Direct, Selective Production of Aromatic Alcohols from Ethanol Using a Tailored Bifunctional Cobalt−Hydroxyapatite Catalyst

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Supporting Information

ABSTRACT: Aromatic alcohols are essential components of many solvents, coatings, plasticizers, fine chemicals, and pharmaceuticals. Traditional manufacturing processes involving the oxidation of petroleum-derived aromatic hydrocarbons suffer from low selectivity due to facile overoxidation reactions which produce aromatic aldehydes, acids, and esters. Here we report a Co-containing hydroxyapatite (HAP) catalyst that converts ethanol directly to methylbenzyl alcohols (MB−OH, predominantly 2-MB−OH) at 325 °C. The dehydrogenation of ethanol to acetaldehyde, which is catalyzed by Co2+, has the highest reaction barrier. Acetaldehyde undergoes rapid, HAP-catalyzed condensation and forms the key intermediate, 2-butenal, which yields aromatic aldehydes through self-condensation and then MB−OH via hydrogenation. In the presence of Co2+, 2-butenal is selectively hydrogenated to 2-butenol. This reaction does not hinder aromatization because cross-coupling between 2-butenal and 2-butenol leads directly to MB−OH without passing through MB═O. Using these insights a dual-bed catalyst configuration was designed for use in a single reactor to improve the aromatic alcohol selectivity. Its successful use supports the proposed reaction mechanism.

KEYWORDS: ethanol, aromatic alcohols, cobalt−hydroxyapatite, dehydrogenation, dehydrocyclization

1. INTRODUCTION

Methylbenzyl alcohols (MB−OH) are essential petrochemical precursors in fine chemical manufacturing, e.g., plasticizers and pharmaceuticals. Traditionally, they are produced principally via the oxidation of petroleum-derived xylenes. Inevitable overoxidation often results in more than 60% conversion to byproducts (e.g., aldehydes, acids, and esters), which represents a waste of raw materials and creates a need for energy-intensive separations. Direct production of MB−OHs without the need for aromatic hydrocarbon feedstocks could be more energy and cost efficient and in particular make use of more sustainable feedstocks. It may also open up alternative routes to phthalic acid, an essential component in plastics.

Ethanol is a widely available, versatile, biomass-derived platform molecule. Its use has been widely explored in the production of value-added chemicals such as acetaldehyde, olefins, and C4−12 aliphatic alcohols via dehydrogenation, dehydration, and C=C coupling. However, achieving selectivity for high molecular weight products, especially aromatic oxygenates, remains a challenge due to the complex network of competing reactions in ethanol cascade processes as well as a lack of versatile catalysts. Recently,
Resasco\textsuperscript{16} and Flaherty\textsuperscript{17} managed to produce methylbenzaldehydes ($\text{MB}^=\text{O}$) from acetaldehyde (instead of ethanol) over MgO and hydroxyapatite, respectively. However, the selectivity was poor (<27%), mainly because of nonselective intermolecular hydrogen transfer between enal intermediates and ethanol, leading to saturated aliphatic products. Kinetic studies indicate that the formation rate of aromatic oxygenates is proportional to the acetaldehyde concentration.\textsuperscript{18} Although solid base materials such as MgO and hydroxyapatite are well known as acid–base catalysts for C–C coupling,\textsuperscript{11,14,15} they are not efficient for alcohol dehydrogenation.\textsuperscript{16} Li and co-workers\textsuperscript{19,20} improved the reactivity for ethanol upgrading by combining transition metal and acid–base catalysts in which dehydrogenation occurs at Pd or Cu sites and aldol condensation is catalyzed by Lewis acid and/or base sites. In that case saturated aliphatic alcohols were mainly obtained because the metal nanoparticles promote not only ethanol dehydrogenation but also enal hydrogenation.\textsuperscript{21–23} The key question is how to protect enals from nonselective dehydrogenation while promoting ethanol dehydrogenation. Recently, homogeneous complexes of 3d transition metal ions, such as $\text{Co}^{2+}_{\text{II}}$ and $\text{Fe}^{2+}_{\text{II}}$, have been reported to catalyze acceptorless alcohol dehydrogenation\textsuperscript{26} as well as selective hydrogenation of unsaturated C=O bonds in $\alpha_\beta$-unsaturated compounds.\textsuperscript{25} We reasoned that the combination of an acid–base catalyst with one of these transition metal species would make it possible to couple ethanol dehydrogenation and C–C coupling to achieve selective production of aromatic oxygenates, which has not been reported so far.

The surface of hexagonal hydroxyapatite [HAP, $\text{Ca}_{10}(\text{OH})_2(\text{PO}_4)_6$] has Lewis acid–base pairs and exhibits high activity for C–C coupling in ethanol upgrading.\textsuperscript{27–30} Moreover, $\text{Ca}^{2+}$ ions on the HAP surface are easily exchanged by other divalent metal cations (such as $\text{Co}^{2+}$, $\text{Ni}^{2+}$, $\text{Fe}^{2+}$, $\text{Cu}^{2+}$, etc.) due to the flexible chemical composition of the hexagonal unit cell, thus presenting broad opportunities for the design of multifunctional catalysts with atomically dispersed metal sites. In this work, a cobalt-doped hydroxyapatite (Co–HAP) was prepared and used to catalyze the conversion of ethanol to methylbenzyl alcohols. While the main products on undoped HAP are aliphatic alcohols, with only traces of aromatics (less than 0.4%), the presence of $\text{Co}^{2+}$ sites dramatically alters the major reaction pathways and shifts the product distribution to MB–$\text{OHs}$. $\text{Co}^{2+}$ sites in HAP catalyze ethanol dehydrogenation to acetaldehyde, which is followed by fast condensation and dehydrocyclization to yield aromatic oxygenates. The process of ethanol to methylbenzyl alcohols represents a new and facile strategy to produce aromatic oxygenates efficiently from renewable carbon.

2. EXPERIMENTAL SECTION

2.1. Synthesis. Hydroxyapatite (HAP) was synthesized by precipitation using $\text{Ca(NO}_3)_2$ and $\text{(NH}_4)_2\text{HPO}_4$ as precursors and $\text{NH}_3\cdot\text{H}_2\text{O}$ as precipitant.\textsuperscript{27} Co–HAP was prepared by the following steps. Briefly, HAP was impregnated with an aqueous solution of Co(NO$_3$)$_2$·6H$_2$O to achieve incipient wetness and held at room temperature for 30 min. As-prepared Co–HAP was obtained by drying at 50 °C in flowing air, calcining at 350 °C for 2 h in static air, and thermal pretreatment at 400 °C for 2 h in 8 vol % H$_2$/N$_2$ in order to mimic reaction conditions. The actual Co content was determined by ICP-OES to be 0.8 wt %.

2.2. Characterization. Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained on JEOL JEM-2100 and JEOL JEM-2100F microscopes, operated at an accelerating voltage of 200 kV. Powder X-ray diffraction patterns were obtained with a Panalytical X’pert Pro Super X-ray diffractometer using Cu Ka radiation (40 kV, 40 mA, $\lambda = 0.15418$ nm). X-ray photoelectron spectroscopy (XPS) data were obtained on a PHI Versaprobe 5000 spectrometer equipped with an Al Ka X-ray source. CO-FTIR experiments were carried out in a custom batch reactor. Spectra were recorded after exposure to $10^{-5}$ Torr CO at $\sim 173$ °C on a Bruker 70 V spectrometer. $^{31}$P MAS NMR spectra were recorded on an Agilent DD2-500 MHz spectrometer operating at 130.2 MHz using a 4 mm MAS NMR probe and a spinning rate of 14 kHz. The type and number of base and acid sites on various HAP surfaces were determined by temperature-programmed desorption mass spectrometry (TPD-MS) of CO$_2$ and NH$_3$, respectively, using a Micromeritics AutoChem II 2920 apparatus. High-sensitivity low-energy ion scattering (HS-LEIS) spectra were collected using an IonTOF Qtaq100 low-energy ion scattering analyzer. Diffuse reflectance infrared Fourier-transform (DRIFT) spectra were collected on a Bruker 70 V spectrometer equipped with an in situ reaction cell (HARRICK) and MCT detector.

2.3. Catalytic Activity Measurements. Catalytic performance was tested in a quartz-tube, packed-bed reactor (8 mm i.d.). All experiments were carried out at atmospheric pressure with a total gas flow rate of 30 mL/min. A gas chromatograph with a flame ionization detector (GC-FID) was
connected to the reactor outlet to quantify the products. Their identities were confirmed by GC-MS analysis (Agilent 7890A GC, interfaced with 5975C MS). Methane was cofed with ethanol as an inert internal standard for carbon balance calculations over the temperature range from 225 to 350 °C at 5–55% ethanol conversion and from 1 to 80% ethanol conversion at 325 °C. The carbon balance is better than 98% (the ±2% imbalance is likely due to analysis uncertainty). Details of the calculations for ethanol conversion and product selectivity are shown in the Supporting Information.

3. RESULTS AND DISCUSSION


Figure 1 compares the light-off profiles for ethanol conversion over Co–HAP (0.8 wt % Co) and HAP only in the temperature range from 250 to 350 °C. The profiles are similar with apparent activation energies for ethanol conversion over HAP and Co–HAP of 70 ± 4 and 89 ± 3 kJ/mol, respectively (Figure S1). However, the product distributions differ dramatically and change with reaction temperature. Over HAP, the products vary in carbon chain length but remain as saturated aliphatic alcohols, including n-butanol and C6–12 alcohols, with only traces of aromatics (less than 0.4%), in agreement with the literature.27 In contrast, the reaction over Co–HAP clearly generates 2-methylbenzyl alcohol (2-MB–OH) even at 250 °C in addition to saturated aliphatic alcohols. The selectivity for 2-MB–OH increases with temperature until it becomes the major product at 325 °C with a selectivity as high as 54% at a conversion of 35%. Thus, Co–HAP has a selectivity for 2-MB–OH that is 2 orders of magnitude higher than that of HAP alone. H2 was detected concomitantly with aromatic oxygenates in an amount proportional to the yield of aromatic oxygenates. The H2 concentration reaches a maximum value of 40 mol % among all products (including water) at 325 °C (Table S1).

The effect of Co loading on the production of aromatic oxygenates was explored. As shown in Figure S2, the ethanol conversion increases slightly with Co content from 0 to 0.8 wt % and then remains constant as the Co loading increases further. Meanwhile, the selectivity for MB=O and MB–OH increases dramatically from 0.4% to 59%, while the yield of aliphatic alcohols is strongly attenuated. As a result, the catalyst containing 0.8 wt % Co was used for further investigation. Interestingly, this loading is very similar to the critical Co content used in the ion-exchanged Co–HAP catalysts as reported for 2-butanol oxidative dehydrogenation.36 These findings reveal significant differences in the reaction pathways for ethanol conversion over the two catalysts.

To investigate how the presence of Co sites in Co–HAP controls the formation of aromatic oxygenates, several catalysts based on Co interacting with various supports (Al2O3, SiO2, carbon, MgAlxOy, CaO, and Ca3(PO4)2) were prepared and tested (Figure S3). These supports represent a range of acidic, neutral, basic, and acidic–basic materials. No aromatics were obtained over Co/Al2O3, Co/SiO2, or Co/carbon. Although MgAlxOy is known to be an acid–base catalyst for ethanol upgrading to n-butanol,11,14,15 the combination of Co and MgAlxOy does not produce aromatics. In contrast, small amounts of MB=O/–OH were detected over Co/CaO and Co/Ca3(PO4)2. These results suggest that synergy between the Co sites and the acid–base sites in Co–HAP is critical for MB=O/–OH production from ethanol.

The stability of the Co–HAP catalyst in the upgrading of ethanol to methylbenzyl alcohols was investigated by operating at an intermediate conversion for 900 min at 325 °C. During this time insignificant declines were observed in both the

Figure 2. Characterization of Co–HAP (0.8 wt % Co) and HAP: (a, b) TEM images of Co–HAP, recorded at two different resolutions, and (c, d) comparison of Co 2p and O 1s XP spectra for the two materials.
ethanol conversion (from 35% to 33%) and the selectivity to 2-MB−OH (from 54% to 53%) (Figure S4).

3.2. Characterization of Co Species. Since H₂ is generated during ethanol conversion over Co−HAP (as described above), the catalyst was pretreated at 400 °C in 8 vol % H₂/N₂ prior to its characterization by HAADF-STEM, XPS, FTIR, 31P MAS NMR, CO₂-TPD, and HS-LEIS. The high-magnification images in Figures 2a, 2b, and S5 show well-crystallized HAP with no evidence for Co-containing aggregates on the surface in any of the regions investigated, which is in accord with the absence of powder X-ray diffraction peaks for any Co-containing species in Co−HAP (Figure S6).

There are two possible explanations for this finding: (1) subnanometer CoOₓ domains are present on the surface of HAP but are not visible due to the lack of Z contrast between Co and Ca or (2) Co incorporation occurs by an ion-exchange-like process during catalyst preparation, leading to atomic dispersion of Co²⁺ ions on the HAP surface. Although the presumed Co²⁺ single sites are not resolved, HAP materials are known to undergo ready ion exchange. The chemical state of Co was explored using XPS. Figure 2c shows the Co 2p³/₂ and 2p₁/₂ binding energies (BEs) at 781.0 and 796.7 eV, respectively. The spin–orbit splitting of 15.7 eV (ΔE = E_(Co 2p¹/₂) − E_(Co 2p³/₂)) is characteristic of Co²⁺ ions. The appearance of satellite peaks at 786.6 and 802.4 eV further confirm that the metal is present as Co²⁺ ions. Figure 2d shows the O 1s BE at 530.6 eV, corresponding to lattice oxygen in HAP. The O 1s peak position and full width at half-maximum (FWHM) are the same for Co−HAP and HAP. Furthermore, when the temperature of H₂ pretreatment was increased to 600 °C, the major form of the metal remains Co²⁺ (Figure S7), demonstrating that the dispersed metal ions interact strongly with HAP.

The local chemical environment of Co²⁺ was further probed using IR spectroscopy with CO as the probe. Under ambient CO pressure at 25 °C, no adsorbed CO was detected on either HAP or Co−HAP. The latter finding reconfirms the absence of metallic Co nanoparticles even after pretreatment in H₂ at 400 °C. Performing the CO-IR analysis on HAP at low temperature (−173 °C) led to the appearance of a sharp peak at 2184 cm⁻¹ assigned to CO adsorbed on Ca²⁺ sites (Figure 3a). The peak is absent from the spectrum of Co−HAP at the same temperature, but there is instead a sharp peak at 2168 cm⁻¹, corresponding to CO bound to Co²⁺. Its linewidth suggests that Co²⁺ is present in a single form on the surface of HAP, supporting the idea that Co²⁺ ions undergo substituting for Ca²⁺. The absence of CO bound to Ca²⁺ sites is a consequence of the low affinity of CO for Ca²⁺. In previous work, only 5% of the HAP surface Ca²⁺ sites (presumably the fraction that is coordinatively unsaturated, located at the edges and defects) was found to bind CO. During the catalyst preparation by incipient wetness these most accessible Ca²⁺ sites are probably replaced by Co²⁺, resulting in CO binding only to the surface Co²⁺ sites of Co−HAP. This conclusion is further supported by the observation of the same signal for adsorbed CO on an ion-exchanged HAP (prepared according to a literature procedure), in which Co²⁺ was shown to be substituted for some of the Ca²⁺ ions. For this material, a single, sharp peak at 2168 cm⁻¹ was observed for adsorbed CO (Figure S8). After use in the reaction of ethanol to MB−OH for 1 h at 325 °C, the IR of the Co−HAP catalyst still shows a single peak for adsorbed CO at 2168 cm⁻¹, confirming that no significant structural changes occur under the reaction conditions.

31P MAS NMR analysis was conducted to shed more light on the possible locations of Co²⁺ species in HAP. Figure 3b shows that the presence of paramagnetic Co²⁺ leads to a doubling of the FWHM of the 31P signal compared to HAP.
only, i.e., 2.2 vs 1.0 ppm. Similar broadening effects have been reported in the literature for Co\textsuperscript{2+}-exchanged HAP materials,\textsuperscript{31} in which the metal ion is believed to interact with phosphate groups through bridging oxygens, and sites denoted [Co–O–P] are probably formed.

The surface of HAP presents base sites\textsuperscript{43} which can be modified by the substitution of Co\textsuperscript{2+} for Ca\textsuperscript{2+} ions. Therefore, the basicity of Co–HAP was compared with that of HAP only by CO\textsubscript{2}-TPD-MS. Figure 3c shows that both materials have three CO\textsubscript{2} desorption peaks in the relatively low-temperature region. For HAP only, the peaks are centered at ca. 160, 220, and 290 °C. These features are assigned to CO\textsubscript{2} desorbing from OH bound to Ca\textsuperscript{2+} (weak, denoted as [Ca–OH]), O\textsuperscript{2–} bound to Ca\textsuperscript{2+} (medium, denoted as [Ca–O–Ca]), and PO\textsubscript{4}\textsuperscript{3–} bound to Ca\textsuperscript{2+} (i.e., Ca\textsubscript{O}PO\textsubscript{4}\textsuperscript{3–} pairs, strong, denoted as [Ca–O–P]), respectively.\textsuperscript{40,44,45} The normalized surface density of [Ca–O–P] sites is 0.62 μmol m\textsuperscript{−2} (Table 1). In the case of Co–HAP, the surface density of [Ca–O–P] sites decreases to 0.32 μmol m\textsuperscript{−2} while the amount of CO\textsubscript{2} desorbed from [Ca–OH] and [Ca–O–Ca] sites remains unchanged. There is also a new high-temperature peak centered at 550 °C. It represents strong base sites whose presence of subsurface Co\textsuperscript{2+} affects the instantaneous formation rates for each product. According to Figure 4a, the steep initial rise in acetaldehyde formation with increasing residence time indicates that this is a primary product over Co–HAP, derived directly from ethanol dehydrogenation. However, the acetaldehyde yield soon reaches a plateau as it is converted to 2-butenal via secondary self-condensation.\textsuperscript{15–17,49} The yield of 2-butenal also reaches a plateau, while 2-MB=O/–OH can only be rationalized by fast conversion of 2-butenal to 2-MB=O/–OH. Thus, 2-butenal is an intermediate whose condensation and dehydrocyclization yields aromatic oxygenates.

In the case of HAP, n-butanol is formed as a primary product (Figure 4b) followed by C\textsubscript{5}–C\textsubscript{12} alcohols as secondary products. This finding is consistent with the result of Meunier et al.\textsuperscript{40} At all residence times, acetaldehyde and 2-butenal are minor products with low initial slopes. With the available time resolution, it is difficult to be sure whether n-butanol arises from acetaldehyde condensation and hydrogenation, although this pathway is widely reported in the literature.\textsuperscript{27,29,30,45,51}

In situ DRIFTS experiments were conducted to observe whether acetaldehyde and 2-butenal are formed on Co–HAP and HAP. Figure 5a shows a weak but discernible peak at 1713

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### Table 1. Physical and Chemical Properties of HAP and Co–HAP Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Co Content (wt %)</th>
<th>Atomic Ratio</th>
<th>Base Amount (μmol m\textsuperscript{−2})\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Ca/P</td>
<td>Co/Ca</td>
</tr>
<tr>
<td>HAP</td>
<td>0</td>
<td>1.67</td>
<td>0.67</td>
</tr>
<tr>
<td>Co–HAP</td>
<td>0.8</td>
<td>1.67</td>
<td>0.07</td>
</tr>
</tbody>
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\textsuperscript{a} Measured by CO\textsubscript{2}-TPD-MS at m/z = 44. \textsuperscript{b} Measured by ICP-OES in the bulk. \textsuperscript{c} Obtained from HS-LEIS upon the surface of Co–HAP.

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**Figure 4.** Comparison of selectivities in ethanol upgrading over Co–HAP (0.8 wt % Co) and HAP at 325 °C showing how product distributions depend on the residence time (1/WHHSV). Dashed lines are present only to guide the eye. Reaction was conducted in a feed gas of 5.7 vol % C\textsubscript{2}H\textsubscript{5}OH in N\textsubscript{2} with WHSV from 2.0 to 33.4 gC\textsubscript{2}H\textsubscript{5}OH g\textsubscript{cat} \textsuperscript{−1} h\textsuperscript{−1}.
assigned to the \( v(C=O) \) mode of acetaldehyde adsorbed on Co–HAP (Figure S9). It is observed immediately after ethanol dosing. A peak at 1672 cm\(^{-1}\) was detected concomitantly, corresponding to the \( v(C=O) \) mode of absorbed 2-butenal (Figure S9). Both peaks become less prominent as the reaction proceeds. After 5 min, the characteristic features of 2-MB–OH dominate the spectrum, as shown by comparison to its reference spectrum. In contrast, neither acetaldehyde nor 2-butenal was detected over HAP under the same experimental conditions (Figure 5b).

Bell et al.\(^{45}\) reported a positive reaction order in acetaldehyde during \( n \)-butanol formation over HAP. We observed a similar effect as well, suggesting that \( n \)-butanol is formed by acetaldehyde condensation followed by hydrogenation. If and how ethanol is dehydrogenated to acetaldehyde over HAP remain a mystery. We investigated the dependence of the ethanol reaction rate on \( p(H_2) \) over Co–HAP and HAP (Figure S10). The rate is completely independent of \( H_2 \) partial pressure over HAP but shows a negative reaction order over Co–HAP. This finding clearly demonstrates that ethanol dehydrogenation (eq 1) does occur over Co–HAP.

\[
\text{CH}_3\text{CHO} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH}
\]

Moreover, some \( n \)-butanol was also detected over Co–HAP, in addition to acetaldehyde, 2-butenal, and MB—OH. The initial slope for \( n \)-butanol formation is lower than that for 2-MB—OH but higher than that for 2-butenal (Figure S11). A sudden increase in the \( n \)-butanol yield occurs at the point when acetaldehyde and 2-butenal level off, suggesting that some 2-butenal is hydrogenated to \( n \)-butanol over Co–HAP. We define the ratio \( \alpha \) as the total selectivity for aromatic oxygenates (MB—OH) relative to the total selectivity for higher aliphatic alcohols (C\(_4\)--C\(_{12}\)OH), i.e., \( \alpha = \frac{\text{sel}[(\text{MB—OH})]}{\text{sel}[(\text{C}4\text{--C}12\text{OH})]} \).

Figure 5. In situ DRIFTS recorded over (a) Co–HAP (0.8 wt % Co) and (b) HAP, both at 300 °C after one dose of ethanol (\( 5 \times 10^{-8} \) mol) using \( \sim 40 \) mg of catalyst. For comparison, spectra of pure \( n \)-butanol (\( n\text{-C}_4\text{H}_9\text{OH} \)) and 2-MB—OH are plotted in gray.

Figure 6. Comparison of selectivities for Co–HAP (0.8 wt % Co) and HAP at 325 °C during ethanol upgrading showing the dependence of \( \alpha = \frac{\text{sel}[(\text{MB—OH})]}{\text{sel}[(\text{C}4\text{--C}12\text{OH})]} \) on the concentrations of acetaldehyde (\( \text{CH}_3\text{CHO} \)) or 2-butenal (\( \text{C}_4\text{H}_6\text{O} \)), each cofed with \( \text{C}_2\text{H}_5\text{OH} \).
both catalysts. Consequently, the product distribution over Co−HAP is determined by the competition between 2-butenal hydrogenation and its aromatization. The key question is which factors tune the dehydrogenation of ethanol to acetaldehyde while suppressing the hydrogenation of 2-butenal to n-butanol.

Both metallic Co nanoparticles22 and Co2+-containing coordination compounds24 are catalytically active in alcohol dehydrogenation; however, they show different behaviors in the selective hydrogenation of 2-butenal.52 To investigate the influence of Co oxidation state on ethanol upgrading to MB−OH, the catalyst was pretreated at various temperatures (325−600 °C) under 8 vol % H2/N2 prior to characterization and catalytic testing. The Co2+/Co0 ratio was determined by XPS (Figure S7 and Table S2). We note that ethanol conversion barely changes with the variation in initial Co oxidation state, suggesting that no structural damage of the HAP occurs during H2 pretreatment (up to 600 °C) because the presence of Co (either as Co0 or Co2+) does not greatly increase the overall rate compared to HAP alone. Figure 1 shows this is the case. Another possibility is that the barriers for ethanol dehydrogenation are almost similar for Co0 and Co2+. This situation was reported recently by a DFT study using a Co0/CoO model system.53 The selectivity toward unsaturated products (acetaldehyde, 2-butenal, and MB−OH) remains constant as long as the Co2+ fraction remains above ∼90%; then it decreases significantly (Figure 7). The selectivity toward saturated aliphatic alcohols shows the opposite trend, suggesting that 2-butenal is more readily hydrogenated to n-butanol as the Co0 fraction increases.

A substantial amount of H2, 2.7 mmol gcat−1 h−1 at 17% ethanol conversion, is produced over Co−HAP during the reaction of ethanol to MB−OH. Since this H2 can be used to hydrogenate 2-butenal, various concentrations of H2 were cofed with 2-butenal to investigate the resulting reactions over Co−HAP. Only traces of 2-butenol were observed, but there was a significant increase in 2-MB−OH selectivity (Figure 8), indicating that carboxyl hydrogenation does occur over Co−HAP. (In contrast, such hydrogenation does not occur over the HAP catalyst.)30,45 Furthermore, no n-butanol was detected, demonstrating that Co−HAP does not catalyze the full hydrogenation of 2-butenal. Consequently, C=C bonds are retained even under H2-rich conditions. The formation of n-butanol during ethanol upgrading over Co−HAP may arise from the direct coupling of ethanol (Figures 4b and 5b) or from the hydrogenation of 2-butenal using ethanol as H-donor via a Meerwein−Ponndorf−Verley (MPV) process.29,30,45

3.4. Mechanistic Investigation. To explore the reaction pathways and identify the key intermediates that control selectivity to aromatic products, each of the proposed reaction intermediates (acetaldehyde and 2-butenal) was fed directly as reactant to Co−HAP and HAP. According to Figure 9a and 9b, 2/4-MB−OH is evident when either acetaldehyde or 2-butenal is the sole feed. Notably, the selectivity to 2-/4-MB−OH was >95% (∼85% as 2-MB−OH) in the direct reactions of 2-butenal. Simultaneously, 2,4,6-octatrienal (C8 enals) was detected over both catalysts. It is likely derived from the self-condensation of 2-butenal.49 The proposed reaction mechanism for 2-MB−OH formation is shown in eqs 2−4.
The similarity in the overall reaction rates of 2-butenal over \( \text{Co}^-\text{HAP} \) and HAP is consistent with the main C–C bond-forming steps (i.e., eqs 2–4) being efficiently catalyzed by HAP alone. Preliminary results suggest that the Lewis base sites on bare HAP surface are responsible for initiating C–C coupling (to be the subject of a future study). Deprotonation of 2-butenal occurs preferentially at the \( \gamma \)-C position due to allylic stabilization of the resulting anion. Nucleophilic attack by the \( \gamma \)-C of the anion at the carbonyl C forms 2,4,6-octatrienial,\(^{49}\) which undergoes dehydrocyclization to 2-MB\(=\text{O} \) as the major product. To a lesser extent, deprotonation at the \( \alpha \)-C position results in the eventual formation of 4-MB\(=\text{O} \). The origin of aromatic aldehyde regioselectivity is summarized in Scheme 1.

Next, ethanol was cofed with acetaldehyde or 2-butenal in an amount similar to that present under ethanol upgrading reaction conditions. For catalysts both with and without Co\(^2+\), the major product switched from MB\(=\text{O} \) to MB\(=\text{OH} \) (Figure 9c and 9d), indicating that aromatic aldehydes are selectively hydrogenated with ethanol as the H-donor (via MPV)\(^{45,49}\) and/or directly by \( \text{H}_2 \) (from ethanol dehydrogenation as well as 2,4,6-octatrienial dehydrocyclization). Moreover, the 2-MB\(=\text{OH}/2\)-MB\(=\text{O} \) ratio (\( \beta = \text{sel}_{2\text{-MB=OH}}/\text{sel}_{2\text{-MB=O}} \)) increased from 6% to 28%/% as the ethanol concentration increased from 1 to 7 vol % (Figure 10a). To explore the hydrogenation mechanism of the aromatic aldehyde, the ratio \( \beta \) was measured over HAP and Co–HAP using 2-butenal and ethanol as cofeeds. High reaction temperatures favor 2-MB\(=\text{OH} \) formation over both catalysts (Figure 10b). In the case of HAP, the \( \beta \) ratio increased dramatically from 0.3%/% to 2.5%/% as the reaction temperature increased from 250 to 350 °C. Given that HAP shows very poor ethanol dehydrogenation activity (Figures 4b and 5b) and almost no MB\(=\text{OH} \) is formed when 2-butenal alone is fed (Figure 9b), the HAP-catalyzed hydrogenation of the aromatic aldehyde is likely to involve intermolecular H transfer in which ethanol serves as a direct H-donor (MPV reaction, Figure 10c). For Co–HAP, the \( \beta \) value is three times larger than that for HAP under the same reaction conditions, suggesting that Co\(^{2+}\) provides additional active sites that activate \( \text{H}_2 \) and catalyze surface-mediated MB\(=\text{O} \) hydrogenation\(^54\) (Figure 10c). The proposed reactions for aromatic aldehyde hydrogenation are shown for 2-MB\(=\text{O} \) in eqs 5 and 6.

In situ DRIFTS experiments were conducted to further explore the feasibility of the reaction steps proposed in eqs 1–6 for Co–HAP. The first spectrum in Figure 11 was measured immediately after a dose of ethanol in order to identify the initial surface species formed. Peaks at 1713 and

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**Figure 9.** Comparison of aldehyde reaction rates and selectivities over Co–HAP (0.8 wt % Co) and HAP at 325 °C upon feeding (a) 1.1 vol % \( \text{CH}_3\text{CHO}/\text{N}_2 \), (b) 0.54 vol % \( \text{C}_4\text{H}_6\text{O}/\text{N}_2 \), (c) 1.1 vol % \( \text{CH}_3\text{CHO}/4.5 \) vol % \( \text{C}_2\text{H}_5\text{OH}/\text{N}_2 \), and (d) 0.54 vol % \( \text{C}_4\text{H}_6\text{O}/4.5 \) vol % \( \text{C}_2\text{H}_5\text{OH}/\text{N}_2 \).

**Scheme 1. Proposed Origin of Regioselectivity in MB\(=\text{O} \) Formation from 2-Butenal**

Next, ethanol was cofed with acetaldehyde or 2-butenal in an amount similar to that present under ethanol upgrading reaction conditions. For catalysts both with and without Co\(^2+\), the major product switched from MB\(=\text{O} \) to MB\(=\text{OH} \) (Figure 9c and 9d), indicating that aromatic aldehydes are selectively hydrogenated with ethanol as the H-donor (via MPV)\(^{45,49}\) and/or directly by \( \text{H}_2 \) (from ethanol dehydrogenation as well as 2,4,6-octatrienial dehydrocyclization). Moreover, the 2-MB\(=\text{OH}/2\)-MB\(=\text{O} \) ratio (\( \beta = \text{sel}_{2\text{-MB=OH}}/\text{sel}_{2\text{-MB=O}} \)) increased from 6% to 28%/% as the ethanol concentration increased from 1 to 7 vol % (Figure 10a). To explore the hydrogenation mechanism of the aromatic aldehyde, the ratio \( \beta \) was measured over HAP and Co–HAP using 2-butenal and ethanol as cofeeds. High reaction temperatures favor 2-MB\(=\text{OH} \) formation over both catalysts (Figure 10b). In the case of HAP, the \( \beta \) ratio increased dramatically from 0.3%/% to 2.5%/% as the reaction temperature increased from 250 to 350 °C. Given that HAP shows very poor ethanol dehydrogenation activity (Figures 4b and 5b) and almost no MB\(=\text{OH} \) is formed when 2-butenal alone is fed (Figure 9b), the HAP-catalyzed hydrogenation of the aromatic aldehyde is likely to involve intermolecular H transfer in which ethanol serves as a direct H-donor (MPV reaction, Figure 10c). For Co–HAP, the \( \beta \) value is three times larger than that for HAP under the same reaction conditions, suggesting that Co\(^{2+}\) provides additional active sites that activate \( \text{H}_2 \) and catalyze surface-mediated MB\(=\text{O} \) hydrogenation\(^54\) (Figure 10c). The proposed reactions for aromatic aldehyde hydrogenation are shown for 2-MB\(=\text{O} \) in eqs 5 and 6.

In situ DRIFTS experiments were conducted to further explore the feasibility of the reaction steps proposed in eqs 1–6 for Co–HAP. The first spectrum in Figure 11 was measured immediately after a dose of ethanol in order to identify the initial surface species formed. Peaks at 1713 and
1672 cm⁻¹ are assigned to the ν(C=O) modes of acetaldehyde and 2-butenal (Figure S9), respectively. They are consistent with rapid ethanol dehydrogenation and subsequent aldol condensation. The intense, broad bands at 1618 and 1601 cm⁻¹ are assigned to the coupled ν(C=C) modes of 2,4,6-octatrienal, which arises from the nucleophilic self-condensation of 2-butenal. The emerging band at 1581 cm⁻¹ as well as a shoulder at 1563 cm⁻¹ are aromatic ring-breathing modes of 2-MB=O. The spectrum suggests that 2-MB=O is produced by intramolecular dehydrocyclization of 2,4,6-octatrienal.

After the second ethanol pulse, the peak at 1581 cm⁻¹ became less pronounced while a new peak appeared at 1593 cm⁻¹. It corresponds to a ring-breathing mode of 2-MB=OH. The blue shift arises because the hydroxymethyl substituent is electron donating compared with the electron-withdrawing formyl substituent. Thus, 2-MB=O is readily hydrogenated to 2-MB=OH. Even after the third ethanol pulse the major products are still acetaldehyde, 2-butenal, and 2,4,6-octatrienal, although the spectrum has become quite complex.

The lowest temperature at which the reaction of ethanol over Co−HAP or HAP can be monitored on a reasonable time scale using DRIFTS is 250 °C; however, feeding acetaldehyde or 2-butenal to Co−HAP or HAP results in conversion to 2-MB=O even below 100 °C (Figure S9). This finding indicates that ethanol dehydrogenation, rather than a C−C coupling step, has the highest reaction barrier in ethanol upgrading to 2/4-MB=O/−OH. Among this dehydrogenation reaction on Co-based catalysts, the rate-limiting step probably involves the α−C−H bond cleavage. Thus, uphill ethanol conversion to acetaldehyde is kinetically relevant and catalyzed by Co²⁺ sites.

As the ethanol conversion increases, the selectivity of Co−HAP for 2-butenol (derived from the selective hydrogenation of 2-butenal according to the results in Figure 10) decreases almost monotonically (Figure S13). Thus, 2-butenol may be involved in the subsequent formation of MB=OH. We examined the effect of cofeeding 2-butenol with 2-butenal on the formation rates of MB=O/−OH over HAP. To exclude any contribution from ethanol, i-C₃H₇OH was used as the H donor. When 2-butenol was present in the 2-butenal feed, the formation rates of both 2-MB=O/−OH and 4-MB=O/−OH nearly doubled (Figure 12). At the same time, the molar ratios of 2-MB=OH/2-MB=O and 4-MB=OH/4-MB=O each increased by a factor of 2.

HAP is almost inactive for 2-butenol dehydrogenation, and self-condensation forms only acyclic diols. Therefore, a C−C bond is likely formed between the 2-butenal carbonyl and either the δ-C or the β-C of 2-butenol, Scheme 2. Subsequent dehydrocyclization yields the aromatic alcohol (either 2-MB=OH or 4-MB=OH) directly, in agreement with the literature. Thus, selective hydrogenation of 2-butenal to 2-butenol using ethanol and/or H₂ as H donors.
H-donor does not hinder aromatic alcohol formation because cross-coupling between 2-butenal and 2-butenol leads to MB−OH without passing through MB=O.

On the basis of the kinetic results as well as the spectroscopic evidence described above, we propose a plausible pathway for 2-MB−OH formation from ethanol over Co−HAP (Scheme 3). First, ethanol dehydrogenation to acetaldehyde occurs on the Co2+ sites. Fast condensation converts acetaldehyde to 2-butenal,56 which then undergoes coupling, dehydrocyclization,57 and hydrogenation to aromatic alcohols, i.e., 2-butenal → 2,4,6-octatrienal → MB=O → MB−OH. Dehydrocyclization occurs readily to form aromatic oxygenates and H2 over basic oxides like MgO16 and HAP.49 Moreover, the coupling of 2-butenal with 2-butenol may contribute to the direct formation of MB−OH. Both high ethanol partial pressures and high reaction temperatures promote aldehyde hydrogenation using H2 (from ethanol dehydrogenation and 2,4,6-octatrienal dehydrocyclization) and/or ethanol as the H donor, thereby favoring 2-MB−OH formation. More importantly, formation of 2-MB−OH interrupts carbon chain growth via aldol condensation. Traces of 2,4-hexadienal (derived from 2-butenal coupling with acetaldehyde) detected during the reaction may also contribute to 2,4,6-octatrienal formation. Finally, coupling of 2-butenal with 2-butenol followed by dehydrocyclization can also produce 4-MB−OH via carbanion resonance structures.58 In contrast, ethanol may undergo direct coupling to form higher aliphatic alcohols (C4−12) over HAP.50

3.5. Improving the Ethanol to Aromatic Alcohols Process by Use of a Dual Catalyst Bed. Thus far we have shown that (1) Co2+ sites in the Co−HAP catalyst are responsible for ethanol dehydrogenation and require reaction temperatures higher than 250 °C and (2) HAP is capable of catalyzing aldol condensations of acetaldehyde and 2-butenal at temperatures as low as 100 °C, leading to the formation of aromatic oxygenates provided hydrogenation of the C=C bond in 2-butenal is suppressed. If these mechanistic conclusions are valid, the yield of aromatic alcohols should be significantly enhanced by using a dual-bed catalyst configuration. Previously, our group reported that metallic Cu-based catalysts are efficient for ethanol dehydrogenation at moderate temperatures (150−260 °C).60 In principle, a simple mixture of Cu and HAP catalysts could be used in the production of MB−OH from ethanol; however, Cu is relatively unstable on oxide supports in the presence of water vapor, as the ethanol upgrading reaction conditions dictate.60 In addition, metallic Cu readily catalyzes C=C bond hydrogenation in enal intermediates,19,23 leading to the undesirable formation of saturated aliphatic alcohols. Therefore, a Cu/carbon catalyst was placed ahead of either HAP or Co−HAP in the reactor in order to achieve ethanol dehydrogenation at a lower temperature.

As expected and shown in Figure 13, the dual-bed combination of Cu/carbon||HAP gives a selectivity to MB−OH/−OH of ca. 64% at 29% ethanol conversion and 225 °C. The yield of MB−OH/−OH is even higher over Cu/carbon||HAP/−OH of ca. 64% at 29% ethanol conversion and 225 °C. The yield of MB−OH/−OH is even higher over Cu/carbon||HAP/−OH of ca. 64% at 29% ethanol conversion and 225 °C. The yield of MB−OH/−OH is even higher over Cu/carbon||HAP/−OH of ca. 64% at 29% ethanol conversion and 225 °C. The yield of MB−OH/−OH is even higher over Cu/carbon||HAP/−OH of ca. 64% at 29% ethanol conversion and 225 °C. The yield of MB−OH/−OH is even higher over Cu/carbon||HAP/−OH of ca. 64% at 29% ethanol conversion and 225 °C.

Figure 13. Selectivity for MB=O/−OH over dual-bed catalysts in a single reactor. First bed consists of Cu/carbon (4 mg) diluted with quartz sands, while second bed is either 400 mg of HAP or Co−HAP. Reaction was conducted at 225 °C in a feed gas of 5.7 vol % C2H5OH/N2 with a WHSV of 0.5 gC2H5OH gcat−1 h−1.
Co–HAP (~71% at 31% conversion). These results are consistent with our conclusion that ethanol dehydrogenation has the highest reaction barrier over both Co–HAP and HAP as single-bed catalysts and support the proposed reaction pathway in Scheme 3. In addition, these aromatic alcohols selectivities are much improved compared to that (<18%) of a dual-bed Cu/ZnO and HAP catalyst (m_{Cu}/m_{ZnO}/m_{HAP} = 1:8). This may be explained by a moderate formation rate of acetaldehyde (catalyzed by Cu) favorable to aromatics formation, because carbonyl groups of acetaldehyde show a much higher adsorption energy than hydroxyl of ethanol (ln(K_{CH3CHO}/K_{CH3OH}) = 8.04), which easily results in overpolymerization of acetaldehyde forming carbonaceous deposits and leading to HAP deactivation (Table S3). Furthermore, the yield of aromatic alcohols from a complex, multistep mechanism is remarkable. For comparison, the commercial process for converting n-butane to maleic anhydride, which is practiced on a very large scale worldwide, has a maximum selectivity of 65%. Therefore, this dual-catalyst bed study provides important fundamental insight into guide the design of a large-scale process for upgrading ethanol to value-added aromatic alcohols.

4. CONCLUSION

We discovered a new, direct route for the production of aromatic alcohols from ethanol via the design of a bifunctional dehydrogenation/aromatization catalyst. At 325 °C, the MB–OH selectivity over a single-bed Co–HAP catalyst reached 54% at an ethanol conversion of 35%. The selectivity can be further increased to 71% by combining Cu/C and Co–HAP in a dual-bed catalyst system at a lower reaction temperature (225 °C) and similar conversion. This study demonstrates that simultaneously promoting ethanol dehydrogenation while preventing hydrogenation of the C=C bonds in unsaturated enal intermediates allows HAP-based materials to catalyze the conversion of ethanol to MB–OH efficiently.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b02566.

General experimental details and additional data including catalytic data, TEM, XPS, XRD, CO-IR, and in situ DRIFTS (PDF)

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Notes

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