C bond or the carbonyl C=O bond. If the C=C hydrogenation is dominant, which may occur over a Pt<sup>2</sup> or Ni surface.<sup>3</sup> the 3methylcyclohexanone and 3-methylcyclohexanol are the main products. However, if the C=O hydrogenation is more favorable, as over Fe or Ni-Fe catalysts,<sup>3</sup> the main product is toluene, which is formed by the hydrogenation of the C=O group followed by dehydration. This new tautomerization mechanism was further extended to the HDO of phenolic compounds over other catalysts to explain the influence of the oxophilicity of metals and reducible supports such as TiO<sub>2</sub>, as the more oxophilic metal and the reducible oxide supports may facilitate the -C=O bond hydrogenation and C-O activation.<sup>12,18</sup>



**Figure 1.** Different mechanisms proposed for the HDO reaction of phenolic compounds with m-cresol as an example. (Left) DDO and HYD mechanisms <sup>14-17</sup>; (right) mechanism involving a keto tautomer <sup>2,3</sup>.

While this tautomerization mechanism can explain experimental results quite well, in this contribution, we have further examined this possible pathway on two different metals (Pt and Ru), using first-principle theoretical methods. To this end, density functional theory (DFT) has enabled us to understand the structure of the catalyst and the chemical reactions at the atomic level, and thus has given a more in-depth understanding of how the specific atomic and electronic structure of the catalyst influence the catalytic performance. In recent work, Lu et al.<sup>19,20</sup> have used DFT calculations to explore the mechanisms of HDO of guaiacol over Pt(111) and Ru(0001) surfaces. Chiu et al.<sup>21</sup> and Lee et al. <sup>13</sup> have also investigated the plausible paths of the HDO of guaiacol over Ru(0001) surface and Pt(111) surface separately. However, since catechol or phenol is the main product for the HDO of guaiacol over Pt(111) and Ru(0001) surfaces, their investigation mainly focused on the removal of CH<sub>3</sub>O- and suggested that dehydrogenation at the methyl group occurs before the C-O bond breaking. Hensley et

al.<sup>22</sup> have also examined five different mechanisms for the HDO of phenol over Fe(110) and Pd(111) surfaces by DFT calculations. They showed that the elementary reaction step for each mechanism is endothermic on the Pd(111) surface while exothermic on Fe(110). They also suggested that the direct cleavage of the C-O bond is likely to be the most energetically and kinetically favorable on Fe(110) surface. Li et al.<sup>23</sup> investigated the hydrogenation of phenol over Pt(111) and Pd(111) surfaces by DFT calculations and suggested that the phenol dissociation is crucial for the different product selectivity over these two metal surfaces, although they only examined the first hydrogenation step at the phenyl ring.

In this work, we have extended our efforts combining experimental HDO of mcresol over  $SiO_2$  supported Pt and Ru catalysts with DFT calculations to compare the fundamental mechanisms of this reaction, including the hydrodeoxygenation and the hydrogenation paths over these two metal surfaces of different oxophilicity. We will show how the nature of the metal catalyst influences the activity and selectivity of the HDO reaction.

## 2. Methods

## 2.1 Catalyst preparation and characterization

The 1 wt.% Pt/SiO<sub>2</sub> and 9.4 wt.% Ru/SiO<sub>2</sub> catalysts used in this study were prepared by incipient wetness impregnation of the SiO<sub>2</sub> support (HiSil 210, PPG,  $S_{BET} = 135 \text{ m}^2/\text{g}$ ) with an aqueous solution of Pt(IV) chloride hydrate and Ru(III) chloride hydrate, respectively. After impregnation, the catalysts were dried at 120 °C for 12 h and calcined at 400 °C for 4 h. Before carrying out the reactions, the catalysts were pelletized, crushed, and sieved to 250-420 µm size range (Mesh no. 40-60). TEM images for the 1% Pt/SiO<sub>2</sub>

 catalyst shown in previous work indicate an average Pt particle size of about about  $3.5 \text{ nm.}^2$  A TEM image for the 9.4% Ru/SiO<sub>2</sub> catalyst is shown in Figure 2. The average particle size for this catalyst was estimated to be 5 nm, as summarized in Table 1. The dispersion of the Pt and Ru particles were estimated accordingly from the observed particle sizes to be about 0.3 and 0.25, respectively.<sup>24</sup>



**Figure 2**. TEM of 9.4 wt.% Ru/SiO<sub>2</sub> after calcination at 400 °C in air, reduction at 400 °C by H<sub>2</sub> and passivation at room temperature.

	Pt/SiO <sub>2</sub>	Ru/SiO <sub>2</sub>
Metal loading	1 wt. %	9.4 wt. %
$d_p$	3.5 nm	5.2 nm
Metal Dispersion	0.3	0.25

#### 2.2 Reaction conditions

The HDO reactions of m-cresol over the  $Pt/SiO_2$  and  $Ru/SiO_2$  catalysts were carried out in a fixed-bed quartz tube reactor (6 mm outer diameter) under  $H_2$  flow at atmospheric pressure. The flow reaction system is equipped with a mass flow controller and a syringe pump for the continuous injection of m-cresol. The pelletized catalysts

were packed in the reactor between two layers of glass beads and quartz wool to improve the temperature uniformity. The catalysts were pre-reduced in flow of H<sub>2</sub> (60 ml/min) for 1 h at 400 °C. After reduction, the reaction was conducted at 300 °C under the same H<sub>2</sub> flow rate. A 0.5 ml/h flow of liquid m-cresol was fed continuously from the syringe pump and vaporized into the H<sub>2</sub> stream. All lines were heated to 250 °C to avoid product condensation. The reaction products were analyzed and quantified online by gas chromatography using an HP-5 column (30 m, 0.25  $\mu$ m) and a flame ionization detector (FID). The selectivity for each product was calculated as:

## Selectivity (%)

= moles of carbon in the target product / moles of carbon in all the products where the moles of carbon in the product are calculated as the number of carbon atoms in

## 2.3 Density Functional Theory Calculations

the product molecule multiplied by the moles of product.

The calculations were carried out using periodic plane-wave gradient-corrected density functional theory methods implemented in the Vienna ab initio Simulation Package (VASP).<sup>25-28</sup> The optPBE-vdW <sup>29,30</sup> exchange correlation functional was used to provide the non-local gradient-corrections to exchange and correlation energies with the correction of van der Walls (vdW) interactions. Projector augmented wave potentials (PAW) <sup>31</sup> within a cutoff energy of 400 eV were used for wave functions.

The close-packed 4x4 Pt(111) and Ru(0001) surfaces, with four metal layers and 15 Å of vacuum separating slabs in the z-direction were used to model the Pt and Ru catalysts. The top two metal layers were allowed to relax in the calculations, whereas the bottom two layers were held fixed to their bulk position. The electronic energies were

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converged to within  $10^{-6}$  eV. The geometric structures for all of reactants, intermediates and products were optimized until the forces were converged to within 0.01 eV/Å. A  $2\times2\times1$  k-point mesh was used to sample the first Brillouin zone.<sup>32</sup> The energies of the adsorbates in vacuum were calculated spin-polarized using an  $18\times18\times18$  Å unit cell with the  $\Gamma$  only k-point mesh.

Transition state searches were performed using the dimer method <sup>33</sup> with the initial guesses for the transition state structure and the reaction trajectory obtained through the nudged elastic band (NEB) method.<sup>34</sup> The located transition states were further verified by vibrational frequency analysis.

The Gibbs free energies for the adsorption of close-shell species at 300 °C and 1 atm were estimated by including the entropy, which in turn was calculated according to standard procedures.<sup>35</sup> That is, the vibrational entropy was calculated from vibrational frequencies derived from DFT frequency calculations. The translational and rotational entropy for adsorbed species were assumed to be zero. For gas phase species, the translational and rotational entropies were calculated by statistical thermodynamics.<sup>35</sup>

## 3. Results and Discussions

## 3.1 Product distribution over Pt/SiO<sub>2</sub> and Ru/SiO<sub>2</sub> catalysts

The product selectivity observed during the conversion of m-cresol over  $Pt/SiO_2$  and  $Ru/SiO_2$  catalysts at 300 °C is summarized in Table 2. Over  $Pt/SiO_2$ , the m-cresol conversion yielded more 3-methylcyclohexanone (60.2%) than toluene (33.3%). This result is consistent with our previous work that showed faster ring hydrogenation than hydrodeoxygenation over pure Pt catalysts.<sup>2</sup> In contrast, the Ru/SiO<sub>2</sub> catalyst favored HDO over ring hydrogenation, with a selectivity to toluene (38.5%) much higher than

that to 3-methylcyclohexanone (7.4%). That is, at comparable conversion levels (5-7 %), the HDO/HYD ratio is only 0.5 on Pt but greater than 5 on Ru. At the same time, significant amounts of CH<sub>4</sub> (43.4%) and C<sub>2</sub>-C<sub>6</sub> hydrocarbons (10.7%) were formed on Ru via C-C bond hydrogenolysis. However, these products were essentially absent over Pt/SiO<sub>2</sub> under the same reaction conditions and comparable conversion levels. Turnover frequencies (TOF) were calculated from the observed conversion, W/F, and estimated metal dispersions for Pt/SiO<sub>2</sub> and Ru/SiO<sub>2</sub> catalysts. Pt/SiO<sub>2</sub> (TOF=19 min<sup>-1</sup>) appears as significantly more active than Ru/SiO<sub>2</sub> (TOF= 0.1 min<sup>-1</sup>).

To further understand how the  $C_1$ - $C_6$  hydrocarbons were formed, we used the two HYD products, 3-methylcyclohexanone and 3-methylcyclohexanol, as feed in two separate sets of experiments as shown in Figure 3. It is found that CH<sub>4</sub>, a product of the C-C hydrogenolysis reaction over Ru/SiO<sub>2</sub> is only observed in very small amounts when the feed was 3-methylcyclohexanone or 3-methylcyclohexanol. It is important to note that  $CH_4$  is clearly a secondary product of both 3-methylcyclohexanone and 3methylcyclohexanol as the rates of CH<sub>4</sub> formation are zero at low conversions (i.e. as W/F approaches zero). By contrast, CH<sub>4</sub> is a primary product when m-cresol is the feed, as demonstrated by the high selectivity to  $CH_4$  at low m-cresol conversion (Table 2). Interestingly, m-cresol is a primary product when feeding the ketone 3methylcyclohexanone, but is a secondary product when feeding the alcohol 3methylcyclohexanol. This suggests that m-cresol is directly formed from the ketone 3methylcyclohexanone rather than the alcohol 3-methylcyclohexanol. However, in both cases, the C-C cracking product CH<sub>4</sub> is directly formed from m-cresol rather than from its hydrogenation products 3-methylcyclohexanone or 3-methylcyclohexanol over Ru/SiO<sub>2</sub>

catalyst. This is an important result that illustrates the radically different reaction paths that occur over Pt and Ru catalysts. It is clear that, over Pt catalyst, the hydrogenation reaction path is more favorable, while over the more oxophilic Ru catalyst, the hydrodeoxygenation and C-C breaking paths are more favorable. This observation suggests that an intermediate may exist over Ru that is ready for C-C breaking immediately following the C-O cleavage, but this does not occur over Pt.

Table 2. Product distributions for the HDO of m-cresol over Pt/SiO2 and Ru/SiO2 catalystsat 300 °C and atmospheric pressure.

	Pt/SiO <sub>2</sub>	Ru/SiO <sub>2</sub>			
W/F (gcat.hr/mol)	4.0	35.3			
Conversion (%)	7.2	4.5			
TOF (min <sup>-1</sup> )	19	0.1			
Selectivity (%)					
3-methylcyclohexanone	60.2	7.4			
3-methylcyclohexanol	6.5	-			
Toluene	33.3	38.5			
C2-C5 hydrocarbon	-	10.7			
CH <sub>4</sub>	-	43.4			



**Figure 3**. Conversion and yields of products of feeds of 3-methylcyclohexanone (*left*) and 3-methylcyclohexanol (*right*) over Ru/SiO<sub>2</sub> as a function of W/F at 300  $^{\circ}$ C with H<sub>2</sub> at the pressure of 1 atm.

In the following sections, we describe the density functional theory (DFT) calculations that we have performed to examine the m-cresol hydrogenation and hydrodeoxygenation pathways over Pt and Ru metal surfaces and explain the experimental observations.

## 3.2 DFT exploration of pathways for hydrogenation and hydrodeoxygenation

## 3.2.1 Adsorption of m-cresol on the Pt(111) and Ru(0001) surfaces

Different adsorption configurations of m-cresol on the Pt(111) and Ru(0001) surfaces were analyzed by DFT. As illustrated in Figure 4, the energy-optimized configuration shows that m-cresol adsorbs flat on 'bridge 30' sites on both Pt(111) and Ru(0001) (i.e. through the aromatic ring carbons). This configuration is similar to previously reported favorable adsorption modes of benzene and phenol on these, as well as other, metal surfaces.<sup>36-39</sup> The adsorption energy of m-cresol on Pt(111) is calculated to be -176 kJ/mol with the vdW corrections as listed in Table 3, which is similar to the reported binding energy of phenol on the Pt(111) surface (-172 kJ/mol).<sup>37</sup> Similarly, the adsorption energy of m-cresol on a Ru(0001) surface is calculated to be -239 kJ/mol, which is similar to the reported adsorption energy of phenol on Ru(0001) surface (-242 kJ/mol).<sup>19</sup> The stronger adsorption of m-cresol on Ru(0001) compared to Pt(111) is probably due to a stronger carbon-metal interaction on the Ru(0001) surface. A similar trend has been reported for benzene, which binds more strongly on Ru(0001) than on Pt(111).<sup>40</sup>



**Figure 4.** DFT optimized structures of m-cresol and its two keto tautomers in gas phase, and on the Pt(111) and Ru(0001) surfaces. The energies shown in the top and bottom are the reaction energies for the tautomerization of m-cresol to each of its keto tautomers (a and b, respectively).

**Table 3.** Adsorption energies (*kJ/mol*) of reactant, products, and close-shell intermediates in the hydrodeoxygenation process of m-cresol on Pt(111) and Ru(0001) surfaces with vdW corrections. KetCO is the keto tautomer of m-cresol, and KetHOH is the intermediate formed by hydrogenation of KetCO tautomer at the carbonyl group. Free adsorption energies  $\Delta G$  were calculated at 300 °C and 1 atm.

	Pt(111)		Ru(0001)		
	ΔΕ	$\Delta G$	ΔΕ	$\Delta G$	
m-cresol	-176	-50	-239	-130	
KetCO	-208	-83	-301	-185	
3-methylcyclohexanone	-116	-5	-165	-63	
Toluene	-170	-44	-225	-121	
Н	-38	-	-48	-	
H <sub>2</sub> O	-37	-	-47	-	
KetHOH	-232	-85	-242	-101	

## 3.2.2 Direct deoxygenation of m-cresol over the Pt(111) surface

As summarized above, the direct deoxygenation mechanism (DDO) for the HDO of phenolic compounds including m-cresol has been proposed in several experimental studies. Some theoretical calculations have also been carried out on HDO of phenol over Fe  $(110)^{22}$  and Pd $(111)^{22}$  surfaces, as well as guaiacol over CoMoS,<sup>41</sup> Pt $(111)^{13}$  and Ru(0001)<sup>19,21</sup> surfaces. Here, we further examine the direct deoxygenation of m-cresol over the Pt(111) surface and compare it to other possible pathways. As shown in Figure 5, m-cresol adsorbs flat on the Pt(111) surface through the aromatic ring. It must be noted that the hydroxyl group -OH does not interact with the metal surface as indicated by the rather long Pt-O distance (3.11 Å). On the other hand, the  $C_{\alpha}$ -OH bond distance in mcresol is about 1.36 Å, which is shorter than a typical C-O bond in aliphatic alcohols (~1.45 Å) and indicates a stronger C-O bond due to the conjugation with the aromatic ring. However, the C-O bond gradually elongates along the reaction coordinate for the direct dehydroxylation over Pt(111). As shown in Figure 5, in the transition state, the C-O bond increases to 2.46 Å from the original 1.36 Å in the reactant. At the same time, the hydroxyl group is bound to the metal surface at the atop site, which stabilizes the transition state. After the C-O bond is cleaved to form the product structure, the hydroxyl group changes from the atop site to the bridge site on the Pt(111) surface as the bridge site binding mode is the most stable for the hydroxyl group on the Pt(111) surface. At the same time, the aromatic ring tilts up about 45° from the flat adsorbed configuration. This tilted configuration is about 23 kJ/mol more stable than the flat configuration, as shown in Figure 5.

However, it is very important to note that the calculated activation energy for this

direct deoxygenation path over Pt(111) is exceedingly high (242 kJ/mol) and the reaction energy is highly endothermic (116 kJ/mol). These energies confirm our previous assumption that the breaking of the aromatic C-O bond is very difficult and may not occur at all on Pt at the temperature (300 °C) of the experimental HDO studies.<sup>2,3</sup>



Figure 5. DFT optimized structures for reactant, transition state, and product (tilted) in the direct dehydroxylation of m-cresol over the Pt(111) surface.

# 3.2.3 Tautomerization of m-cresol to its keto tautomer

Based on our previous kinetic analyses of the HDO of m-cresol over SiO<sub>2</sub>-supported Ni-Fe and Pt catalysts,<sup>3</sup> we propose a mechanism that involves the tautomerization of the phenolic compound to their corresponding keto tautomer. This tautomer could undergo ring hydrogenation (forming a hydrogenated ketone) or hydrogenation of the carbonyl group followed by dehydration (forming the deoxygenated aromatic product). This mechanism explains the experimental kinetic results. Here, we have used DFT calculations to examine the reaction pathways involved in this mechanism.

It is well-known that phenol exhibits keto-enol tautomerism with its unstable keto tautomer (cyclohexadienone), even though only a tiny fraction may exist as the ketone form.<sup>42</sup> A similar keto-enol tautomerism should exist for m-cresol. The structures of the two keto tautomers of m-cresol (*KetCO-a* and *KetCO-b*) are shown in Figure 4 above. The reaction energy for the keto-enol tautomerization of m-cresol in the gas phase to

*KetCO-a* and *KetCO-b* is calculated to be 73 kJ/mol and 79 kJ/mol respectively, which suggests the phenol form of m-cresol is much more stable than its keto tautomers due to its aromaticity. Therefore, the keto tautomer can only be in a very small amount in the gas phase, similar to the case of phenol.<sup>42</sup> The calculations also suggest that *KetCO-b* with the -CH<sub>2</sub>- at the ortho position of methyl group is more stable than *KetCO-a*, in which the -CH<sub>2</sub>- is at the para position of methyl group. As shown in Figure 4, *KetCO-b* is not only more stable than *KetCO-a* in the gas phase, but also on Pt(111) and Ru(0001) surfaces. Thus, in this paper, we have only examined the reaction paths involving the more stable tautomer *KetCO-b* of m-cresol. In the following sections this keto tautomer is referred as KetCO, for simplicity.

On the Pt(111) surface, this keto tautomer (KetCO) may adsorb through the two C=C bonds and form four carbon-metal bonds with the metal surface, as shown in Figure 4. However, the carbonyl group does not bind to the metal surface, but instead tilts away from the surface with a carbonyl C-Pt distance of 2.86 Å and a carbonyl O-Pt distance of 3.67 Å. This adsorption configuration is similar to the reported adsorption mode of butadiene<sup>43</sup>, furan,<sup>40</sup> and furfural<sup>41</sup> on Pd(111) and Pt(111) surfaces, all molecules containing two C=C bonds. The adsorption energy of KetCO on the Pt(111) surface is calculated to be -208 kJ/mol, which is stronger than the adsorption energy of m-cresol on the Pt(111) surface, as shown in Table 3. The reaction energy for the tautomerization of m-cresol over Pt(111) surface is calculated to be 41 kJ/mol. That is, compared to the gas phase, the keto tautomer KetCO is more stable on the Pt(111) surface, with a much less endothermic tautomerization reaction.

Similarly, the keto tautomer KetCO adsorbs on Ru(0001) surface, also through the

two C=C double bonds. However, different from the Pt(111) surface, the -C=O binds to the metal surface in the 'di- $\delta$ ' mode, as shown in Figure 4, due to the stronger oxophilicity of Ru. The adsorption energy of KetCO on the Ru(0001) surface is calculated to be -301 kJ/mol, which is also stronger than m-cresol on the Ru(0001) surface, as shown in Table 3. Thus, the reaction energy for the tautomerization of mcresol is calculated to be 11 kJ/mol, which is much less endothermic compared to the Pt(111) surface and in the gas phase. This result suggests that the more oxophilic the metal is, the more strongly the keto tautomer is stabilized on the metal surface.

We now discuss in detail the energy barrier for the tautomerization of m-cresol over Pt(111) and Ru(0001) surfaces (Figure 6). Hensley et al.<sup>22</sup> studied the tautomerization of phenol over Fe(110) surface, and found a very high energy barrier (196 kJ/mol). However, it is important to note that, in their study, the tautomerization proceeded via direct H transfer from the hydroxyl group onto the adjacent carbon. Recently, Li et al.<sup>23</sup> suggested that the tautomerization on metal surfaces may proceed via metal-assisted O-H dissociation, followed by metal-assisted C-H combination. We have analyzed the metal-assisted tautomerization of m-cresol over Pt(111) and Ru(0001) surfaces and the results are shown in Figure 6.

It can be observed that, over both Pt(111) and Ru(0001) surfaces, the O-H dissociation of m-cresol is easy with energy barriers of 39 kJ/mol over the Pt(111) surface and 45 kJ/mol over Ru(0001) to form an m-cresoxy intermediate and H\*. This O-H dissociation step is endothermic over Pt(111) with a reaction energy of 22 kJ/mol, while it is very exothermic over the Ru(0001) surface with a reaction energy of -89 kJ/mol. After the O-H bond is dissociated, the H\* can then be combined with the  $\beta$ -C of the m-cresoxy

intermediate to form the ketone tautomer KetCO. The energy barrier for this C-H combination step is calculated to be 77 kJ/mol over the Pt(111) surface and 80 kJ/mol over Ru(0001). As shown in Figure 6, the overall barrier for this metal-assisted tautomerization process is about 99 kJ/mol over Pt(111) surface and about 45 kJ/mol over Ru(0001) surface, which are much lower than the 196 kJ/mol barrier calculated by Hensley et al. for the direct tautomerization path over Fe(110).<sup>22</sup> The lower overall barrier for this tautomerization process over Ru(0001) than over Pt(111) also suggests that an oxophilic metal not only stabilizes the keto tautomer more efficiently, but also lowers the energy barrier for the tautomerization reaction.



**Figure 6.** DFT optimized structures for reactant, transition state and product in the metal assisted tautomerization reactions of m-cresol over Pt(111) surface (top) and Ru(0001) surface (bottom). The energies listed are in reference to the reactant.

### 3.2.4 Hydrogenation and hydrodeoxygenation of the keto tautomer over Pt(111)

Four sequential hydrogenation steps are required to saturate the two C=C bonds of

keto tautomer KetCO and form the hydrogenated product 3-methylcyclohexanone. The different sequences of hydrogenation of the four different carbons lead to 24 different pathways from KetCO to 3-methylcyclohexanone as shown in Figure S1. After examination of the different pathways, it was found that the pathway for hydrogenating KetCO in the order C3-C4-C5-C6 is the most favorable as shown in Figure 7. This result is consistent with the reported hydrogenation of furan on Pd(111), in which the most favorable hydrogenation pathway of the four carbons follows the order C1-C2-C3-C4.44 The structures for the intermediates in the step-wise hydrogenation of KetCO (KetHCO,  $KetH_2CO$  and  $KetH_3CO$ , as well as the final product 3-methylcyclohexanone on Pt(111), are shown in Figure 7. We can see that in the structures of intermediates KetHCO and *KetH*<sub>2</sub>*CO* that are formed by addition of one H and two H, respectively, the carbonyl group C=O does not bind to the metal surface, as indicated by the long O-Pt distances (3.64 - 4.07 Å) and the C-Pt distance of ~2.90 Å, similar to that in KetCO. By contrast, in the subsequent  $KetH_3CO$  and 3-methylcyclohexanone species formed by hydrogenation of three carbons and four carbons, respectively, the carbonyl group C=O binds to the metal surface through the carbonyl O due to the saturation of the carbons in the ring that releases the steric constraint. The transition state structures for each hydrogenation step are shown in Figure 7. All hydrogenation steps proceed through the metal insertion mechanism. In each case, the adsorbed H inserts into the C-metal bond forming an H-Cmetal triangular transition state. The calculated energy barriers and reaction energies for each hydrogenation step are included in Figure 7. The activation barriers for the four hydrogenation steps are similar at 93~107 kJ/mol. These four hydrogenation steps are endothermic with the reaction energy of 22 kJ/mol, 11 kJ/mol, 3 kJ/mol and 15 kJ/mol

respectively, which is consistent with the reported energy trends for hydrogenation of furan and benzene over Pt(111) and Pd(111) surfaces. <sup>44,45</sup>

After 3-methylcyclohexanone is formed, it desorbs with a desorption energy of 116 kJ/mol (Table 3). It must be noted that the vdW interaction contributes significantly to this energy compared to desorption energies calculated without vdW corrections, such as that for cyclohexanone (26 kJ/mol) on Pt.<sup>23</sup> It is noted that even though the calculated desorption energy for 3-methylcyclohexanone is high (116 kJ/mol), the desorption process may be entropy driven. When entropy is considered, the free energy of 3-methylcyclohexanone adsorption (at 300 °C and 1 atm) becomes only -5 kJ/mol as shown in Table 3.

The overall energy diagrams for the hydrogenation of the KetCO intermediate is summarized in Figure 8. Starting at the adsorbed keto tautomer KetCO and adsorbed hydrogen ( $KetCO^{*}+4H^{*}$ ) the overall energetics is uphill along the reaction coordinate, with the last hydrogenation step transition state at the highest energy. The resulting energy barrier for the hydrogenation of the KetCO intermediate is 143 kJ/mol. The overall energy barrier, including the tautomerization step, from the adsorbed m-cresol and adsorbed hydrogen  $(Cre^{+}4H^{+})$ the final to hydrogenation product (3methylcyclohexanone) is calculated to be 181 kJ/mol. Of course, even though the tautomerization reaction and each hydrogenation step over a Pt(111) surface are endothermic, the heat of adsorption of the reactants makes the overall reaction from gas phase m-cresol and  $H_2$  is exothermic, with a reaction energy of -121 kJ/mol, as expected.



**Figure 7**. DFT optimized structures for the intermediates, transition state, and product in the step-wise hydrogenation of KetCO at the ring carbons over the Pt(111) surface.



**Reaction Coordinate** 

**Figure 8**. Energy diagrams for the hydrogenation of m-cresol to form 3-methylcyclohexanone (red) and the hydrodeoxygenation of m-cresol to form toluene (blue) through the keto tautomer KetCO over the Pt(111) surface.

In addition to the hydrogenation of the keto tautomer KetCO at the carbon ring that

leads to 3-methylcyclohexanone, the keto tautomer KetCO can also be hydrogenated at the carbonyl group C=O. In this case, subsequent dehydration would form the HDO product toluene. Therefore, we have also examined this path with DFT calculations.

First, we must note that the hydrogenation of the carbonyl group can proceed by two alternative pathways: 1) through a hydroxyl-alkyl intermediate by first H addition to the O of the carbonyl group; or 2) through an alkoxide intermediate by first H addition to the C of the carbonyl group.<sup>46</sup> However, the formation of the alkoxide would require the four ring C that bind to the metal surface to all tilt away, resulting in a high reaction energy of 177 kJ/mol. Therefore, the more favorable pathway for the hydrogenation of KetCO at the carbonyl group is through the hydroxyl-alkyl intermediate, followed by the second hydrogenation at the carbonyl C. In the first hydrogenation of the carbonyl O of KetCO, the tilted away carbonyl group gradually gets closer to the metal surface. The distance between the carbonyl C decreases from 2.88 Å in the reactant to 2.56 Å in the transition state, as shown in Figure 9A. At the same time, the H atom adsorbed on the metal surface shifts from the fcc hollow site to the atop site and binds to the carbonyl O of KetCO. This reaction has a low energy barrier (26 kJ/mol) and an exothermic reaction energy (-16 kJ/mol). The subsequent hydrogenation of the hydroxyl-alkyl intermediate at the C proceeds through the metal insertion mechanism, as shown in Figure 9B, similar to the hydrogenation of KetCO at the ring carbons described above. The energy barrier is calculated to be 88 kJ/mol, which is higher than the first hydrogenation step at the carbonyl oxygen. This reaction is also endothermic with a reaction energy of 29 kJ/mol. It can be noted that in the intermediate (KetCHOH) that is formed by the hydrogenation of the carbonyl group of the keto tautomer KetCO, the hydroxyl group also tilts away

from the metal surface rather than binding to the metal surface due to the constraints caused by the adsorption of the ring carbons, as shown in Figure 9B.

After the intermediate KetCHOH is formed by hydrogenation of the carbonyl group of the keto tautomer KetCO, it can then undergo dehydration to remove the hydroxyl group and H at the  $\beta$ -carbon as H<sub>2</sub>O to form toluene, as shown in Figure 9C. The C-OH and  $\beta$ -C–H bonds gradually elongate, with the C-OH bond changing from 1.45 Å to 1.89 Å and the C-H bond changing from 1.11 Å to 1.36 Å. Simultaneously, the distance between the hydroxyl group and the H at the  $\beta$ -carbon gradually decreases from 2.25 Å in the reactant to 1.31 Å in the transition state. After the C-OH bond and the  $\beta$ -C-H bond are completely broken, a H<sub>2</sub>O molecule is formed, leaving toluene adsorbed at the metal surface, as shown in Figure 9C. Toluene desorbs with a desorption energy of 170 kJ/mol (Table 3). This reaction is exothermic with a reaction energy of -69 kJ/mol because two stable molecules (water and toluene) are formed as products. However, the calculated energy barrier is rather high (152 kJ/mol). If KetCHOH desorbed and re-adsorbed with the OH group facing the metal surface, the dehydration of KetCHOH would have a lower energy barrier. However, the desorption energy of KetCHOH is calculated to be 232 kJ/mol, as listed in Table 3, which is even higher than the energy barrier for the direct dehydration path of KetCHOH shown above (152 kJ/mol).

Therefore, the dehydration step rather than the hydrogenation steps is likely to be rate-limiting in the HDO process over Pt(111) surface (Figure 8). However, in any case, the overall energy barrier relative to the adsorbed m-cresol and adsorbed hydrogen (Cre\* + 4H\*) is about 203 kJ/mol, which is still about 39 kJ/mol lower than the energy barrier required for the direct deoxygenation pathway (242 kJ/mol). This tautomerization-

hydrogenation-dehydration path is more favorable than the direct deoxygenation path for the HDO of m-cresol over the Pt(111) surface, which supports our previous assumptions.

The energy diagram for the hydrogenation of m-cresol towards 3methylcyclohexanone can be compared in Figure 8 with the energy diagrams for the mcresol HDO towards toluene. It is shown that the energy barrier for the deoxygenation of m-cresol towards toluene is about 22 kJ/mol higher than that for hydrogenation of mcresol towards 3-methylcyclohexanone, which is in agreement with the experimental observations of higher selectivity to 3-methylcyclohexanone rather than toluene over Pt/SiO<sub>2</sub> catalysts.



**Figure 9**. DFT optimized structures for the reactant, transition state and product over a Pt(111) surface in the reaction of (A) hydrogenation of KetCO at the carbonyl oxygen; (B) continuing hydrogenation of KetCO at the carbonyl carbon; (C) dehydration of the KetCHOH intermediate formed from hydrogenation of KetCO.

#### 3.2.5 Hydrogenation and hydrodeoxygenation of keto tautomer over Ru(0001)

While the mechanism involving the keto tautomer KetCO over Pt(111) surface is in agreement with experimental observations, the same may not be necessarily true over

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other metals. Therefore, we examined on a Ru(0001) surface the same pathways for hydrogenation of the keto tautomer as those studied on Pt(111). Similar to the case of Pt, the most favorable path for hydrogenation of KetCO at the ring carbons on Ru(0001) follows the sequence of C3-C4-C5-C6. However, as shown in Figure 10, an important differences between the two metals are observed in the structures for the intermediates and transition states involved in the sequential hydrogenation of KetCO (KetHCO,  $KetH_2CO$  and  $KetH_3CO$ , as well as that for the final product 3-methylcyclohexanone. In contrast to Pt(111), over Ru(0001) the carbonyl group -C=O of all the three intermediates and final product binds to the surface in a 'di- $\sigma$ ' mode due to the stronger oxophilicity of Ru. Each hydrogenation step also proceeds via the metal insertion mechanism, with the formation of a H-C-metal triangular transition state. The activation energies for these four sequential hydrogenation steps are calculated to be 87, 81, 75, and 90 kJ/mol, respectively, which are similar to those over Pt(111). These hydrogenation reactions are all endothermic with positive reaction energies, consistent with those over the Pt(111) surface.

From the energy diagram in Figure 11, we can see that along the reaction coordinate of the hydrogenation of keto tautomer KetCO at the ring carbons over Ru(0001), the energetics is also uphill, with the last hydrogenation step transition state having the highest energy, similar to the case over Pt(111). Thus, in reference to the state with the lowest energy, (i.e. adsorbed m-cresol and the adsorbed hydrogen ( $Cre^*+4H^*$ )), the overall energy barrier for the hydrogenation of m-cresol is calculated to be 224 kJ/mol, which is higher than that obtained over the Pt(111) surface (181 kJ/mol). This is consistent with previous calculations for the benzene hydrogenation over Pt(111) and

 Ru(0001) surfaces showing that the overall barrier over Ru(0001) is higher than over Pt(111).<sup>40,47</sup>



**Figure 10**. DFT optimized structures for the intermediates, transition state, and product in the step-wise hydrogenation of KetCO at the ring carbons over Ru(0001).



**Figure 11**. Energy diagrams for the hydrogenation of m-cresol to form 3-methylcyclohexanone (red) and the hydrodeoxygenation of m-cresol to form toluene (blue) through the keto tautomer KetCO over Ru(0001) surface.

To complete the HDO reaction as done above for Pt, the pathways for the

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hydrogenation of the keto tautomer KetCO at the carbonyl group followed by dehydration to form toluene were also examined over Ru(0001). The corresponding structures are summarized in Figure 12.

Similar to the case of Pt(111), the favorable path for hydrogenation of the carbonyl group of KetCO on Ru(0001) is through the hydroxyl-alkyl intermediate formed by the first hydrogenation at the carbonyl O. The transition state for the first hydrogenation at the carbonyl O moves from the bridge site to the atop site and, at the same time, the adsorbed H inserts into the O-Ru bond, as shown in Figure 12A. This hydrogenation step is very endothermic with a reaction energy of 60 kJ/mol, more endothermic than over Pt(111) (-16 kJ/mol). The energy barrier (136 kJ/mol) is also much higher than on Pt(111) (26 kJ/mol). Clearly, the higher reaction energy and energy barrier for the hydrogenation of the O in the carbonyl is due to the stronger interaction of the carbonyl O with Ru(0001) than with Pt(111). This trend is consistent with the reported hydrogenation of other ketones and aldehydes over Pt(111) and Ru(0001) surfaces.<sup>48</sup>

Next, the structures of the reactant, transition state, and product for the continuing hydrogenation of the hydroxyl-alkyl intermediate (KetCOH\*) are shown in Figure 12B. In the transition state, the adsorbed H inserts into the C-Ru bond and forms a H-C-Ru triangle, similar to the transition state structures of the hydrogenation of KetCO at the ring carbons shown above for Pt. This reaction is also very endothermic, with a reaction energy of 78 kJ/mol. The energy barrier is calculated to be 106 kJ/mol. Similar to Pt(111), the intermediate (KetCHOH\*) formed by hydrogenation of the carbonyl group adsorbs on Ru(0001) with the –OH tilting away rather than binding to the metal surface.

After this intermediate (KetCHOH\*) is formed it can dehydrate leading to toluene

on the metal surface and water in the gas phase, as shown in Figure 12C. The transition state structure is similar to that on Pt(111), as shown in Figure 9C. This reaction over Ru(0001) is even more exothermic (-145 kJ/mol) than over Pt(111) (-69 kJmol), due to the stronger adsorption of the product toluene on a Ru(0001) surface (-225 kJ/mol), as listed in Table 3. The energy barrier is calculated to be 120 kJ/mol, which is also about 30 kJ/mol lower than on Pt(111).



**Figure 12**. DFT optimized structures for the reactant, transition state and product state over the Ru(0001) surface in the reaction of (A) hydrogenation of KetCO at the carbonyl oxygen; (B) continuing hydrogenation of KetCO at the carbonyl carbon; (C) dehydration of KetCOH intermediate formed from hydrogenation of KetCO.

As shown in Figure 11, similar to Pt(111), all the energies go uphill, with the transition state for the dehydration step at the highest energy. Thus, the overall energy barrier referred to the adsorbed m-cresol and adsorbed hydrogen (*Cre*\*+4*H*\*) is about 283 kJ/mol, about 80 kJ/mol higher than that over Pt(111). Even though the energy barrier for the dehydration step of KetCHOH is lower over Ru(0001), the more endothemic nature of the hydrogenation step of the keto tautomer KetCO leads to a

higher overall energy barrier for the hydrodeoxygenation path to toluene on Ru(0001) than over Pt(111).

Comparing the paths of the hydrogenation of m-cresol to 3-methylcyclohexanone and the deoxygenation to toluene over the Ru(0001) surface through the keto tautomer KetCO, one finds a higher overall energy barrier for the deoxygenation path (by 59 kJ/mol) than for the hydrogenation path. This result is in contradiction with the experimental results that show a higher selectivity to toluene rather than 3methylcyclohexanone. Therefore, we will examine other possible paths over Ru(0001), such as the direct dehydroxylation, which was unfavorable for Pt(111).

# 3.2.6 Direct deoxygenation of m-cresol over Ru(0001)

Recently, Chiu et al. <sup>21</sup> and Lu et al. <sup>19</sup> have independently investigated the deoxygenation of guaiacol over Ru(0001) using DFT calculations. They both have found that the energy barrier for the direct C-O bond breaking of catecholate  $C_6H_4(OH)O$  is rather low, about 100 kJ/mol. Hensley et al. <sup>22</sup> also investigated the mechanism of the deoxygenation of phenol on Fe(110) and found that a plausible path for the deoxygenation of phenol on the oxophilic Fe(110) surface is the direct dehydroxylation. They did not consider the hydrodeoxygenation path via the keto tautomer discussed here. Therefore, we have analyzed the direct deoxygenation path of m-cresol over Ru(0001) and compared the results with those of the keto tautomer path.

The structures for the reactant, transition state, and product for the direct dehydroxylation of m-cresol over the Ru(0001) surface are shown in Figure 13A. Similar to Pt(111), the dehydroxylation of m-cresol over Ru(0001) proceeds via the gradual

elongation of the C-OH bond. In the transition state, the C-OH bond distance increases to 1.93 Å and the  $\alpha$ -C also moves from the atop site to the neighboring bridge site. After the C-OH bond is broken, the OH group moves to an hcp hollow site, which is the most favorable binding site for the OH group on the Ru(0001) surface. Meanwhile, the C ring still binds flat on the metal surface, which is different from the case on Pt(111) in which, after dehydroxylation, the carbon ring tilts up from metal surface, as shown in Figure 5. The energy barrier for the direct dehydroxylation of m-cresol over Ru(0001) is 98 kJ/mol, which is similar to the reported value for the dehydroxylation of catecholate C<sub>6</sub>H<sub>4</sub>(OH)O over Ru(0001).<sup>21</sup> This energy barrier is much lower than the overall energy barrier for the tautomerization-hydrogenation-dehydration path we showed above (283 kJ/mol), indicating that, over Ru(0001), the direct dehydroxylation path.

The reaction energy is calculated to be -30 kJ/mol, which is also more exothermic than over Pt(111), 116 kJ/mol. The much lower energy barrier and the more exothermic reaction energy for the direct dehydroxylation of m-cresol over the Ru(0001) surface than over Pt(111) is certainly due to a stronger oxophilicity. Oxophilic metals bind the OH group strongly and can stabilize the transition state for the dehydroxylation reaction, as shown in Figure 13A.

To draw a more general conclusion, we have calculated the intrinsic energy barriers for the direct dehydroxylation of m-cresol on different metal surfaces with varying oxophilicities, as measured in terms of the adsorption energy of atomic O. The direct dehydroxylation of m-cresol over Pd(111) and Rh(111) surfaces were shown in Figure S6. As shown in Figure 14, the intrinsic energy barrier for dehydroxylation can be

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correlated to the oxophilicity of the metal surface. We can conclude that the oxophilicity of the metal surface can regulate what reaction path is more favorable. On a strong oxophilic metal, such as Ru(0001) or Fe(110), the direct deoxygenation is the favorable path, while on weaker oxophilic metals such as Pt(111), the direct deoxygenation become less favorable and the tautomerization-hydrogenation-dehydration mechanism is the favorable path. This conclusion might also apply to explain, at least partially, our previous experimental observations of different product distributions from the m-cresol conversion over Ni, Fe, and Ni-Fe catalysts.<sup>3</sup> Over Ni catalyst, the HDO of m-cresol may proceed through the tautomerization-hydrogenation-dehydration path while over the more oxophilic Fe or Ni-Fe catalyst, the HDO of m-cresol may include contributions of the direct dehydroxylation path, similar to the results on Pt(111) and Ru(0001) surface that we show here.



 **Figure 13.** DFT optimized structures for the reactant, transition state and product state over Ru(0001) surface in the reaction of (A) direct dehydroxylation of m-cresol; (B) hydrogenation of  $C_7H_7^*$  radical intermediate that is formed via dehydroxylation of m-cresol; (C) hydrogenation of OH\* that is formed via dehydroxylation of m-cresol



**Figure 14**. Correlation between the intrinsic energy barrier for the direct dehydroxylation of m-cresol on different metal surfaces and the adsorption energies of the atomic oxygen on these metal surfaces.

#### 3.2.7 Fate of the OH and $C_7H_7^*$ species left over Ru(0001) upon direct dehydroxylation

After dehydroxylation, an adsorbed OH group and the  $C_7H_7^*$  carbon ring are formed over Ru(0001), as illustrated in Figure 13A. Hydrogenation of the  $C_7H_7^*$  forms the final product toluene and the hydrogenation of the hydroxyl group forms water, as shown in Figure 13B and 13C. The former is a rather easy reaction, with an energy barrier of 46 kJ/mol and an exothermic reaction energy of -18 kJ/mol for the formation of toluene. By contrast, the latter is more difficult, with an energy barrier of 128 kJ/mol and an endothermic reaction energy of 50 kJ/mol. The energy diagram for the dehydroxylation of m-cresol followed by the hydrogenation to form toluene and water is summarized in Figure 15. We can see that, along the reaction coordinate, the highest energy occurs at the first dehydroxylation step for the surface reaction steps. However,

the intrinsic energy barrier for the hydrogenation of the OH group, which is formed from the dehydroxylation of m-cresol, is relatively high (128 kJ/mol). This observation suggests that the hydroxyl group -OH may build up over the Ru(0001) surface and poison active sites. Therefore, even though the strong oxophilicity of a metal can facilitate the dehydroxylation of m-cresol, it may also lead to a more difficult hydrogenation of the OH groups formed on the surface, leading to lower activity. The desorption energy of the product toluene is also high (225 kJ/mol) (Table 3). However, as discussed above for the desorption of 3-methylcyclohexanone, the desorption process is entropy driven and is not likely to be rate limiting at the reaction temperature.

Comparing the energy diagrams for the hydrodeoxygenation path of m-cresol through the direct dehydroxylation path to form toluene and the hydrogenation path of m-cresol to form 3-methylcyclohexanone over the Ru(0001) surface in Figure 15, we can see that the overall energy barrier for the hydrodeoxygenation path is about 134 kJ/mol lower than the ring hydrogenation path. This is in agreement with the experimentally observed higher selectivity to toluene than to 3-methylcyclohexanone. However, as shown above, the adsorbed OH\* is difficult to remove from the surface with an energy barrier of 128 kJ/mol. Rather, it is more readily dehydrogenated to O\* with a moderate energy barrier (75 kJ/mol) and a negative reaction energy (-70 kJ/mol), as shown in Figure S2. Thus, we anticipate that the Ru(0001) surface may be covered by OH\* or O\* under the reaction conditions, which may influence the dehydroxylation and the hydrogenation of m-cresol over Ru(0001) surface. While the coverage of the surface species is not exactly known, we have investigated the dehydroxylation and ring hydrogenation paths of m-cresol over the Ru(0001) surface with an arbitrary coverage of

 6/16 ML O\*, to illustrate the effects of coverage. As shown in Figure S3-S5, the energy barrier for the dehydroxylation of m-cresol towards toluene increases from 98 kJ/mol over the clean Ru(0001) surface to 116 kJ/mol for a 6/16 ML O\*-covered Ru(0001) surface. By contrast, the overall energy barrier for the hydrogenation of m-cresol to 3-methylcyclohexanone (in reference to Cre\*+4H\*) decreases from 224 kJ/mol over the clean Ru(0001) to 145 kJ/mol over the O\*-partially covered Ru(0001) surface, as shown in Figure S3. However, even on an O\*-partially covered Ru(0001) surface, the energy barrier for the dehydroxylation path is still about 30 kJ/mol lower than the ring hydrogenation path, which keeps the same trends predicted on a clean Ru(0001) surface.



**Figure 15.** Energy diagrams for the hydrogenation of m-cresol to form 3-methylcyclohexanone (red) and the hydrodeoxygenation of m-cresol to form toluene through the direct dehydroxylation (blue) over the Ru(0001) surface.

Significant amounts of  $CH_4$  and other  $C_2$ - $C_5$  hydrocarbons are observed in the products of the HDO of m-cresol over Ru catalysts. These  $CH_4$  and  $C_2$ - $C_5$  hydrocarbons

in the products are formed by C-C bond breaking on the metal surface. Such C-C bond breaking of hydrocarbons on metal catalysts to form short chain hydrocarbons always proceeds via intermediates that are formed by activating several C-H bonds. 49 The study of the decomposition of benzene on Pt(111) surface by Tsai et al.<sup>50</sup> shows that the decomposition of benzene starts from the C-H bond breaking. Similarly, Weststrate et al.<sup>51</sup> studied the decomposition of benzene on Ir(111) and suggested that two possible benzene decomposition mechanisms are possible. In the first mechanism, about one third of the adsorbed benzene decomposes via C-C bond-breaking, forming six CH species, while the other two-thirds of the adsorbed benzene decomposes via C-H fragmentation, forming  $C_6H_v$  (y<6), which then further decomposes to  $C_xH_v$  (x<6) and CH species. Thus, we believe that in our case, the unsaturated surface species C<sub>7</sub>H<sub>7</sub>\* formed from the dehydroxylation of m-cresol is an intermediate that continues undergoing C-C bond breaking to form products such as CH<sub>4</sub> and C<sub>2</sub>-C<sub>5</sub> hydrocarbons. This reaction proceeds by either further activating C-H bond to generate  $C_7H_y$  ( y < 7 ) species or cleaving C-C bonds to form  $C_xH_y$  species (x<7, y<7) and CH species, similar to the benzene decomposition on Ir(111) surface. <sup>51</sup> In this case, the C<sub>x</sub>H<sub>y</sub> species and CH species can be hydrogenated to form CH<sub>4</sub> and C<sub>2</sub>-C<sub>5</sub> hydrocarbons. However, the detailed investigation of the pathways and the energetics for the C-C bond breaking of  $C_7H_7^*$  towards  $CH_4$  and  $C_2$ - $C_5$  hydrocarbons are beyond the scope of this paper.

As shown earlier, the HDO of m-cresol over Pt(111) proceeds through the tautomerization-hydrogenation-dehydration mechanism, in which the partially unsaturated hydrocarbon surface species  $C_7H_7^*$  is not formed. Thus, there are no C-C bond breaking products formed during HDO of m-cresol over the Pt(111) surface. Hence,

the C-C bond breaking products  $CH_4$  and  $C_2$ - $C_5$  hydrocarbons in the HDO of m-cresol experimentally observed only over the Ru catalyst, but not over Pt is an additional support to the theoretical analysis developed to explain the opposing behavior of the two metals.

As discussed above, the OH\* (or more likely O\*) may build up on the Ru(0001) surface and partially block active sites. The C-C bond breaking of the unsaturated surface species  $C_7H_7^*$  on Ru(0001) surface will generate  $C_xH_y$  (x<7, y<7) and CH species, which may also partially cover the surface. These may be the main reasons for the experimental observation that the Ru/SiO<sub>2</sub> catalyst is much less active than Pt/SiO<sub>2</sub>.

# 4. Conclusions

We have investigated the hydrodeoxygenation of m-cresol over SiO<sub>2</sub>-supported Pt and Ru catalysts and found different product distributions. Over Pt/SiO<sub>2</sub> catalysts, the hydrogenation product 3-methylcyclohexanone is dominant and much more abundant than the deoxygenation product, toluene. By contrast, over Ru/SiO<sub>2</sub>, toluene is favored over 3-methylcyclohexanone. In addition, significant amounts of C-C bond breaking products (C<sub>1</sub>-C<sub>5</sub> hydrocarbons) are generated over Ru/SiO<sub>2</sub>, but were not present over Pt/SiO<sub>2</sub>.

Density functional theory (DFT) calculations were conducted to understand the mechanisms of the hydrodeoxygenation of m-cresol over Pt and Ru catalysts and determine how the nature of the metal influences the product selectivity. It was found that the direct dehydroxylation of m-cresol over Pt(111) is unfavorable. A more favorable path for the hydrodeoxygenation of m-cresol over Pt(111) involves a keto tautomer (KetCO)

of m-cresol, which can be hydrogenated at the carbonyl group, and following dehydration, form the deoxygenation product toluene. In parallel, the hydrogenation of this keto tautomer at the carbon ring leads to the experimentally observed hydrogenation product, 3-methylcyclohexanone. The higher energy barrier for the deoxygenation path compared to the hydrogenation path is in agreement with the experimental observation that over the  $Pt/SiO_2$  catalyst the selectivity to 3-methylcyclohexanone is higher than that to toluene.

By contrast, over Ru(0001), the hydrogenation of the carbonyl group of the keto tautomer KetCO is more difficult than over Pt(111) due to the stronger oxophilicity of Ru, which leads to a high energy barrier for the tautomerization / hydrogenation / dehydration path. However, the strong oxophilicity of Ru facilitates the direct dehydroxylation of m-cresol with much lower energy barier and more exothermic reaction energy. Over the Ru(0001) surface, the favorable path for hydrodeoxygenation of m-cresol proceeds via direct dehydroxylation. The lower energy barrier for the deoxygenation path than the hydrogenation path over Ru(0001) is in agreement with the experimental observation that the selectivity to toluene is greatly enhanced over the Ru/SiO<sub>2</sub> catalyst.

The direct dehydroxylation of m-cresol over the Ru(0001) surface forms an unsaturated hydrocarbon surface species  $C_7H_7^*$ , which can be an intermediate for the production of C-C bond breaking products CH<sub>4</sub> and C<sub>2</sub>-C<sub>5</sub> hydrocarbons over Ru/SiO<sub>2</sub>. The  $C_7H_7^*$  intermediate is not formed over Pt(111), and thus no C-C bond breaking products are formed, which is also in good agreement with the experiments.

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## **Supporting Information Available**

The sequential hydrogenation of the keto tautomer of m-cresol KetCO over Pt(111)

and Ru(0001) surfaces. The paths for the dehydroxylation and hydrogenation of m-cresol

over 6/16 ML O\* covered Ru(0001) surface. This information is available free of charge

via the Internet at http://pubs.acs.org/.

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<b>Table 1.</b> Characteristics of the P	<b>le 1.</b> Characteristics of the Pt/SiO <sub>2</sub> and Ru/SiO <sub>2</sub> catalysts.			
	Pt/SiO <sub>2</sub>	Ru/SiO <sub>2</sub>		
Metal loading	1 wt. %	9.4 wt. %		
$d_p$	3.5 nm	5.2 nm		
Metal Dispersion	0.3	0.25		

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	Pt/SiO <sub>2</sub>	Ru/SiO <sub>2</sub>			
W/F (gcat.hr/mol)	4.0	35.3			
Conversion (%)	7.2	4.5			
TOF (min <sup>-1</sup> )	19	0.1			
Selectivity (%)					
3-methylcyclohexanone	60.2	7.4			
3-methylcyclohexanol	6.5	-			
Toluene	33.3	38.5			
C <sub>2</sub> -C <sub>5</sub> hydrocarbon	-	10.7			

**Table 2.** Product distributions for the HDO of m-cresol over  $Pt/SiO_2$  and  $Ru/SiO_2$  catalysts.

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**Table 3.** Adsorption energies (*kJ/mol*) of reactant, products, and close-shell intermediates in the hydrodeoxygenation process of m-cresol on Pt(111) and Ru(0001) surfaces with vdW corrections. KetCO is the keto tautomer of m-cresol, and KetHOH is the intermediate formed by hydrogenation of KetCO tautomer at the carbonyl group. Free adsorption energies  $\Delta G$  were calculated at 300 °C and 1 atm.

	Pt(111)		Ru(0001)	
	ΔΕ	ΔG	ΔΕ	ΔG
m-cresol	-176	-50	-239	-130
KetCO	-208	-83	-301	-185
3-methylcyclohexanone	-116	-5	-165	-63
Toluene	-170	-44	-225	-121
Н	-38	-	-48	-
H2O	-37	-	-47	-
KetHOH	-232	-85	-242	-101

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**Figure 1.** Different mechanisms proposed for the HDO reaction of phenolic compounds with m-cresol as an example. (Left) DDO and HYD mechanisms <sup>14-17</sup>; (right) mechanism involving a keto tautomer <sup>2,3</sup>.



**Figure 2.** TEM of 9.4 wt.% Ru/SiO<sub>2</sub> after calcination at 400 °C in air, reduction at 400 °C by  $H_2$  and passivation at room temperature.



**Figure 3**. Conversion and yields of products of feeds of 3-methylcyclohexanone (*left*) and 3-methylcyclohexanol (*right*) over Ru/SiO<sub>2</sub> as a function of W/F at 300 °C with H<sub>2</sub> at the pressure of 1 atm.



Figure 4. DFT optimized structures of m-cresol and its two keto tautomers in gas phase, and on the Pt(111)





**Figure 5.** DFT optimized structures for reactant, transition state, and product (tilted) in the direct dehydroxylation of m-cresol over the Pt(111) surface.



**Figure 6.** DFT optimized structures for reactant, transition state and product in the metal assisted tautomerization reactions of m-cresol over Pt(111) surface (top) and Ru(0001) surface (bottom). The energies listed are in reference to the reactant.



Figure 7. DFT optimized structures for the intermediates, transition state, and product in the step-wise hydrogenation of KetCO at the ring carbons over the Pt(111) surface.



**Figure 8**. Energy diagrams for the hydrogenation of m-cresol to form 3-methylcyclohexanone (red) and the hydrodeoxygenation of m-cresol to form toluene (blue) through the keto tautomer KetCO over the Pt(111) surface.



**Figure 9**. DFT optimized structures for the reactant, transition state and product over a Pt(111) surface in the reaction of (A) hydrogenation of KetCO at the carbonyl oxygen; (B) continuing hydrogenation of KetCO at the carbonyl carbon; (C) dehydration of the KetCHOH intermediate formed from hydrogenation of KetCO.





Figure 10. DFT optimized structures for the intermediates, transition state, and product in the step-wise hydrogenation of KetCO at the ring carbons over Ru(0001).



Figure 11. Energy diagrams for the hydrogenation of m-cresol to form 3-methylcyclohexanone (red) and the hydrodeoxygenation of m-cresol to form toluene (blue) through the keto tautomer KetCO over Ru(0001) surface.



**Figure 12**. DFT optimized structures for the reactant, transition state and product state over the Ru(0001) surface in the reaction of (A) hydrogenation of KetCO at the carbonyl oxygen; (B) continuing hydrogenation of KetCO at the carbonyl carbon; (C) dehydration of KetCOH intermediate formed from hydrogenation of KetCO.





**Figure 13**. DFT optimized structures for the reactant, transition state and product state over Ru(0001) surface in the reaction of (A) direct dehydroxylation of m-cresol; (B) hydrogenation of  $C_7H_7^*$  radical intermediate that is formed via dehydroxylation of m-cresol; (C) hydrogenation of OH\* that is formed via dehydroxylation of m-cresol.



Figure 14. Correlation between the intrinsic energy barrier for the direct dehydroxylation of m-cresol on different metal surfaces and the adsorption energies of the atomic oxygen on these metal surfaces.



**Figure 15.** Energy diagrams for the hydrogenation of m-cresol to form 3-methylcyclohexanone (red) and the hydrodeoxygenation of m-cresol to form toluene through the direct dehydroxylation (blue) over the Ru(0001) surface.