

Experimental and Theoretical Insights into the Hydrogen-Efficient Direct Hydrodeoxygenation Mechanism of Phenol over Ru/TiO₂

Ryan C. Nelson,[†] Byeongjin Baek,[‡] Pamela Ruiz,[§] Ben Goundie,[†] Ashley Brooks,[†] M. Clayton Wheeler,^{||} Brian G. Frederick,[§] Lars C. Grabow,^{*,‡} and Rachel Narehood Austin^{*,†,⊥}

[†]Department of Chemistry, Bates College, Lewiston, Maine 04240, United States

[‡]Department of Chemical and Biomolecular Engineering, University of Houston, Houston, Texas 77204-4004, United States

[§]Department of Chemistry and Laboratory for Surface Science and Technology (LASST), ^{||}Department of Chemical and Biological Engineering, University of Maine, Orono, Maine 04469, United States

S Supporting Information

ABSTRACT: Catalytic reduction of pyrolyzed biomass is required to remove oxygen and produce transportation fuels, but limited knowledge of how hydrodeoxygenation (HDO) catalysts work stymies the rational design of more efficient and stable catalysts, which in turn limits deployment of biofuels. This work reports results from a novel study utilizing both isotopically labeled phenol (which models the most recalcitrant components of biofuels) with D₂O and DFT calculations to provide insight into the mechanism of the highly efficient



HDO catalyst, Ru/TiO_2 . The data point to the importance of interface sites between Ru nanoparticles and the TiO_2 support and suggest that water acts as a cocatalyst favoring a direct deoxygenation pathway in which the phenolic OH is replaced directly with H to form benzene. Rather than its reducibility, we propose that the amphoteric nature of TiO_2 facilitates H₂ heterolysis to generate an active site water molecule that promotes the catalytic C–O bond scission of phenol. This work has clear implications for efforts to scale-up the hydrogen-efficient conversion of wood waste into transportation fuels and biochemicals.

KEYWORDS: hydrodeoxygenation, ruthenium, TiO₂, biofuels upgrading, DFT

INTRODUCTION

Concerns about global climate change and energy security motivate efforts to develop biofuels and biochemicals from nonedible lignocellulosic biomass. The U.S. DOE and USDA have estimated that approximately 1.3 billion dry tons, the equivalent of more than 1/3 of the demand for transportation fuel in 2005, of this renewable resource can be sustainably grown and is readily available.¹ Furthermore, pyrolysis technologies that convert biomass into bio-oils have the potential to diversify the global energy mix and to develop high-tech jobs in rural locations.² However, current pyrolysis technologies produce oils that are too oxygenated to serve as suitable transportation fuels or as platform chemicals that could substitute for certain petrochemicals.¹ Even recent breakthrough technologies such as formate-assisted pyrolysis (FAsP) still produce oils that contain phenolic compounds incompatible with current fuel standards.² Thus, a complete biomass-tofuel process requires a catalytic upgrading step in which a catalyst, a reducing agent, and the crude bio-oil are combined to catalytically remove oxygen, ideally without removal of carbon. When the reductant is hydrogen gas and the byproduct is water, this upgrading process is called hydrodeoxygenation (HDO).

The complex, amorphous chemical structure of lignocellulosic biomass leads to hundreds of oxygenated bio-oil compounds and makes detailed HDO studies of this feedstock quite difficult.^{1a} Thus, phenol or substituted phenols, representative of a large fraction of oxygenated bio-oil compounds, are often used as model substrates.³ Figure 1 schematically shows the two main reaction pathways by which oxygen can be removed from phenol. The upper pathway shows the direct deoxygenation (DDO) of phenol to benzene, which utilizes a single hydrogen equivalent for reduction. The lower pathway is initiated by a catalytic hydrogenation (HYD) of phenol to cyclohexanone. Additional reduction and dehydration steps are necessary to reach a deoxygenated product, cyclohexene, which under HDO reaction conditions is rapidly reduced by an additional hydrogen equivalent to cyclohexane.⁴ Overall, this process consumes four hydrogen equivalents for deoxygenation. For upgrading biofuels, it is desirable to selectively remove oxygen because hydrogenation of the double bonds uses expensive reduction equivalents while decreasing the octane value of the naphtha fraction of the product.⁵ Selectivity in the context of the present work refers specifically to the extent to which reducing equivalents are used to directly remove oxygen, as opposed to the reduction of double bonds.

Received: July 21, 2015 Revised: September 15, 2015



Figure 1. Two schematic HDO pathways for phenol. The top pathway represents the direct deoxygenation (DDO) route and utilizes hydrogenreducing equivalents most efficiently. The lower pathway (HYD) utilizes a total of four hydrogen-reducing equivalents to arrive at the final deoxygenated, but saturated product.

HDO catalyst design has been inspired by closely related hydrodesulfurization catalysts (HDS) used for decades in the petroleum industry to remove sulfur contaminants in crude oil and to meet low sulfur fuel standards.^{3a,d-h,k,4,6} MoS₂ catalysts are archetypal HDS catalysts whose catalytic activity relies on the formation of sulfide vacancies at the Mo-promoted edge sites.⁷ Although many HDS catalysts are also effective at catalyzing HDO reactions, they require a continual feed of H₂S to prevent catalyst degradation. Lignocellulosic biomass inherently has little sulfur, so adding sulfur during an upgrading step is not desirable.^{3d} Recent efforts have turned instead to metal oxide- and supported metal particle-based catalysts, which do not require a sulfide regeneration step.^{3a,d,h,k,6d,8}

Rational catalyst design relies on understanding the mechanism by which catalysts operate. In our initial work in this area, we screened a number of supported Ru catalysts for HDO of liquefied phenol, which contains 10 wt % water.^{3a} Uncalcined Ru/TiO₂ catalysts with particle sizes of ~2 nm showed the best activity and DDO selectivity of all the catalysts screened, consistent with several other literature reports.^{3m,9} Our findings supported the hypothesis that metallic Ru(0) was the primary ruthenium species in the active catalyst.^{3a} We and others hypothesized that TiO₂'s superior support properties were attributable to its redox activity, ^{3a,m,9c} which can be enhanced by hydrogen spillover. This interpretation was also suggested in literature reports on reducible ZrO₂ and Fe₂O₃ supports.^{3a,h,q,10}

Conclusive information on the mechanism of catalytic direct deoxygenation (DDO) of phenolic compounds is scarce. Although the direct C–O bond scission pathway (Figure 2, mechanism A) is fully consistent with observed product distributions, it has been widely discarded because it requires breaking a strong C–O bond.^{3q,11} Indeed, density functional theory (DFT) calculations on the flat Ru(0001) surface support this assessment.¹² However, a recent DFT study on stepped Ru reported that C–O activation may occur with a moderate activation barrier of $E_a = 0.78 \text{ eV}.^{13}$ Similarly, McEwen and coworkers identified direct C–O bond scission as the dominant pathway on Fe and Pd/Fe surfaces.^{10,14}

As an alternative to direct C–O bond scission, an initial hydrogenation (HYD) step was proposed to weaken the C–O bond, followed by an acid-catalyzed dehydration reaction (Figure 2, mechanism B).^{6a,15} Resasco's group, however, convincingly argues that the product distributions observed on selective DDO catalysts, such as Ru/TiO₂, Pd/ZrO₂, Fe, and bimetallic Ni–Fe catalysts are inconsistent with the hydrogenation/dehydration sequence.^{3j,m,q} They suggest instead that the DDO pathway is initiated by a tautomerization step leading to a keto intermediate, which undergoes hydrogenation and dehydration (Figure 2, mechanism C).^{3j,q}

We have expanded our examination of the Ru/TiO_2 catalyst system using a combination of experimental work and first-



Mechanism B



Figure 2. Three possible reaction mechanisms for DDO emphasizing the isotopic signature predicted for each pathway when starting with D_2 as the reductant. Mechanism A is the direct C–O cleavage mechanism with hydrogen attack at the ipso position. Mechanism B requires initial hydrogenation at the ortho position, followed by dehydration. Mechanism C is initiated by tautomerization, followed by hydrogenation and dehydration. In the presence of D_2O , the hydroxyl can be deuterated through H/D exchange. Reductive H/D equivalents and H/D atoms exchanged with water are highlighted in red.

principles calculations to resolve the debate regarding the mechanism of selective DDO catalysts. The addition of polar and nonpolar additives provides direct evidence for the crucial role of water in the activity and selectivity of these catalysts, and a series of isotopic labeling experiments imply that the phenolic hydroxyl is directly replaced by a single hydrogen atom. Theoretical calculations indicate that H₂ undergoes heterolytic cleavage at an interfacial site between ruthenium nanoparticles and a basic bridging hydroxyl at the TiO2 surface. The heterolytic cleavage of hydrogen generates an active site consisting of a Brønsted acid on the support in close proximity to a reductive ruthenium hydride. The lowest energy reduction pathway is a proton-mediated, direct substitution of the aromatic hydroxyl with this ruthenium hydride. The exceptional activity and selectivity of TiO2 is attributed to its amphoteric character rather than its reducibility. TiO₂ can both accept a proton from H₂ to generate the active site and donate a proton to assist in cleaving the C–O bond of phenol; both steps have

almost identical activation energies. This novel mechanism, which does not require the formation of an oxygen vacancy site on TiO_2 , is supported by theory and experiments using isotopically labeled reactants and is capable of explaining the observed activity and selectivity reported for other metal catalysts on amphoteric oxide supports.

2. EXPERIMENTAL SECTION

2.1. Materials. Titanium dioxide (Aldrich, 21 nm particle size, $33-55 \text{ m}^2 \text{ g}^{-1}$ surface area), RuCl₃·3H₂O, phenol, hexadecane, cyclohexane, cyclohexene, cyclohexanol, cyclohexanone, hexamethyldisilazine, trace metal grade nitric acid, and trace metal grade hydrochloric acid were all purchased from Sigma-Aldrich. Deuterium oxide, deuterated phenol, and deuterated benzene were purchased from Cambridge Isotopes.

2.2. Catalyst Preparation. Supported ruthenium catalysts were prepared by a wet impregnation method, as previously reported, but without high-temperature calcination.^{3a} Catalysts were reduced in a 25 mL Parr reactor. After sealing an appropriate amount of catalyst in the reactor, the temperature of the system was increased under flowing H₂ gas at a rate of 20 K min⁻¹ until it reached the 573 K set point. Upon temperature equilibration, the system was maintained under flowing H₂ for 0.5 h. At that point, the reactor was sealed and pressurized with H₂ to 550 psig and maintained at this temperature for 1 h. At the end of this reaction time, the reactor was cooled to room temperature before venting the remaining H₂. This reduced catalyst was quickly weighed in air before being immediately transferred back to the reactor along with the phenol.

2.3. Catalyst Characterization. *2.3.1. Metal Determination.* Ru content analysis was performed by Galbraith Laboratories or done using a Thermo Scientific iCAP 600 ICP-OES spectrometer with microwave-assisted digestion. Additional details on metal analysis are provided in the Supporting Information (SI).

2.3.2. High-Resolution TEM (HRTEM). High-resolution TEM was carried out at the MIT Center for Material Science and Engineering (CMSE) using the JEOL 2010 Advanced High Performance TEM. The catalysts were dispersed in isopropyl alcohol, and a drop of this suspension was placed on a lacey carbon Cu grid. Simultaneously with TEM analysis of the selected samples, energy dispersive X-ray microanalysis (EDX) experiments were also performed on selected regions of the catalysts to confirm the presence of Ru metal and to demonstrate the absence of residual chlorine.

2.4. Catalytic Conversion of Phenol. 2.4.1. Standard Reaction Conditions. The phenol HDO reactions were carried out in a 25 mL autoclave reactor operating in batch mode. In a typical reaction, liquefied phenol (5 g, ~10 wt % water, Fisher Scientific) was introduced into the reactor along with $\sim 100 \text{ mg}$ of freshly reduced catalyst. The system was closed, and to avoid any air contamination, H₂ was bubbled through the solution for 10 min. This was followed by three reactor purges with 75 psig of H₂. The closed reactor, still under H₂ atmosphere, was heated to the reaction temperature of 573 K while stirring at 700 rpm. When the reaction temperature was reached, the total pressure was adjusted to 650 psig (45.8 bar) by regulating the H₂ pressure. The pressure was kept constant during the progress of the 1 h experiment. After the reaction, the reactor was cooled to room temperature. Samples were immediately frozen until they could be analyzed by GC/MS.

2.4.2. Modified Reaction Conditions for Isotopic Labeling and the Effect of Additives. These experiments were conducted as described above (section 2.4.1), except that either anhydrous D_0 -phenol or anhydrous D_6 -phenol (4.5 g) was added to the reactor along with an optional addition of water (deionized or deuterated) or octane. We use the notation D_x to indicate extent of deuteration, e.g. D_0 -phenol is regular phenol, whereas D_6 -phenol is fully deuterated. In all cases, 0.5 g of additive was used for a final concentration of 90 wt % phenol. A catalytic experiment was also conducted with D_0 phenol (liquified, ~10 wt % water) and 200 μ L of NMR quality D_6 -benzene. This reaction was run for a total of 15 min.

Samples from the isotopic labeling experiments were derivitized with trimethylsilane (TMS) by taking $\sim 100 \ \mu$ L of the reaction mixture and mixing it with 50 μ L of hexamethyldisilazine. After shaking the samples for 10 min, excess silylating agent was removed using a stream of argon gas.

2.4.3. Gas Chromatography Mass Spectrometry (GC/MS). Two microliters of the reaction product was diluted in 1 mL of hexadecane. The samples were injected without a solvent delay. Samples were analyzed using an Agilent 689N Network GC System with a 6890 series injector and 5973N network mass selective detector with a HP-5MS cross-linked 5% PH ME siloxane capillary column (dimensions of 30 m × 0.25 mm × 0.25 μ m) using UHP He. The analysis method contained a 6 min hold at 308 K, followed by a ramp at 5 K/min to 398 K. This temperature was held for another 10 min before ramping at 30 K/min to 573 K, which was held for 10 min. The mass detector was turned off after the elution time of all potential products but before the solvent (hexadecane) eluted. Product yields were obtained from calibrated GC/MS spectra.

2.4.4. Isotopic Distribution Analysis. For HDO reactions conducted with isotopically labeled starting materials, the isotopologue distribution of the products and remaining starting materials were determined by non-negative least-squares fitting of a portion of the experimental MS data with a reference array of simulated isotopologue MS data.

Experimental MS data were extracted from the GC/MS spectra of the reaction products. Under our GC/MS conditions, benzene and cyclohexane elute at very similar retention times, so the experimental MS intensity data for the entire elution region containing both compounds was considered simultaneously. Samples of TMS-protected phenol were prepared separately (see above), so the MS of this material was extracted and analyzed independently. The analysis window was 73-97 m/z for benzene/cyclohexane and 161-175 m/z for TMS-protected phenol. The experimentally observed intensities for each reaction are shown in Table S1.

To prepare the reference MS matrices for all isotopologues, initial reference spectra were obtained from the NIST Webbook¹⁶ for benzene and cyclohexane or from a MS of an authentic sample of TMS-protected phenol. The intensity values for the molecular ion and several lighter fragments were then extracted from this data: 73-78 m/z for benzene, 81-84m/z for cyclohexane, and 161–166 m/z for TMS-protected phenol. MS data for heavier deuterium-containing isotopologues were simulated using a simple probability-based approach for loss of H or D in the molecular fragments, which was shown to give an approximation very close to the experimentally observed mass spectrum of D₁-benzene.¹⁷ To account for heavier ¹³C-containing isotopologues, the reference MS data for each deuterium-containing isotopologue were convoluted with the ratios of the ¹³C isotopologues calculated from the natural isotopic abundance of ${}^{12}\hat{C}$ and ${}^{13}C$. The full

reference matrices for benzene (73-86 m/z), cyclohexane (81-96 m/z), and TMS-protected phenol (161-174 m/z) are found in Tables S2–S4. The matrices for benzene and cyclohexane were combined before fitting the data. The raw and normalized non-negative least-squares fit coefficients are found in Table S5. Plots of the experimental MS data versus the fit-simulated MS data are shown in Figures S1–S5.

2.5. Computational Approach. Density functional theory (DFT) calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) in combination with the Atomic Simulation Environment (ASE).¹⁸ The projector augmented wave (PAW) method¹⁹ and the generalized gradient approximation (GGA) with the revised Perdew-Burke-Ernzerhoff (RPBE) functional were employed to solve the Kohn-Sham equations.²⁰ All DFT calculations were performed with a cutoff energy of 400 eV and a Gaussian smearing of $k_{\rm B}T = 0.1$ eV with subsequent extrapolation of the total energies to $k_{\rm B}T = 0$ eV.²¹ To correct for on-site Coulombic interaction of the localized Ti 3d state, we used the DFT+U approach by Dudarev et al. with $U_{\rm eff} = 2.0 \text{ eV.}^{22}$ This value is in good agreement with the value obtained by Hu and Metiu.²³ To model the Ru/TiO₂ interface, we emulated our previous approach to modeling the Au/TiO₂ interface.²⁴ We placed a 10 atom Ru cluster, initially in the hcp structure, on a fully hydroxylated rutile h-TiO₂(110) surface, the most stable surface facet of TiO_2 , as shown in Figure 3. The



Figure 3. Side and top views of Ru_{10}/h -TiO₂(110) with enumerations at the locations used in the DFT calculations to investigate the effect of water. (1) Water adsorbed in the V_O^{le} vacancy site near the Ru_{10}/h -TiO₂ interface. (2) A gas-phase water molecule used to approximate the effects of the additive water. (3) Water adsorbed directly on the Ru_{10} cluster. For visual clarity, the bridging hydroxyl group shown in black dotted circles was removed in the side view. Color code: hydrogen, white; oxygen, red, ruthenium, teal; and titanium, light gray.

Ru₁₀ cluster was placed on three adjacent bridging oxygen vacancy sites, which can serve as nucleation sites for cluster growth.²⁵ The supported Ru₁₀/*h*-TiO₂(110) cluster model is representative for very small particles, whereas the more frequently used periodic Ru(0001) surface is a model for very large particles. Comparisons based on these two extreme models, neither one of which is an exact representation of the real catalyst, enable a computationally aided interpretation of the experimental measurements and allow rationalizing the observed particle size and support effect.

The optimized lattice constants for rutile TiO_2 are a = 4.712Å, c/a = 0.640, and u = 0.306, in good agreement with experimental data.²⁶ The TiO₂(110) surface was represented in a 5 × 4 periodic unit cell with four TiO₂ layers, of which the top two layers were fully relaxed, while the bottom two layers were fixed at their bulk positions. Subsequent slabs were separated by 16 Å of vacuum space in the *z* direction, a dipole correction was applied to compensate for the effect of adsorbing molecules only on one side of the surface,²⁷ and spin polarization was included. The Brillouin zone was integrated using a (2 × 2 × 1) Monkhorst–Pack mesh,²⁸ and geometries were optimized using a force convergence criterion of 0.05 eV/Å. Convergence with respect to the *k*-point set and the force criterion were confirmed.

The binding energies of stable intermediate states ($E_{\rm BE}$) were calculated with respect to the clean surface and gas phase reference molecules according to $E_{\rm BE} = E_{\rm slab+adsorbate} - (E_{\rm slab} + E_{\rm gas})$, where $E_{\rm slab+adsorbate}$ is the total energy of the slab with adsorbates; $E_{\rm slab}$ is the energy of the clean surface; and $E_{\rm gas}$ is a gas phase reference state based on phenol, water, and hydrogen. All reported DFT energies are electronic energies at T = 0 K unless otherwise noted. Where the use of Gibbs free energies is indicated, those were calculated according to $\Delta G = \Delta E + E_{\rm ZPE} - T\Delta S$ (ZPE = zero point energy) at T = 573 K, $P_{\rm phenol} = 11.43$ bar, $P_{\rm H_2} = 33.37$ bar, and $P_{\rm H_2O} = 1.00$ bar.

The climbing image nudged elastic band method was implemented to locate the transition state (TS) of each elementary reaction step with five or six intermediate images, which were fully optimized to a force criterion of 0.1 eV/ Å.^{24,29,30} We confirmed that this convergence criterion is sufficient to obtain transition states within 0.1 eV accuracy, a generally accepted error bar in DFT calculations. Vibrational analysis was performed to confirm the existence of a single imaginary mode, corresponding to the reaction coordinate along the reaction pathway. For each calculated elementary reaction step, the hydrogen coverage was kept minimal by adding or removing 1/2 H₂ to or from the surface as needed. We note that the associated adsorption/desorption energy changes depend on lateral surface interactions within the local surface environment to or from which the H atom is added or removed. These interactions are included in the hydrogen adsorption/desorption energies, leading to variations of these values.

To study the effect of water on phenol HDO, we investigated three plausible scenarios, as shown in Figure 3: (1) water adsorbed in a bridging oxygen vacancy site ($V_{O^{br}}$) at the Ru_{10}/h -TiO₂ interface, (2) a single gas-phase water molecule near a $V_{O^{br}}$ site on *h*-TiO₂, and (3) water adsorbed on the Ru metal cluster. The binding energies (E_{BE}) for water in these positions are (1) -0.06, (2) -0.11, and (3) -0.40 eV, respectively. For comparison, the water binding energy on the flat Ru(0001) surface is $E_{BE} = -0.14$ eV.

3. RESULTS AND DISCUSSION

There are at least two separate reduction reaction pathways by which phenol can react on a supported Ru catalyst in the presence of hydrogen (Figure 1).^{4a,31} In the hydrogenation pathway (HYD), phenol is involved in a multistep hydrogenation sequence to form the ketone cyclohexanone and the alcohol cyclohexanol. Dehydration of cyclohexanol provides the first deoxygenated product cyclohexene, which is rapidly reduced to the ultimate deoxygented product cyclohexane.³² The second pathway is a direct deoxygenation (DDO) that



Figure 4. High-resolution transmission electron microscopy (HRTEM) images of Ru/TiO_2 (a) after H₂ reductive activation and (b) after a subsequent calcination. Both figures are magnified 200 000× at 200 kV. The black scale bar represents 5 nm.

Entry	Additive	%	%	%	% OH	% O	% conv	% deox	DDO HYD
1	Water	95	2.5	0.8	0.8	0.8	30	98	19
2	None	38	40	5	3	14	22	83	0.8
3	Octane	40	24	1	15	20	13	65	1.6

Table 1. Results of Catalytic Tests of Ru/TiO₂ for Phenol HDO^a

^{*a*}The product distribution is reported as the average percent of each product formed relative to all phenol products. Percent conversion (% conv) gives the percentage of phenol converted to products. The percentage of all oxygen-free products (% deox) and the ratio of products that come from direct deoxygenation (benzene) to those that come from the hydrogenation pathway (all other products) are reported.

converts phenol into benzene without saturating its aromatic ring.³³

It has been suggested that HDO catalysts can have three distinct sites: a site for hydrogenation, a site for dehydration (these two sites would need to work in concert for HDO to occur), and a site for hydrogenolysis of the C–O bond for direct deoxygenation.^{32e,34} We postulate that HYD preferentially occurs on larger Ru particles and that DDO occurs at the interface between small Ru particles and an activated interfacial site. Below, we describe our use of HRTEM, isotopically labeled substrates, and DFT calculations to test this postulate.

3.1. Catalyst Characterization with HRTEM. EXAFS and CO chemisorption measurements in our previous report indicated uncalcined Ru/TiO₂ catalysts with a particle size of \sim 2 nm showed the best DDO activity and selectivity.^{3a} In contrast, calcined Ru/TiO₂ catalysts had a particle size of 33 nm and were not selective for DDO, producing only 20% deoxygenated products from phenol.^{3a} To confirm the effect of calcination on the particle sizes, we acquired high-resolution transmission electron microscopy (HRTEM) images on selected catalysts (Figure 4). These HRTEM images confirm the presence of small 2–3 nm Ru particles in catalysts treated only under a high-pressure reducing environment (Figure 4a). Upon calcination, the Ru particles aggregate to form much larger clusters of Ru metal (Figure 4b), which is consistent with our previously reported chemisorption data.^{3a}

3.2. The Effects of Additives on Catalytic Activity and Selectivity. To explore the effects of polar and nonpolar additives as well as the possible role of water on the reaction mechanism, we conducted three sets of experiments: a reference experiment with liquefied phenol (10 wt % water); an experiment with anhydrous phenol; and an experiment with a nonpolar additive (octane).

The reference experiments (Table 1, entry 1) were done under conditions similar to our previously published work, with only a minor modification to the pretreatment conditions.^{3a,35} The product selectivity is similar to that reported in our earlier work; however, slightly higher conversion is reported in this paper (30% conversion in this paper vs 12% in prior work), which we attribute to the more aggressive pretreatment conditions.³⁵

Although the overall efficiency of the catalysts to deoxygenate phenol is similar whether water is present or absent in the reaction, the dominant deoxygenation reaction pathway is quite different. When water is excluded from the initial reaction, cyclohexane is the major deoxygenated product, with a DDO/HYD ratio of 0.8 (Table 1, entry 2). In the presence of water, benzene is the dominant product, with a DDO/HYD ratio of 19 (Table 1, entry 1).

When octane (10 wt %) is added to anhydrous phenol at the start of the reaction to reduce the polarity of the reaction medium, the reaction shows both lower conversion (13% conversion) and low selectivity toward DDO (DDO/HYD ratio of 1.6) (Table 1, entry 3). The presence of 10 wt % octane alters the reaction trajectory and slows the dehydration of cyclohexanol. Clearly, the presence of water plays an important role in the overall reaction, as these experiments done with and without water and with octane demonstrate.

The primary focus of this work is to develop catalysts that efficiently produce benzene directly from phenol; however, the pathway where phenol is hydrogenated and then dehydrated can also lead to products suitable for combustion. Different engines and different countries require fuels with differing compositions, so understanding the structural factors that control the HYD pathway is also of interest. As described in our prior work, under standard pressure at 573 K, both formation of cyclohexanone and reduction to cyclohexanol are thermodynamically unfavorable, but the subsequent steps in the HYD pathway are favorable.^{3a} The dehydration of cyclohexanol has been used as a probe of surface acidity of heterogeneous materials.^{36,37} In this work, the ratio of cyclohexanol to cyclohexane varies from a low of 0.075 in the reaction with no water additive to a ratio of 0.63 in the reaction with octane additive, suggesting that there are fewer acidic sites suitable for catalyzing the dehydration of cyclohexanol when nonpolar octane is added as an additive.

3.3. Isotopic Labeling Experiments. To distinguish between the various proposed mechanisms for DDO, several reactions were carried out with isotopically labeled substrates. Figure 2 provides the expected isotopic signature of benzene from each pathway when the starting material is D_0 -phenol and the reductant is D_2 . Mechanism A, a direct substitution of a hydride for a hydroxide, should generate benzene with a single reductive hydrogen substituting the phenolic hydroxyl. The isotopic composition of benzene from mechanism B, ring hydrogenation followed by dehydration, and mechanism C, hydrogenation of the ketone tautomer of phenol followed by dehydration, is a bit more complicated to predict, but in each case, the isotopic composition of benzene should include more than one of the reductive hydrogen atoms.

The isotopic labeling experiments in this work were conducted with different mixtures of isotopically labeled substrates, and the final isotopic compositions of the products were determined using simple least-squares fitting methods of the acquired GC/MS data. Phenol undergoes an inevitable H/ D exchange of the phenolic protons with ambient water during sample workup and GC/MS analysis.³⁸ To minimize the complications this induces in isotopic analysis, aliquots of each reaction sample were treated with a silylating agent, which derivitizes free hydroxyl groups and leaves phenol with a maximum of five aromatic protons. These samples were used for isotopic distribution analysis of phenol.

3.3.1. H/D Ring Exchange in Phenol from Tautomerization. Phenol tautomerization (Scheme 1) provides a route to

Scheme 1. Deuterium Incorporation into Phenol through Tautomerization^{*a*}



^{*a*}The initial deuterium is a result of H/D exchange with D_2O .

incorporate the isotopic signature of water into the aromatic ring.^{3q} DFT calculations estimate that the water-assisted tautomerization step at the Ru/TiO₂ interface is likely equilibrated with a moderate activation barrier of $E_a = 0.38$ eV and $\Delta E = -0.22$ eV (Figure S6 in the SI). The extent of tautomerization expected under these reaction conditions was measured by a control reaction consisting of 10 wt % D₂O in

 $D_0\text{-}phenol$ and a sample of activated Ru/TiO_2 catalyst. This reaction mixture was heated to the normal reaction temperature (573 K) under an atmosphere of inert gas (N_2). The isotopic distribution of phenol observed at the end of this reaction is shown in Figure 5a. $D_0\text{-}phenol$ remains the major isotopologue



Figure 5. Isotopic distributions for benzene (blue) and phenol (red) for two control experiments. (a) The isotopologue distribution of phenol when a mixture of D_0 -phenol and D_2O was used without H_2 showing H/D exchange due to tautomerization. Phenol was derivitized prior to analysis, so it contains a maximum of five H + D atoms. (b) The isotopologue composition of benzene after a reaction in which a spike of D_6 -benzene was added to D_0 -phenol with H_2O and H_2 at the start of the reaction. This experiment indicates that H/D metal hydride exchange for the benzene product (via Scheme 2) is very minor under these conditions. (Note: D_6 -benzene overlaps with D_0 -cyclohexane in the MS. However, very small amounts of cyclohexane are typically observed in reactions with this catalyst under these conditions, so it can be assumed that the majority of the intensity shown here comes from D_6 -benzene.).

in this mixture; however, the presence of D_{1} - (~22%) and D_{2} -phenol (~4%) suggests that tautomerization occurs and that care must be taken in the interpretation of other isotopic labeling experiments.

3.3.2. H/D Ring Exchange in Benzene under Reaction Conditions. Aromatic H/D exchange is commonly observed in metal hydride-catalyzed reactions (Scheme 2)^{38,39,40} and has

Scheme 2. Possible Aromatic H/D Scrambling Pathways for Phenol (X = OH) or Benzene $(X = H)^{a}$

- (a) H-[Cat] + D₂O ____ D-[Cat] + DHO
- (b) $XC_6H_5 + D-[Cat] \longrightarrow XC_6H_4D + H-[Cat]$
- (c) $XC_6D_5 + H-[Cat] \longrightarrow XC_6D_4H + D-[Cat]$

a'(a) The H/D exchange of a metal hydride with water.⁴¹ (b, c) Metalcatalyzed H/D ring exchange alters the isotopic composition of the aromatic ring.

the potential to complicate mechanistic interpretations of isotopic distributions. To assess the extent of this process under our reaction conditions, a reaction was conducted in which 200 μ L of D₆-benzene was added at the start of a standard HDO reaction. The isotopic composition of all benzene (spike + reaction product) at the end of this reaction is shown in Figure Sb.

The results of this experiment indicate that benzene is effectively inert to H/D ring exchange under these reaction conditions. $D_{0^{-}}$ and $D_{6^{-}}$ benzene are the two most prominent isotopologues of benzene, each representing >40% of the product composition. $D_{0^{-}}$ benzene is the product of the catalytic

DDO of D_0 -phenol. The low levels of intermediate isotopologues are evidence that aromatic H/D exchange is a minor reaction pathway for benzene under these reaction conditions. It is also worth noting that this experiment confirms an assumption made in our earlier work: namely, that benzene is not fully hydrogenated under these reaction conditions, and therefore, the cyclohexane produced is entirely derived from the HYD pathway.^{3i,42} This is also confirmed by the lack of heavier cyclohexane isotopologues in this experiment (Table S5).

3.3.3. H/D Ring Exchange in Phenol from Metal-Catalyzed *H/D Exchange*. Direct H/D exchange of the phenolic aromatic protons, in a manner analogous to that described above for benzene, would provide another route by which the isotopic composition of phenol could shift to reflect either the isotopic composition of the reducing gas or the isotopic composition of water (Scheme 2). An HDO experiment conducted with D_{6} phenol and H₂ without water present at the start of the reaction was used to assess the level of aromatic H/D exchange in phenol. This reaction was stopped after only 15 min of total reaction time (rather than 1 h under normal conditions) to minimize side reactions with water, which is a reaction product. The distribution of phenol isotopologues in this experiment is shown in Figure 6. The phenol distribution shifts to lighter isotopologues as the reaction proceeds, which is indicative of metal-catalyzed H/D ring exchange.



Figure 6. Isotopologue distribution for phenol in an HDO experiment with D_6 -phenol and H_2 but without water showing that significant aromatic H/D exchange occurs for phenol.

3.3.4. Involvement of Water in H/D Exchange and Reduction Mechanism. To better understand both the mechanistic role played by water and its possible involvement in H/D exchange, an HDO reaction was conducted with 10 wt % D₂O, H₂, and anhydrous D₀-phenol. The isotopologue distributions for phenol (red bars) and benzene (blue bars) from this reaction are shown in Figure 7a. Some deuterium incorporation into phenol is observed. The levels are slightly higher than the amount of deuterium incorporation from the tautomerization experiment (Figure 5a), suggesting that both tautomerization and metal-catalyzed H/D ring exchange in phenol (but not benzene) are operative (as illustrated in Scheme 2) and lead to a change in the isotopic composition of phenol relative to its initial composition. Deuterium incorporation is also seen in benzene, but at levels that precisely mirror that of phenol starting material. The lack of additional deuterium incorporation into benzene leads to a mechanistic interpretation that water plays an important role in dictating



Figure 7. Isotopologue distributions for benzene (blue) and phenol (red) for two HDO isotopic labeling experiments. (a) Isotopologue composition from a reaction with D_0 -phenol, 10 wt % D_2O , and H_2 . (b) Isotopologue composition from a reaction with D_6 -phenol, 10 wt % D_2O , and H_2 . Phenol was derivitized prior to analysis, so it contains a maximum of five H + D atoms.

activity and selectivity but does not directly participate in the reductive proton transfer.

3.3.5. Mechanistic Insights from Determining the Number of Reductive Hydrides Transferred to Product. The primary purpose of the isotope experiments was to elucidate the reduction mechanism by assessing the total number of hydrogen equivalents being transferred to benzene (Figure 2). To determine this, we compare the isotopologue distribution of benzene and phenol in HDO reactions that use either D_0 -phenol or D_6 -phenol in the presence of 10 wt % D_2O and H_2 (Figure 7). In both experiments, the isotopologue distribution of benzene mirrors that seen for phenol. Given that benzene is inert to H/D exchange under these reaction conditions, this result implies that the phenolic hydroxyl is being substituted by a single reductive hydrogen. Other mechanisms would lead to notably lighter distributions (i.e. more ¹H incorporation) of benzene isotopologues. Figure 7a shows the nearly identical distribution of benzene and phenol isotopologues. Taken in total, these data are consistent with the direct C-O bond cleavage pathway (Figure 2, mechanism A), but inconsistent with the mechanistic hypotheses that involve hydrogenation of the tautomerized keto form of phenol or multiple hydrogenation/dehydration steps (Figure 2, mechanisms B and C), which would be expected to add additional reductive equivalents to benzene.

3.4. First Principle Analysis of HDO Pathways on Ru/ TiO2. To propose a DDO reaction mechanism that is consistent with our isotopic labeling experiments and can simultaneously explain the promotional effect of water, multiple pathways were explored using DFT calculations on a Ru_{10}/h - $TiO_2(110)$ surface model. The key calculated energetics are summarized in Table 2. Guided by the experimental observation that a single reducing hydrogen equivalent is exchanged, the most probable DDO pathway for phenol in the absence of water is presented as DDO1 in Figure 8. The promotional effect of water on DDO activity and selectivity is then explored for three different cases (DDO2–DDO4), which are also summarized in Figure 9. Our results are contrasted with data on the thermodynamically most stable Ru(0001) facet, which is a good representation of larger Ru particles and has been used in several previous DFT investigations of HDO of phenolic compounds.¹² All of the most probable DDO mechanisms explored occur at interfacial sites between small Ru particles and the TiO₂ support. Such interfacial sites are known to play important roles in heterogeneous catalysis, and

no.	elementary steps	ΔE^{b}	E_{a}^{b}	ΔG^{c}	G_{a}^{c}
Ι	$(C_6H_5)OH_{(g)} + V_{O^{br}} + Ru \rightarrow (C_6H_5)OH^*$	-1.60		-0.56	
II	C_6H_6 -Ru $\rightarrow C_6H_{6(g)}$ + Ru	1.40		0.41	
III	$H_2O_{(g)} + V_{O^{br}} \rightarrow H_2O^{br}$	-0.06		0.69	
IV	$H_2(g) + 2Ru \rightarrow 2H-Ru$	-0.25	$\sim 0.0^d$	е	
V	$H-Ru + HO^{br} \rightarrow H_2O^{br} + Ru$	0.94	1.15	е	е
VI(a)	$H_{2(g)} + Ru + HO^{br} \rightarrow H_2 - Ru + HO^{br}$	-0.05	0.11	0.67	$(0.67)^{f}$
VI(b)	$H_2 - Ru + HO^{br} \rightarrow H - Ru + H_2O^{br}$	0.22	0.47	0.36	0.51
VII	DDO1: $(C_6H_5)OH^* \rightarrow (C_6H_5)-Ru + HO^{br}$	-1.02	0.66	-1.09	0.65
VIII	DDO2: $(C_6H_5)OH^* + H_2O^{br} \rightarrow (C_6H_5)-Ru + HO^{br} + H_2O_{(g)}^g$	-1.25	0.42	-1.25	0.58
IX	DDO3: $(C_6H_5)OH^* + H_2O_{(g)} \rightarrow (C_6H_5) - Ru + HO^{br} + H_2O_{(g)}$	-0.83	0.94	е	0.90
Х	DDO4: $(C_6H_5)OH^* + H_2O-Ru \rightarrow (C_6H_5)-Ru + HO^{br} + H_2O-Ru$	-0.79	0.79	е	1.05
XI	(C_6H_5) -Ru + H-Ru $\rightarrow (C_6H_6)$ -Ru + Ru	-0.67	0.18	-0.52	0.19

Table 2. Summary o	f Key E	lementary Ste	eps at the Ru ₁₀	/h-TiO ₂	(110)) Interface Model"
--------------------	---------	---------------	-----------------------------	---------------------	-------	--------------------

^{*a*}The table shows the electronic energy change (ΔE), the activation energy (E_a), the Gibbs free energy change (ΔG), and the Gibbs free energy of activation (G_a) for each step. $V_{O^{br}}$ denotes the bridging oxygen vacancy site on *h*-TiO₂ near the interface. Species X bound only to the Ru cluster are shown as X–Ru. The simultaneous binding of phenol to both the $V_{O^{br}}$ site and the Ru cluster is indicated with an asterisk, for example, (C_6H_5)OH*. Additional data for the individual contributions of ΔE_{ZPE} and $T\Delta S$ are available in Table S6. ^{*b*} ΔE and E_a are the total energy change and activation energy barriers without zero point energy (E_{ZPE}) or entropy correction in electronvolts. ^{*c*}Gibbs free energies are calculated as $\Delta G = \Delta E + E_{ZPE} - T\Delta S$ at T = 573 K, $P_{phenol} = 11.43$ bar, $P_{H_2} = 33.37$ bar, and $P_{H_2O} = 1.00$ bar. ^{*d*}The H₂ molecule dissociated spontaneously upon adsorption on a Ru metal site away from the Ru/TiO₂ interface. ^{*e*}Values were not calculated. ^{*f*}The Gibbs free energy of activation G_a is set equal to ΔG because entropy corrections render the calculated Gibbs free energy of the transition state more stable than the final state. ^{*g*}Instead of binding to the V_O^{br} site, the phenolic OH group interacts with the H₂O^{br} molecule occupying the V_O^{br} site.



Figure 8. DDO1 pathway of phenol without water at the Ru_{10}/h - $TiO_2(110)$ interface: (a) calculated geometries of the initial state, transition state, and final state; (b) potential energy surface (PES). The energy of the initial and final state is calculated with respect to phenol and the Ru_{10}/h - TiO_2 model with bridging oxygen vacancy site (V_O^{br}). At the transition state (TS), the activation barrier, E_{ar} is indicated in bold face. Color code: hydrogen, white; oxygen, red; carbon, gray; ruthenium, teal; and titanium, light gray.

all of our computational results implicate them in the observed chemistry reported in this work.⁴³

3.4.1. Direct Deoxygenation (DDO) in the Absence of Water. The DDO of phenol without water is shown in Figure 8

and begins with its adsorption onto a Ru/TiO₂ interface site near a bridging oxygen vacancy (V_O^{br}) on TiO₂. The calculated binding energy of phenol at the interface is exothermic by $E_{\rm BE} =$ -1.60 eV. In comparison, phenol binding to the flat Ru(0001) surface is weaker, with $E_{\rm BE} = -0.47$ eV (Figure S7 in the SI), indicating a preferential adsorption at the interface site. Binding occurs primarily by charge transfer from Ru metal to the adsorbate and strong π interactions between the aromatic ring and the *d*-states of the Ru cluster.⁴⁴

The binding of phenol is followed by direct C–O scission, which requires a moderate activation energy barrier of $E_a = 0.66$ eV. The cleaved OH group heals the V_O^{ter} site at the Ru/TiO₂ interface, rendering the reaction exothermic by $\Delta E = -1.02$ eV. The same step on Ru(0001) is activated by $E_a = 1.23$ eV (Figure S7 in the SI), which compares well with previously calculated values of $E_a = 1.15$ eV^{12a} and $E_a = 1.29$ eV.^{12b} The resulting C₆H₅-Ru intermediate undergoes easy H atom transfer on the Ru cluster. The reaction C₆H₅-Ru + H-Ru \rightarrow C₆H₆-Ru + Ru has an activation barrier of only $E_a = 0.18$ eV and is exothermic by $\Delta E = -0.67$ eV (Figure S8 in the SI). On Ru(0001), the corresponding activation barrier increases to $E_a = 0.55$ eV.¹²

Benzene is also strongly adsorbed on the Ru cluster, and its desorption requires $\Delta E = 1.40$ eV from the Ru₁₀/h-TiO₂ interface and $\Delta E = 0.60$ eV from the Ru(0001) surface. Thus, it may at first seem as if product desorption could be rate-limiting, but when Gibbs free energies (ΔG) are considered under realistic reaction conditions (e.g., conditions other than T = 0 K and ultrahigh vacuum), the adsorption and desorption steps are associated with a much smaller Gibbs free energy change. For example, Chiu et al. have calculated the ground state desorption energy for phenol and benzene from Ru(0001) as 1.35 and 1.41 eV and tabulated the Gibbs free energies at 523 K and 40 bar as 0.50 and 0.55 eV, respectively.^{12b} These values are in good agreement with the Gibbs free energies of adsorption of phenol and desorption of benzene shown in Table 2 obtained under the conditions of our experiments. Temperature and pressure effects on adsorbed



Figure 9. Potential energy surface (PES) of the H_2O -assisted DDO pathways. Initial and final state energies in electronvolts are given with respect to phenol and the respective (water-modified) Ru/TiO₂ model with oxygen vacancy (see Figure 3). Activation energy barriers (E_a) in electronvolts are shown in bold face, and the roman numerals refer to the elementary steps in Table 2. The dotted black line serves as a reference to the DDO1 pathway in the absence of water, as shown in Figure 8. The final state energies vary slightly as a result of different binding orientations of benzene on the Ru particle and different binding environments, that is, the presence of H_2O .

intermediate and transition states are generally small.^{12b} As shown in Table 2 and contrasted in Figure S9 of the SI, the Gibbs free energies change, and activation barriers for surface steps are similar to the ground state electronic energies. This allows us to neglect entropy contributions for our qualitative discussion of surface reaction mechanisms. Overall, our analysis suggests that the kinetics of the DDO pathway on Ru/TiO₂ and Ru(0001) are largely determined by the initial C–O scission step and that the Ru/TiO₂ interface site is more active than Ru(0001).

Phenol DDO on a V_0^{hr} vacancy site of the fully hydroxylated *h*-TiO₂(110) surface in the absence of a Ru cluster was also considered. Although vacancy formation by hydrogen activation and water elimination on *h*-TiO₂ is kinetically unfavorable,⁴⁵ it has been suggested that a vacancy site may form via hydrogen spillover in the presence of transition metal clusters.⁴⁶ If such a vacancy site exists, then the calculated activation energy barrier of the direct C–O scission step is $E_a = 1.02$ eV (Figure S10 in the SI), which is lower than on Ru(0001), yet 0.36 eV larger than at the Ru/TiO₂ interface. Thus, the Ru/TiO₂ interface site remains the most favorable site for DDO.

3.4.2. Site Regeneration: Vacancy Formation and Hydrogen Activation. After phenol dehydroxylation via DDO1, the $V_{O^{br}}$ site at the Ru/TiO₂ interface is healed with the abstracted OH group, denoted as HO^{br}. To close the catalytic cycle and regenerate the oxygen vacancy, several mechanistic possibilities were explored, including H₂ activation on a Ru site followed by spillover of atomic H. Although H₂ dissociation is nonactivated, the spillover from Ru to TiO₂ requires an activation barrier of $E_a = 1.15$ eV (Table 2). The most likely pathway according to our study is a TiO2-assisted heterolytic cleavage of H2, as illustrated in Figure 10. It is initiated with activated H₂ adsorption on the Ru cluster near the TiO₂ support, which has an $E_a = 0.11$ eV and $\Delta E = -0.05$ eV (Figure 10a). The adsorbed H₂ species then dissociates heterolytically across the Ru/TiO₂ interface to protonate a bridging hydroxyl group (HO^{br}) on TiO₂, as shown in the enlarged transition and final state of Figure 10b. The protic character of the hydrogen being transferred to the support is evidenced by a fractional Bader charge of +0.38 e⁻ in the transition state. This dissociation mechanism generates a support Brønsted acid site and an H adatom, with significant negative charge density, on the bridge site of two Ru atoms. The calculated energy barrier and reaction energy for this H₂ dissociation step are $E_{2} = 0.47$ eV and $\Delta E = 0.22$ eV, respectively. After H₂O^{br} is formed at the interface, it may desorb as water and recreate the interfacial $V_{O^{br}}$ site with Lewis acid character. The H atom remaining on the Ru cluster is required for the hydrogenation of C₆H₅-Ru to benzene, as described earlier. H₂ dissociation on the Ru cluster followed by atomic hydrogen spillover to TiO₂-with or without the assistance of water as suggested by Xi et al.⁴⁷—was also tested; however, both atomic hydrogen spillover pathways involved at least one step with a barrier of ~ 1.1 eV or more (Figure S11 in the SI).

3.4.3. HYD Reactivity. Molecular hydrogen adsorbs dissociatively without barrier on a Ru site of Ru/TiO₂, and hydrogen delivery can be assumed to be quasi-equilibrated. Hence, to assess the HYD pathway, only the activation barrier for the first phenol hydrogenation step was calculated. On Ru(0001), hydrogen addition to the ortho position is more favorable than addition to either the meta and para positions on phenol. The calculated activation barrier for H addition at the ortho position is $E_a = 0.91$ eV on Ru(0001) (Figure S7 in the SI) and $E_a = 0.81$ eV on the supported Ru cluster (Figure S12 in the SI). These energetics are in line with the same reaction pathway studied on water-solvated Pt(111) and Ni(111), which fell between 0.84 and 1.00 eV.^{6a}

3.4.3. DDO/HYD Selectivity and the Effect of Particle Size. Our calculations show that the Ru_{10}/h -TiO₂ interface with a bridging V_{O^{bt}} vacancy site, representative of small Ru particles on partially reduced TiO₂, has very good DDO activity ($E_a =$ 0.66 eV) and moderate HYD activity ($E_a =$ 0.81 eV). The Ru(0001) surface, representative of large Ru particles, has low HYD activity ($E_a =$ 0.91 eV) and even lower DDO activity ($E_a =$ 1.23 eV). Thus, small Ru particles with a large number of metal/support interface sites should have higher DDO/HYD selectivity and activity compared with large Ru particles with fewer interface sites.

This theoretical assessment of the DDO and HYD pathways and activity/selectivity trends for Ru_{10}/h -TiO₂ and Ru(0001) is consistent with the experimental data. The HRTEM images in Figure 4 showed fairly uniform 2–3 nm Ru particles on the H₂activated catalysts. These small particles have relatively more Ru/TiO₂ interface area in comparison with bulk Ru, which is



Figure 10. DFT calculated models for hydrogen binding and heterolytic cleavage at the Ru_{10}/h -TiO₂(110) interface. (a) H₂ adsorbs on the Ru particle: $H_{2(g)} + Ru \rightarrow H_2$ -Ru. (b) Heterolytic dissociation of H_2 -Ru occurs across the Ru/TiO₂ interface: H_2 -Ru + HO^{br} \rightarrow H-Ru + H_2O^{br} . The charge density difference, $\Delta \rho = \rho_{H_3Ru/TiO_2} - (\rho_{RuTiO_2} + \rho_{H_2})$, shown with blue and red represent charge accumulation and depletion, respectively. The numerical values indicate the Bader charge at the transition state and final state. Color code: hydrogen, white; oxygen, red; ruthenium, teal; and titanium, light-gray.

consistent with the most favorable DDO mechanism (DDO1). The aggregated Ru particles (\sim 30 nm) obtained after calcination show reversed selectivity toward HYD, in agreement with our predictions for the Ru(0001) surface model. The proposed HYD and DDO pathways proceed independently, that is, ring hydrogenation is not necessary for C–O cleavage, which is consistent with observed product distributions.^{3j} Although this proposed mechanism and active site model is congruent with the vast majority of experimental observations, it cannot explicitly account for the promotional effect of water.

3.4.4. The Mechanistic Role of Water: Cocatalyzing C–O Cleavage. The additive exchange experiments clearly demonstrate a strong beneficial effect of water on DDO selectivity and are in agreement with the observations of others.^{9c} To investigate the mechanistic role of water during DDO, three scenarios were considered in which water might assist the C–O scission step.

In the first water-assisted scenario, DDO2, H2O^{br} formed during the site regeneration process does not desorb from the $V_{O^{br}}$ site, that is, it remains in position 1 in Figure 3. This is likely to occur in water-rich environments that would shift the equilibrium to the surface-bound water state. As explained earlier in section 3.4.2, this motif is created by heterolytic H_2 bond dissociation, which leads to the creation of a Brønsted acidic H₂O^{br} group. Brønsted acids can catalyze the elimination of OH groups from saturated reaction intermediates (e.g., cyclohexanol) during HDO.^{9b,15} In the DDO2 pathway shown in Figure 9, H_2O^{br} was retained on the surface and acts as a proton donor to the hydroxyl group of phenol. Although phenol binding is weaker at this active site model ($E_{\rm BE} = -1.29$ eV), the proton-assisted activation barrier is greatly reduced (E_a = 0.42 eV) compared with the nonassisted pathway, DDO1 (Figure 8). This mechanism is consistent with data from prior researchers⁴⁸ and supports the speculation that protonation of the lone pair orbital of oxygen could facilitate C-O bond cleavage.

An important observation about this pathway is that the proton originating from H_2O^{br} is not incorporated into the aromatic ring. This is consistent with our isotopic labeling

experiments using D₀-phenol, with or without D₂O, which exclude the possibility of direct water involvement during the reductive proton transfer, that is, the isotopic signature from water does not end up in benzene, except to the extent that it is exchanged into phenol through one of the two possible mechanisms discussed earlier. As discussed for DDO1, the benzene radical (C₆H₅-Ru) on the Ru particle reacts rapidly with the remaining H–Ru adatom.

The precise details of the C-O bond-breaking and C-H bond-forming steps are difficult to determine from our work and may depend on the hydrogen surface coverage. Lu and Heyden have considered the inverse sequence consisting of an initial hydride attack to the ispo carbon of phenol on Ru(0001)followed by C–O bond-breaking.^{12a} Their reported barriers along both alternative routes are within 0.1 eV, yet their microkinetic model predicts a ~2.5 times faster rate for C-H bond-forming followed by C-O bond-breaking, presumably caused by higher hydrogen coverage. In Figure S13 of the SI, we present a similar sequence of HYD, followed by C-O scission for the water-assisted DDO2 mechanism at 1/9 ML hydrogen coverage; that is, one hydrogen atom is adsorbed on nine exposed Ru atoms. We find that hydrogen does not change the adsorption strength of phenol as long as it does not block the Ru sites near the VObr vacancy. We also find that the adsorption complex after the ipso C-H bond formation step has a binding energy of -1.48 eV, which is even 0.19 eV stronger than phenol binding along the DDO2 pathway. Furthermore, the activation barrier for H₂O-assisted C-O scission remains identical at $E_a = 0.42$ eV. These findings do not implicate a strong hydrogen coverage dependence of the promotional effect of H₂O on the C–O dissociation barrier; yet a stronger effect at higher coverages cannot be excluded.

Despite several attempts, a direct hydride attack pathway to generate a transition state, in which C–H bond formation and C–O bond breaking occur in concert, was not identified. In practice, both bond-forming/-breaking sequences are competitive, and the actual mechanism may depend on the extent of hydrogen coverage on Ru, which in turn depends on reaction conditions.^{12a} A full microkinetic model, including all relevant

Table 3. Estimated Relative Reaction Rates at 7	' = 573 K for the Four Diffe	erent HDO Pathways Based	on the DFT-Calculated
Binding and Activation Energies Tabulated in '	Table 2 ^a		

no.	$\Delta G_{\rm BE}$, eV	$E_{\rm a\prime}~{\rm eV}$	ΔS^{\ddagger} , eV K ⁻¹	k_1^+ , bar ⁻¹ s ⁻¹	k_1^- , s ⁻¹	k_{2}^{+}, s^{-1}	$ heta_{ ext{phenol}}$	r _{norm} ^b
DDO1	-0.56	0.66	-0.00012	8.86×10^{03}	9.70×10^{-02}	4.28×10^{06}	2.32×10^{-02}	1.0
DDO2	-0.37^{c}	0.42	-0.00021	9.22×10^{04}	5.06×10^{01}	2.19×10^{08}	4.80×10^{-03}	10.6
DDO3	-0.74°	0.94	-0.00007	2.06×10^{03}	6.14×10^{-04}	2.79×10^{04}	4.59×10^{-01}	0.1
DDO4	-0.78°	0.79	-0.00011	8.59×10^{03}	1.22×10^{-03}	3.62×10^{05}	2.14×10^{-01}	0.8

 ${}^{a}\Delta G_{\text{BE}}$ is the Gibbs free binding energy of phenol, ΔS^{\ddagger} is the entropy change from adsorbed phenol to the transition state of C–O bond scission, and the fugacity of phenol is taken as $f_{\text{phenol}} = 11.48$ bar. b Rate is normalized to DDO1. Conly the entropy change for phenol was considered in the calculation of ΔG_{BE} .

steps, is required to address these details, but our main conclusion that the presence of H_2O lowers the C–O scission barrier appears to be independent of hydrogen coverage.

3.4.5. Alternative Role of Water: Phenol Stabilization. In addition to actively lowering the C-O scission barrier, water may passively stabilize reaction intermediates and transition states by pure solvation effects without transferring a proton.^{6a} Rather than attempting to fully model the aqueous reaction environment, two simplified systems were considered: (1) physisorption of a single water molecule near the phenolic OH group (position 2 in Figure 3), and (2) water chemisorption on the Ru cluster (position 3 in Figure 3). These two pathways, DDO3 and DDO4, respectively, are illustrated in Figure 9. In the DDO3 pathway, a single physisorbed (\approx gas-phase) water molecule is located near the hydroxyl group of phenol, which adsorbs in the interfacial $V_{O^{br}}$ site (see the schematic of DDO3 in Figure 9). By acting as a hydrogen bond acceptor, the water molecule stabilizes the adsorbed phenol by -0.25 eV, resulting in a stronger phenol binding energy of $E_{\rm BE} = -1.85$ eV, which is consistent with hydrogen bonding between water and the hydroxyl group of phenol. This stabilization, however, does not translate to a lower energy transition state barrier for C-O cleavage. The barrier for DDO3 (solid blue line in Figure 9) is $E_{\rm a}$ = 0.94 eV, therefore 0.28 eV higher than the barrier for DDO1 in the absence of water ($E_a = 0.66$ eV). Hence, this scenario, which approximates the effect of water on hydrogen bonding, is not alone capable of explaining the promotional effect of water on DDO activity.

The DDO3 pathway is, in fact, similar to the proton-assisted mechanism (DDO2), and the drastic activity difference between these two paths can qualitatively be understood in terms of reversed electronic interactions. In DDO2, hydrogen bond donation to the departing phenolic hydroxyl decreases the electron density in the C–O bond, facilitating its cleavage. In DDO3, however, the phenolic oxygen acts as a hydrogen bond donor, increasing the electron density in the C–O bond, making it more difficult to cleave.

Another potential role for water is modulating the density of states by binding to ruthenium near the active site (DDO4; see the schematic of DDO4 in Figure 9). Again, the presence of water stabilizes the initial binding of phenol by -0.22 eV relative to DDO1 ($E_{BE} = -1.82$ eV) while having relatively little effect on the activation energy ($E_a = 0.78$ eV for DDO4 vs $E_a = 0.66$ eV for DDO1). Overall, the potential energy diagram for DDO4 (solid green line in Figure 9) suggests that water chemisorbed on the Ru cluster lowers the potential energy of the initial and transition state equally, without significantly changing the C–O bond breaking barrier. We note, however, that the effect of adsorbing water molecules on a Ru cluster will depend on the number of water molecules or size of the metal

cluster, making it difficult to extrapolate the quantitative results of this pathway to other scenarios.

Calculations on the role of water in the DDO2 mechanism have led to a number of conclusions. Most importantly, a Brønsted acidic H₂O^{br} is able to act as a hydrogen bond donor to the ruthenium-bound phenol. This interaction decreases the activation barrier for C-O bond scission, which was thought to be the rate-determining step in our water-free model pathway DDO1. Notably, the formation of a vacancy site on TiO_2 is not required. This should lead to increased DDO activity in the presence of water, which mirrors the experimental increase in activity seen with water present (Table 1; compare entries 2 and 1). This observation is also in agreement with the conclusions of Behtash et al., who noted that polar solvents such as water and *n*-butanol not only increase the catalytic activity for HDO of propanoic acid but also stabilize the key intermediates.⁴⁹ When water acts as a hydrogen bond acceptor from bound phenol or is passively bound to the ruthenium cluster, decreased binding energies are observed, but the effect on the C-O cleavage energy barriers is minimal.

3.5. Kinetic Evaluation of Water-Assisted DDO Pathways. A simple kinetic model was developed to discriminate between C-O scission mechanisms in the possible DDO pathways. This model should not be understood as a quantitative microkinetic model; it is rather a tool that allows us to predict whether the favorable binding and higher coverage of phenol in DDO3 and DDO4 can compensate for the larger C-O cleavage barrier when compared with DDO2. In this model, the adsorption of phenol is assumed to occur reversibly on the (water-modified) vacancy site at the interface of Ru/ TiO_2 denoted as "*", followed by irreversible C–O scission.¹³ Note that for weak phenol binding, the desorption of phenol may become faster than the C-O scission reaction, which will lower the consumption of phenol. Importantly, we do not assume that phenol adsorption is quasi-equilibrated, but that the fractional phenol coverage is at steady-state (θ_{phenol} = constant). As indicated by our DFT analysis, the benzene radical formed after the C-O scission step is quickly hydrogenated to the final DDO product benzene. Because the hydrogenation barrier of $E_a = 0.18$ eV is so low, we make this last assumption irrespective of the presence or absence of water. Finally, it is sufficient for our purposes to consider only the intrinsic activity of each active site model, and we do not attempt to estimate the concentration of vacancy sites or water coverage. This reduces the kinetic analysis to the three elementary steps, of which only the first two are kinetically relevant. The simplified mechanism is then given by

phenol + $* \rightleftharpoons$ phenol*

with
$$r_1 = k_1^+ f_{\text{phenol}} \theta^* - k_1^- \theta_{\text{phenol}}$$
 (1)

phenol*
$$\rightarrow C_6 H_5 - Ru + HO^{br}$$
 with $r_2 \approx k_2^+ \theta_{phenol}$ (2)

$$C_6H_5-Ru + HO^{br} + H_2 \rightarrow benzene + H_2O + * (fast)$$
(3)

Assuming steady state for the fractional coverage of phenol θ_{phenol} leads to $r_1 - r_2 = k_1^+ f_{\text{phenol}} \theta^* - k_1^- \theta_{\text{phenol}} - k_2^+ \theta_{\text{phenol}} = 0$, which allows the estimation of θ_{phenol} as a function of the fugacity of phenol (f_{phenol}).

$$\theta_{\rm phenol} = \frac{k_1^+ f_{\rm phenol}}{k_2^+ + k_1^- + k_1^+ f_{\rm phenol}} \tag{4}$$

The site balance $\theta_{\text{phenol}} + \theta^* = 1$ was used to obtain eq 4. The reaction rate can then be approximated from eqs 2 and 4 as

$$r = r_2 = k_2^+ \frac{k_1^+ f_{\text{phenol}}}{k_2^+ + k_1^- + k_1^+ f_{\text{phenol}}}$$
(5)

The fugacity of phenol at T = 573 K is approximated as its pure vapor pressure of 11.48 bar.⁵⁰ The DFT-derived energetics from Table 2 were used to calculate the expected reaction rates of the four different DDO pathways; the results are summarized in Table 3. Herein, the preexponential factors for the rate constants $k_i = A_i \exp(-E_{a,i}/k_bT)$ were calculated as $A_i = (k_bT/h) \exp(\Delta S_i^{\ddagger}/k_b)$.

The simplified kinetic analysis clearly shows that the direct water-assisted pathway, DDO2, is the fastest reaction channel. Its rate is ~ 11 times faster than the reference rate for the DDO1 pathway without water, even though the phenol coverage decreases by one order of magnitude (Table 3). Without overemphasizing the quantitative agreement and assuming that the HYD rate is not altered by water, we note that the ca. 11-fold increase is similar to the experimentally obtained DDO/HYD ratio of 19 in the presence of water (Table 1, entry 1), whereas the DDO/HYD ratio is approximately unity in the absence of water (Table 1, entries 2 and 3). The less intuitive result of this analysis is that the stabilizing effect of water in pathways DDO3 and DDO4 is, in fact, detrimental because it slows the C-O scission rate, even though the phenol coverage is increased. The reason is that the phenol reactant in the initial state is stabilized with respect to the transition state, and although the surface coverage of phenol increases, the rate constant, k_2^+ , becomes smaller.

3.6. Active Site Formation for DDO Catalysis: The Specific Role of TiO₂. Titania has generated interest as a HDO support primarily as an alternative to alumina because alumina has known instability problems under typical HDO conditions of high temperatures and humidity.^{3d,6d} In addition, titania is also a reducible support, which has been linked to ease of oxygen vacancy formation,^{9c} and it has been noted that the use of reducible supports enhances the catalytic hydrogenation of carbonyls by group VIII metals.^{8d} The calculations presented in this work support this beneficial role of an oxygen vacancy in the energetics of C-O bond scission pathways in the absence of water (DDO1) or with passive water stabilization of phenol (DDO3 and DDO4). The HDO experiments of McEwen and Wang also support the hypothesis that DDO selectivity is enhanced by the combination of a reducible support (Fe₂O₃) and transition metal (Pd).¹⁰ A comparison of Pd/SiO₂, Pd/ Al₂O₃, and Pd/ZrO₂ showed that only the reducible ZrO₂ support leads to selective DDO, because it has oxophilic

undercoordinated Zr⁴⁺ sites with Lewis acid character,^{3q} which is similar to the role our calculations indicate TiO₂ is playing.

As an intrinsic biofuel component and a reaction product, water is a key player in phenolic HDO reactions, and as such, its presence on the catalyst surface cannot be avoided. Most previous studies have neglected to account for the presence of water, but our results confirm that water greatly enhances HDO activity and selectivity for the DDO pathway. On the basis of isotopic labeling studies and DFT simulations, we conclude that selective DDO of phenol occurs on a bifunctional reaction site at the interface between Ru nanoparticles and a Brønsted acidic surface hydroxyl/water on the TiO₂ support. In the proposed proton-assisted DDO mechanism (DDO2, Figure 9), phenol binds at this interfacial site. It is here that the acid site catalyzes C-O cleavage while the Ru metal component catalyzes the hydride attack. In this case, the active site motif is regenerated through heterolytic H–H bond cleavage, yielding a ruthenium hydride and a Brønsted acidic water on the surface of hydroxylated TiO_2 (Figure 10). A number of homogeneous Ru-based hydrogenation catalysts, for example, Shvo's catalyst, show a similar ability to simultaneously transfer acidic and hydridic hydrogens in the reduction of carbonyl substrates and ultimately regenerate the active site through H₂ bond heterolysis.⁵¹ The proposed proton-assisted DDO mechanism (DDO2) does not require formation of an oxygen vacancy site on the reducible TiO₂ support.

Our newly obtained insights into the mechanism and active site location for DDO on Ru/TiO_2 allows us to revise the prevailing notion that the support reducibility is the key property for selective and hydrogen-efficient HDO catalysts. None of the intermediate states shown in the PES in Figure 11



Figure 11. Full potential energy surface (PES) for the DDO2 pathway. Binding energies (electronvolts) are calculated with respect to gasphase phenol, H_2 , H_2O , and the *h*-Ru/TiO₂ model with H_2O^{br} acid site (model 1 in Figure 3). Activation energy barriers (E_a) in electronvolts are shown in bold red font, and the roman numerals refer to the elementary steps in Table 2. Reactants adsorbing to the surface are shown in blue; products desorbing from the surface are shown in green. For consistency with the modeled reaction steps, compensating hydrogen atoms (1/2 H_2) have been added and removed.

for the most favorable DDO2 pathway involves an oxygen vacancy site. Instead of its reducibility, we propose that TiO₂ is unique among reducible metal oxide supports because of its amphoteric character, that is, it can act as both an acid and a base. In the full PES for the water-promoted DDO2 mechanism, shown in Figure 11, the two largest, and almost identical, activation barriers are obtained for proton-assisted dehydroxylation of phenol ($E_a = 0.42$ eV) and the regeneration of the acid site by heterolytic H₂ dissociation across the Ru/ TiO_2 interface ($E_a = 0.47$ eV). These proton transfers to and from the support are ideally balanced such that neither the acidcatalyzed dehydroxylation nor the active site regeneration step are highly activated. If TiO_2 had a higher proton affinity (lower acidity), the dehydroxylation step would require a higher activation energy; however, on the other hand, if TiO₂ was more acidic (lower proton affinity), the surface protonation during heterolytic H₂ dissociation would be more difficult.

This explanation is congruent with the fact that ZrO_{2} , another amphoteric oxide with tunable Brønsted and Lewis acidity/basicity,⁵² has also been identified as a suitable support for transition metal catalysts for selective DDO.^{3h,q} The Lewis acid Zr⁴⁺ cations may be transformed to Brønsted acid sites in the presence of water and form an active site motif similar to what we propose for Ru/TiO₂. Similarly, Pd/Fe₂O₃ has shown high DDO selectivity, which was attributed to the reducibility of Fe_2O_{3} ,^{10a} but the authors did not investigate the role of water or support hydroxyl species. However, a combined STM/ DFT study has shown that protons on iron oxide surfaces are highly mobile in the presence of water⁵³ and could assist the dehydration reaction, as proposed here for TiO₂. Finally, the availability of mobile protons has also been implicated as a key mechanistic component during water-assisted CO oxidation on Au/TiO_2 ²⁴

4. CONCLUSIONS

This work reports that the DDO selectivity of Ru/TiO_2 catalyst with small Ru particles is enhanced by the presence of water. At 573 K and 550 psig H₂, these catalysts show unprecedented activity (30% conversion) and selectivity for direct deoxygenation of phenol (DDO/HYD ratio of 19). In the absence of water or the presence of 10% octane, there is a 10–20 fold reduction in the ratio of DDO/HYD products and a 30–60% reduction in the overall conversion of phenol to products.

We propose a novel DDO mechanism for phenol, which is consistent with the bulk of the experimental and theoretical literature and explains the cocatalytic effect of water. Isotopic labeling experiments indicate that a single reductive hydrogen atom is exchanged along the DDO path. This provides strong evidence against mechanisms involving multiple (de)hydrogenation/dehydration steps (Figure 2, mechanism B) because the overall number of reductive proton transfers would be expected to be greater than one. On the basis of product distributions, Resasco and co-workers proposed a reaction pathway initiated by a tautomerization step followed by hydrogenation and dehydration (Figure 2, mechanism C).^{3j,q} Isotopic labeling control experiments and low calculated activation barriers for water-assisted tautomerization in this work confirm the presence of phenol tautomerization. The hydrogenation/dehydration sequence along the tautomerization pathway, however, would increase the number of reductive H atoms transferred, which is not shown in our isotopic labeling data.

The novel mechanism we propose allows us to attribute the exceptional activity and selectivity of Ru/TiO₂ to the ability of TiO₂ to act as a conjugated acid/base pair rather than its reducibility. Water molecules adsorbed on hydroxylated or partially reduced TiO₂ can easily accept and donate protons across the Ru/TiO₂ interface and lower the C-O scission barrier by donating a proton during the abstraction of the phenolic OH group. The OH group is replaced in a hydride attack with a single reductive proton. Small Ru particles that create a maximal number of interface sites are necessary for optimal DDO performance. Because of the strong Carvi-O bond, the direct scission pathway has received very little attention in the past. The DFT results presented here, however, identified a bifunctional site with metal and Brønsted acid functionality at the Ru/TiO₂ interface that provides a lower C-O bond scission barrier ($E_a = 0.42 \text{ eV}$) than the most favorable hydrogenation step ($E_a = 0.81$ eV). This proposed mechanism fully explains the beneficial effect of water (maintaining the Brønsted acid site) and small Ru particles (maximizing the ratio of interface/bulk Ru active sites) on DDO selectivity and the observation that a single reductive hydrogen is transferred to the product. Although we have taken all necessary care in the pathway and active site determination, we have concentrated our theoretical efforts on pathways that are consistent with our catalytic and isotopic labeling experiments, and we acknowledge the possibility that other more complex reaction pathways or multisite reactions may exist.

Ring hydrogenation (HYD) occurs preferentially on large Ru particles, as indicated by DFT simulations on the idealized Ru(0001) surface. In the absence of the Ru/TiO₂ interface the lowest barrier to hydrogenation is $E_a = 0.91$ eV, whereas the direct C–O scission is more difficult ($E_a = 1.23$ eV). This is in line with previous results obtained using calcined Ru/TiO₂ catalysts, which have aggregated Ru particle sizes of about 30 nm.^{3a} Higher amounts of cyclohexanone and cyclohexanol were also seen in this work when octane was added to the reaction mixture. This is consistent with the hypothesis that octane may occlude and reduce the number of dehydroxylation sites at the Ru/TiO₂ interface.

In conclusion, our detailed understanding of the DDO mechanism and novel interpretation of the role of the support material will aid future efforts to design more efficient, less expensive catalysts or catalytic processes for bio-oil upgrading by hydrodeoxygenation. Our results suggest that by tuning the support Brønsted acidity, an optimal balance for proton acceptance and donation can be found, which is critical for selective C–O cleavage. Furthermore, the process conditions can be optimized to yield a desired DDO/HYD ratio by adjusting the amount of water present or modifying the Ru particle size.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.Sb01554.

Additional experimental and computational details for MS and DFT simulations, reaction energetics, illustrations of alternative reaction pathways (PDF)

Relevant geometry files to facilitate viewing computational models (ZIP)

AUTHOR INFORMATION

Corresponding Authors

*E-mail: grabow@uh.edu.

*E-mail: raustin@barnard.edu.

Present Address

¹(R.N.A.) Department of Chemistry, Barnard College, Columbia University, New York, NY 10027.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Thanks to Dr. Yong Zhang for assistance with the highresolution TEM. This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Nos. DE-SC0011983 and DOE EPSCoR Grant DE-FG02-07ER46373. This research used resources of the National Energy Research Scientific Computing (NERSC) Center, a DOE Office of Science User Facility supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231; and of the Center for Nanoscale Materials (CNM), supported by the U.S. DOE, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357. Additional computational resources were provided through the Extreme Science and Engineering Discovery Environment (XSEDE), which is supported by National Science Foundation (No. ACI5681053575). We also acknowledge the use of the Maxwell/Opuntia Cluster and the advanced support from the Center of Advanced Computing and Data Systems (CACDS) at the University of Houston to carry out the research presented here. This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof.

REFERENCES

(1) (a) Huber, G. W.; Iborra, S.; Corma, A. *Chem. Rev.* **2006**, *106*, 4044–4098. (b) Garcia-Perez, M.; Chaala, A.; Pakdel, H.; Kretschmer, D.; Roy, C. *Biomass Bioenergy* **2007**, *31*, 222–242.

(2) Mukkamala, S.; Wheeler, M. C.; van Heiningen, A. R. P.; DeSisto, W. J. Energy Fuels **2012**, *26*, 1380–1384.

(3) (a) Newman, C.; Zhou, X.; Goundie, B.; Ghampson, I. T.; Pollock, R. A.; Ross, Z.; Wheeler, M. C.; Meulenberg, R.; Austin, R. N.; Frederick, B. G. Appl. Catal., A 2014, 477, 64–74. (b) Badawi, M.; Paul, J.-F.; Cristol, S.; Payen, E. Catal. Commun. 2011, 12, 901–905.
(c) Chang, J.; Danuthai, T.; Dewiyanti, S.; Wang, C.; Borgna, A. ChemCatChem 2013, 5, 3041–3049. (d) Boullosa-Eiras, S.; Løpdeng, R.; Bergem, H.; Stocker, M.; Hannevold, L.; Blekkan, E. A. Catal. Today 2014, 223, 44–53. (e) Echeandia, S.; Arias, P. L.; Barrio, V. L.; Pawelec, B.; Fierro, J. L. G. Appl. Catal., B 2010, 101, 1–12.
(f) Huynh, T. M.; Armbruster, U.; Pohl, M.-M.; Schneider, M.; Radnik, J.; Hoang, D.-L.; Phan, B. M. Q.; Nguyen, D. A.; Martin, A. ChemCatChem 2014, 6, 1940–1951. (g) Leiva, K.; Sepulveda, C.; Garcia, R.; Fierro, J. L. G.; Escalona, N. Catal. Commun. 2014, 53, 33– 37. (h) Mortensen, P. M.; Grunwaldt, J.-D.; Jensen, P. A.; Jensen, A. D.

ACS Catal. 2013, 3, 1774-1785. (i) Romero, Y.; Richard, F.; Brunet, S. Appl. Catal., B 2010, 98, 213-233. (j) Nie, L.; de Souza, P. M.; Noronha, F. B.; An, W.; Sooknoi, T.; Resasco, D. E. J. Mol. Catal. A: Chem. 2014, 388-389, 47-55. (k) Gao, D.; Schweitzer, C.; Hwang, H. T.; Varma, A. Ind. Eng. Chem. Res. 2014, 53, 18658-18667. (1) Resasco, D. E.; Crossley, S. P. Catal. Today 2014, 257, 185. (m) Boonyasuwat, S.; Omotoso, T.; Resasco, D. E.; Crossley, S. P. Catal. Lett. 2013, 143 (8), 783-791. (n) Sun, J.; Karim, A. M.; Zhang, H.; Kovarik, L.; Li, X. S.; Hensley, A. J. R.; McEwen, J.-S.; Wang, Y. J. Catal. 2013, 306, 47-57. (o) Song, W.; Liu, Y.; Barath, E.; Zhao, C.; Lercher, J. A. Green Chem. 2015, 17 (2), 1204-1218. (p) Prasomsri, T.; Shetty, M.; Murugappan, K.; Roman-Leshkov, Y. Energy Environ. Sci. 2014, 7 (8), 2660-2669. (g) de Souza. P. M.: Rabelo-Neto. R. C.: Borges. L. E. P.: Jacobs, G.; Davis, B. H.; Sooknoi, T.; Resasco, D. E.; Noronha, F. B. ACS Catal. 2015, 5 (2), 1318-1329. (r) Lu, J.; Heyden, A. J. J. Catal. 2015, 321, 39-50.

(4) (a) Echeandia, S.; Pawelec, B.; Barrio, V. L.; Arias, P. L.; Cambra, J. F.; Loricera, C. V.; Fierro, J. L. G. Fuel 2014, 117, 1061–1073.
(b) Laurent, E.; Delmon, B. Ind. Eng. Chem. Res. 1993, 32, 2516–2524.
(5) Albahri, T. A.; Riasi, M. R.; Alqattan, A. A. Fuel Chemistry Division Preprints 2002, 47, 710–711.

(6) (a) Yoon, Y.; Rousseau, R.; Weber, R. S.; Mei, D.; Lercher, J. A. J. Am. Chem. Soc. **2014**, 136, 10287–10298. (b) Bu, Q.; Lei, H.; Zacher, A. H.; Wang, L.; Ren, S.; Liang, J.; Wei, Y.; Liu, Y.; Tang, J.; Zhang, Q.; Ruan, R. Bioresour. Technol. **2012**, 124, 470–477. (c) Parsell, T. H.; Owen, B. C.; Klein, I.; Jarrell, T. M.; Marcum, C. L.; Haupert, L. J.; Amundson, L. M.; Kenttamaa, H. I.; Ribeiro, F.; Miller, J. T.; Abu-Omar, M. M. Chem. Sci. **2013**, 4, 806–813. (d) Pucher, H.; Schwaiger, N.; Feiner, R.; Pucher, P.; Ellmaier, L.; Siebenhofer, M. Int. J. Energy Res. **2014**, 38, 1964–1974.

(7) Moses, P. G.; Grabow, L. C.; Fernandez, E. M.; Hinnemann, B.; Topsøe, H.; Knudsen, K. G.; Nørskov, J. K. *Catal. Lett.* **2014**, *144*, 1425–1432.

(8) (a) Zhao, F.; He, L. Prep. Pap.—Am. Chem. Soc., Div. Fuel Chem.
2012, 57, 766. (b) Stoch, J.; Dao, H. Q.; Czeppe, T. Bull. Polym. Acad. Sci. 1987, 35, 387–391. (c) He, L.; Wu, C.; Cheng, H.; Yu, Y.; Zhao, F. Catal. Sci. Technol. 2012, 2, 1328–1331. (d) Mendes, M. J.; Santos, O. A. A.; Jordao, E.; Silva, A. M. Appl. Catal., A 2001, 217, 253–262. (e) Lugo-Jose, Y. K.; Monnier, J. R.; Williams, C. T. Appl. Catal., A 2014, 469, 410–418.

(9) (a) Wildschut, J.; Mahfud, F. H.; Venderbosch, R. H.; Heeres, H. J. Ind. Eng. Chem. Res. 2009, 48, 10324–10334. (b) Wan, S.; Pham, T. T.; Zhang, S.; Lobban, L. L.; Resasco, D. E.; Mallinson, R. AIChE J. 2013, 59, 2275–2285. (c) Omotoso, T.; Boonyasuwat, S.; Crossley, S. P. Green Chem. 2014, 16, 645–655.

(10) (a) Hensley, A. J. R.; Hong, Y.; Zhang, R.; Zhang, H.; Sun, J.; Wang, Y.; McEwen, J.-S. ACS Catal. 2014, 4 (10), 3381–3392.
(b) Hong, Y.; Zhang, H.; Sun, J.; Ayman, K. M.; Hensley, A. J. R.; Gu, M.; Engelhard, M. H.; McEwen, J.-S.; Wang, Y. ACS Catal. 2014, 4 (10), 3335–3345.

(11) Furimsky, E. Appl. Catal., A 2000, 199, 147.

(12) (a) Lu, J.; Heyden, A. J. Catal. 2015, 321, 39–50. (b) Chiu, C.-

C.; Genest, A.; Borgna, A.; Rosch, N. ACS Catal. 2014, 4, 4178–4188. (13) Chiu, C.-C.; Genest, A.; Borgna, A.; Rösch, N. Phys. Chem. Chem. Phys. 2015, 17, 15324–15330.

(14) Hensley, A. J. R.; Wang, Y.; McEwen, J.-S. ACS Catal. 2015, 5, 523-536.

(15) Zhao, C.; Kou, Y.; Lemonidou, A. A.; Li, X.; Lercher, J. A. Angew. Chem., Int. Ed. 2009, 48, 3987–3990.

(16) Stein, S. E. Mass Spectra. NIST Chemistry WebBook, NIST Standard Reference Database Number 69; National Institute of Standards and Technology: Gaithersburg, MD, 20899, http://webbook.nist.gov; accessed July 17, 2015.

(17) Mohler, F. L.; Dibeler, V. H.; Williamson, L.; Dean, H. Journal of Research of the National Bureau of Standards **1952**, 48, 188–192.

(18) (a) Kresse, G.; Hafner, J. Phys. Rev. B: Condens. Matter Mater. Phys. 1993, 47, 558-561. (b) Kresse, G.; Hafner, J. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 49, 14251-14269. (c) Kresse, G.; Furthmüller, J. Phys. Rev. B: Condens. Matter Mater. Phys. 1996, 54,

11169-11186. (d) Bahn, S. R.; Jacobsen, K. W. Comput. Sci. Eng. 2002, 4, 56-66.

(19) Blöchl, P. E. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 50, 17953-17979.

(20) (a) Hammer, B.; Hansen, L. B.; Nørskov, J. K. Phys. Rev. B: Condens. Matter Mater. Phys. 1999, 59, 7413-7421. (b) Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865-3868.

(21) Stevens, E. D.; Rys, J.; Coppens, P. J. Am. Chem. Soc. 1978, 100, 2324-2328.

(22) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. Phys. Rev. B: Condens. Matter Mater. Phys. 1998, 57, 1505-1509.

(23) Hu, Z.; Metiu, H. J. Phys. Chem. C 2011, 115, 5841-5845.

(24) Saavedra, J.; Doan, H. A.; Pursell, C. J.; Grabow, L. C.; Chandler, B. D. Science 2014, 345, 1599-1602.

(25) Campbell, C. T. Acc. Chem. Res. 2013, 46, 1712-1719.

(26) (a) Morgan, B. J.; Watson, G. W. J. Phys. Chem. C 2009, 113, 7322-7328. (b) Chueh, Y. L.; Hsieh, C. H.; Chang, M. T.; Chou, L. J.; Lao, C. S.; Song, J. H.; Gan, J. Y.; Wang, Z. L. Adv. Mater. 2007, 19, 143 - 149

(27) Bengtsson, L. Phys. Rev. B: Condens. Matter Mater. Phys. 1999, 59, 12301-12304.

(28) Monkhorst, H. J.; Pack, J. D. Phys. Rev. B 1976, 13, 5188-5192. (29) Sheppard, D.; Terrell, R.; Henkelman, G. J. Chem. Phys. 2008, 128, 13410601-13410610.

(30) (a) Farberow, C. A.; Dumesic, J. A.; Mavrikakis, M. ACS Catal. 2014, 4, 3307-3319. (b) Deng, J.; Li, H.; Xiao, J.; Tu, Y.; Deng, D.; Yang, H.; Tian, H.; Li, J.; Ren, P.; Bao, X. Energy Environ. Sci. 2015, 8, 1594-1601. (c) Sun, X. Y.; Li, B.; Metiu, H. J. Phys. Chem. C 2013, 117, 7114-7122. (d) Wang, S.; Vorotnikov, V.; Vlachos, D. G. ACS Catal. 2015, 5, 104-112.

(31) Hong, D.-Y.; Miller, S. J.; Agrawal, P. K.; Jones, C. W. Chem. Commun. 2010, 46, 1038-1040.

(32) (a) Romero, Y.; Richard, F.; Reneme, Y.; Brunet, S. Appl. Catal., A 2009, 353, 46-53. (b) Elliott, D. C.; Hart, T. R. Energy Fuels 2009, 23, 631-637. (c) Gutierrez, A.; Kaila, R. K.; Honkela, M. L.; Slioor, R.; Krause, A. O. I. Catal. Today 2009, 147, 239-246. (d) Bunch, A. Y.; Wang, X.; Ozkan, U. S. Appl. Catal., A 2008, 346, 96-103. (e) Senol, O. I.; Viljava, T.-R.; Krause, A. O. I. Catal. Today 2005, 100, 331-335. (f) Bunch, A. Y.; Ozkan, U. S. J. Catal. 2002, 206, 177-187. (g) Prochazkova, D.; Zamostny, P.; Bejblova, M.; Cerveney, L.; Cejka, J. Appl. Catal., A 2007, 332, 56-64. (h) Wang, W.; Yang, Y. Q.; Luo,

H.; Hu, T.; Liu, W. Catal. Commun. 2011, 12, 436-440.

(33) Zhao, H. Y.; Li, D.; Bui, P.; Oyama, S. T. Appl. Catal., A 2011, 391, 305-310.

(34) Massoth, F. E.; Politzer, P.; Concha, M. C.; Murray, S.; Jakowski, J.; Simons, J. J. Phys. Chem. B 2006, 110, 14283-14291.

(35) In the previous study, the catalysts were activated by heating in an atmospheric pressure flow of 3:1 N₂/H₂ gas for several hours. In this study, a sample of unactivated catalyst was placed in a highpressure Parr reactor and heated (575 K) in a static atmosphere (550 psig) of pure H₂ gas for 2 h. Upon cooling, the activated catalyst was weighed and immediately returned to the Parr reactor along with the phenol necessary for the reaction.

(36) El-Sharkawy, E.-S. A. Monatsh. Chem. 2006, 137, 1487-1498.

(37) (a) Martin, D.; Duprez, D. J. Mol. Catal. A: Chem. 1997, 118, 113-128. (b) Datka, J.; Gil, B.; Vog, O.; Rakoczy, J. Stud. Surf. Sci. Catal. 1999, 125, 409-415.

(38) Sajiki, H.; Ito, N.; Esaki, H.; Maesawa, T.; Maegawa, T.; Hirota, K. Tetrahedron Lett. 2005, 46, 6995-6998.

(39) Ito, N.; Watahiki, T.; Maesawa, T.; Maegawa, T.; Sajiki, H. Adv. Synth. Catal. 2006, 348, 1025-1028.

(40) Kawazoe, Y.; Ohnishi, M. Chem. Pharm. Bull. 1966, 14, 1413-1418.

(41) Prins, R. Chem. Rev. 2012, 112, 2714-2738.

(42) Moreau, C.; Aubert, C.; Durand, R.; Zmimita, N.; Geneste, P. Catal. Today 1988, 4, 117-131.

(43) An, K.; Alayoglu, S.; Musselwhite, N.; Plamthottam, S.; Melaet, G.; Lindeman, A. E.; Somorjai, G. A. J. Am. Chem. Soc. 2013, 135 (44), 16689-16696.

- (44) Hensley, A. J. R.; Wang, Y.; McEwen, J.-S. Surf. Sci. 2014, 630, 244-253.
- (45) Hammer, B.; Wendt, S.; Besenbacher, F. Top. Catal. 2010, 53, 423-430.

(46) Rekoske, J. E.; Barteau, M. A. J. Phys. Chem. B 1997, 101, 1113-1124.

(47) Xi, Y.; Zhang, Q.; Cheng, H. J. Phys. Chem. C 2014, 118, 494-501

(48) (a) Zhu, X.; Lobban, L. L.; Mallinson, R. G.; Resasco, D. E. J. Catal. 2011, 281, 21–29. (b) Zhu, X.; Nie, L.; Lobban, L. L.;

Mallinson, R. G.; Resasco, D. E. Energy Fuels 2014, 28, 4104-4111. (49) Behtash, S.; Lu, J.; Faheem, M.; Heyden, A. Green Chem. 2014, 16. 605-616.

(50) Green, D. W.; Perry, R. H. Perry's Chemical Engineers' Handbook; McGraw-Hill: New York. 2008.

(51) Conley, B. L.; Pennington-Boggio, M. K.; Boz, E.; Williams, T. J. Chem. Rev. 2010, 110 (4), 2294-2312.

- (52) Arce-Ramos, J. M.; Grabow, L. C.; Handy, B. E.; Cardenas-Galindo, M.-G. J. Phys. Chem. C 2015, 119, 15150-15159.

(53) Merte, L. R.; Peng, G.; Bechstein, R.; Rieboldt, F.; Farberow, C. A.; Grabow, L. C.; Kudernatsch, W.; Wendt, S.; Laegsgaard, E.;

Mavrikakis, M.; Besenbacher, F. Science 2012, 336, 889-893.