



Mechanistic analysis of the role of metal oxophilicity in the hydrodeoxygenation of anisole



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ABSTRACT

A combined experimental and theoretical comparative study of the hydrodeoxygenation (HDO) of anisole was conducted over Pt, Ru, and Fe metals. In the experimental part, an inert silica support was used to directly compare the catalytic activity and selectivity of the three metals at 375 °C under H₂ flow at atmospheric pressure. In parallel, for density functional theory (DFT) calculations the close-packed Pt(111), Ru(0001), and Fe(110) surfaces were employed to compare the possible mechanisms on these metals. It was observed that over Pt/SiO₂ and Ru/SiO₂ catalysts, both phenol and benzene were the major products in a phenol/benzene ratio that decreased with the level of conversion. By contrast, over the Fe/SiO₂ catalyst, no phenol formation was detected, even at low conversions. The DFT results show that over all the three metal surfaces the dehydrogenation at the –CH₃ side group occurs before the C–O bond breaking. This removal of H atoms from the –CH₃ group facilitates the activation of the aliphatic C_{alkyl}–O bond. Therefore, it can be concluded that a common intermediate for the three metals is a surface phenoxy and the significant differences between the three metals are related to the reactivity of this surface phenoxy. That is, over Pt(111) and Ru(0001) the phenoxy intermediate is hydrogenated to phenol, which in turn, can undergo further HDO to form benzene. This result is in agreement with the experiments over Pt/SiO₂ and Ru/SiO₂ catalysts. Over these catalysts, both phenol and benzene are major products, with the selectivity to benzene increasing with conversion at the expense of phenol. In contrast, over the Fe(110) surface, the strong metal oxophilicity makes the direct cleavage of the C–O bond in the surface phenoxy easier than hydrogenation to phenol. Thus, it is predicted that phenol is not formed over iron, but only benzene should be observed as HDO product at all conversion levels, which is also in agreement with the experimental observations.

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1. Introduction

The development of catalysts for the catalytic hydrodeoxygenation (HDO) of lignin-derived phenolic compounds is a very important step in the upgrading of biomass-derived streams to fuels and chemicals. Lignin-derived phenolic compounds include guaiacol, cresol, vanillin, eugenol, syringol, and others, which contain both –OH and –OCH₃ functional groups attached directly to the aromatic ring [1–9]. Thus the hydrodeoxygenation of these phenolic compounds requires catalysts that can break the aromatic C–O bond to remove the –OH or –OCH₃ groups and form C–H bonds instead. While different catalysts including metals [2–11], metal sulfides [12–14], metal phosphides [15–19] and metal carbides

[20–22] have been investigated in the HDO process, the supported metal catalysts such as Pt, Pd, Ru and Fe have been shown to be promising for the hydrodeoxygenation reactions of phenolic compounds [2–10]. Various aspects of the metal catalysts such as the incorporation of bifunctionality [23–31], use of bimetallics [32–38], and metal-support effects [39–42] have been extensively studied. However, to determine how the chemical role of the different metals leads to different reaction pathways further investigation is needed.

Indeed, it is clear that different metals show different activity and selectivity for HDO reactions. Our previous experiments of HDO of m-cresol over SiO₂-supported Pt, Ru, Ni, Fe and Ni-Fe catalysts at 300 °C showed that the hydrogenation products 3-methylcyclohexanone and 3-methylcyclohexanol are the major products over Pt and Ni catalysts, while the selectivity to the HDO product (toluene) is significantly enhanced over oxophilic

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metals, such as Ru, Fe, and Ni-Fe [5,6,9]. In a recent study, to understand how different metal catalysts lead to different product distributions in the HDO of *m*-cresol, we carried out DFT calculations and explored the reaction paths of *m*-cresol conversion on Pt(111) and Ru(0001) surfaces [9]. We found that direct deoxygenation (DDO) is unfavorable over Pt(111). On this metal, the reaction is thought to proceed through a keto tautomer intermediate, which undergoes hydrogenation of the carbonyl group followed by dehydration to form toluene and water. This HDO path occurs in parallel with the hydrogenation of the ring, which leads to 3-methylcyclohexanone and 3-methylcyclohexanol as major products. By contrast, over the more oxophilic Ru(0001) surface, the DDO pathway becomes more favorable than the tautomerization route. Moreover, our DFT calculations demonstrated a general correlation between the energy barrier for direct deoxygenation and the oxophilicity of metal surfaces, as assessed by the binding energy of O to the metal surface. Similar trends have been reported by Hensley et al. [43] by comparing the paths of HDO of phenol over Pd(111) and Fe(110) surfaces. They found that the direct C–O cleavage is not favorable over Pd(111) surface but favorable over the more oxophilic Fe(110) surface.

As opposed to the HDO of *m*-cresol and phenol, which requires the removal of –OH group, the HDO of anisole or guaiacol requires the removal of an –OCH₃ group, which might proceed through different mechanisms since their molecular structures comprise two kinds of C–O bonds: the aromatic C_{aryl}–O bond and the aliphatic C_{alkyl}–O bond. The HDO of guaiacol has been investigated over different metal catalysts, such as Pd [44,45], Pt [46–49], Ru [50–52], and Fe [44,53–55]. The product distribution seems to vary with the specific catalyst. For example, working with MgO-supported Pt catalysts, Gates et al. [48] found that catechol, phenol, and cyclohexanone are dominant products at low conversion (6%), with selectivities of 25%, 51%, and 17%, respectively. This result would indicate that if both are primary products, phenol and catechol could be produced via demethoxylation and demethylation, respectively. Also, on a Pt/C catalyst, Gao et al. [49] found that guaiacol yielded 40% phenol and 10% catechol. In this case, it was suggested that phenol production could follow two alternative pathways, direct demethoxylation and sequential demethylation/dehydration via catechol. Similarly, Boonyasuwat et al. [50] investigated the HDO of guaiacol over Ru catalysts on different supports, including C, SiO₂, Al₂O₃, and TiO₂. They found that, similar to the Pt catalyst, Ru/C, Ru/SiO₂ and Ru/Al₂O₃ produced catechol and phenol as major products. However, on Ru/TiO₂ catalyst, the deoxygenation activity was significantly enhanced and catechol quickly converted, leaving phenol as the only major product. This unique behavior of Ru/TiO₂ is ascribed to the creation of synergic sites between Ru and TiO₂ at the metal/support interface [56,57].

In parallel, DFT calculations have been used to explore the mechanisms of guaiacol conversion on Pt(111) and Ru(0001) surfaces. For example, Chiu et al. [51] and later Lu et al. [52] have independently explored the reaction pathways of guaiacol on Ru(0001). Both groups found that the most plausible path starts with the removal of H from the –OH group in the guaiacol molecule (HO-Ph-OCH₃) to form the O^{*}-Ph-OCH₃ intermediate, which then goes through sequential dehydrogenation steps of the –CH₃ group to form an O^{*}-Ph-OCH^{*} intermediate. Then, this O^{*}-Ph-OCH^{*} species is able to cleave the aliphatic C_{alkyl}–O bond, forming a surface catecholate (O^{*}-Ph-O^{*}). Subsequent hydrogenation of catecholate yields catechol, which in a second deoxygenation step can form phenol. These calculations agree well with the observed experimental results. Similar paths have been obtained by Lee et al. [47] for the conversion of guaiacol over the Pt(111) surface. They also have concluded that dehydrogenation of the –OH and –CH₃ groups occurs before the cleavage of the C–O bond.

The HDO of guaiacol over Fe catalysts has been studied by Olcese et al. [53]. They found that, similar to the case of Pt and Ru catalysts, Fe/SiO₂ produces phenol as the main product. However, in contrast to Pt and Ru, on which catechol is observed as an intermediate product, on Fe catechol is barely detected. Interestingly, it was observed that selectivity to catechol increased when co-feeding H₂O. That is, the near absence of catechol in the products over Fe may be ascribed to the fast conversion of catechol on clean Fe, or alternatively, it can be due to the high oxophilic of Fe, which may facilitate the direct cleavage of the aromatic C–O bond, preventing the evolution of catechol to the gas phase. In that case, the inhibition of this direct cleavage pathway by water would explain the observed increase in catechol selectivity.

Anisole is an attractive model compound since it only has the –OCH₃ group pendant on the aromatic ring. Our group has previously studied the HDO of anisole over Pt/SiO₂ as well as bifunctional Pt/H-Beta catalysts [58]. We found that over a Pt/SiO₂ catalyst, phenol and CH₄ are the major products at low space time (W/F), but at higher W/F the yield of benzene increased at the expenses of phenol. Thus, we suggested that over Pt demethylation to phenol is the primary reaction, while benzene is produced by secondary HDO of phenol, rather than directly from anisole. Similar results were observed by Pichaikaran et al. [10] in the study of HDO of anisole over aluminosilicate-supported Ru and Ni catalysts. They found that phenol was the major product at low conversions.

In summary, while a number of experimental efforts have been reported about HDO of methoxy-aromatics, such as anisole and guaiacol, over different metals, the mechanism for the removal of the aromatic –OCH₃ groups is not clear, as both possible paths, demethoxylation and demethylation, have been proposed. Also, the influence of the chemical nature of the metal catalyst, such as its oxophilicity, on the reaction pathways and hence the product distribution is not completely established yet. Therefore, in this work, we have carried out experiments probing HDO of anisole over Pt, Ru and Fe catalysts, each one displaying a different degree of oxophilicity. The experiments have been combined with the DFT calculations to elucidate the mechanisms of the HDO of anisole over the three metal surfaces with the goal of determining the role of metal oxophilicity on reaction mechanisms.

2. Experimental

2.1. Catalyst preparation and characterization

Three silica-supported catalysts, Pt/SiO₂ (1 wt.%), Ru/SiO₂ (9.4 wt.%) and Fe/SiO₂ (5 wt.%) catalysts were prepared by incipient wetness impregnation of the SiO₂ support (HiSil 210, PPG, S_{BET} = 135 m²/g) with an aqueous solution of Pt(IV) chloride hydrate and Ru(III) chloride hydrate and with an aqueous solution of Fe(III) nitrate hydrate, respectively, as described in previous work [5,6,9,59]. The Pt/Fe₂O₃ (1 wt.%) catalyst was prepared by incipient wetness impregnation of Fe₂O₃ (S_{BET} = 29.5 m²/g) with the aqueous solution of Pt(IV) chloride hydrate. After impregnation, the catalysts were dried at 120 °C for 12 h and calcined at 500 °C for 4 h. Before carrying out the reactions, the samples were pelletized, crushed, and sieved to 250–420 μm size range (Mesh No. 40–60). Transmission Electron Microscopy (TEM) images of catalyst samples were obtained in a JEOL 2000FX system. The samples were prepared by dispersing the catalyst powder in isopropanol, sonicating for 30 s and placing one drop of solution on holey-carbon coated Cu grids followed by drying. TEM images of the Pt/SiO₂, Ru/SiO₂ and Fe/SiO₂ samples have been shown in previous work, indicating average metal particle sizes of about 3.5, 5.2, and 23.4 nm, respectively, as summarized in Table 1 [5,6,9,59]. These particle sizes suggest the flat planes dominate in all the three metal

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