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Controlling phenolic hydrodeoxygenation by tailoring metal –O bond strength via specific catalyst metal type and particle size selection



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ABSTRACT

Experimental and theoretical studies of hydrodeoxygenation (HDO) of *m*-cresol show that on metals of low oxophilicity, such as Pt or Pd, the direct C–O bond cleavage is not possible. Therefore, HDO requires an indirect pathway via tautomerization. In contrast, on metals of higher oxophilicity, such as Ru or Rh, the direct C–O bond cleavage is possible and toluene can be directly obtained from *m*-cresol. These studies show that the HDO activity correlates directly with the metal oxophilicity, which in turn depends on the position of the d-band center relative to the Fermi level. This catalytic descriptor depends on (1) the type of metal and (2) the extent of coordination of the metal atoms. The present contribution investigates the effect of the second factor. It is demonstrated that a Rh/SiO₂ catalyst with small particles (low-coordination sites) is more active for HDO than one with larger particles (high-coordination sites). At the same time, the low coordination site is more prone to deactivation and loss of HDO selectivity. These experimental results are combined with the density functional theory calculations, which show that the energy barrier for direct C–O bond cleavage is lower on a step site than on a terrace site. At the same time, it is shown that a step site requires a higher energy barrier to remove adsorbed molecular fragments to regenerate the activity than a terrace site, which explains the faster deactivation rate observed on catalysts with small more defective metal clusters.

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1. Introduction

The lignin-derived phenolic compounds are among the main components in pyrolysis bio-oil. For example, the vapors evolved during torrefaction of red oak contain about 19% phenolics (on a dry basis) [2]. The oxygen functionalities in phenolic compounds, usually in the form of hydroxy–OH or methoxy–OCH₃, make them reactive for many different C–C bond formation chemistries such as alkylation, hydroxyalkylation, acylation [3–5], and so forth to create longer chain molecules that fit into the fuel pool. However,

after the C–C bond forming step, these oxygen functionalities still remain on the aromatic ring, and it is necessary to perform hydrodeoxygenation (HDO) chemistry to remove oxygen and create hydrocarbon fuels. This work focuses on the removal of hydroxy–OH functionality, with *m*-cresol as the model compound, because it is one of the dominant functionalities in biomass-derived compounds.

The HDO reaction of phenolic compounds has been extensively studied and reported in the literature over different metals and bimetallic alloys [6–10], different supports [11–13], or in cooperation with an acidic function [14–21]. Understanding the reaction mechanisms and finding relationships between the observed catalytic behavior and the catalyst structure is of crucial significance for optimizing catalyst design and selection.

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In our previous studies, we have shown that the oxophilicity of the metal catalysts, reflecting the metal–O bond strength, is a crucial descriptor of their HDO activity [22]. In a series of studies on the HDO of *m*-cresol and phenol as the model compounds, we have compared the reactivity and prevalent mechanisms over different metals, including monometallic (Pt, Pd, Ru, Fe, and Ni) and bimetallic catalysts supported on inert SiO₂ [1,22–24] or more oxophilic supports [12]. In particular, SiO₂ is an inert support with minimum participation in the reaction, which has allowed us to focus on the catalytic behavior of the metals.

In this contribution, honoring Prof. Francois Gault, we analyze the observed trends with the oxophilicity of the metals and present new results on the effect of extent of metal atom coordination, which can be controlled by varying the metal cluster size, which in turn affects oxophilicity, and consequently the HDO activity. Throughout his illustrious career, Prof. Gault called attention to the dramatic changes in selectivity of hydrocarbon conversion (e.g., hydrogenolysis and isomerization) over metal catalysts as the particle size changes. He recognized that the changes commonly observed in product selectivity with varying particle size can be traced to changes in reaction mechanisms, which in turn are related to the number of low-coordination (corner and edge) atoms relative to high-coordination (face or terrace) atoms [25–29]. Here, we are using these concepts to interpret changes in HDO reaction mechanism and selectivity changes for the conversion of phenolics on different metal catalysts.

2. HDO of *m*-cresol on different types of metal

As depicted in Fig. 1, when *m*-cresol is converted in the presence of H₂ over different metal catalysts, two types of products are typically observed: (1) hydrogenation products (3-methylcyclohexanone and 3-methylcyclohexanol) and (2) HDO products (toluene [TOL], methylcyclohexane, and 3-methylcyclohexene). In principle, TOL could be produced via two different pathways: (1) hydrogenation of *m*-cresol to 3-methylcyclohexanol, followed by dehydration to 3-methylcyclohexene and further dehydrogenation to TOL, and (2) direct HDO from *m*-cresol.

2.1. HDO of *m*-cresol over Pt catalyst

In a detailed kinetic study conducted with a Pt/SiO₂ catalyst [1,30], we showed that pathway (1) only occurs to a

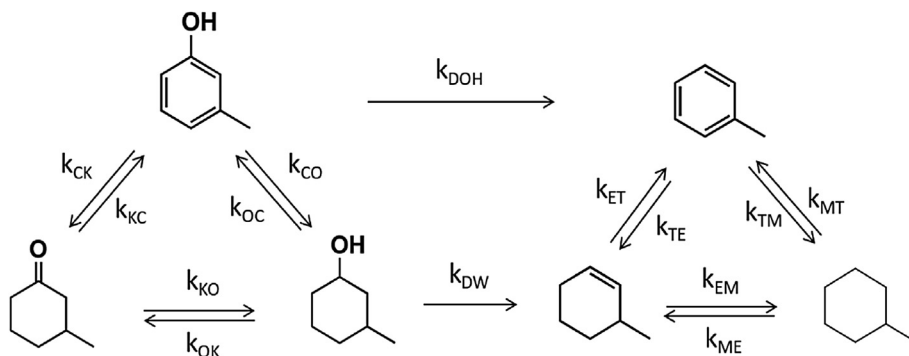


Fig. 1. Reaction pathway for HDO of *m*-cresol (modified with permission from Ref. [1]).

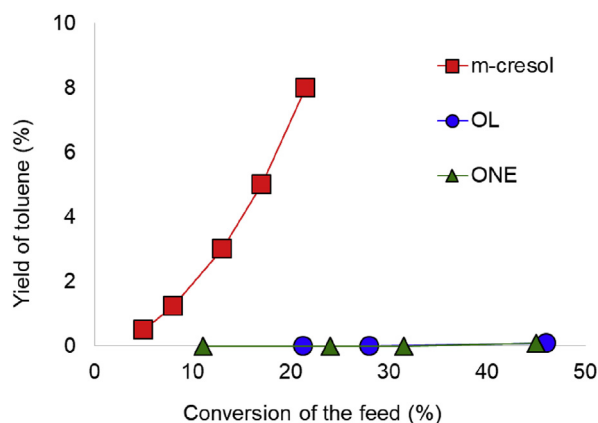


Fig. 2. The yield of TOL vs conversion of feed over Pt/SiO₂ at 300 °C with different feeds including *m*-cresol, 3-methylcyclohexanol (OL) and 3-methylcyclohexanone (ONE) (modified with permission from Ref. [1]).

very low extent due to the low acidity of the SiO₂ support. As shown in Fig. 2, the yield of TOL increases with increasing *m*-cresol conversion but when 3-methylcyclohexanol or 3-methylcyclohexanone was used as feed, the yield of TOL remains almost zero in all cases, even at high feed conversions, which shows that TOL is not obtained from the alcohol or the saturated ketone.

It was also clearly demonstrated that TOL was not derived from methylcyclohexene either. In fact, as shown in Table 1, at low conversions over Pt/SiO₂, methylcyclohexene results in a TOL/methylcyclohexane ratio of about unity. This ratio gradually increases to its equilibrium value (~11 at 300 °C) with feed conversion. That is, far from equilibrium, the methylcyclohexene to TOL and methylcyclohexene to methylcyclohexane reactions occur at similar rates, but as conversion increases, the secondary methylcyclohexane to TOL reaction drives the TOL/methylcyclohexane ratio close to the equilibrium of 11. This was indeed the trend observed when the feed was either 3-methylcyclohexanol or 3-methylcyclohexanone over the Pt/SiO₂ catalyst.

As shown in Fig. 3, when 3-methylcyclohexanol or 3-methylcyclohexanone was fed over the Pt/SiO₂ catalyst, the TOL/methylcyclohexane ratio was near unity at low feed conversion and only increased to near 10–11 as the feed conversion increased. This is reasonable because 3-

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