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Regulating Aromatic Alcohols Distributions by Cofeeding Methanol with Ethanol over Cobalt-Hydroxyapatite Catalyst

Bai-Chuan Zhou, Qing-Nan Wang, Xue-Fei Weng, Lei He, Wen-Cui Li and An-Hui Lu*[a]

Abstract: Aromatic alcohols, often used for the synthesis of plasticizers, coatings and pharmaceuticals, are currently produced from the oxidation of petroleum-derived aromatic hydrocarbons. Herein, we report a non-petroleum and environmentally friendly route for the production of aromatic alcohols: cofeeding methanol with ethanol over cobalt-hydroxyapatite catalyst, in which the distribution of aromatic alcohols products can be regulated by varying methanol pressure. Co species on hydroxyapatite can activate both methanol and ethanol to yield their corresponding aldehydes (formaldehyde and acetaldehyde). The followed cross- and self-condensations of aldehydes are catalyzed by hydroxyapatite to produce acrolein and 2-butenal, which are the key intermediates for the formation of aromatic oxygenates. The sequential cross-condensation and dehydrocyclization of acrolein and 2-butenal yield benzaldehyde, which is then hydrogenated to benzyl alcohol. The direct production of benzyl alcohol from methanol and ethanol could be regarded as a cutting-edge example, which ensures a promising route for sustainable aromatic alcohols production.

Introduction

Aromatic alcohols with oxygen functional groups are essential precursors in pharmaceuticals manufacturing.[1,2] In industry, aromatic alcohols are mainly produced via the oxidation of petroleum-derived aromatic hydrocarbons, such as methylbenzene, xylene, etc.[3] Moreover, shifting refinery targets towards gasoline production certainly causes a global shortage of aromatic hydrocarbons.[4] Although the supply of aromatic hydrocarbons has been explored by other non-oil routes, such as lignocellulose conversion,[5,6] sugar-derived furans cycloaddition,[7] aromatization of alcohols,[8,9] syngas transformation,[10,11,12] ethylene trimerization and cycloaddition,[13,14] and methane nonoxidative conversion,[4] the production of aromatic alcohols by using any sustainable feedstock rather than aromatic hydrocarbons would be more environmentally benign.

Ethanol, an available platform molecule, has been investigated for the production of value-added chemicals, such as acetaldehyde, butadiene, and higher aliphatic alcohols (C_{4-12}) by dehydrogenation,[15,16] dehydration,[17] and C–C coupling.[18,19,20] However, by far, few studies were reported to produce aromatic oxygenates from ethanol and its derivates. Resasco[21] and Flaherty[22] observed the formation of methylbenzaldehydes (MB=O) from acetaldehyde (instead of ethanol) over MgO and hydroxyapatite, respectively. Nevertheless, the selectivity was unsatisfying, mainly because of the presence of non-selective intermolecular hydrogen transfer between enal intermediates and ethanol, leading to the dominant formation of saturated aliphatic alcohols. Recently, our group reported a direct production of methylbenzyl alcohols (MB-OH) from ethanol, using a bifunctional cobalt-hydroxyapatite catalyst.[23] The existent Co^{2+} promotes ethanol dehydrogenation and simultaneously suppresses the non-selective hydrogenation of unsaturated enal intermediates, thereby allowing the selective production of 2-methylbenzyl alcohol (2-MB-OH) from ethanol. In this process, 2-butenal, a key intermediate, undergoes self-condensation and/or coupling with 2-butenol derived from the selective hydrogenation of 2-butenal to form the targeted aromatic alcohols. Inspired by the synthesis route, we attempt to regulate the distribution of aromatic alcohols by altering either the structure or the carbon number of enal intermediates.

Benzyl alcohol is also commonly used for fine chemical manufacturing.[24] Thus, exploring its sustainable synthesis route from lower alcohols is challenging, which has not been reported yet. Methanol is known as an abundant C1 platform molecule from syngas chemistry.[25,26] Cofeeding of methanol and ethanol was recently reported to form acrolein,[27] iso-butanal,[28] and iso-butanol[29,30] over metal and/or acid-base catalysts. During these reactions, formaldehyde as a key intermediate for subsequent cascade reactions was confirmed as the primary product from methanol dehydrogenation and its cross-condensation with acetaldehyde yields acrolein. We therefore propose that the cofeeding of methanol (which holds an odd carbon number) with ethanol could be an attractive potential route to regulate the aromatic alcohols distributions. In this study, catalytic results proved that the formaldehyde (CH_xO) derived from methanol can regulate the structure of enal intermediates, and in turn, change the product distributions of aromatic alcohols. As a result, benzyl alcohol (BA-OH) is formed over cobalt-hydroxyapatite, and its selectivity increases with the increment of methanol pressure. The possible reaction pathways for BA-OH production was proposed from kinetic experiments and in situ IR studies.

Results and Discussion

Dependence of product distributions on methanol concentration

Figure 1 shows that the distribution of aromatic alcohols over Co-HAP is greatly switched from methylbenzyl alcohol (C8, MB-OH) to benzaldehyde (C7, BA=O) and benzyl alcohol (C7, BA-OH) by cofeeding methanol with ethanol. When ethanol is fed alone, MB=O/-OH are presented as the only aromatic products, in accordance with our previous report.[23] Strikingly, after cofeeding methanol with ethanol, BA=O/-OH are clearly observed. The distribution of aromatic alcohols depends strongly on the ratio of methanol to ethanol, that is, the selectivity of

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MB=O/-OH decreases monotonically, while the selectivity of BA=O/-OH gradually increases and reaches a maximum of 27% in the feed of methanol mole fraction of 0.67 at 325 °C. The total selectivity towards aromatic oxygenates reaches 45% under these reaction conditions. A combination of kinetic experiments and in situ FTIR studies demonstrates that ethanol undergoes dehydrogenation, self-condensation, dehydrocyclization, and rehydrogenation to MB-OH, in which 2-butenal is the key intermediate.[23] The carbon number of BA=O/-OH (C_7) shown in Figure 1, together with their structure, indicates that cross-condensation reactions of different enal intermediates derived from methanol and ethanol take place. Simultaneously, the product distributions of saturated aliphatic alcohols (C_3 and C_5, C_4 and C_6) show an opposite trend (Table 1). These findings reveal that high concentration of methanol possibly favors the formation of enal intermediates with odd carbon number, such as acrolein,[27] which then undergoes cross-condensation with 2-butenal and dehydrocyclization to BA=O/-OH, rather than hydrogenation to *n*-propanol. As shown in Table 1, approximately 60% carbon atoms in the consumption of CH_3OH are incorporated into the aromatic alcohols. Notably, formaldehyde, dimethyl ether, CO_x (>90 mol%) and no aromatic oxygenates were observed when methanol was only fed over Co-HAP (Table 2). CO_x likely arises from the over oxidation and decomposition of formaldehyde in the presence of water, which was coproduced from the C-C coupling under reaction conditions.[31] Nevertheless, in the case of methanol-ethanol cofeeding, the CO_x selectivity is below 0.5 mol% among all the products, indicating that the cross-condensation of formaldehyde with acetaldehyde is dominant by overwhelming its oxidation/decomposition reactions.

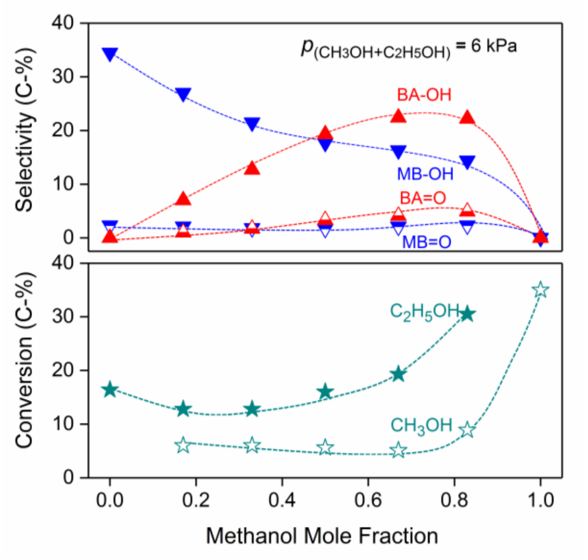

Figure 1. Dependence of product distributions on the partial pressure of methanol. Reaction activity was measured over Co-HAP (0.8 wt%) at 325 °C in a feed gas of 6 vol% (CH_3OH+C_2H_5OH) balanced with N_2 (30 mL·min^{-1}).

Table 1. Reactivity of methanol and ethanol over Co-HAP catalyst [a]

Temperature (°C)	Conversion (%)		Selectivity (%)								
	C_2H_5OH	CH_3OH	CH_3CHO	C_3H_4O	C_4H_6O	$C_{3-6}OH$	BA=O	BA-OH	MB=O	MB-OH	Others [b]
300	10.9	2.5	19.4	trace.	2.8	35.5	1.9	20.3	1.4	15.2	3.5
325	19.3	5.1	22	0.5	3.4	22.1	4.1	22.4	2.1	16.7	6.7
350	36.8	7.8	21.3	0.9	3.9	16.5	8.5	24.6	3.2	11.7	9.4
375	59.8	12.5	19.3	1.4	2.2	14.1	14.7	20.6	5.2	10	12.5

[a] Reaction activity was measured over Co-HAP (0.8 wt%) at 325 °C with a feed gas of 4vol% CH_3OH and 2vol% C_2H_5OH, N_2 balanced. [b] Other products include ethyl acetate and C_4 olefins, with minor acetone, ethylene, and diethyl ether.

Table 2. Reactivity of methanol over HAP and Co-HAP catalyst [a]

Catalyst	Conversion (%)	Selectivity (%)		
	CH_3OH	CH_3OCH_3	CO_x	Others [b]
HAP	2.1	100	-	-
Co-HAP	37.1	6.2	93.5	0.3

[a] Reaction activity was measured over HAP and Co-HAP (0.8 wt%) at 325 °C with a feed gas of 4vol% CH_3OH. [b] Other products include methyl formate.

Table 3. Reactivity of methanol and ethanol over HAP catalyst [a]

Temperature (°C)	Conversion (%)		Selectivity (%)								
	C_2H_5OH	CH_3OH	CH_3CHO	C_3H_6O	C_3-OH	*n*-C_4-OH	*i*-C_4-OH	C_5-OH	C_6-OH	Aromatics	Others [b]
300	14.9	0.3	2.5	1.0	30.5	32.5	5.3	10.9	6.3	0.1	10.9
325	25.9	3.1	2.8	1.1	28.6	26.2	7.8	13.3	7.6	0.2	12.4
350	37.6	5.8	3.2	1.7	23.0	18.6	10.6	16.3	7.5	0.3	18.8
375	54.3	12.2	4.3	3.4	18.6	11.3	13.1	14.6	5.8	0.3	28.6

[a] Reaction activity was measured over HAP at 325 °C with a feed gas of 4vol% CH_3OH and 2vol% C_2H_5OH, N_2 balanced. [b] Other products include ethyl acetate, methyl acetate and C_4 olefins, with minor acetone, ethylene, and diethyl ether.

On the other hand, when bare HAP is used, feeding ethanol or methanol-ethanol mainly produces saturated aliphatic alcohols (>80%, Table 3), with only traces of aromatics (less than 0.3%), which agrees well with the literature.[32] The condensation reaction of methanol with ethanol produces a mixture of C_3、C_4、C_5 and C_6 alcohols. The selectivity of C_3 alcohol decreases with the increase in temperature, while the selectivity of iso-butanol and C_5 alcohols shows a slight increase. Moreover, only dimethyl ether was observed over HAP by feeding methanol (Table 2). The suitable acid/base property endows HAP a good catalyst for C-C bond coupling.[22,23,32,33,34,35,36] The catalysts acid/base property modified by Co was carefully considered that 0.8wt% loading of Co reduced ca. 15% of base sites, which should decrease the C-C coupling rate if the acid/base property is the only factor,[33,35,36,37,38] however, Co-HAP shows higher catalytic reactivity as compared to bare HAP towards both acetaldehyde condensation[23] and methanol conversion (Table 1-3). These results indicate that the presence of Co is more important than the acid/base property modification in shifting reaction route of lower alcohols upgrading.

Furthermore, good stability of the Co-HAP catalyst in the reaction is evidenced by its operation for 50 h at 325 °C, where a slight decline was observed in terms of ethanol conversion (from 47% to 38%) and aromatic oxygenates selectivity (from 45% to 40%) (Figure 2).

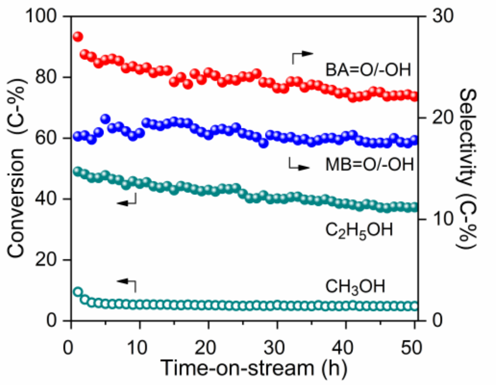

Figure 2. Reaction stability test was measured at 325 °C over Co-HAP (0.8 wt%) catalyst with a feed gas of 6 vol% (CH_3OH+C_2H_5OH)/N_2. The weight hourly space velocity of ethanol and methanol is 0.37 g_{C2H5OH}·$g_{Cat.}^{-1}$·h^{-1} and 0.51 g_{CH3OH}·$g_{Cat.}^{-1}$·h^{-1}, respectively.

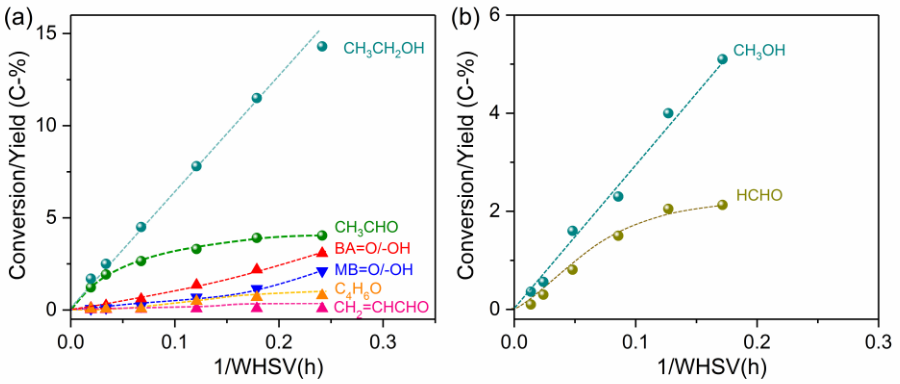

Figure 3. Dependence of the product distributions on the residence time, (a) 1/WHSV$_{C2H5OH}$ and (b) 1/WHSV$_{CH3OH}$. The dash lines are presented only to guide the eye. Reaction was conducted at 325 °C over Co-HAP (0.8 wt%) in a feed gas of 4 vol% CH_3OH and 2 vol% C_2H_5OH balanced with N_2.

Identifying the reaction intermediates

To reveal the possible reaction route of methanol-ethanol over Co-HAP, the effect of residence time on product distributions was investigated. As shown in Figure 3, the steep initial rise in acetaldehyde formation with residence time (1/WHSV) indicated that acetaldehyde is a primary product obtained directly from ethanol dehydrogenation. What's more, formaldehyde was also a primary product via the dehydrogenation of methanol, which acts as an active electrophile.[39] The yields of acetaldehyde and formaldehyde soon reached plateaus as they converted to 2-butenal and acrolein via secondary self- or cross-condensation. The yield of 2-butenal or acrolein also reached a plateau, while the formation rate of BA=O/-OH and MB=O/-OH increased with the residence time. The low yields and slopes of 2-butenal and acrolein, compared to aromatic oxygenates, could only be rationalized by the fast transformation to BA=O/-OH and MB=O/-OH. 2-butenal has been verified to undergo self-condensation and dehydrocyclization to form MB=O, which was then hydrogenated to MB-OH.[22,23] Therefore, BA=O is likely produced from the cross-condensation of 2-butenal and acrolein, and the following dehydrocyclization (vide infra). In these upgrading reactions, cross-condensation of 2-butenal with acrolein competes with its self-condensation. The data from Figure 1 display that increasing methanol pressure efficiently improves BA=O/-OH selectivity, possibly by boosting the formation of formaldehyde and acrolein. Therefore, the formation rate of BA=O/-OH is proportional to the concentration of these aldehydes intermediates under reaction conditions. In addition, a small amount of 2-propenol and 2-butenol is also observed; thus their cross-condensation with enals is possibly existing, which yields aromatic alcohols directly.[23] Neither cyclohexanone nor phenol is observed, thereby indicating that the self-condensation and dehydrocyclization of acrolein do not occur. Moreover, aliphatic $C_{3\text{-}6}$ alcohols were also yielded, via the hydrogenation of unsaturated intermediate aldehydes, using either alcohols or hydrogen as the H-donor.[40]

In the case of HAP, saturated aliphatic alcohols ($C_{3\text{-}6}$) are always the major products (Figure 4), in consistence with the prior work.[32] Based on our kinetic studies and literature report,[29] ethanol and methanol proceed direct cross- and self-condensation reactions and form aliphatic alcohols ($C_{3\text{-}6}$). At all residence times (1/WHSV < 0.5 h), acetaldehyde and formaldehyde are always minor products, and the selectivity of aromatic oxygenates is below 0.3%. These results demonstrate that the Co^{2+} sites change the activation behavior of alcohols, thus shifting the major products from saturated aliphatic alcohols to aromatic oxygenates, such as BA=O/-OH and MB=O/-OH.

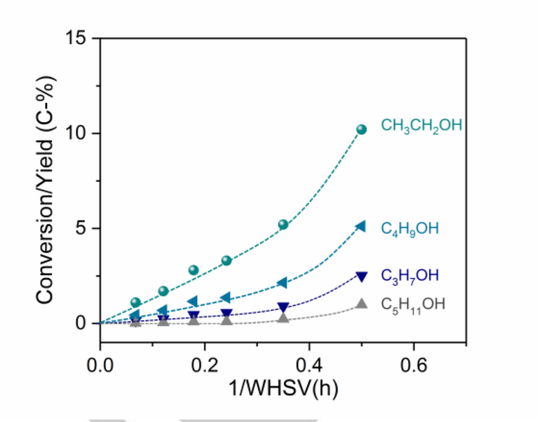

Figure 4. Dependence of the product distributions on the residence time, (1/WHSV$_{C2H5OH}$). Reaction activity was measured over HAP at 325 °C with a feed gas of 4 vol% CH_3OH and 2 vol% C_2H_5OH balanced with N_2.

In situ DRIFTS experiments were conducted to better understand the activation of methanol over Co-HAP and HAP. As shown in Figure 5, a weak signal at 2956 cm^{-1} appears after methanol dosing over both Co-HAP and HAP, corresponding to the v(C−H) mode of adsorbed methoxy species, which transform quickly into formate species (2830, 2710, 1596 and 1353 cm^{-1}) over Co-HAP but not over HAP. This finding clearly demonstrates that methanol dehydrogenation occurs over Co-HAP, and the CH_xO species (such as formaldehyde) derived from methanol possibly further participate in subsequent reactions, which is in line with our previous study.[23]

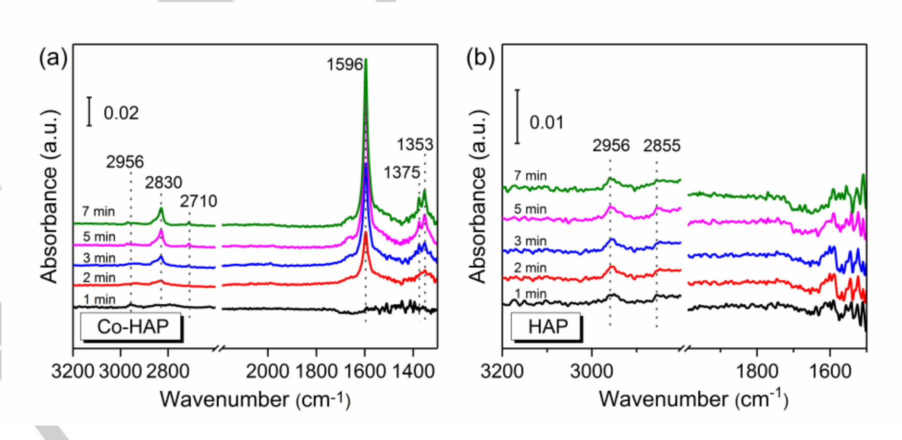

Figure 5. In situ DRIFTS spectra recorded over (a) Co-HAP (0.8 wt% Co), and (b) HAP, both at 300 °C after one dose of methanol.

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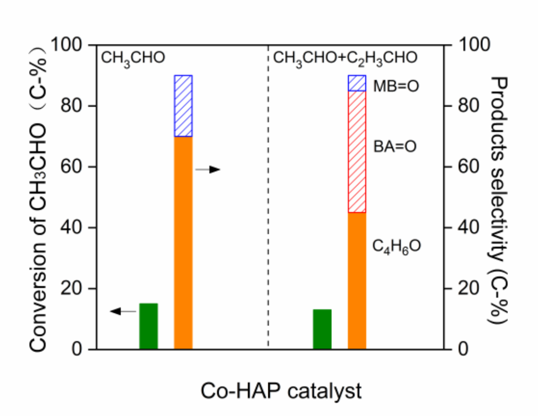


Figure 6. Product distributions from acetaldehyde (CH_3CHO, 1 kPa) alone and cofed with acrolein ($CH_2{=}CHCHO$, 1 kPa). Catalytic measurement was conducted at 325 °C.

To explore the reaction pathways and identify the key intermediates that control the selectivity of aromatic products, the reaction intermediates (acetaldehyde and acrolein) were fed directly as reactants onto Co-HAP catalyst. As shown in Figure 6, MB=O is observed to be sole aromatic products by feeding acetaldehyde. Interestingly, when acrolein was cofed with acetaldehyde, BA=O is obviously observed and becomes major aromatics. These results indicate that 2-butenal and acrolein both act as key intermediates for the formation of aromatic alcohols with odd carbon number.

Scheme 1 illustrates the possible reaction network for methanol and ethanol conversion over Co-HAP. According to our previous study, Co^{2+} sites are able to catalyze dehydrogenation of ethanol to acetaldehyde, which rapidly undergoes HAP-catalyzed condensation and dehydrocyclization to form MB=O. 2-butenal, the key intermediate, undergoes self-condensation, dehydrocyclization, and hydrogenation to 2-MB-OH. More importantly, Co^{2+} sites could prevent hydrogenation of the C=C bonds in unsaturated enal intermediates. For methanol, it proceeds dehydrogenation to form formaldehyde, which is subjected to nucleophilic attack from acetaldehyde to produce acrolein. The subsequent cross-condensation and dehydrocyclization of 2-butenal with acrolein probably yields BA=O, which is then hydrogenated to BA-OH by alcohols or H_2 as H-donor, i.e., $C_3H_4O + C_4H_6O \rightarrow$ BA=O $\rightarrow$ BA-OH.

Conclusions

We have demonstrated that by cofeeding methanol together with ethanol, benzyl alcohol can be produced over Co-HAP. The distribution of aromatic alcohols can be regulated from methylbenzyl alcohols by feeding ethanol to benzaldehyde (C_7, BA=O) and benzyl alcohol (C_7, BA-OH) by cofeeding methanol and ethanol, and to aromatic alcohols free by feeding methanol only. This study provides a direct route for the selective production of aromatic alcohols from methanol and ethanol over a tailored bifunctional Co-HAP catalyst. The introduction of methanol results in the formation of acrolein, which undergoes secondary cross-condensation with 2-butenal, dehydrocyclization, and hydrogenation to benzyl alcohols.

Experimental Section

Catalyst preparation

Hydroxyapatite (HAP) was synthesized by precipitation method according to the literature.[32] Briefly, an aqueous solution of $Ca(NO_3)_2$ (0.6 M, Sinopharm) was added dropwise to a solution of $(NH_4)_2HPO_4$ (0.4 M, Sinopharm). Then, $NH_3{\cdot}H_2O$ (25 wt%, Sinopharm) was added to the solution to achieve an initial system pH of 10.3. The slurry was stirred for 24 h at 80 °C. After filtration, drying, and calcination (600 °C for 2 h in static air), white HAP was obtained. The overall Ca/P ratio was ca. 1.67, as measured by inductively-coupled plasma optical emission spectrometry (ICP-OES, Optima2000DV).

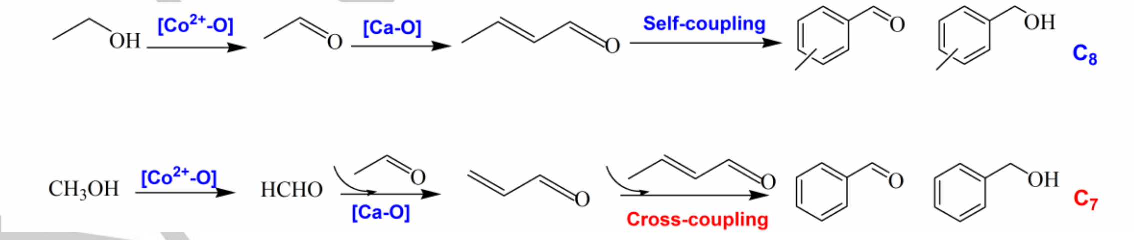
HAP was impregnated with an aqueous solution (0.35 M) of $Co(NO_3)_2$ (Sinopharm) by incipient wetness impregnation and held at room temperature for 30 min. After drying at 50 °C for 12 h in air and calcination at 350 °C for 2 h in air, the as prepared Co-HAP catalyst was obtained. The actual Co content was determined to be 0.8 wt% by ICP-OES.

Characterization

The characterization of HAP and Co-HAP catalysts refers to our previous work.[23] Briefly, the Co species of cobalt-hydroxyapatite (Co-HAP) exist as atomically dispersed Co^{2+} located into the lattice on HAP (Ca/P= 1.67) surface. In this study, the actual Co content was determined by ICP-OES to be 0.8wt % and the chemical state of Co was +2, as confirmed by XPS.

DRIFTS spectra were collected at a resolution of 4 cm^{-1} on a Bruker 70V spectrometer equipped with an in situ reaction cell (HARRICK) and MCT detector. 50 mg catalyst powder was pre-treated at 400 °C for 1 h in a flow of 8% H_2/N_2. Then, the sample was maintained at 300 °C in

Scheme 1. Proposed Pathways to Form Aromatic Oxygenates from Ethanol and Methanol.



flowing N_2 to collect the background spectrum. Methanol vapor was fed into the chamber by N_2 bubbling, and the spectra were simultaneously collected at different reaction time. The amount of methanol (6×10^{-8} mol) delivered to the cell was controlled by a sample loop and the saturated vapor pressure at a given temperature.

Catalytic tests

Catalytic performance was tested in a quartz-tube, packed-bed reactor (8 mm inner diameter). The reaction temperature was maintained using a vertically aligned tube furnace equipped with a YuDian AI controller (series 708P) and a K-type thermocouple.

The Co-HAP catalyst was pre-treated at 400 °C for 2 h in 8% H_2/N_2 prior to reaction. All experiments were carried out under atmospheric pressure with a total gas flow rate of 30 mL/min. For cofeeding of methanol with ethanol experiments, the methanol and ethanol partial pressures were varied while the total alcohol mixture pressure for all experiments were ensured, (i.e. $p_{(CH3OH+C2H5OH)} = 6$ kPa). The outlet of the reactor was connected with a Gas Chromatograph (GC) equipped with a Flame Ionization Detector (FID) and a thermal conductivity (TCD) to analyze the products. The residence time for each specific component was determined using the corresponding standard chemicals (Benzaldehyde, Benzyl alcohol, AR; C_1-C_6 alcohols, 2- and 4-methylbenzyl alcohols, Sinopharm; acrolein, Energy chemical; Acetaldehyde, Aladdin; E-2-butenal, AcroSeal; 2- and 4-tolualdehyde, J&K). The identities of products were further confirmed by GC-MS analysis (Agilent 7890A GC interfaced with 5975C MS).

The conversion and product selectivity were calculated based on moles of carbon in the products, as follows:

Ethanol conversion:

$$Con.(\%) = (1 - \frac{n_{out,C2H5OH} \times A_{out,C2H5OH} \times f_{out,C2H5OH}}{n_{in,C2H5OH} \times A_{in,C2H5OH} \times f_{in,C2H5OH}}) \times 100\% \quad (1)$$

Methanol conversion:

$$Con.(\%) = (1 - \frac{n_{out,CH3OH} \times A_{out,CH3OH} \times f_{out,CH3OH}}{n_{in,CH3OH} \times A_{in,CH3OH} \times f_{in,CH3OH}}) \times 100\% \quad (2)$$

Product selectivity:

$$Sel.(\%) = \frac{n_i \times A_i \times f_i}{\sum_{i\geq2} n_i \times A_i \times f_i} \times 100\% \quad (3)$$

The carbon number, FID peak area, response factor, and molar yield of each product are designated n_i, A_i and f_i, respectively.

The Co-HAP catalyst exhibited good stability in a 50 h-test, showing a carbon deposition rate of 0.0012 mg/min. As the feed rate of methanol and ethanol is 1.18 mg/min, so the carbon deposition only accounts for 0.1%/min. Therefore, the carbon balance is close to 100%. The selectivity of formaldehyde was calculated on basis of TCD （equiped with a porapak-Q column）determination, because of its low response (whose reciprocal f_M is equal to 136) on FID detector. Note that the conversion of methanol and ethanol were calculated by the external standard method, respectively. The product selectivity was obtained by the corrected area normalization method.

For studies of reaction pathways, the catalytic performance was measured at 325 °C after the system reached a steady-state. Ethanol and methanol conversions were varied by changing the catalyst mass from 2.6 to 50 mg. The bed height was kept constant during the tests with the aid of quartz sand. Ethanol conversion was maintained below 14 % to minimize the effects caused by diffusion limitation.

Acknowledgements

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Keywords: lower alcohols • aromatic alcohols • cobalt-hydroxyapatite • dehydrogenation • dehydrocyclization

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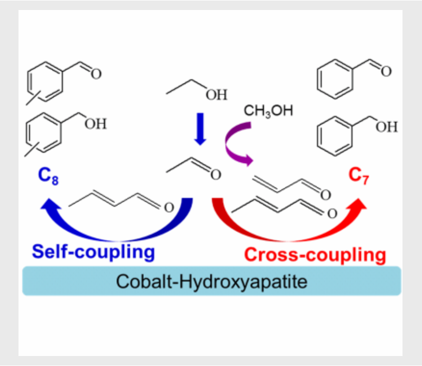
FULL PAPER

The distribution of aromatic alcohols on cobalt-hydroxyapatite is greatly switched from methylbenzyl alcohol (feeding ethanol) to benzaldehyde (C_7, BA=O) and benzyl alcohol (C_7, BA-OH) by cofeeding of methanol and ethanol.



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Regulating Aromatic Alcohols Distributions by Cofeeding Methanol with Ethanol over Cobalt-Hydroxyapatite Catalyst