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 is 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.

Keywords

hydrodeoxygenation, HDO, anisole, platinum, ruthenium, iron, oxophilicity, density functional theory, DFT, phenolics

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 -OCH_3 functional groups attached directly to the aromatic ring [1-9]. Thus the hydrodeoxygenation of these phenolic compounds require catalysts that can break the aromatic C-O bond to remove the -OH or -OCH_3 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 SiO_2 -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 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 to 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,[46-50] Ru,[51-53] and Fe [44, 54-56]. 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. [51] 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 [57, 58].

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.[52] and later Lu et al. [53] 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-OCH_3) to form the $\text{O}^*\text{-Ph-OCH}_3$ intermediate, which then goes through sequential dehydrogenation steps of the $-\text{CH}_3$ group to form an $\text{O}^*\text{-Ph-OCH}^*$ intermediate. Then, this $\text{O}^*\text{-Ph-OCH}^*$ species is able to cleave the aliphatic $\text{C}_{\text{alkyl}}\text{-O}$ bond, forming a surface catecholate ($\text{O}^*\text{-Ph-O}^*$). 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. [50] for the conversion of guaiacol over the Pt(111) surface. They also have concluded that dehydrogenation of the –OH and $-\text{CH}_3$ groups occurs before the cleavage of the C-O bond.

The HDO of guaiacol over Fe catalysts has been studied by Olcese et al. [54] They found that, similar to the case of Pt and Ru catalysts, Fe/SiO_2 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 H_2O . 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 $-\text{OCH}_3$ group pendant on the aromatic ring. Our group has previously studied the HDO of anisole over Pt/SiO_2 as well as bifunctional Pt/H-Beta catalysts [59]. We found that over a Pt/SiO_2 catalyst, phenol and CH_4 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 $-\text{OCH}_3$ 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, $S_{\text{BET}} = 135 \text{ m}^2/\text{g}$) with an aqueous solution of Pt(IV) chloride hydrate, Ru(III) chloride hydrate and with an aqueous solution of Fe(III) nitrate hydrate, respectively, as described in previous work [5, 6, 9, 60]. The Pt/Fe₂O₃ (1 wt.%) catalyst was prepared by incipient wetness impregnation of Fe₂O₃ ($S_{\text{BET}} = 29.5 \text{ m}^2/\text{g}$) 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 seconds 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, 60]. These particle sizes suggest the flat planes dominate in all the three metal particles and the particle size effects are thus minimized, and the surface models can thus be used in the following DFT calculations.[61] A TEM image of the Pt/Fe₂O₃ catalyst is shown and discussed below. Thermogravimetric analysis (TGA) of the Pt/Fe₂O₃ catalyst sample was carried out in a H₂:Ar (80:20) gas mixture with a total flow rate of 100 cm³/min and a linear temperature increase of 10 °C/min.

2.2 Reaction Conditions

The HDO activity and product distribution from conversion of anisole over the three catalysts were measured in a fixed-bed quartz-tube reactor (6 mm outer diameter) under H₂ flow at atmospheric pressure. The flow reaction system is equipped with a mass flow controller and a syringe pump for the continuous injection of anisole. Pelletized catalysts were packed in the reactor between two layers of glass beads and quartz wool to improve flow and temperature uniformity. The catalysts were pre-reduced in flowing H₂ (60 ml/min) for 1 h at 400 °C for Pt/SiO₂ and Ru/SiO₂ while at 450 °C for Fe/SiO₂ and Pt/Fe₂O₃. After reduction, the reaction was conducted at 375 °C under the same H₂ flow rate. A 0.3 ml/h flow of liquid anisole was fed continuously from the syringe pump and vaporized into the H₂ stream. Space time (W/F), defined as the ratio of catalyst mass (W) to mass flow rate (F), was adjusted for different runs to investigate the reaction kinetics. In each run at a different W/F, the products were collected and analyzed after 15 min on stream, which is long enough to allow steady state to be established, and also short enough to minimize the effect of catalyst deactivation. The reaction products were analyzed and quantified by online gas chromatography, using an HP-5 column (30 m, 0.25 μm) and a flame ionization detector (FID). All lines were kept heated at 250 °C to avoid product condensation. The carbon selectivity for each product was calculated according to the expression:

$$\text{Selectivity (\%)} = \text{moles of C in the target product} / \text{moles of C in all the products}$$

where the moles of C in each product are calculated as the number of C atoms in the particular product molecule multiplied by the moles of this product. Methane formed from the side group of anisole was not counted in the analysis of selectivity. When the total moles of methane in the product exceed the sum of phenol and benzene moles, it can be concluded that this additional methane arises from cracking of some of the aromatic rings. Therefore the “methane from cracking” value was obtained by subtracting the moles of phenol + benzene in the products from the total moles of methane.

2.3 Density Functional Theory Calculations

The calculations were carried out using periodic plane-wave gradient-corrected density functional theory methods implemented in the Vienna ab initio Simulation Package (VASP)[62-65]. The PBE functional was used to calculate the exchange correlation energy within the

generalized gradient approximation (GGA) [66]. The DFT-D3 method was used to account for van der Waals (vdW) interactions [67]. The projector augmented wave method (PAW) which uses the exact shape of the valence wave functions instead of pseudo-wave functions, was employed to describe the electron-ion interactions [68]. The cutoff energy of 400 eV was applied for the plane-wave basis set to represent valence electrons.

The close-packed 4x4 Pt(111), Ru(0001) and Fe(110) surfaces with four metal layers and 15 Å of vacuum separating the slabs in the z-direction were used to model the Pt and Ru and Fe catalysts. The top two metal layers were allowed to relax during the calculations, whereas the bottom two layers were held fixed to their initial bulk position. The electronic energies were converged within 10^{-6} eV limit. The geometric structures for all of reactants, intermediates and products were optimized until the forces on each atom were below 0.01 eV/Å. A $3\times 3\times 1$ k-point mesh was used to sample the first Brillouin zone [69]. The energies of the adsorbates in vacuum were calculated spin-polarized using an $18\times 18\times 18$ Å unit cell with the Γ only k-point mesh.

Transition state searches were performed using the dimer method[70] with the initial guesses for the transition state structure and the reaction trajectory obtained through the nudged elastic band (NEB) method [71].

The Gibbs free energies for the adsorption of closed-shell species at 375 °C and 1 atm were estimated by including the entropy, which in turn was calculated according to standard thermodynamic procedures [72]. That is, the vibrational entropy was calculated from vibrational frequencies derived from DFT frequency calculations; the translational and rotational entropies of adsorbed species were assumed to be zero. For gas-phase species, the translational and rotational entropies were calculated from statistical thermodynamics [72].

3. Results and Discussion

3.1 Product distribution from anisole conversion over Pt/SiO₂, Ru/SiO₂ and Fe/SiO₂

The product selectivity observed during the conversion of anisole over the Pt/SiO₂, Ru/SiO₂ and Fe/SiO₂ catalysts at 375 °C is summarized in Table 2. Over Pt/SiO₂ at a low conversion of 15%, phenol was the dominant product with 93% selectivity. Benzene was also produced, but at a much lower selectivity (7%). No ring hydrogenation products (e.g. methoxycyclohexanone or methoxycyclohexanol) were observed, since at 375 °C hydrogenation is thermodynamically unfavorable.

Methane, generated from the methoxy side group and/or the hydrogenolysis (ie. cracking) of the aromatic ring, was observed in the products. In contrast, no methanol was observed, which suggests that demethylation rather than demethoxylation is the preferred reaction path of the methoxy group in anisole. In fact, the $\text{CH}_4/(\text{phenol}+\text{benzene})$ molar ratio was calculated to be about 1.0. Since no toluene or other methylated products are observed, this value indicates that, on Pt, CH_4 comes exclusively from the anisole methoxy group rather than cracking of the aromatic ring. A comparable product distribution has been previously reported for the HDO of anisole on Pt [59].

The evolution of products as a function of space-time (W/F) was also investigated on the Pt/SiO₂ catalyst. As shown in Figure 1A, at low conversion, the primary product is clearly phenol, the only product with a non-zero initial derivative with respect to W/F. As conversion increases with W/F, the yield of benzene keeps increasing until finally reaches 100% at the expense of phenol that reaches a maximum at about W/F = 0.05, and finally decreases progressively to zero. Clearly, this trend demonstrates a series $\text{A} \rightarrow \text{B} \rightarrow \text{C}$ reaction such that over the Pt/SiO₂ catalyst anisole first undergoes demethylation to form CH_4 and phenol, which then undergoes the HDO reaction to form benzene and water. It is also clear that the direct demethoxylation of anisole to benzene does not occur over Pt.

Over Ru/SiO₂ catalyst at low conversion (5 %), both phenol and benzene products were observed, as found using Pt/SiO₂. However, even at this low conversion the phenol/benzene ratio on Ru was much lower than that observed on Pt. Similarly, methane rather than methanol was observed in the products on Ru/SiO₂ suggesting demethylation rather than demethoxylation occurs in the HDO of anisole. However, the $\text{CH}_4/\text{aromatics}$ ratio, which is about 22, is much higher than the stoichiometric ratio of 1.0 observed on Pt, indicating that significant cracking of the aromatic rings occurs over Ru/SiO₂. In fact, as shown in Table 2, the selectivity towards methane from cracking (75%) is even higher than the selectivity of phenol and benzene combined (9% and 16%) at 5% conversion. The significant extent of cracking of the aromatic ring is consistent with that previously observed during the HDO of m-cresol over Ru/SiO₂ [9]. As discussed previously in the HDO of m-cresol over Ru/SiO₂, the cracking of the aromatic ring may also lead to lower turnover frequencies over the Ru catalyst (Table 2), as the carbon species generated from cracking can block the metal surface [9]. Figure 1B shows the evolution of products as a function of space-time (W/F) over Ru/SiO₂. It is observed that as anisole

conversion increases the yields of both benzene and phenol increase, but the yield of the latter remains low over the entire range of W/F investigated.

Finally, over the Fe/SiO₂ catalyst the differences versus Pt are even more striking. As shown in Table 2, benzene is the dominant product with a selectivity of 85% at a low anisole conversion (8%). Interestingly, toluene is also formed with the selectivity of 9%. As previously discussed, this product is obtained via transalkylation catalyzed by acid sites resulting from unreduced iron oxide, followed by hydrodeoxygenation on the metal particles. Still no methanol, but rather methane, was observed in the products. The CH₄/aromatics ratio is calculated to be 1.4, indicating about 6% anisole underwent cracking reactions. Remarkably, even at the low conversion of this run, no phenol was observed in the products, which is dramatically different from the cases of Ru and particularly Pt. This result is consistent with the observation that no catechol was observed from guaiacol conversion over Fe/SiO₂ [54].

The corresponding evolution of products from anisole conversion on Fe/SiO₂ as a function of W/F is shown in Figure 1C. It is remarkable that no phenol was observed in the products in the broad anisole conversion range investigated (8-50 %).

Another way to illustrate the differences displayed by a highly oxophilic metal (Fe) and a less-oxophilic metal (Pt) in the HDO of anisole is to follow the change in selectivity as a function of catalyst deactivation over the two metals. Figure 2 summarizes the variation of the relative molar fractions of phenol (P) and benzene (B), calculated as $P/(P+B)$ and $B/(P+B)$, respectively, as a function of time-on-stream over the Pt and Fe catalysts. It is clear that on Pt/SiO₂, as the catalyst deactivates with time-on-stream and the conversion decreases, the molar fraction of benzene decreases and the molar fraction of phenol in turn increases. By contrast, on Fe/SiO₂ the relative molar fraction of benzene remains at 100% and no phenol is observed at any time-on-stream.

Clearly, the absence of phenol suggests that a different mechanism is operative over Fe/SiO₂ from that over Pt/SiO₂ and Ru/SiO₂. As shown in previous temperature programmed reduction (TPR) studies, oxidized Fe/SiO₂ is more difficult to reduce than Pt or Ru catalysts. In fact, it may require temperatures as high as 650 °C to complete the hydrogen uptake. However, XRD shows that partial reduction occurs at 450 °C, and a significant fraction of metallic Fe is formed at these temperatures [60]. The addition of small amounts of Pt, greatly facilitates the reduction of Fe oxide. Therefore, to examine the active sites on metallic Fe, a Pt-doped Fe₂O₃ catalyst was

compared to undoped Fe oxide. The TGA of Fe_2O_3 and $\text{Pt/Fe}_2\text{O}_3$ are shown in Figure 3. It is clear that the reduction of the undoped Fe_2O_3 proceeds in two steps (from Fe_2O_3 to Fe_3O_4 which later converts to metallic Fe). The first step finishes at about 300 °C, while the second finishes at about 550 °C, in agreement with previous studies [73]. It is clear that doping with small amounts of Pt (1%) facilitates the reduction of Fe_2O_3 , shifting the two steps to lower temperatures, as seen before in Ni-Fe and Pd-Fe catalysts [60, 74]. At about 450 °C, the Pt-doped Fe_2O_3 is totally reduced to metallic Fe. This is further confirmed by the TEM images and the selected area electron diffraction (SAED) patterns of $\text{Pt/Fe}_2\text{O}_3$ after reduction, as shown in Figure 4. The TEM images show that Fe_2O_3 , originally displaying a geometric and crystalline shape, adopts a “glassy-like” morphology upon reduction, corresponding to metallic Fe coated with a thin layer of oxide, which is formed upon exposure to air. The SAED patterns of Fe_2O_3 before and after the reduction were compared with the standard diffraction data of metallic Fe and Fe oxides structures, as shown in the Figure S1. The comparison clearly shows that the $\gamma\text{-Fe}_2\text{O}_3$ phase is present in the unreduced sample; but, after reduction, it becomes metallic $\alpha\text{-Fe}$.

The HDO of anisole was then conducted over the $\text{Pt/Fe}_2\text{O}_3$ catalyst. The product distribution, summarized in Table 2, shows that at low conversion (7%), the dominant product is benzene (selectivity 80%) while no phenol is formed. This behavior is typical of the Fe/SiO_2 catalyst rather than Pt. In fact, the only primary product on Pt/SiO_2 is phenol. That is, the dominant active function in $\text{Pt/Fe}_2\text{O}_3$ is iron. More importantly, although Fe/SiO_2 contains both oxide and metallic Fe, the dominant HDO activity is due to metallic Fe. Therefore, the observed differences in product distributions over Pt, Ru and Fe catalysts are due to the different nature of the three metals, rather than differences in oxidation state. In the following sections, we describe the DFT calculations that we have carried out to explore the reaction pathways of the HDO of anisole over Pt, Ru and Fe metal surfaces and explain the different product distributions experimentally observed over the Pt/SiO_2 , Ru/SiO_2 , and Fe/SiO_2 catalysts.

3.2 Adsorption of Anisole on $\text{Pt}(111)$, $\text{Ru}(0001)$ and $\text{Fe}(110)$ surfaces

The energies of different adsorption configurations of the anisole molecule over $\text{Pt}(111)$, $\text{Ru}(0001)$ and $\text{Fe}(110)$ surfaces were calculated and compared as shown in Figure S2. From this analysis it can be concluded that the most favorable adsorption mode on these three surfaces is the ‘bridge 30’ configuration, as shown in Figure 5. In this adsorption mode, anisole binds flat to

four metal (Pt, Ru, or Fe) atoms via the six aromatic C atoms. This mode is similar to those reported for other adsorbed phenolic compounds such as phenol, cresol, and guaiacol on Pt(111), Ru(0001), Fe(110), and other surfaces [9, 43, 50, 52, 53, 75]. The corresponding adsorption energy for anisole on Pt(111) surface is calculated to be -225 kJ/mol (Table 3), which is close to the reported adsorption energy of guaiacol on Pt(111) (-233 kJ/mol) [50]. The adsorption energy of anisole on Ru(0001) is calculated to be -263 kJ/mol, slightly higher than the reported adsorption energy of guaiacol on Ru(0001) (-237 kJ/mol) [52]. This calculated adsorption energy of anisole on Ru(0001) is also higher than the adsorption energy of anisole on Pt(111), indicating a stronger binding of anisole to Ru(0001) than Pt(111). This trend is consistent with the differences in m-cresol adsorption energy between Pt(111) and Ru(0001) surfaces [9]. Finally, the adsorption energy of anisole on Fe(110) surface is calculated to be -232 kJ/mol, slightly higher than that on Pt(111) but lower than that on Ru(0001).

The adsorption energy of atomic oxygen on Pt(111), Ru(0001) and Fe(110) surfaces were also calculated and used as a measurement of the oxophilicity of these three metals. The adsorption energies for O on Pt(111), Ru(0001), and Fe(110) were calculated to be -481 kJ/mol, -650 kJ/mol and -698 kJ/mol respectively (Table 3), indicating that the order of metal oxophilicity is Pt(111) << Ru(0001) < Fe(110).

3.3 Reaction paths for HDO of anisole over Pt(111)

3.3.1 C_{aryl}-O activation of anisole

One might predict that after adsorption on Pt(111) surface, the adsorbed anisole could undergo C_{aryl}-O breaking (demethoxylation) to remove the -OCH₃ and form a phenyl intermediate, which could be successively hydrogenated to benzene. However, this is neither supported by experiments, nor as shown below, by DFT calculations. As shown in Figure 6A, the calculation for this unfavorable path predict that the C_{aryl}-O bond would gradually elongate from 1.35 Å in the reactant to 2.53 Å in the transition state. At the same time, the OCH₃ group would approach the metal surface with the Pt-O distance decreasing from 3.31 Å in the reactant to 2.06 Å in the transition state. This transition state structure is similar to the one we reported previously for the direct dehydroxylation of m-cresol over Pt(111)[9] and, as in that case, the resulting activation energy is predicted to be exceedingly high (258 kJ/mol). The corresponding activation energy for the dehydroxylation of m-cresol that we reported previously was similarly

high (242 kJ/mol)[9] and of the same order as that calculated for guaiacol on Pt(111), 243 kJ/mol [50]. Likewise, the reaction energy for the demethoxylation reaction of anisole over Pt(111) is calculated to be highly endothermic (147 kJ/mol) and similar to the one reported for the demethoxylation of guaiacol (140 kJ/mol) [50]. That is, the exceedingly high barrier and the highly endothermic nature confirm that the direct demethoxylation of anisole is unfavorable over Pt, as deduced from the experimentally observed evolution of products with conversion (Fig. 1.A).

3.3.2 $C_{alkyl}-O$ activation of anisole

We should also consider the possibility that the adsorbed anisole on Pt(111) could undergo demethylation to remove the $-CH_3$ group to form the phenoxy intermediate, which can then form phenol via hydrogenation. Figure 6A shows the reactant, transition state, and product structures for this demethylation reaction. Here, in the transition state, the $C_{alkyl}-O$ bond stretches to 2.11 Å from the original 1.44 Å in the reactant. The corresponding activation energy for this step is predicted to be 200 kJ/mol, slightly higher than the one reported for the demethylation of guaiacol over Pt(111) (181 kJ/mol) [50]. While this energy barrier is about 60 kJ/mol lower than the one for demethoxylation described above, it is still significantly high. Therefore, other optional reaction paths were analyzed, as shown below.

3.3.3 $C-H$ activation of anisole

It has been reported that initial dehydrogenation steps can facilitate the cleavage of C-O and C-C bonds in hydrogenolysis of alcohols, polyols, cyclic ethers and alkanes [76-78]. Thus, we have investigated the possibility that dehydrogenation of anisole at the $-CH_3$ group might be the initiation step. As shown in Figure 6A, one H atom can be removed from the $-CH_3$ group to form adsorbed $-CH_2^*$ and H^* species with a relatively low energy barrier (125 kJ/mol) in comparison to the demethoxylation (258 kJ/mol) and demethylation (200 kJ/mol) pathways described above. The reaction energy is only slightly endothermic (12 kJ/mol), which indicates that this pathway is kinetically and thermodynamically more favorable than the others.

3.3.4 Subsequent dehydrogenations and C-O bond cleavage:

After one H atom was removed from the $-CH_3$ substituent, the $Ph-O-CH_2^*$ species formed

could undergo cleavage of the $C_{\text{aryl}}\text{-O}$ or $C_{\text{alkyl}}\text{-O}$ bonds. However, as shown in Figure 6B, the successive dehydrogenation of the Ph-O-CH_2^* intermediate to form the Ph-O-CH^* has a lower energy barrier and more favorable reaction energy than the direct cleavage of any of the two C-O bonds. Thus, the activation energy for successive dehydrogenation is only 79 kJ/mol, compared to 227 and 90 kJ/mol for the cleavages of the $C_{\text{aryl}}\text{-O}$ and $C_{\text{alkyl}}\text{-O}$ bonds, respectively. This second dehydrogenation step is also about 34 kJ/mol more exothermic than the first dehydrogenation step with an overall reaction energy of -22 kJ/mol. This trend is consistent with the results found for the hydrogenolysis of methyltetrahydrofuran [78]. In that case, removal of a second H atom was found to be easier than removal of the first H atom at the same C. Also, compared to the $C_{\text{alkyl}}\text{-O}$ and $C_{\text{aryl}}\text{-O}$ bond breaking, the dehydrogenation paths of the Ph-O-CH_2^* intermediate is less endothermic, indicating that the second step in the reaction should be a second dehydrogenation to form Ph-O-CH^* . This trend is consistent with results of Lee et al. [50] who found that in the conversion of guaiacol the less saturated is the C of the side group, the easier is the demethylation. This trend also holds for the $C_{\text{aryl}}\text{-O}$ breaking reactions of Ph-O-CH_x ($x=1\sim3$). Thus, the activation energy and reaction energy for the $C_{\text{aryl}}\text{-O}$ breaking of Ph-O-CH^* (150/70 kJ/mol) are lower than for the $C_{\text{aryl}}\text{-O}$ breaking of Ph-O-CH_3 (258/147 kJ/mol) and Ph-O-CH_2^* (227/126 kJ/mol).

As shown in Figure 6C, once the Ph-O-CH^* species has been formed, removal of the last H from the C becomes more difficult with a barrier of 124 kJ/mol and an endothermic reaction energy (32 kJ/mol). This finding is in agreement with DFT calculations of the sequential dehydrogenation of CH_4 over Pt(111), in which the last dehydrogenation step has a higher barrier (120 kJ/mol) than the first three dehydrogenation steps [79]. Nevertheless, the $C_{\text{alkyl}}\text{-O}$ bond can now be easily broken to remove the CH^* group and form the phenoxy intermediate, with an activation energy of only 83 kJ/mol and an exothermic reaction energy of -49 kJ/mol. Thus, this seems to be the most favorable path.

3.3.5 Proposed reaction pathway for HDO of anisole over Pt(111)

From the discussions above, the most plausible path over Pt(111) starts with anisole undergoing two sequential dehydrogenation steps from the $-\text{CH}_3$ substituent to form a Ph-O-CH^* intermediate, which then breaks the $C_{\text{alkyl}}\text{-O}$ bond and forms a phenoxy intermediate. Moreover, comparing the $C_{\text{alkyl}}\text{-O}$ breaking and $C_{\text{aryl}}\text{-O}$ breaking reactions of anisole (Ph-O-CH_3), Ph-O-

CH_2^* and Ph-O-CH^* respectively in Figure 6, we see that the energy barriers for the $\text{C}_{\text{alkyl-O}}$ cleavage are always lower than those for $\text{C}_{\text{aryl-O}}$ cleavage, suggesting that over Pt(111), demethylation is always more favorable than demethoxylation.

The final step to consider is the fate of the phenoxy intermediate formed on the surface. As shown in Figure 7, this intermediate can either undergo hydrogenation to form phenol or C-O cleavage to form surface phenyl. The activation energy for hydrogenation is indeed very low on Pt(111), 17 kJ/mol, with an exothermic reaction energy of -22 kJ/mol. The low barrier and exothermicity of this reaction suggest that phenol should be readily formed on Pt catalysts, as experimentally verified (see Table 2 above). In contrast, the deoxygenation of the phenoxy intermediate to form a phenyl intermediate that would lead to benzene as a primary product is extremely difficult on Pt, with an activation energy as high as 270 kJ/mol and an endothermic reaction energy of 140 kJ/mol. Figure 8A shows the energy diagrams for the hydrogenation and deoxygenation reactions of phenoxyl to form respectively phenol and benzene on Pt(111). It is clear that the hydrogenation path towards phenol is more favorable with a much lower overall energy barrier than deoxygenation. Therefore, we can conclude that the HDO of anisole over Pt(111) proceeds via demethylation to phenol rather than the demethoxylation to benzene, as experimentally verified (see Section 3.1). Once phenol is formed and desorbs to the gas phase, it can further undergo HDO to benzene by the tautomerization-hydrogenation-dehydration mechanism previously demonstrated in the HDO of m-cresol over Pt catalyst [9]. This anisole $\rightarrow$ phenol $\rightarrow$ benzene (A $\rightarrow$ B $\rightarrow$ C) series reaction for HDO of anisole on Pt is in agreement with the typical behavior observed experimentally as a function of conversion (Fig. 1 A).

3.4 Reaction Paths for HDO of Anisole over Ru(0001)

Ru(0001) was the second surface investigated by DFT calculations as a catalyst for the HDO of anisole. As summarized in Figure 9, the transition state structure for the $\text{C}_{\text{aryl-O}}$ bond breaking (demethoxylation) of the adsorbed anisole on Ru(0001) is similar to that obtained over Pt(111), with the $\text{C}_{\text{aryl-O}}$ bond distance increasing from 1.39 to 2.01 Å and the $-\text{OCH}_3$ binding to one neighboring Ru atom with a Ru-O distance of 2.15 Å. However, the activation energy for this step on Ru(0001), 99 kJ/mol, is much lower than that calculated for the same reaction on Pt(111), 258 kJ/mol, but very close to the barrier (98 kJ/mol) that we previously calculated for the cleavage of $\text{C}_{\text{aryl-O}}$ bond of m-cresol over Ru(0001) [9]. Similarly, Chiu et al. [53] reported an

activation energy of 102 kJ/mol for the demethoxylation of guaiacol over the same surface. The difference between the barriers over Ru and Pt is consistent with the trend that we previously reported for the activation energies of the m-cresol dehydroxylation [9]. The direct demethoxylation via C_{aryl}-O bond cleavage is highly exothermic over Ru(0001), -63 kJ/mol, while being highly endothermic (147 kJ/mol) over Pt(111).

The second reaction path investigated over Ru(0001) was the cleavage of the C_{alkyl}-O bond that results in the formation of CH₃* and phenoxy surface intermediates, as shown in Figure 9. This path is more exothermic on Ru(0001) (-91 kJ/mol) and it involves a lower energy barrier (135 kJ/mol) than on Pt(111) (200 kJ/mol), due to the stronger oxophilicity of Ru. However, this activation energy is higher than that for the C_{aryl}-O bond breaking. Moreover, as described below, the removal of a H atom at the -CH₃ group to form Ph-O-CH₂* has an even lower activation energy (73 kJ/mol). This difference suggests that dehydrogenation is the most favorable path for the adsorbed anisole over Ru(0001), similar to the case on the Pt(111) surface. Also, it can be expected that after the first dehydrogenation at the -CH₃ side group, the Ph-O-CH₂* intermediate could undergo one of these three possibilities: cleavage of one of the two C-O bonds, or further dehydrogenation of the -CH₂ group. As shown in Fig. 9, the dehydrogenation of Ph-O-CH₂* to Ph-O-CH* on Ru exhibits the lowest activation energy (only 14 kJ/mol), with the overall reaction energy being exothermic (-32 kJ/mol). This energy barrier is significantly lower than the first dehydrogenation step (73 kJ/mol), while also lower than the corresponding step over Pt(111) (79 kJ/mol). However, the breaking of the C_{alkyl}-O bond to form CH₂* and the phenoxy intermediate is also very easy, with a barrier of only 24 kJ/mol and a very exothermic reaction energy, -127 kJ/mol. By contrast, the activation of the C_{aryl}-O bond that would lead to a phenyl intermediate and benzene as primary product has a somewhat higher barrier (89 kJ/mol). While none of these paths has a very high barrier, the one which seems to dominate on Ru is the dehydrogenation of Ph-O-CH₂* to Ph-O-CH*.

Similarly, the three possible paths, C_{alkyl}-O and C_{aryl}-O bond breaking, and continuing dehydrogenation were also calculated for the Ph-O-CH* intermediate, as shown in Figure 9. Among the three options, the C_{alkyl}-O bond breaking was the one with the lowest barrier (51 kJ/mol), while both the C_{aryl}-O bond breaking (121 kJ/mol) and finally dehydrogenation (88 kJ/mol) are subject to significantly higher activation energies.

According to this analysis, we propose that on Ru(0001) the HDO of anisole starts with two

sequential dehydrogenation steps on the $-\text{CH}_3$ side group to form a Ph-O-CH^* intermediate, which then breaks the $\text{C}_{\text{alkyl}}\text{-O}$ bond to form a phenoxy intermediate. This pathway is consistent with previous DFT calculations of guaiacol on $\text{Ru}(0001)$ that show catecholate is formed by $\text{C}_{\text{alkyl}}\text{-O}$ breaking of a $^*\text{OPh-O-CH}^*$ intermediate [52, 53]. It may also be noted in Fig. 9 that the energy barrier for breaking the $\text{C}_{\text{alkyl}}\text{-O}$ bond of the Ph-O-CH_2^* intermediate is comparable enough (24 kJ/mol) to occur in parallel. Thus, the phenoxy intermediate may also be formed from Ph-O-CH_2^* . Similar to the behavior predicted for Pt, the surface phenoxy is a crucial intermediate on $\text{Ru}(0001)$ and the product selectivity should be determined by the fate of this intermediate. It can undergo hydrogenation to form phenol or C-O bond cleavage to form a surface-bound phenyl species, as shown in Figure 7. The activation energy for the former is 134 kJ/mol, about 117 kJ/mol higher than the same step on $\text{Pt}(111)$ and very endothermic with a reaction energy of 89 kJ/mol, as opposed to the exothermic value obtained over $\text{Pt}(111)$ (-22 kJ/mol). The higher energy barrier and reaction energy calculated for hydrogenation of the phenoxyl oxygen on $\text{Ru}(0001)$ is due to the strong interaction of oxygen with the metal. This is consistent with our previously reported trend for hydrogenation of the ketone tautomer of m-cresol over $\text{Ru}(0001)$ and $\text{Pt}(111)$ surfaces [9, 80]. As a result, one would not expect a very high selectivity towards phenol on Ru catalyst, which is confirmed experimentally. Still, the phenoxy intermediate could cleave the $\text{C}_{\text{aryl}}\text{-O}$ bond to form O^* and a phenyl intermediate, which can undergo hydrogenation to form benzene. In fact, the calculated energy barrier for this deoxygenation step to phenyl and O^* is 165 kJ/mol, which due to the stronger oxophilicity of Ru is about 105 kJ/mol lower than that over $\text{Pt}(111)$. This result is consistent with the demethoxylation reaction of anisole discussed above and the dehydroxylation of m-cresol reported previously over $\text{Pt}(111)$ and $\text{Ru}(0001)$ surfaces [9]. The energy diagrams for the hydrogenation and deoxygenation pathways of phenoxy to phenol and benzene are shown in Figure 8B. It can be concluded that after phenol is formed by hydrogenation of the phenoxy intermediate on $\text{Ru}(0001)$, it may be difficult to desorb since the binding energy is -260 kJ/mol (Table 3). While entropy plays important roles in the desorption process, the adsorption free energy (ΔG) of phenol on $\text{Ru}(0001)$ at 375 °C is still highly negative -110 kJ/mol (Table 3). Thus, although the energy barrier for the hydrogenation of the phenoxy intermediate to form phenol (134 kJ/mol) is lower than the barrier for its deoxygenation to form phenyl intermediate on $\text{Ru}(0001)$, due to the extreme endothermicity of the hydrogenation step (89 kJ/mol) and the

strong binding of phenol on Ru(0001) surface, the total barrier for the gas phase phenol formation is still higher than the deoxygenation path to form benzene, as shown in Figure 8B. However, as previously shown, the O* formed during the HDO reaction may build up on the Ru surface due to its difficulty to be removed; hence, the energetics for hydrogenation and deoxygenation of the phenoxy intermediate may change as a function of conversion [9]. The results of the calculations for the hydrogenation of the surface species O* and OH* on Ru(0001) are summarized in the supplemental information (Figure S3). It is found that hydrogenation of both O* and OH* are very endothermic (70 kJ/mol and 50 kJ/mol) and involve high energy barriers (145 kJ/mol and 128 kJ/mol, respectively). Therefore, we have calculated the hydrogenation and deoxygenation of phenoxy in the presence of a moderate oxygen coverage, 7/16 ML O* on Ru(0001) surface, as shown in Figure 10. It is observed that on the O*-covered Ru(0001) surface, the hydrogenation reaction of phenoxy is facilitated, lowering the energy barrier and making the reaction less endothermic (103 and 29 kJ/mol, respectively) in comparison to those over the clean Ru(0001) surface (134 and 89 kJ/mol, respectively). In contrast, the deoxygenation reaction of phenoxy is hindered on the O* covered Ru(0001) surface. Indeed, the energy barrier becomes higher and the reaction energy more endothermic (182 and 42 kJ/mol, respectively). Clearly, the energy diagram also shown in Figure 10 for the hydrogenation and deoxygenation paths of phenoxy on O* covered Ru(0001) surface demonstrates that the hydrogenation path to release phenol is more favorable. This result correlates well with the results of the conversion of guaiacol over Ru(0001) that show that once catecholate ($C_6H_4O_2$) is formed, it undergoes hydrogenation to form catechol $C_6H_4(OH)_2$ or a $C_6H_4(O)(OH)$ intermediate before the dehydroxylation to C_6H_4O that yields phenol and benzene [52, 81]. Thus, over Ru catalyst, benzene may result from both the direct deoxygenation of the phenoxy intermediate and/or further HDO of phenol as a secondary product. It is worth noting that the phenyl intermediate (C_6H_5) that is converted into benzene is in fact a crucial intermediate in the reaction that can also lead to cracking products, as discussed in our previous work [9]. In this case, cracking will proceed by either further activating C-H bonds to generate C_6H_y ($x < 5$) species or cleaving C-C bonds to form C_xH_y ($x < 6$, $y < 5$) species and CH species, similar to benzene decomposition observed on Ir(111) surfaces [82].

3.5 Reaction paths for HDO of anisole over Fe(110)

The same set of reaction pathways described for Pt and Ru were analyzed over Fe(110), as shown in Figure 11. Over the oxophilic Fe(110) the C_{aryl}-O bond breaking of anisole is very exothermic (-124 kJ/mol) and it has a lower activation energy (79 kJ/mol) than those calculated for Pt(111) and Ru(0001), i.e. 258 and 99 kJ/mol, respectively. Similarly, the activation energy for the C_{alkyl}-O bond breaking of anisole over Fe(110) of 103 kJ/mol is the lowest among the three metals. However, these two paths are still less favorable than the dehydrogenation of anisole at the -CH₃ side group to form Ph-O-CH₂* over Fe(110) (70 kJ/mol). This suggests that dehydrogenation is still the most favorable initial step over Fe(110), similar to Pt(111) and Ru(0001), although the direct demethoxylation (C_{aryl}-O bond breaking) becomes more competitive due to the stronger oxophilicity of Fe.

Similar to the behavior on Pt(111) and Ru(0001) surfaces, the removal of H atoms from the CH₃ substituent facilitates both C_{aryl}-O and C_{alkyl}-O bond breaking over Fe(110). The barrier for the C_{alkyl}-O bond cleavage in Ph-O-CH₂* is only 17 kJ/mol, which is particularly low suggesting the C_{alkyl}-O bond breaking to form CH₂* and the phenoxy intermediate is the most favorable path for Ph-O-CH₂*. The barrier for successive dehydrogenation of Ph-O-CH₂* to Ph-O-CH* is also low (32 kJ/mol), suggesting that it may also happen. Although being generated by a different reaction path relative to Pt(111) and Ru(0001), the formation of the phenoxy intermediate is still favored on Fe(110). This is consistent with the experimental observations that no CH₃OH, rather only CH₄, is formed over the Fe/SiO₂ and Pt/Fe₂O₃ catalysts. However, the major difference is the fate of the phenoxy intermediate after it is formed on Fe(110). As mentioned above, it can undergo hydrogenation to phenol, or cleavage of the C-O bond. As shown in Figure 7, the energy barrier for hydrogenation is relatively high (147 kJ/mol), but the cleavage of the C_{aryl}-O bond to form the phenyl group is much lower (101 kJ/mol). That is, the deoxygenation path toward benzene is more favorable than the hydrogenation path toward phenol over Fe(110), and benzene instead of phenol should be the primary product from the HDO of anisole over Fe catalysts as shown in the energy diagram in Figure 8C. Similarly, we also calculated the deoxygenation and hydrogenation of the phenoxy intermediates over Fe(110) with a moderate 7/16 ML O* coverage in Figure 12, as the removal of O* on Fe(110) is even more difficult than Ru(0001) as shown in Figure S3. On the Fe(110) surface with 7/16 O* coverage, the energy barrier for the deoxygenation of the phenoxy intermediate to form the phenyl group increases slightly to 110 kJ/mol while the energy barrier for the hydrogenation of it to form phenol

decreases to 125 kJ/mol, similar to that on Ru(0001). This observation suggests that the preference of the Fe(110) surface to deoxygenation over hydrogenation of the phenoxy intermediate holds for a rather wide range of O* coverages. This prediction is in fact validated by the experimental observations, showing the complete absence of phenol from the Fe/SiO₂ catalyst, even at the lowest conversions investigated.

As a general trend, it is interesting to compare the important effect of oxophilicity on the different reactions involved in HDO. As summarized in Figure 13, the intrinsic energy barriers for the direct deoxygenation of phenoxy via C_{aryl}-O bond cleavage over different metal surfaces decrease with the binding energy of the atomic O to these metals, while those for hydrogenating the surface phenoxy increase. Therefore, while on Fe is more favorable for the phenoxy intermediate to break its C_{aryl}-O bond than hydrogenating to form phenol the opposite is true on Pt. It must be noted that the correlation between HDO activity and oxophilicity of Pt, Ru and Fe is also valid for the binding energies of carbon on the three metals (Table 3). Clearly, both can be attributed to the position of the d band center of the three metals, as shown in Table 3. That is, the closer is the d band center to the Fermi level the higher are both C-M and O-M bond strengths. Table 4 summarizes the DFT calculated reaction energies and activation barriers for all the reaction steps investigated. All the trends discussed above are clearly evident in this table.

4. Conclusion

In this work, the conversion of anisole at 375 °C under H₂ flow at atmospheric pressure has been compared over SiO₂-supported Pt, Ru, and Fe catalysts. Over Pt/SiO₂, phenol and benzene are produced sequentially. Thus, the selectivity of benzene increases at the expense of phenol as conversion increases. Over a more oxophilic catalyst as Ru/SiO₂, the trend is similar, but phenol is observed in lower yields while benzene increases with conversion. Over this catalyst, significant amounts of CH₄ are produced by cracking. Over Fe/SiO₂, the most oxophilic catalyst investigated, benzene is the major product. Moreover, the most dramatic difference with the other metals is the complete absence of phenol in the products even at low conversions.

DFT calculations were carried out to explore the mechanism of these reactions and understand how the oxophilicity of the metal influences the reaction pathways. It was found that on all three metals, the dehydrogenation at the -CH₃ side group is the most favorable reaction before any C-O bond breaking. Removal of the H atoms at the -CH₃ side group facilitates the

subsequent C-O bond breaking, especially the aliphatic C_{alkyl}-O breaking. The surface phenoxy formed by this C-O cleavage can either undergo hydrogenation to form phenol as a primary product or break the C_{aryl}-O bond to form the surface phenyl that leads finally to benzene via hydrogenation. The former dominates on Pt and to a certain extent on Ru, over which phenol is the primary product from anisole conversion, but the latter is definitely dominant on Fe, which explains why no phenol is observed from this catalyst.

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Table 1
Summary of the characterization of the Pt/SiO₂, Ru/SiO₂ and Fe/SiO₂ catalysts

	Pt/SiO ₂	Ru/SiO ₂	Fe/SiO ₂
Metal loading*	1 wt. %	9 wt. %	5 wt. %
d _p	3.5 nm	5.2 nm	23.4 nm
Metal Dispersion	0.3	0.25	0.05

(*) different loadings were used due to the disparity in the intrinsic activity of the metals

Table 2

Product distributions for the HDO of anisole over the Pt/SiO₂, Ru/SiO₂, Fe/SiO₂ and Pt/Fe₂O₃ catalysts at 375 °C and atmospheric pressure.

	Pt/SiO ₂	Ru/SiO ₂	Fe/SiO ₂	Pt/Fe ₂ O ₃
W/F (gcat.hr/g)	0.02	0.10	0.12	0.08
Conversion (%)	15	5	8	7
TOF (min⁻¹)	75	0.4	2.3	-
Selectivity (%)				
Phenol	93	9	-	-
Benzene	7	16	85	80
CH₄ from cracking	-	75	6	7
Toluene	-	-	9	13
CH₄/Aromatics	1	22	1.4	1.5

Table 3

Adsorption energies (kJ/mol) of reactant, products and intermediates in the hydrodeoxygenation of anisol on Pt(111), Ru(0001) and Fe(110) surfaces.

	Pt(111)		Ru(0001)		Fe(110)	
	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG
Anisole	-225	-	-263	-	-232	-
Phenol	-218	-71	-260	-110	-230	-83
Benzene	-212	-31	-250	-69	-227	-46
H	-43	-4	-54	-14	-70	-30
O	-481	-	-650	-	-698	-
C	-692	-	-740	-	-826	-
d-band center	-2.32 eV		-1.94 eV		-1.56 eV	

(*) Free energies of adsorption (ΔG) were calculated at 375 °C and 1 atm.

Table 4

Summary of the DFT calculated energetics (kJ/mol) of the elementary steps in the HDO of anisole over the Pt(111), Ru(0001), and Fe(110) surfaces.

Reactions		Pt(111)		Ru(0001)		Fe(110)	
		E _{act}	E _{rxn}	E _{act}	E _{rxn}	E _{act}	E _{rxn}
Dehydrogenation	Ph-O-CH ₃ * + * → Ph-O-CH ₂ * + H*	125	12	73	-12	70	-26
	Ph-O-CH ₂ * + * ↔ Ph-O-CH* + H*	79	-22	14	-32	32	-38
	Ph-O-CH* + * ↔ Ph-O-C* + H*	124	32	88	-24	30	-82
C _{aryl} -O Breaking	Ph-O-CH ₃ * + * ↔ Ph* + OCH ₃ *	258	147	99	-63	79	-124
	Ph-O-CH ₂ * + * ↔ Ph* + OCH ₂ *	227	103	89	-45	64	-43
	Ph-O-CH* + * ↔ Ph* + OCH*	150	47	121	-40	59	-38
C _{alkyl} -O Breaking	Ph-O-CH ₃ * + * ↔ Ph-O* + CH ₃ *	200	-4	135	-91	103	-75
	Ph-O-CH ₂ * + * ↔ Ph-O* + CH ₂ *	90	-7	24	-127	17	-117
	Ph-O-CH* + * ↔ Ph-O* + CH*	83	-49	51	-154	16	-166
Fate of Ph-O*	Ph-O* + H* ↔ Ph-OH* + *	17	-22	134	89	147	103
	Ph-O* + * ↔ Ph* + O*	270	140	165	-11	101	-42

Fig. 1. Conversion and yields of products of HDO of anisole over Pt/SiO₂(A), Ru/SiO₂(B), and Fe/SiO₂ (C) as a function of W/F at 375 °C and atmospheric pressure

Fig. 2. Molar fraction of phenol and benzene in the products of HDO of anisole over Pt/SiO₂(A) and Fe/SiO₂ (B) with different time on stream at 375 °C and atmospheric pressure

Fig. 3. Thermogravimetric analysis of Fe_2O_3 and 1% $\text{Pt}/\text{Fe}_2\text{O}_3$ with mass loss (A) and H_2O mass spectrometry signal (B).

Fig. 4. TEM and electron diffraction patterns of (A) Fe_2O_3 before reduction; and (B) Pt-doped Fe_2O_3 after reduction.

Fig. 5. DFT calculated adsorption configuration of anisole on Pt(111), Ru(0001), and Fe(110) surfaces

Fig. 6. DFT calculated reactant, transition state and product structures for the $\text{C}_{\text{aryl}}\text{-O}$ bond breaking, $\text{C}_{\text{alkyl}}\text{-O}$ bond breaking and dehydrogenation reaction of different Ph-O-CH_x ($x=1\sim3$) intermediates over Pt(111).

Fig. 7. DFT calculated reactant and product structures for the hydrogenation and deoxygenation of the phenoxy intermediate over Pt(111), Ru(0001) and Fe(110) surfaces. The energetics ($E_{\text{ACT}}/E_{\text{RXN}}$) are in kJ/mol.

Fig. 8. Energy diagrams for the hydrogenation and deoxygenation of the phenoxy intermediate over Pt(111) (A), Ru(0001) (B) and Fe(110) (C). The energetics ($E_{\text{ACT}}/E_{\text{RXN}}$) are in kJ/mol.

Fig. 9. DFT calculated reactant, transition state and product structures for the C_{aryl}-O bond breaking, C_{alkyl}-O bond breaking and dehydrogenation reactions of different Ph-O-CH_x (x=1~3) intermediates over Ru(0001). The energetics (E_{ACT}/E_{RXN}) are in kJ/mol.

Fig. 10. DFT calculated deoxygenation (A) and hydrogenation (B) of the phenoxy intermediate on 7/16 ML O*-covered Ru(0001) and their corresponding energy diagrams.

Fig. 11. DFT calculated reactant, transition state and product structures for the C_{aryl}-O bond breaking, C_{alkyl}-O bond breaking and dehydrogenation reactions of different Ph-O-CH_x (x=1~3) intermediates over Fe(110). The energetics (E_{ACT}/E_{RXN}) are in kJ/mol.

Fig. 12. DFT calculated deoxygenation (A) and hydrogenation (B) of the phenoxy intermediate on 7/16 ML O*-covered Fe(110).

Fig. 13. Correlation between the intrinsic energy barrier for the hydrogenation reaction and deoxygenation reaction of phenoxy on different metal surfaces and the adsorption energies of the atomic oxygen (oxophilicity) on these metal surfaces.

*Graphical Abstract (for review)