

Enhanced Selective Hydrogenolysis of Phenolic C–O Bonds over Graphene-Covered Fe–Co Alloy Catalysts

Jianghao Zhang, Junrui Li, Berlin Sudduth, Junming Sun,* Changbin Zhang, Hong He, and Yong Wang*

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several graphene overlayers in the Cs-G@CoFe catalyst. In





contrast to the inhibited C–O cleavage product by the addition of Cs in the Cs-G@Fe catalyst, the addition of Cs on Cs-G@ CoFe improved the activity for selective C–O bond cleavage. The surface chemistry has been probed using H_2 chemisorption to identify the enhanced activity in the selective hydrogenolysis of phenolics.

KEYWORDS: enhanced selective hydrodeoxygenation, phenolic compounds, Co-Fe alloy, graphene, cesium, inhibition of tautomerization

INTRODUCTION

As a promising approach to remove the oxygen in feedstock, catalytic hydrodeoxygenation (HDO) has attracted extensive research interest in biomass utilization processes,¹⁻³ the petroleum industry,^{4,5} etc. Among the numerous oxygenates derived from biomass, phenolics are one type of recalcitrant species in the HDO process.^{6,7} HDO of phenolics can be categorized into two major routes: hydrogenation of an aromatic ring followed by deoxygenation (HYD) that leads to the ring-saturated products and direct deoxygenation (DDO) that produces aromatic hydrocarbons.^{8,9} Since DDO minimizes the consumption of valuable H₂ and provides higher octane gasoline blending stock, it has been generally recognized as a desirable reaction route.^{2,10} However, due to the high bond dissociation enthalpy of $C_{aromatic}$ -O (465 kJ/ mol),¹¹ DDO exhibits a much higher activation energy than HYD.^{12,13} A facile HYD and thus its ring-saturation products usually dominate in the HDO process.¹⁴⁻¹⁶ Therefore, great efforts have been devoted to developing highly selective catalysts for DDO. In addition, alkali metals are present in biooil with a broad range of concentrations^{2,17} and have been reported showing negative impact on the HDO catalysts.^{18–20} Therefore, it is critical to design such catalysts to withstand or even take advantage of the potential alkali metals.²

Metal oxophilicity, i.e., the tendency to form metal oxide,²¹ has been reported to critically influence the performance of

catalysts in the HDO reaction.^{7,22–24} Based on the Sabatier principle, active catalysts should have a moderate binding strength to adsorbates. Tan et al.^{7,22} studied the DDO of cresol and anisole over the surface of metals with different oxophilicities (Pt, Pd, Rh, Ru, and Fe). It was found that Fe showed promising activity for the lower barrier for DDO. However, the metals with oxophilicities higher than those of Fe and Mo (e.g., W and Nb²⁵) show negligible reactivity,^{26,27} likely due to the strong binding of oxygen and thus overoxidation of the metal. A recent comprehensive study also revealed the volcano-type dependence of the rate of C–O bond cleavage on the oxophilicity of metals.²⁸ As a result, a moderate oxophilic metal, such as Fe and Co,²⁵ has been identified as a promising candidate for selective DDO of phenolics.

Although Fe-based catalysts were shown to be highly selective in HDO of phenolics,^{29,30} the difficulty in removing oxygen species generated from the elimination of the hydroxyl group in phenols over Fe has been shown to oxidize and

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rapidly deactivate the Fe-based catalysts.^{31,33} We have developed platinum-group-metal (PGM)-promoted Fe catalysts that displayed high arene selectivity and durability in vapor-phase HDO of phenolics.^{29,31} The PGMs, at appropriate loadings, were found to facilitate the dissociation of H₂ and thus enhance the removal of oxygen species on the catalysts. Over these catalysts, the direct C-O bond cleavage mechanism was proposed for gas-phase HDO reaction, as supported by kinetic study³² and theoretical calculation.³³ Unfortunately, ring saturation dominated when these PGMpromoted Fe catalysts were applied in liquid-phase HDO.³⁴ Our further mechanistic studies revealed that enhanced ketoenol tautomerization is the main contributor to ring saturation in liquid-phase reaction conditions over the (PGM-promoted) Fe catalyst.³⁴ Alternatively, Fe wrapped with several graphene overlayers has been demonstrated to be effective in maintaining the activity of Fe via a weakened Fe-OH interaction and a proposed electron tunneling through the graphene overlayer.^{35,36} Furthermore, alkali-metal (i.e., Cs)doped graphene-wrapped Fe was found to significantly inhibit the tautomerization, leading to 100% arene selectivity even in liquid-phase conditions under high H₂ pressure albeit with a low reactivity.^{35,37}

Recent DFT studies suggest that alloying Fe with metals in Group B regulates the Fe-O binding strength, which is weakened by increased d-band filling for metals in Period 4.³⁸ According to the Sabatier principle, metal-O binding strength needs to be optimized to balance the oxygen abstraction from phenols and oxygen elimination from the surface.³⁹ Co shows slightly increased d-band filling and similar nature to Fe²⁵ that likely endows the bimetallic Co-Fe alloy with a modified surface chemistry in C-O bond cleavage. Herein, we report highly active and selective DDO catalysts with a bimetallic Co-Fe alloy core covered by a graphene shell doped with Cs. In the HDO of phenol, a simplest phenolic model compound, a significant improvement (\sim 3.5-fold) in the HDO reactivity was observed with high benzene selectivity (>95%). Complementary characterizations including powder X-ray diffraction (XRD), in situ Raman spectroscopy, high-resolution transmission electron microscopy (HRTEM), temperature-programmed surface reaction with H₂ (H₂-TPR), temperatureprogrammed desorption of H₂ (H₂-TPD), and in situ attenuated total reflectance Fourier transformation infrared spectroscopy (ATR-FTIR) were employed to elucidate the active sites and reaction mechanisms.

EXPERIMENTAL SECTION

Preparation of Catalysts. First, 5 wt % Co/Fe₂O₃ was prepared with an incipient wetness impregnation method. Typically, 2.5 mL of Co(NO₃)₂ (Alfa Aesar, ≥99.999%, 0.68 M) solution was added dropwise to 2 g of Fe₂O₃ powder (Alfa Aesar, 99.95%, pore volume: 1.25 mL/g). After stirring for 10 min to ensure an even dispersion of solution over the support surface, the sample was transferred into a convection oven for drying at 80 °C overnight. The obtained solid sample was then calcined at 450 °C for 3 h.

G@CoFe was synthesized with tandem carburization and reduction. Reduction was performed to remove any possible carbide phase. In a typical synthesis, the obtained Co/Fe₂O₃ powder was transferred into an alumina boat placed in a quartz tube. Then, 10 vol % CO/He (50 mL/min) was used to purge the whole system for 1 h before ramping the temperature to 350 °C (5 °C/min) and holding for another 4 h. After cooling to ambient temperature, the gas was switched to 50% H_2/N_2 (50 mL/min) purge for 1 h, and then, the temperature was ramped to 350 °C (5 °C/min) and held for another

4 h. After cooling to ambient temperature and purging with UHP N₂ (50 mL/min) for 1 h, 0.2 vol % O₂/N₂ (50 mL/min) was introduced to passivate the sample. G@Fe and G@Co were prepared with the same procedure except using a monometallic oxide precursor (after 450 °C calcination), while CoFe (i.e., carbon-free sample) was obtained by direct reduction with 50% H₂/N₂ (50 mL/min) at 350 °C for 4 h.

To obtain 1.7 wt % Cs-doped catalysts, a Cs₂CO₃ (Sigma-Aldrich, 99.9%, metal basis) solution was mixed with the above samples for incipient wetness impregnation. The mixture was then transferred into a quartz tube with flowing UHP N₂ (50 mL/min). After purging for 1 h, the temperature was increased to 80 °C (5 °C/min) and held for 6 h and then to 400 °C and held for another 2 h. After cooling to ambient temperature in flowing UHP N₂ (50 mL/min), the sample was passivated with 0.2 vol % O_2/N_2 (50 mL/min) for 2 h.

Characterizations. XRD was performed with a Rigaku Miniflex II X-ray diffractometer with $Cu_{x\alpha}$ radiation ($\lambda = 1.54178$ Å) operating at 40 kV and 50 mA. The patterns were collected at a scanning rate of 1°/min with a step-size of 0.01°. In situ Raman spectra were collected with a Horiba LabRAM HR Raman/FTIR microscope equipped with a 532 nm (Ventus LP 532) laser source and Synapse charge coupled device detector (CCD). In a typical measurement, the sample was loaded in a Linkam CCR1000 in situ cell and purged with N₂ (50 mL/min) for 20 min to avoid the possible laser-induced oxidation of the surface by O₂. After calibration using the silicon reference, the spectrum of the sample was recorded at room temperature.

HRTEM analysis of the catalysts was performed using a JEM-2100F operated at 200 kV equipped with a 4 k CCD camera. In a typical preparation of the sample, the ground catalyst was dispersed into ethanol, and then, a drop of the nanoparticle suspension was dispensed onto a 3 mm lacey-carbon-coated copper grid. Excess ethanol was removed by an absorbent paper, and the sample was dried at 80 $^\circ$ C for 12 h.

H₂-TPD was carried out using a chemisorption analyzer (Micromeritics AutoChem 2920) equipped with a quadrupole mass spectrometer (Omnistar gas analyzer GSD 301). About 50 mg of sample was loaded into a quartz tube and purged with 5%Ar/He (50 mL/min) for 10 min. The gas was then switched to 10 vol % H₂/Ar (50 mL/min), and the temperature was ramped (10 °C/min) to 300 °C holding for 2 h to simulate the surface in HDO reaction. After the pretreatment, the sample was cooled down to -60 °C in 10 vol % H₂/Ar, followed by purging with 5%Ar/He (50 mL/min) for 20 min. Then, the temperature was ramped to 300 °C with a rate of 10 °C/min.

In situ ATR-FTIR was performed to study the adsorbed phenol over the surface of catalysts. The experiments were conducted with a Bruker Tenser II spectrometer and a custom-designed ATR cell.⁴⁰ Before each test, the as-prepared catalyst was ground into fine powder so that it could be suspended in hexane by sonication. Then, the catalyst was deposited on the ZnSe internal reflection element by dip coating. The thin layer of catalyst coating was then reduced in 10% H_2/He (40 mL/min) at 300 °C for 1 h. After this, the sample was cooled down to 250 °C (due to an uncontrolled background shift and poor signal-to-noise ratio at 300 and 250 °C used for this experiment) followed by N₂ purging for 1 h. After a background collection, phenol vapor (30 Pa, balanced by N₂, 50 mL/min) was introduced into the catalyst for 20 min, followed by purging in flowing N₂ (40 mL/min) for 20 min. The spectra were then collected by averaging 64 scans at a resolution of 4 cm⁻¹.

Evaluation of Catalytic Performance. The performance of the catalysts was evaluated for HDO of phenol in a stainless-steel batch reactor (Parr Instrument, Series 4560, 300 mL) equipped with a glass liner. In a typical test, a specific amount of catalyst, 0.6 g of phenol (Sigma-Aldrich, \geq 99%), and 50 mL of hexadecane (Sigma-Aldrich, 99%) were placed into a reactor. After 3 times of purging with 4 MPa H₂, the temperature was ramped to reacting temperature (15 °C/min). Then, the reactor was pressurized with H₂ to 1.6 MPa where the stirring (800 rpm) of the mixed slurry solution and reaction started. The stability of the catalyst was evaluated by a set of recycling tests. After each cycle of the test, the product/solvent mixture was



Figure 1. Catalytic performances of Cs-G@Co, Cs-G@Fe, and Cs-G@CoFe. (a) Benzene formation rate; (b) product distribution; (c) stability test of Cs-G@CoFe. Reacting condition: $300 \degree$ C, 1.6 MPa H₂, 0.15 g of catalyst, 0.6 g of phenol, 1 h for Cs-G@Co and 4 h for Cs-G@Fe and Cs-G@CoFe to control the conversion below 20%.



Figure 2. (a) XRD patterns and (b) Raman spectra of catalysts. Inset: magnification of the region of (110) diffraction.

removed/analyzed, while the catalyst was retained in a reactor vessel by sedimentation and carefully washed with 50 mL of hexadecane. After the reaction was completed, the product was analyzed using a gas chromatograph (GC, Agilent 7890A) equipped with a DB-FFAP column (30 m, 0.32 mm, 0.25 μ m) and flame ionization detector (FID), as well as a GC–MS (Shimadzu, GC-MS-QP2020) equipped with an HP-5 column (30 m, 0.32 mm, 0.25 μ m) connected to an FID. The benzene formation rate (measured with conversion below 20%) and selectivity were defined as follows: benzene formation rate [mmol/g/h] = mole of produced benzene/amount of catalyst/spent reacting time; selectivity [%] = (moles of carbon in the specific product/moles of carbon in all products) × 100%. The carbon balance was in the range of 90 to 100%.

RESULTS AND DISCUSSION

Catalytic Performance. Liquid-phase HDO of phenol was employed to study the performance of the catalysts. A comparison of Cs-G@Co, Cs-G@Fe, and Cs-G@CoFe is shown in Figure 1a,b (the detailed product distribution is shown in Figure S1). Cs-G@Co displays a low benzene production rate (0.42 mmol/g_{catal}/h) and benzene selectivity (11%). The main product is cyclohexanol, implying the strong capability of hydrogen activation over the Co-based catalyst. Cs-G@Fe exclusively produces benzene (100% selectivity), while the production rate (0.43 mmol/g_{catal}/h) is comparable with that of Cs-G@Co. It indicates that the Fe-based catalyst is highly selective but with a low reactivity. In contrast, the bimetallic catalyst (i.e., 5 wt % Co and Fe) showed a promoted more than threefold to 1.42 mmol/ g_{catal}/h , while the high benzene selectivity (95%) is maintained. A physical mixture containing 5 wt % Cs-G@Co and 95 wt % Cs-G@Fe displayed no promoting effect to the reactivity of benzene production but decreased benzene selectivity (Figure S2), indicating the pivotal role of Co-Fe interaction in the catalyst. The promotion effect by different amounts of Co was probed, and reactivity showed a volcano-type dependence on the Co amount with 5 wt % as the apex (Figure S3). The stability of Cs-G@CoFe in the recycling tests was studied with phenol HDO at 300 °C, as shown in Figure 1c. There was a slight deactivation in the first two cycles in terms of reactivity, whereas it stabilized in the 3rd and 4th cycles. Moreover, the arene selectivities in the tested four cycles were all maintained above 95%. Under the optimized reaction condition (i.e., 325 $^{\circ}$ C and 3 MPa H₂), Cs-G@CoFe converted ~90% phenol with 90% benzene selectivity (Table S1). Note that, to our best knowledge, this remarkable performance has rarely been reported among sulfur-free base-metal catalysts in liquidphase HDO of phenolics (Table S1). Structural Characterization. XRD patterns of catalysts

remarkable synergic effect: the benzene production rate is

Structural Characterization. XRD patterns of catalysts are measured as shown in Figure 2a to investigate the structure of catalysts. The G@Fe catalyst displays the diffractions that can be indexed to the body-centered cubic crystal structure (JCPDS no. 06-0696). G@CoFe and Cs-G@CoFe show similar diffraction peaks though there is a shift to a higher angle

(0.05°, inset plot), indicating the decreased lattice parameters.⁴¹ No diffraction associated with monometallic Co^{42,43} was detected although the Co species was clearly observed in the elemental mapping (vide infra). The shift to a higher angle was also observed over the carbon-free catalysts (Figure S4). These results suggest the formation of the Co-Fe alloy (JCPDS no. 48-1816, primitive cubic structure), which is consistent with a recent study⁴⁴ showing the alloy formation after H_2 reduction at 350 °C (the same pretreating condition for our catalysts). The bimetallic nature of CoFe was studied with carbon-free Fe and CoFe. As shown in Figure S5, CoFe shows the H₂ uptake appearing at 181 °C and reaching the apex at 219 °C. In contrast, both the onset and peak temperatures for H₂ uptake over Fe are much higher (217 and 281 °C, respectively). These results further confirm the formation of the CoFe alloy, leading to significantly modified nature of the catalyst relative to that of bare Fe. Raman spectra were employed to study the surface structure, as shown in Figure 2b. All three studied catalysts display two peaks at 1344 (D band) and 1586 cm⁻¹(G band), which are assigned to the zone center phonons of E_{2g} symmetry and K-point phonons of A1g symmetry of graphitic carbon, respectively.⁴⁵ The observation of both D and G bands indicates the disordered nature of graphitic species over catalysts' surface.^{46,47} Raman spectra of bare CoFe and graphene-covered CoFe (Figure S6) showed the oxide peaks in the region of 200-700 cm⁻¹ over bare CoFe but none on G@CoFe.48 It should be noted that metallic CoFe has no Raman signal since its primitive cubic structure has no opticalbranch zero wavevector vibrational modes. The flat spectrum suggests that oxidation of CoFe does not occur on G@CoFe, an indication of full coverage of graphene on CoFe.

The structures of both fresh and spent catalysts were also characterized with HRTEM. Figure 3a,b shows the representative images of fresh G@Fe and G@CoFe, respectively. The continuous and stacked overlayers with an interlayer spacing of



Figure 3. Microscopic study of G@Fe, G@CoFe, and Cs-G@CoFe catalysts. (a) HRTEM image of G@Fe; (b) HRTEM image and (c) elemental mapping of G@CoFe; (d) HRTEM image of spent Cs-G@ CoFe collected after 4 cycles of HDO reaction.

0.34 nm are clearly observed over the metal substrate and identified as graphene.⁴⁹ The elemental mapping of G@CoFe shows that C, Co, and Fe are uniformly dispersed in the particles, which is consistent with the XRD results about the formation of the Co–Fe alloy and suggests that the graphene overlayer fully covers the CoFe metal. The spent catalyst of Cs-G@CoFe collected after 4 cycles of the stability test was also studied with HRTEM, as shown in Figure 3d. The graphene layers are observed over the spent catalyst particle, indicating that the graphene-wrapped structure was well maintained during the catalysis. The lattice distance of the crystal substrate is 0.205 nm, which is indexed to the (110) plane of the CoFe alloy. Based on these characterizations, the surface structure of the catalyst is essentially identified as the graphene-coated CoFe alloy that is modified with Cs.

Unravel the Possible Active Sites. As one of the reactants, H_2 was used to probe the surface active sites and possible synergic effect in the bimetallic catalyst. In H_2 -TPD (Figure 4), G@Fe displays the desorption in the range of -50



Figure 4. Temperature-programmed desorption of H_2 over the catalysts. The intensity is normalized by surface area.

to 175 °C that can be deconvoluted into four sub-bands, which are denoted as α , β , γ , and δ from low to high temperatures. α and β bands located below 50 °C can be attributed to the weakly adsorbed H on the surface, while γ and δ at higher temperatures indicate a stronger interaction.⁵⁰ Different from G@Fe, the nature and amount of each chemisorbed hydrogen over G@CoFe change significantly. For example, the γ and δ sub-bands of G@CoFe have a much higher area (twofold) and percentage (1.5-fold) than that of G@Fe, indicating that G@ CoFe has a higher amount and concentration of strongly adsorbed H. This is consistent with the DFT calculations showing enhanced hydrogen adsorption on the CoFe alloy.³⁸ After doping with Cs, the G@Fe sample shows a significant decrease of all bands. In contrast, the α and β bands are obviously enhanced over Cs-G@CoFe with decayed γ and δ



Figure 5. (a) Benzene formation rate and (b) product distribution over different catalysts. Reaction condition: 300 °C, 1.6 MPa H₂, 0.15 g of catalyst, and 0.6 g of phenol.



Figure 6. In situ ATR-FTIR spectra of phenol adsorption over G@CoFe and Cs-G@CoFe at 250 °C: (a) C-H stretching region; (b) C=O and C-C vibration regions.

bands. Since alkali metals typically decrease the surface concentration of hydrogen^{37,51} in the case of Cs-G@Fe, the enhanced hydrogen adsorption (α and β bands) suggests that the unique electronic structure of the CoFe alloy may have changed the electron donation from Cs.³⁵

It should be mentioned that, although addition of Cs inhibited the ring saturation on both G@Fe and G@CoFe, leading to >95% benzene selectivity in the HDO of phenol, its effect on the benzene formation was different on those two catalysts. With Cs doping, a significant decrease of the benzene formation rate was observed on Cs-G@Fe compared to G@Fe (Figure 5). In contrast, the benzene formation rate of Cs-G@ CoFe was improved substantially with respect to G@CoFe. This phenomenon is well correlated with the amount of weakly adsorbed hydrogen (α and β) shown in Figure 4, indicating that the α and β hydrogen may be associated with the selective hydrogenolysis of the C–O bond. Our recent studies about Febased catalysts³¹⁻³³ have shown that the direct C-O bond cleavage in phenols produces the hydroxyl on the surface, which needs to be eliminated by H (surface reduction) such that the catalytic cycle can be closed. Although the intrinsic reasons behind the enhanced hydrogen adsorption remain unclear, the unique surface chemistry presented on Cs-G@ CoFe may have promoted the formation of α and β hydrogens

and thus the removal of hydroxyl formed by direct C–O bond cleavage.

The recent work^{52,53} has shown that the thin graphene overlayer enables electron tunneling from the metal substrate to the surface such that these composite materials are still catalytically active.^{35,37} Directly doping Cs on bare CoFe led to significantly decreased reactivity (Figure S7), while doping Cs on G@CoFe showed a different behavior; i.e., the activity is further promoted by Cs, indicating the indispensability of graphene layers in this catalyst system. Similar to the present work, the previous studies showed that direct interaction between Cs and Fe completely deactivated the catalyst.^{35,37} These results suggested that Cs tends to poison the catalyst even though it contributes to the increased benzene selectivity. Therefore, the interaction between Cs and the metal substrate must be tailored to improve the selectivity while avoiding the poisoning effect. To this end, graphene must play critical roles in modulating the interaction of Cs and the CoFe alloy, leading to an optimal electronic hybridization of Cs and CoFe for selective and highly active C-O bond cleavage. Bare CoFe and G@CoFe were also investigated with electron microscopy. The mean particle size (d_M) and size distribution were analyzed statistically by sampling ~100 particles from randomly chosen areas of the TEM image (Figure S8). The d_M value of CoFe (86.0 nm) is much higher than that of G@CoFe (27.6 nm),



Figure 7. Structures and catalytic performances of catalysts with different promoters. (a) XRD of catalysts; (b) benzene formation rate and benzene selectivity over Cs-modified catalysts with different promoters. Reaction condition: 300 °C, 1.6 MPa H₂, 0.15 g of catalyst, 0.6 g of phenol, 4 h.

suggesting that the graphitic layer mitigates the aggregation of CoFe particles so that more active sites could be maintained under the reaction conditions, which is consistent with the higher activity of G@CoFe than that of CoFe as shown in Figure S7.

The role of Cs in influencing the phenol adsorption was studied with in situ ATR-FTIR. The spectra were recorded after N₂ purging for 20 min to evaluate the physically adsorbed phenol. Figure 6a displays the region of C-H bond vibration in spectra of G@CoFe and Cs-G@CoFe. Three peaks, located at 3044, 2972, and 2895 cm⁻¹, appear in the spectrum of G@ CoFe. The peak at 3044 cm⁻¹ is attributed to the vibration of C_{sp2} -H in phenol species,⁵⁴ while the latter two peaks are assigned to the C_{sp3} -H vibration.⁵⁵ This implies the robubic direction of C_{sp3} -H rehybridization of C electrons concurrent with the formation of δ -bonds between the carbon atoms and the catalyst surface⁵⁶ or the tautomerization of phenol to form cyclohexadienone species.⁵⁷ In contrast, Cs-G@CoFe exclusively shows the bands for C_{sp2}-H stretching, located at 3044 and 3004 cm^{-1} , indicating that the aromaticity is still preserved. This is consistent with the exclusive C-C ring stretching (1573 and 1465 cm⁻¹) and C-O stretching (~1245 cm⁻¹) vibration in the spectrum of Cs-G@CoFe,^{54,55} as shown in Figure 6b. Besides sharing the same peaks with Cs-G@CoFe, G@CoFe also displays absorptions of other functional groups at 1725, 1374, and 1313 cm⁻¹ that are attributed to stretching vibration of $C=O^{57}$ and wagging and twisting vibration of CH₂,⁵⁸ respectively. The above results suggest the formation of cyclohexadienone from the tautomerization of phenol over the G@CoFe surface, while the tautomerization is inhibited by the Cs doping. In our previous study, the tautomerization has been demonstrated as the main contributor to the ring saturation over Fe-based catalysts.³⁴ Since Cs inhibited the tautomerization on Cs-G@CoFe, a highly selective hydrogenolysis was achieved.

To further investigate the role of Co, we also studied the catalysts with Ni and Pd (5 wt %) as promoters. Ni shares a similar crystal structure to Fe and thus also has the tendency to form NiFe alloy. Moreover, in terms of d-band filling, these three metals have an order of Fe < Co < Ni. The electronic structure of Pd is distinct to Fe, showing a lower tendency to form alloy. These two metals have been reported to enhance the reactivity of Fe-based catalysts in HDO of phenolics.^{31,59}

The XRD pattern of Cs-G@PdFe in Figure 7a shows the diffraction of metallic Pd crystals, besides the peaks from Fe⁰. Cs-G@NiFe displays the shift of the diffraction peak to a higher angle, and no peak associated with Ni⁰ is detected. This suggests that Pd forms nanoparticles on Fe, while Ni incorporates into Fe, forming alloy. The performance of catalysts (Figure 7b, the detailed product distribution is shown in Figure S9) displays a volcano-type relation between activity with the d-band filling in the 3d metals (i.e., Fe, Co, and Ni). This suggests that a finely and reciprocally tuned electronic structure of M-Fe (M = Fe, Co, Ni) is essential to regulate the catalytic performance. The Cs-G@PdFe bimetallic catalyst shows no obvious promotion to the C-O bond cleavage reactivity (i.e., benzene formation), compared to Cs-G@Fe, likely due to the absence of alloy effect. These results suggest that the modification of the electronic structure on Fe through the alloy formation with Fe is critical in tuning the surface-O binding strength and surface hydrogen species, which in turn significantly influences the HDO performance of the catalysts.

CONCLUSIONS

We have presented a highly selective and stable Cs-G@CoFe catalyst for the hydrogenolysis of phenol. Our results on the Fe-based bimetallic catalysts reveal that formation of the bimetallic alloy can finely tune the electronic properties of the Fe surface to regulate the selective hydrogenolysis of the C-O bond. The graphene overlayers not only protect the metallic surface from oxidation/poisoning by hydroxyl/Cs but also mitigate the agglomeration and sintering of bimetallic nanoparticles at high temperatures. The doped Cs inhibits the tautomerization of phenol over the catalyst surface, consequently achieving high selectivity to direct hydrogenolysis. Alloying Fe with Co modifies its electronic structure, facilitating the formation of surface weakly adsorbed H species, especially in the presence of Cs. As a result, an enhanced conversion of phenol (>threefold) was achieved on the composite Cs-G@CoFe catalysts at a 90% benzene selectivity, in comparison with the Cs-G@Fe catalyst.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.2c02075.

Detailed product distributions of Cs-G@Co, Cs-G@Fe, and Cs-G@CoFe; catalytic performances of Cs-G@ CoFe and physical mixture containing 5% Cs-G@Co and 95% Cs-G@Fe; benzene formation rate and benzene selectivity over Cs-G@CoFe with different Co loadings; XRD patterns of monometallic Fe and bimetallic CoFe; H2-TPR profiles of Fe and CoFe with surface oxidation (signal has been reversed); Raman spectra of fresh CoFe and G@CoFe; benzene formation rate and product distribution over CoFe-alloy-based catalysts; TEM images, size distribution, and mean particle size of CoFe and G@CoFe; detailed product distributions of Cs-G@Fe, Cs-G@CoFe, Cs-G@NiFe, and Cs-G@PdFe; comparison of HDO reactivity in the conversion of phenolics to arenes for Cs-G@CoFe with other HDO catalysts from the literature (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Junming Sun The Gene & Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, Washington 99164, United States; orcid.org/0000-0002-0071-9635; Phone: 509-335-1880; Email: junming.sun@wsu.edu
- Yong Wang The Gene & Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, Washington 99164, United States; © orcid.org/ 0000-0002-8460-7410; Phone: 509-371-6273; Email: yong.wang@pnnl.gov

Authors

- Jianghao Zhang The Gene & Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, Washington 99164, United States; State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China; orcid.org/0000-0002-5245-507X
- Junrui Li The Gene & Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, Washington 99164, United States
- Berlin Sudduth The Gene & Linda Voiland School of Chemical Engineering and Bioengineering, Washington State University, Pullman, Washington 99164, United States
- Changbin Zhang State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China; orcid.org/0000-0003-2124-0620
- Hong He State Key Joint Laboratory of Environment Simulation and Pollution Control, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China; orcid.org/0000-0001-8476-8217

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.2c02075

Author Contributions

J.Z., J.S., and Y.W. conceived the research ideas and designed the experiments. Y.W. and J.S. supervised and led the project. J.Z. and J.L. synthesized and evaluated the catalysts. J.Z. performed the XRD, HRTEM, temperature-programmed experiments, and ATR-FTIR characterizations. J.Z. and J.S. wrote the manuscript. C.Z., H.H., and Y.W. revised the manuscript. All authors discussed the results and commented on the manuscript.

Notes

The authors declare no competing financial interest.

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