




Understanding the effect of co-reactants on ketonization of carboxylic acids in the aqueous-phase pyrolysis oil of wood

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Abstract

Ketonization of carboxylic acids is one of the crucial reactions to produce sustainable bio-fuel and bio-chemicals from the pyrolysis oil of wood. Ketonization using different mixed solutions of carboxylic acids, furfural, and hydroxyacetone has been explored to understand the influence of co-feed reactants on the performance of ketonization of carboxylic acid over the selected CeZrOx catalyst. Furfural (7% in water) inhibited the catalytic activity for ketonization of acetic acid (20% solution) with reversible blocking of active sites, but for a mixed solution of hydroxyacetone (7%) and acetic acid (20%), both reactants influenced each other, resulting in very low conversions and slow and uncompleted recovery to 50% after removing hydroacetone from the mixture. For the mixed solution (20% acetic acid + 7% furfural + 7% hydroxyacetone in water), hydroxyacetone was the most reactive compound on CeZrOx and the conversions of reactants reached below 10%, due to the inhibition of co-existing carbonyl components. This work provides guidance for ketonization of carboxylic acids in the aqueous-phase pyrolysis oil.

Introduction

Currently, renewable bio-fuels are receiving extensive interest as drop-in fuels, especially as governments consider a carbon-neutral growth strategy for the mitigation of carbon dioxide emissions. Lignocellulosic biomass is one of the promising resources from which renewable transportation fuel and chemicals can be produced through thermochemical transformation such as gasification and pyrolysis technologies. In particular, a high yield of liquid product (bio-oil) can be obtained from fast pyrolysis

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of wood (Westerhof et al. 2012; Park et al. 2019). It is well known that the crude bio-oil can be upgraded into bio-fuel via hydro-upgrading processes and a number of studies including research on catalysts, reaction mechanisms and reaction conditions have been conducted (Han et al. 2019; Yu et al. 2017). Since wood consists of cellulose, hemicellulose, and lignin, if it is pyrolyzed, various organic compounds derived from cellulose and hemicellulose will be present in the crude bio-oil as well as diverse phenolic compounds derived from lignin. Up to 40 wt% of the bio-oil can be quantified due to the limited analysis tools and the heterogeneity of the oil strongly depending on the type of wood and pyrolysis conditions (Lyu et al. 2015). Furthermore, the typical bio-oil contains a large amount of water (17–30 wt%) with a high level of oxygen (36–52 wt%) and low pH (Wang et al. 2013). In other words, many issues should be overcome to chemically transform crude bio-oil into bio-fuel via hydro-upgrading processes.

One of the issues raised during the hydro-upgrading processes is severe coke formation originating from the unstable and reactive low-molecule oxygenates in the bio-oil, making long-term operation difficult. In general, the typical crude bio-oil contains large amounts of these lightweight components including acids, aldehydes, ketones and ethers, having a carbonyl functional group, C=O (Wang et al. 2013). Therefore, a hydro-stabilization step is adopted for easier operation of the subsequent hydro-deoxygenation step (Boscagli et al. 2015; Han et al. 2020). However, the lightweight oxygenates still contain lower carbon number than jet and diesel fuels even though they undergo the hydro-stabilization and hydro-deoxygenation reactions, owing to their low-carbon numbers. On this account, the crude bio-oil has been separated into an oily phase and an aqueous phase. Low-molecule compounds in the aqueous-phase bio-oil have been further fractionated and converted to larger carbon chains via C–C bond formation reactions (oligomerization, hydroalkylation and aldol condensation reactions) in order to enhance the yield of useful liquid fuels from lignocellulosic biomass (Raguindin et al. 2020; Shao et al. 2020).

Aldol condensation reaction is a well-known C–C bond formation reaction, and many studies have been carried out to produce liquid fuel intermediates using various model compounds such as furfural (FF, C₅H₄O₂) and acetone (C₃H₆O) (Su et al. 2017; Dubnová et al. 2020). In this case, carboxylic acids (RCOOH) should be removed or be limited from the reactants prior to the aldol condensation reaction, because of the stability of the basic catalysts such as MgO and hydrotalcites. Practically, acetic acid (AA, CH₃COOH) is the most abundant carbonyl compound in the aqueous-phase bio-oil. Here, ketonization (R₁COOH + R₂COOH → R₁COR₂ + CO₂ + H₂O) is crucial to reduce carboxylic acids in the aqueous-phase bio-oil and to form larger carbon chains (ketones, R₁COR₂). The produced ketones can be used as intermediates in the production of longer carbon-chain oxygenates, finally being converted into fuel-range hydrocarbons. Many different catalysts and the reaction mechanisms of ketonization have been reported in previous studies (Boekaerts and Sels 2021). In summary, high lattice energy oxides such as CeO₂ and ZrO₂ are available for the ketonization reaction with relatively high catalytic activity and are often used in biomass conversion reactions (Kumar et al. 2018). However, ketonization has been mostly studied using simple model compounds such as AA, even though different carboxylic acids and diverse

oxygenate compounds exist in the real aqueous-phase bio-oil. These carbonyl components including acids, aldehydes, ketones, and alcohols may interact with catalyst surfaces and/or with each other to undergo chemical transformation to diverse products under the reaction conditions for ketonization. The ketonization of a 16 vol% AA solution was conducted over $\text{Fe}_{0.2}\text{Ce}_{0.2}\text{Al}_{0.6}\text{O}_x$ catalyst in the presence of different components such as hydroxyacetone (HA, $\text{C}_3\text{H}_6\text{O}_2$), FF, eugenol, and guaiacol. (Jackson 2013). 10 vol% HA and 2 vol% FF had little impact on the ketone yield and phenolics at high concentrations (e.g., 5 vol% guaiacol) inhibited the catalytic activity. However, there are some limitations to understand the inhibition effects of co-existence components on the ketonization reaction due to the high reaction temperatures (above 400 °C), because HA already disappeared at 400 °C over mixed oxide catalysts (Mansur et al. 2013). Furthermore, it was difficult to reveal why phenolics and FF at high concentrations in the mixed solution reduced ketone yield without evaluation of carbon balance and analysis of spent catalysts after reactions. Catalytic upgrading of an aqueous pyrolygneous acid derived from slow pyrolysis of wood-chips was carried out to investigate the effect of ZrO_2 content in $\text{ZrO}_2\text{-FeO}_x$ catalyst on ketone yields (Mansur et al. 2013). The presence of metal impurities (K and Mg) in the feedstock reduced ketone yield, but the pre-treatment of the pyrolygneous acid using a cation-exchange resin solved this problem. However, the respective effects of co-existence carbonyl compounds have hardly been discussed due to the complexity of the pyrolygneous acid. Consequently, it is impossible to reveal all-chemical transformations occurring among oxygenates owing to the diversity and heterogeneity of bio-oil. As the first step, it is very important to understand the effects of co-existing compounds with carboxylic acids on the catalytic behavior during the ketonization reaction. Therefore, in the present work, experimental observations are provided to understand the influence of co-reactants on the performance of ketonization over the selected CeZrOx catalyst. Different mixed model solutions were prepared representative of the light fraction of the aqueous-phase bio-oil, and ketonization has been studied in the coupling of different carboxylic acids, FF, HA, and mixed solutions. The effects of various reaction conditions (FF or HA concentrations in a 20 wt% AA solution and reaction temperatures) were investigated on the catalytic performance for the ketonization of AA. Coke analysis of the spent catalysts and a time-on-steam (TOS) testing were involved to understand the behavior of co-reactants during the ketonization reaction of AA over CeZrOx catalyst.

Materials and methods

Catalyst preparation and characterization

A powder type CeZrOx mixed oxide catalyst was prepared by the co-precipitation method. Aqueous solutions of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich, 99%) and $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ (Aldrich, 99%), as precursors, were mixed according to the molar ratio of cerium and zirconium (1:1). NH_4OH solution (Aldrich, 28~30%) was added to the mixed precursor solution to obtain the precipitate. The slurry was aged by mild stirring at room temperature for 24 h, followed by filtration, washing with ethanol and

distilled water, and drying at 110 °C overnight. The dried solid was calcined at 450 °C for 2 h in air. Prior to use, the powder-type catalyst was pressed to a disk and then crushed and sieved to 40–60 mesh particles.

An X-ray diffraction (XRD) analysis of metal oxides was carried out using a Rigaku Smartlab XRD system with Cu K α radiation. The textural properties of the prepared catalysts were determined using the Brunauer–Emmett–Teller (BET) technique using a BELSORP-mini II (MicrotracBEL Co. Ltd.). A thermogravimetric analysis (TGA) of the used catalysts was conducted using a TGA Q500 with air to provide information on coke deposited on the used catalysts. TGA data were divided into three regions: weight loss below 300 °C corresponding to the desorption of water and volatile components, weight loss between 300 and 500 °C corresponding to the thermal coke, and weight loss between 500 and 750 °C corresponding to catalytic coke (Rezaei et al. 2015). Note that thermal coke is mainly deposited on the exterior of the catalyst as a result of thermal polymerization of components in gas phase, and catalytic coke is formed on the active sites in the pores of catalyst through reactions including condensation of oxygenates, oligomerization, etc.

Catalytic reaction and product analysis

A schematic drawing of the experimental set-up for the catalytic reaction is presented in Fig. 1. The prepared reactant solution was fed to a quartz bulb-reactor using an HPLC pump (Eldex Laboratories). The amount of loaded reactant solution was reported using a data logger, connected to a balance (A&D Company) during the experiments. The sieved catalysts were placed in the reactor (ID = 1/4 inch), and

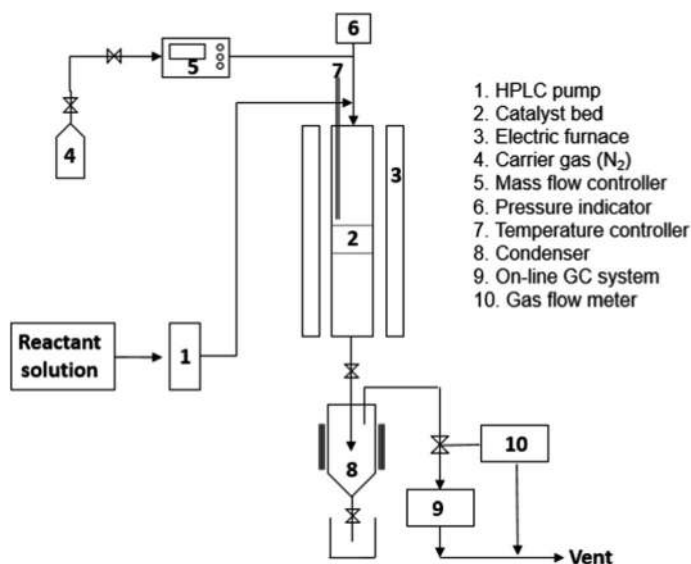


Fig. 1 Schematic drawing of the experimental set-up for catalytic reaction

a K-type thermocouple was located in the reactor to control the reaction temperature. Nitrogen was used as a carrier gas (15 ml/min). To select the representative model reactants, the light fraction separated from the pyrolysis oil of saw-dust was analyzed using a gas chromatograph (GC, Agilent 7890A) equipped with a mass spectrometer (5975C). An HP-5 column (30 m×0.32 mm×0.2 μm) and a flame ionization detector (FID) were used, and the compounds were identified using the National Institute of Standards and Technology (NIST) Mass Spectral Library. For the ketonization reaction, a carboxylic acid solution (20 wt% in water) was prepared, and 7 wt% of FF and 7 wt% of HA were added to the carboxylic acid solution, unless specifically stated.

The collected liquid product from the condenser after the reaction was analyzed using a high-performance liquid chromatograph (HPLC, Shimadzu) with a refractive index detector and an Aminex HPC-87H column to determine the conversion of carboxylic acid and the product yield. A glycerol solution, 5 v/v%, was used as an internal standard, and a H₂SO₄ solution (0.005 N) was used as a mobile phase for the HPLC analysis. The conversion of carboxylic acid and the yield of ketone product were calculated by the following equations.

$$\text{Conversion(\%)} = \left(1 - \frac{\text{mole of unreacted carboxylic acid}}{\text{initial mole of carboxylic acid}} \right) \times 100$$

$$\text{Ketone yield (\%)} = \left(\frac{\text{mole of produced ketone}}{\text{initial mole of carboxylic acid}} \right) \times 100$$

The non-condensable gas was analyzed using an on-line gas chromatograph (GC, Agilent 7890A) equipped with a thermal conductivity detector (TCD) and FID. The columns were a Carboxen-1004 stainless steel column (Supelco, 2 m/16in.×0.75 mm) for TCD and a GS-Alumina capillary column (Agilent J&W, 50 m×0.53 mm) for FID, respectively.

Results and discussion

Model compounds of the fractionated aqueous-phase bio-oil and catalyst characteristics

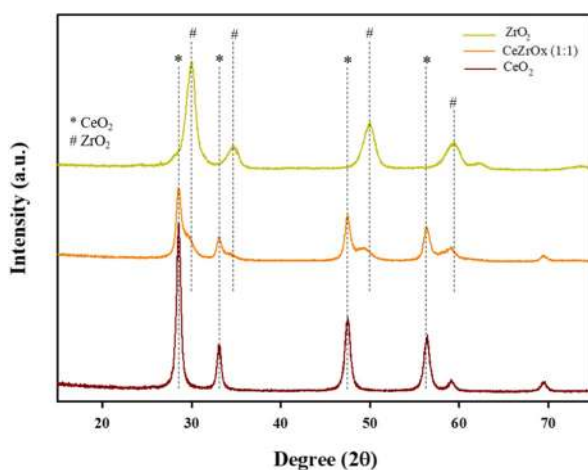
Although the composition of bio-oil is dependent on the type of wood as feedstock and the conditions of pyrolysis, the typical bio-oil contains a large amount of water and a vast variety of oxygenates and can be divided into two phases, oil and aqueous-phase oil (Wang et al. 2013). Crude pyrolysis oil of pine saw-dust was obtained from a bench-scale fast-pyrolyzer installed in the institute in order to analyze the composition of oil. The aqueous-phase bio-oil separated from the as-received crude bio-oil was fractionated to obtain low-molecule carbonyl compounds at 180 °C. Table 1 presents a summary of oxygenates in the fractionated aqueous-phase oil, analyzed using GC/MS. Large amounts of acids, ketones, and aldehydes

Table 1 Summary of low-molecule carbonyl components in the fractionated aqueous-phase oil at 180 °C

Group	Oxygenates	GC peak area (%)
Acid	Acetic acid	23.55
	Propionic acid	2.48
	Butyric acid	3.08
Alcohol	2-butanol	1.02
	2-methyl-1-propanol	1.20
Aldehyde	Furfural	10.94
	Furfural, 5-methyl-	1.28
Ketone	2,3-butanedione	2.34
	2-propanone, 1-hydroxy-	28.35
	2-cyclopenten-1-one	1.94
Phenol	1-hydroxy-2-butanone	2.18
	Phenol	3.09
	Phenol, 2-methoxy-4-methyl-	6.96
	Phenol, 2-methoxy-	9.65
	Phenol, 4-ethyl-2-methoxy-	1.92

are included in the light fraction oil. The water content and pH of the fractionated oil were 45% and 2.9, respectively. Therefore, different mixed model solutions representative of the light fraction in bio-oil were prepared, and ketonization was studied in the coupling of different carboxylic acids (AA and propionic and butyric acids), FF as aldehyde, HA as ketone, and the mixed solutions.

The XRD patterns of the prepared catalyst (CeZrOx) including individual metal oxides (ZrO₂ and CeO₂) for comparison purpose are shown in Fig. 2. Characteristic peaks (28.5°, 33.1°, and 47.5°) of CeO₂ were presented in pure and mixed oxide catalysts (Hwang et al. 2011), and the tetragonal phase of ZrO₂ (30.2°, 35.2° and 50.6°) was observed in pure and mixed oxide catalysts (Basahel et al. 2015). However, an

Fig. 2 XRD patterns of the prepared catalysts (ZrO₂, CeZrOx, and CeO₂)

asymmetric (111) CeO_2 diffraction peak ($2\theta=28.5^\circ$) and shift of the ZrO_2 diffraction peak to lower 2θ values were observed in the CeZrOx catalyst, indicating that cations of different sizes were partially incorporated in the structure of each oxide. The BET surface area and pore volume of the prepared catalyst are $72.9 \text{ m}^2/\text{g}$ and $0.154 \text{ cm}^3/\text{g}$, respectively.

Ketonization of carboxylic acids

Basically, ketonization of AA, a simple and abundant carboxylic acid in aqueous-phase oil, has been conducted over the CeZrOx catalyst, presented in Fig. 3. AA was converted completely into acetone over the CeZrOx catalyst ($2\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COCH}_3 + \text{CO}_2 + \text{H}_2\text{O}$) and acetone yield (46%) nearly reached the theoretical value (50%) at above 350°C . Note that some acetone loss should be considered during sampling from the condenser due to its high volatility, despite complete conversion of AA. During the ketonization reaction at above 400°C , a trace amount of methane was observed in the gas products, owing to decarboxylation of AA over the CeZrOx catalyst ($\text{CH}_3\text{COOH} \rightarrow \text{CH}_4 + \text{CO}_2$) (Fig. 3b) (Lemonidou et al. 2013).

Figure 4 shows the results of ketonization of different carboxylic acid solutions on the CeZrOx catalyst. It has been reported the ketonization progresses through a surface carboxylate mechanism on Ce-Zr mixed oxides, where the formation of the β -ketoacid intermediate between enolate and acylium intermediates is the key step (Kumar et al. 2018). The formation of β -ketoacid does not appear to be directly related to the chain-length of carboxylic acids (for normal, not branched, carboxylic acids), because the reaction starts from the adsorption of the carbonyl group in acids on the active site of the catalyst, followed by dehydrogenation of α -hydrogen forming enolate, as described in Fig. S1 in Electronic Supplementary Material. However, relatively higher reaction temperatures are required for the ketonization reaction to proceed with an increase in the number of carbons in the molecules of carboxylic acids. The required temperature for the complete conversion of carboxylic acids followed the order: butyric acid (450°C) > propionic acid (375°C) > AA (350°C). Through the initial rate studies, the measured apparent activation energy was 98.5 kJ/mol for the ketonization of AA in the solution (20 wt% in water) over CeZrOx catalyst, which is in line with the previously reported value (117.6 kJ/mol for ZrO_2) (Ignatchenko and Kozliak 2012). Given that the activation energy value in the previous study, however, was determined from the ketonization of pure AA without any interference of water molecule, the measured value in the present study was relatively very low. This is likely due to the low-temperature (450°C) calcined CeZrOx catalyst, based on the results that Snell and Shanks (2013) reported for the ketonization of AA on two different CeO_2 catalysts; 450°C calcined CeO_2 showed a lower activation energy (78 kJ/mol) than 900°C calcined CeO_2 (161 kJ/mol), resulting from the differences in the crystallinity of the catalyst and internal mass transfer limitations on the catalyst. The apparent activation energies increased with the increase in the carbon number in carboxylic acids (127.4 kJ/mol for propionic

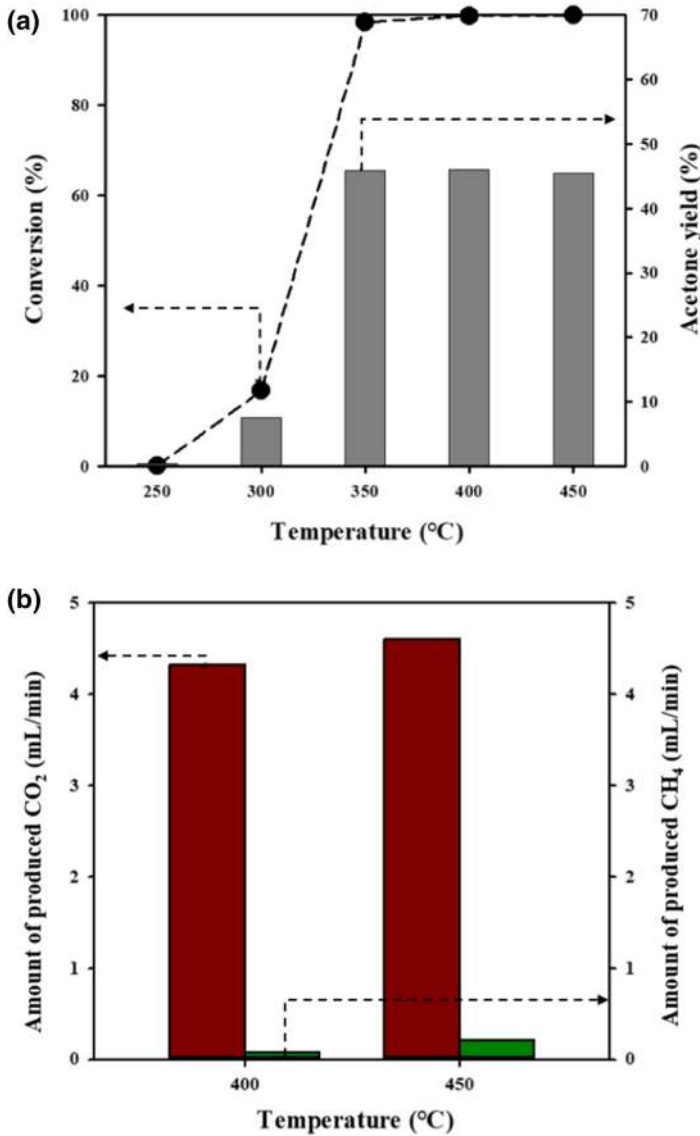


Fig. 3 Results of ketonization of AA solution (20% in water) over the CeZrOx catalyst at WHSV = 3 h⁻¹: **a** conversion of AA and acetone yield and **b** the amount of gas products

acid and 137.3 kJ/mol for butyric acid, respectively), due to the steric effect of acids (Kulik et al. 2020). As shown in Fig. S2 in Electronic Supplementary Material, the difference in the conversions between pure AA and AA solution reactants indicates that the water molecules competitively adsorbed on the active sites on

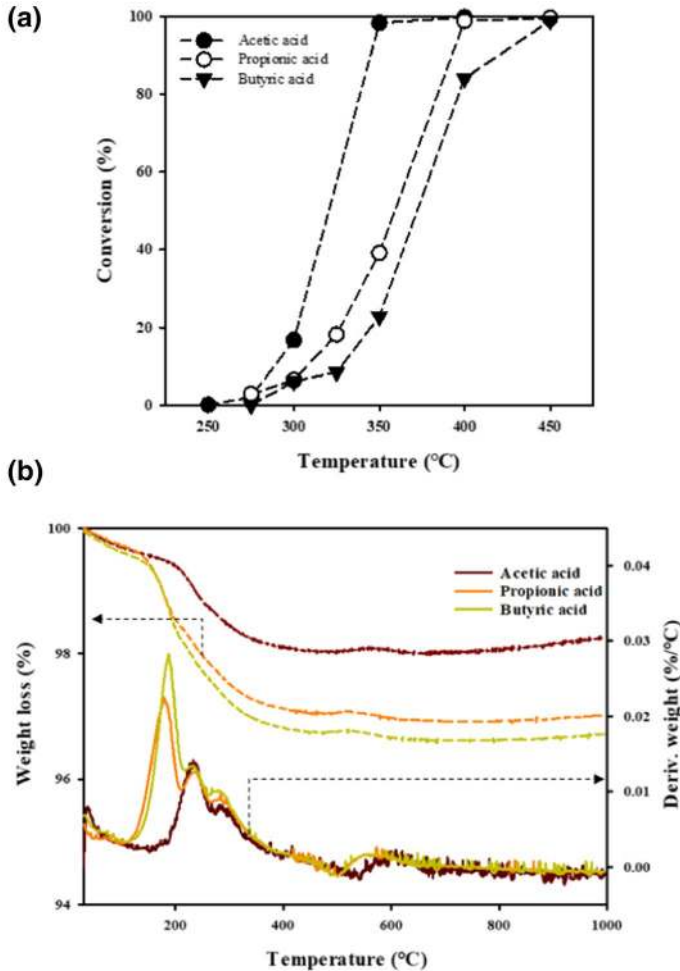


Fig. 4 Results of ketonization of different carboxylic acids (20% in water) on CeZrOx catalyst at $WHSV = 3 \text{ h}^{-1}$: **a** conversion of carboxylic acids and **b** TGA profiles of used catalysts

CeZrOx hinder the adsorption of AA molecules (Pham et al. 2012), resulting in the low catalytic activity.

After the reactions, a TGA analysis of the catalyst was carried out to examine coke formed over the surface of the catalyst, as shown in Fig. 4b. The catalysts after reactions using propionic acid and butyric acid had three significant weight loss peaks at around 100–300 °C, unlike AA. Since weight loss at below 300 °C corresponds to the desorption of water and volatile components, the large weight loss peaks are likely due to unconverted acids, having higher molecular weight than AA, adsorbed on the surface of the catalyst. Table 2 summarizes the contents of thermal coke, catalytic coke, and total coke deposited on the used catalysts. The weight loss region below 300 °C is excluded in the calculation of thermal and catalytic

Table 2 Comparison of coke deposited on the CeZrOx catalyst after a 250 °C to 450 °C reaction testing using different carboxylic acid solutions at WHSV = 3 h⁻¹

% g _{coke} /g _{catalyst}	AA solution	Propionic acid solution	Butyric acid solution
Thermal coke	0.41	0.46	0.47
Catalytic coke	0.02	0.14	0.14
Total coke	0.43	0.60	0.61

coke contents. There is no significant difference in the thermal coke contents, but a significant amount of catalytic coke was observed in the case of ketonization of propionic and butyric acids. Coke might be produced as a result of secondary and tertiary self-/cross-aldol condensation of formed ketones and further oligomerization on the active sites in the pores at relatively high temperatures. The longer the carbon-chain in the molecule of the reactant, the greater the potential for the formation of high molecule compounds through the consecutive aldol condensation-type surface reactions. CeZrOx has catalytic activity for aldol condensation and because of that various long-chain adducts originated from C₃ and C₄ acids-derived ketones might result in coke deposition on the active sites in the pores of catalyst. Because the same amount (20 wt%) of acids was added in the water for each reactant solution (2.8 mmol/ml of propionic acid and 2.4 mmol/ml of butyric acid, respectively), a comparable amount of coke appeared to be formed for C₃ and C₄ acid solutions. For all reactants, the amount of thermal coke originated from the thermal polymerization of components in gas phase was obviously more than that of catalytic coke.

Co-feeding reactants effect on the catalytic performance

Reactions of FF or HA over CeZrOx have been observed under the reaction conditions of ketonization, prior to studying the effect of co-feeding reactants on ketonization of carboxylic acid. The results of FF (a) and HA (b) are shown in Fig. 5. When the FF solution (7 wt%) was fed into the CeZrOx catalyst bed, the conversion of FF increased with an increase in reaction temperature and reached 100% conversion at 450 °C (Fig. 5a). However, significant products were not detected in the liquid product. Instead, a large amount of thermal coke was observed on the wall of the reactor and on the catalyst bed, which is more significant than HA. Some light components (<C₅) were detected in the gas products and the number and the intensity of gas components increased with the reaction temperature. (Unfortunately this could not be analyzed quantitatively.) Moreover, small amounts of H₂, CO, and CO₂ were present from the reaction temperature of 400 °C, likely due to partial steam reforming of FF on the CeZrOx catalyst. The produced hydrogen was about 7.6% of the hydrogen generated theoretically from global steam reforming of FF at 100% conversion (C₅H₄O₂ + 8H₂O ↔ 5CO₂ + 10H₂). FF is one of the important molecules when considering C–C coupling reactions for the fuel precursor owing to the higher carbon number of the molecule. However, most of FF appears to disappear into thermal coke at a relative low reaction temperature and into various gas-phase products above 400 on the CeZrOx catalyst.

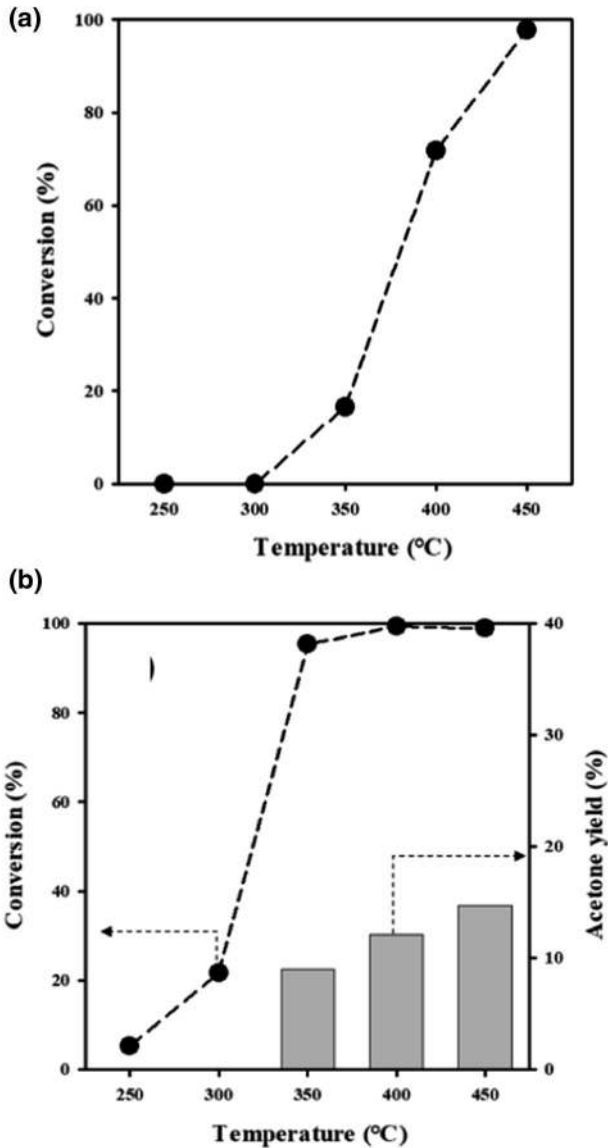


Fig. 5 Results of reactions of FF (7% in water) and HA (7% in water) over CeZrOx at WHSV = 1 h⁻¹: **a** conversion of FF and **b** conversion of HA and acetone yield

In the case of HA (Fig. 5b), the conversion was similar to that of AA, but the yield of acetone was very low, 15% at 450 °C. Various different carbonyl compounds in the liquid products were observed, and we tried to analyze qualitatively some of them using HPLC-MS (shown in Fig. 6): acetone, propanal (C₃H₆O), 3-methyl-2-cyclopentenone (CH₃C₅H₅O), 2,5-hexanedione (C₆H₁₀O₂), AA, etc. Hakim et al. (2013) proposed that pyruvaldehyde (C₃H₄O₂) and 1,2-propylene glycol (C₃H₈O₂),

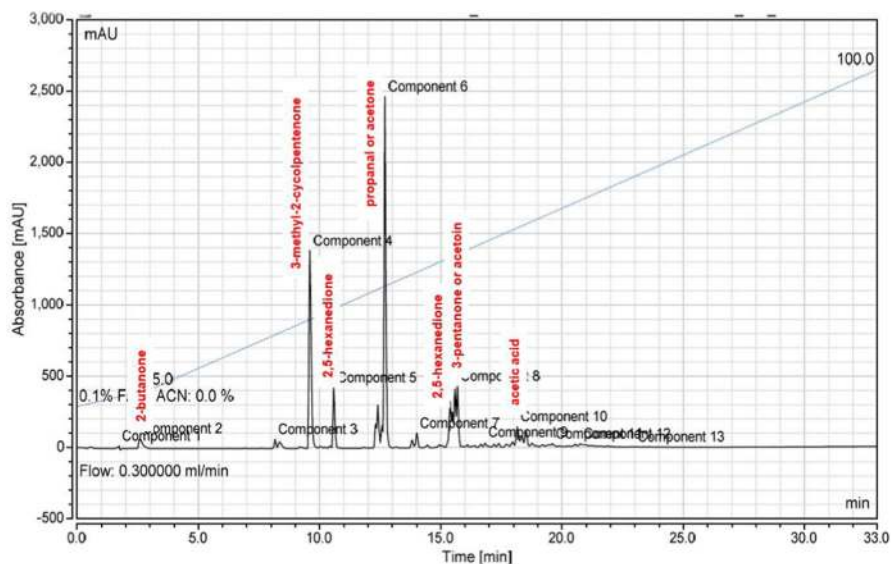


Fig. 6 Possible components in the liquid product obtained from HA solution (7 wt%) under the ketonization reaction condition (350 °C, CeZrOx)

as important reaction intermediates, are formed from the hydrogen transfer reaction between two HA molecules. Based on their results, propanal and acetone can be produced from dehydration of 1,2-propylene glycol and AA formed from pyruvaldehyde can produce 3-methyl-2-cyclopentenone and 2,5-hexanedione via the aldol condensation reaction. As a result, HA was highly reactive on the CeZrOx catalyst and produced these various carbonyl compounds with less oxygen and below carbon number of 6 in their molecules. The physical appearance of the used catalyst bed and the reactor indicates that the amount of thermal coke appears to be much lower than when feeding FF. Small amounts of H₂, CO, and CO₂ were detected from 400 °C, likely due to partial steam reforming of HA ($\text{CH}_3\text{COCH}_2\text{OH} + 4\text{H}_2\text{O} \rightarrow 3\text{CO}_2 + 7\text{H}_2$) on the CeZrOx catalyst, similar to FF. However, the amount of gases was half of the amount of gases from the steam reforming of FF. Table 3 summarizes the contents of thermal coke, catalytic coke and total coke deposited on the used catalysts, when feeding FF or HA under the reaction conditions for the ketonization reaction. As observed, FF formed much more thermal coke than HA. Although the amount

Table 3 Comparison of coke deposited on the CeZrOx catalyst after a 250 °C to 450 °C reaction testing using different reactants at WHSV = 1 h⁻¹

% g _{coke} /g _{catalyst}	7 wt% FF in water	7 wt% HA in water
Thermal coke	1.31	0.43
Catalytic coke	0.05	0.07
Total coke	1.36	0.50

of catalytic coke was much lower than the amount of thermal coke in the present conditions, if FF and HA interact with the phenolic components present in the real pyrolysis oil at a relatively high temperature of around 300–400 °C, a large amount of catalytic coke can be deposited on the surface of the catalyst (Xiong et al. 2020). Furthermore, the contents of thermal and catalytic cokes of FF and HA were much higher than those of AA, considering the WHSV of FF or HA was three times lower than that of AA.

Ketonization using two mixtures (AA and FF or AA and HA) has been conducted over CeZrOx at 350 °C in the fixed bed reactor. The effects of FF or HA concentrations on the ketonization of AA in the mixture were examined (Fig. S3 in Electronic Supplementary Material). As expected, FF and HA reduced the catalytic activity for the ketonization of AA. HA at high concentration (7 wt%) inhibited the initial catalytic activity slightly more than FF at 350 °C, likely due to the high reactivity of HA on CeZrOx giving various carbonyl compounds as shown in Figs. 5b and 6. The catalytic activity loss by HA was overcome by proceeding the ketonization reaction at 450 °C (Fig. S4 in Electronic Supplementary Material), which is consistent with that reported by Jackson (2013) that at above 400 °C, 10 vol% HA did not hinder the ketonization of a 16 vol% AA solution over $\text{Fe}_{0.2}\text{Ce}_{0.2}\text{Al}_{0.6}\text{O}_x$. To further understand the behavior of FF and HA over the surface of catalyst, the ketonization of AA in the mixture as a function of TOS was carried out, and the results are shown in Figs. 7 and 8, respectively. When feeding the mixture of AA and FF (Fig. 7a), the initial conversion of AA was about 40% and decreased to below 5% within 4 h on steam. In comparison with the ketonization reaction of pure AA (20 wt% solution) (conversion = 100% and acetone yield = 46%), the presence of FF appears to significantly inhibit the ketonization reaction. However, FF does not appear to be significantly affected from AA, because the conversion of FF was about 20% (Fig. 7b), which is similar to the conversion of FF solution alone (Fig. 5a). After the reaction, bright brown products were found, having accumulated on the inner-wall of the quartz reactor between the furnace and the condenser. The brown products recovered using acetone mainly consisted of furfuralacetone ($\text{C}_8\text{H}_8\text{O}_2$) including some carbonyl components, based on the results of the GC/MS analysis. In other words, the aldol condensation reaction ($\text{C}_5\text{H}_4\text{O}_2 + \text{C}_3\text{H}_6\text{O} \rightarrow \text{C}_8\text{H}_8\text{O}_2 + \text{H}_2\text{O}$) between unreacted FF and produced acetone occurred during the ketonization of AA over CeZrOx at 350 °C. Furfuralacetone is an important reaction product in the present catalytic reaction condition in terms of reduction of acidity and formation of larger carbon chains. When removing FF from the feed, the conversion of AA and acetone yield was restored to about 80% and above 30%, respectively. This means that the FF induces reversible poisoning on the surface of the catalyst by merely blocking active sites. The complete recovery in the conversion and yield was not achieved, likely due to thermal coke, derived from FF, on the surface of the catalyst (Table 4). The co-presence of HA (7%) in the AA solution showed different behaviors from the case of the FF mixed solution (Fig. 8a). The conversion of AA and acetone yield was about 20% and 10%, respectively, with about 40% HA conversion. When comparing with the results of ketonization using each solution (AA or HA), the conversions were one-tenth and a half of each conversion, respectively. This indicates that the co-existence of AA and HA significantly influences their counterpart reactions:

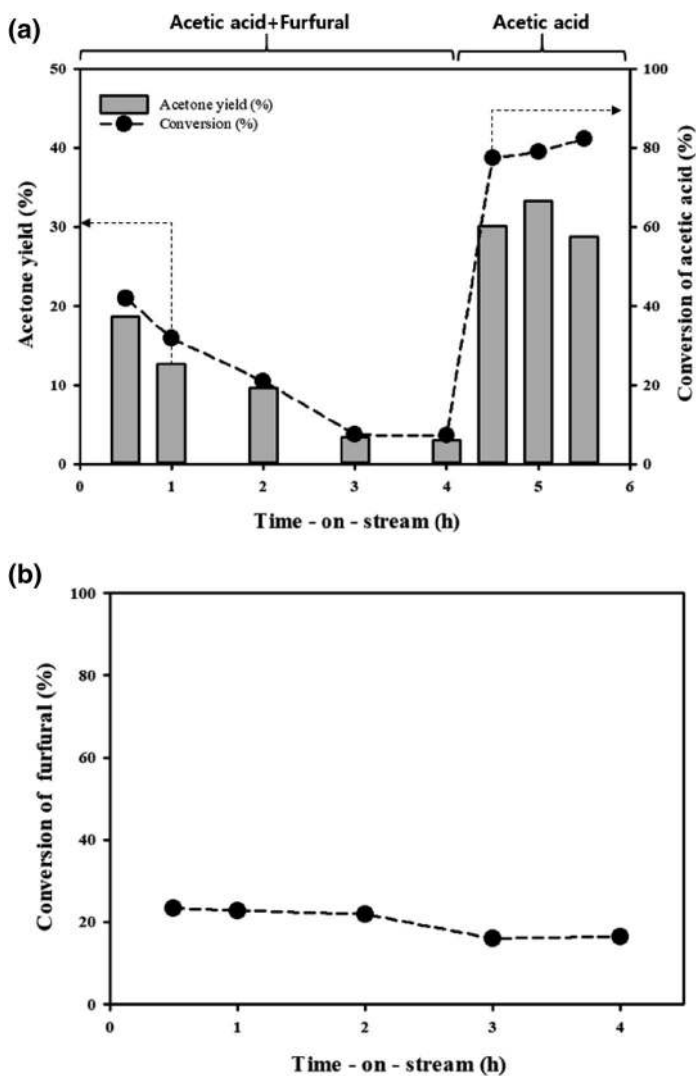


Fig. 7 Results of ketonization of AA in the mixture (20% AA+7% FF in water) over CeZrOx at WHSV = 3 h⁻¹ (based on AA) and 350 °C: **a** conversion of AA and acetone yield and **b** conversion of FF

ketonization of AA and complex reactions of HA for forming other carbonyl compounds. These results contrast with those of Hakim et al. (2013) who found that the presence of HA (5 wt%) did not influence the ketonization activity (20 wt% of AA) and both reactants (AA and HA) achieved more than 99% conversion at 350 °C. The conversion of AA was not dramatically recovered as soon as HA was removed from the mixed solution, but appeared to be slowly restored. However, the conversion still reached 50% after removing HA from the mixed solution (2 h). This indicates that

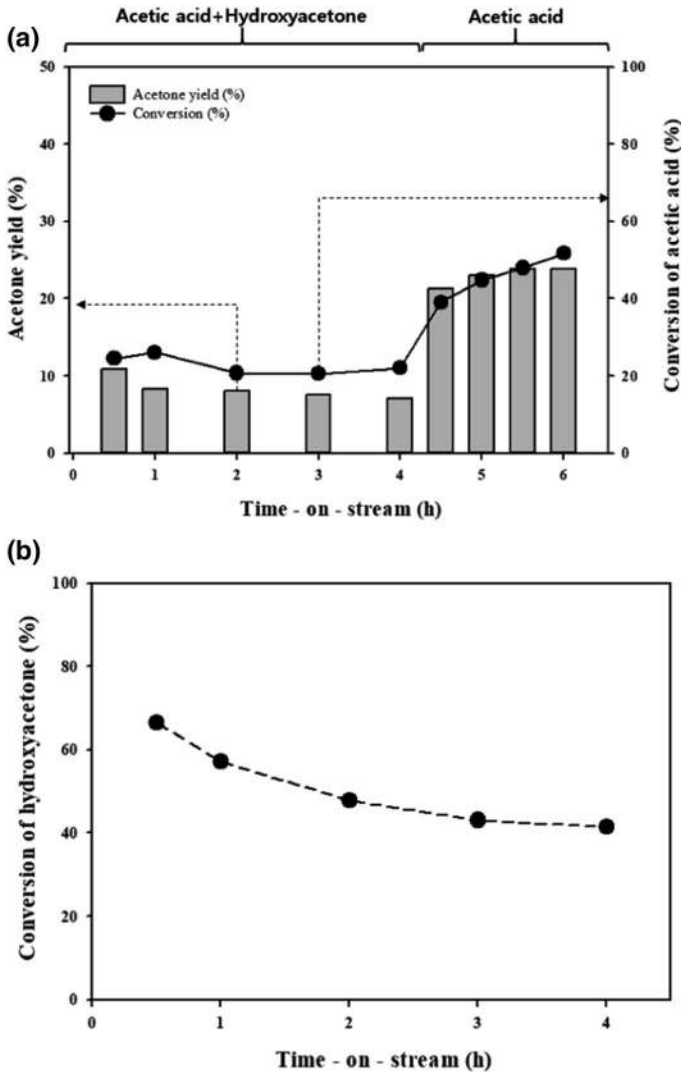


Fig. 8 Results of ketonization of AA in the mixture (20% AA+7% HA in water) over CeZrOx at WHSV=3 h⁻¹ (based on AA) and 350 °C: **a** conversion of AA and acetone yield and **b** conversion of HA

Table 4 Comparison of coke deposited on the CeZrOx catalyst after ketonization reaction (6 h TOS) using the different mixed solutions at 350 °C at WHSV=3 h⁻¹ (based on AA)

% g _{coke} /g _{catalyst}	20 wt% AA + 7 wt% FF	20 wt% AA + 7 wt% HA	20 wt% AA + 7 wt% FF + 7 wt% HA
Thermal coke	1.46	0.53	0.5
Catalytic coke	0.00	0.03	0.09
Total coke	1.46	0.56	0.59

various carbonyl compounds derived from HA, unlike FF, adsorb strongly on the surface of the catalyst (severe poisoning).

The results of ketonization of AA in the mixed solution (20% AA + 7% FF + 7% HA in water) at 350 °C are shown in Fig. 9. As expected, the conversion of AA and acetone yield was, unfortunately, about 10% and below 10%, respectively, due to the co-existing reactants. HA was the most reactive on CeZrOx among the reactants early in the reaction (initial conversion = 46%), but its conversion dramatically dropped to about 10% on stream. The significant reduction in the catalytic activity is likely due to the competitive adsorption of AA, FF and carbonyl components formed from HA on the active sites, as demonstrated before. As shown in Table 4, the amount of catalytic coke deposited in the spent catalysts increased as the number of reactants in the solution increased, but thermal coke decreased even if FF was co-fed. Instead, the larger amount of humin-like products were adhered on the inner surface of the tubular reactor, when using the AA + FF + HA mixed solution rather than the AA + FF solution. As shown in Fig. S4, the inhibition of the ketonization of AA by adding HA and FF could be overcome by proceeding the reaction at 450 °C. Long-term operation (5 cycles) for ketonization of AA in the mixture, therefore, was conducted at 450 °C, and the spent catalyst was in situ regenerated periodically using air at 450 °C for 2 h. The conversions of reactants and acetone yield as a function of TOS are shown in Fig. 10, giving acetone without any unreacted AA remaining on stream. Acetone yield (about 40%) was reasonable considering the following: product loss during the sampling and coke formation originated from the high temperature operation, as mentioned earlier. The conversions of HA and FF followed similar trends to those in Fig. S3. Severe thermal coke formation was, however, unavoidable on top of the catalyst bed during the long-term operation using the mixed solution.

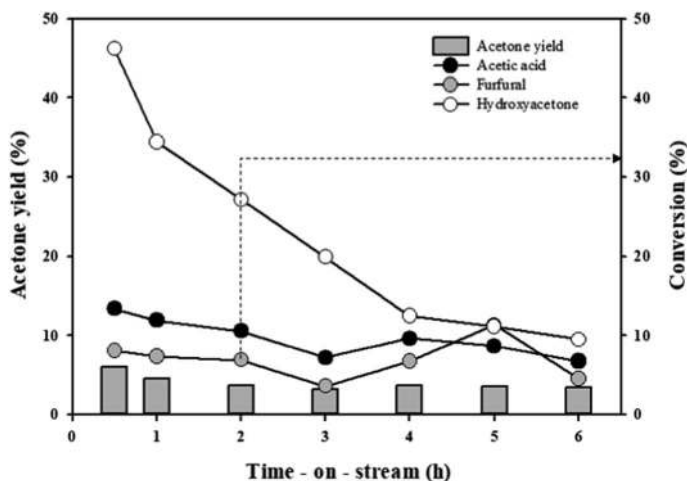


Fig. 9 Results of ketonization of AA in the mixture (20% AA + 7% FF + 7% HA in water) over CeZrOx at WHSV = 3 h⁻¹ (based on AA) and 350 °C

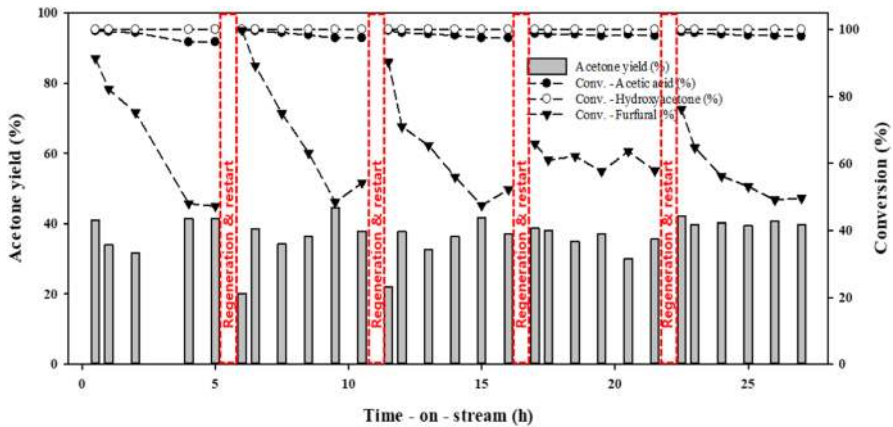


Fig. 10 Results of long-term operation using the mixture (20% AA + 7% FF + 7% HA in water) over CeZrOx at WHSV = 3 h⁻¹ (based on AA) and 450 °C (catalyst regeneration using air at 450 °C for 2 h)

To produce sustainable bio-fuel and bio-chemicals from the pyrolysis oil of woods, the first important reaction is the ketonization of carboxylic acid, which not only reduces a large amount of carboxylic acid but also converts it to less reactive intermediates with larger carbon numbers. However, based on the present results, just a few co-feed reactants significantly influence the catalytic activity for ketonization of carboxylic acids. In practice, abundant carbonyl components are present in the aqueous-phase bio-oil and different chemical reactions including self-/cross-ketonization, aldol condensation and carbonyl-forming reactions are involved under the reaction conditions. There are limitations to obtain enough information due to the heterogeneity of the present species and a merely qualitative analysis. If a comprehensive qualitative and quantitative analysis is established, more strategic and systematic studies would be possible to gain more information on these effects.

Conclusion

Ketonization has been investigated in mixed model solutions of different carboxylic acids, FF and HA, to understand the influence of co-feed reactants on the performance of ketonization of AA over the selected CeZrOx catalyst, and the experimental observations are as follows.

- (1) In the case of self-ketonization of different carboxylic acids, relatively higher reaction temperature is needed for complete conversion of carboxylic acids with the increase in carbon number in the molecules.
- (2) When FF (7%) was co-fed with AA solution, FF largely inhibited the catalytic activity within 4 h on stream, but the blocking of active sites by FF was immediately removed by removing FF from the feed. However, the complete recovery

in the conversion and yield was not achieved, likely due to thermal coke ($1.46\% \text{ g}_{\text{coke}}/\text{g}_{\text{catalyst}}$), derived from FF, on the surface of the catalyst. Aldol condensation also occurred during ketonization with the mixture of FF and AA over CeZrOx at $350\text{ }^{\circ}\text{C}$, producing furfuralacetone ($\text{C}_8\text{H}_8\text{O}_2$) adduct.

- (3) In the case of co-feeding HA(7%) with AA solution, both reactants influenced each other, resulting in very low conversions: one-tenth and a half of each conversion of pure solution at $350\text{ }^{\circ}\text{C}$. Reactive HA over CeZrOx produced various carbonyl compounds with less oxygen and some catalytic coke ($0.03\% \text{ g}_{\text{coke}}/\text{g}_{\text{catalyst}}$), unlike the FF mixture. The catalytic activity was slowly restored, but the conversion still reached 50%, after removing HA from the mixture.
- (4) For the mixed solution (20% AA + 7% FF + 7% HA in water), HA was the most reactive on CeZrOx among the co-feed reactants early in the reaction at $350\text{ }^{\circ}\text{C}$, but its conversion dramatically dropped to about 10% on stream, due to the inhibition of co-existing carbonyl components. The inhibition of the ketonization of AA by adding HA and FF could be overcome by proceeding the reaction at $450\text{ }^{\circ}\text{C}$. Severe thermal coke formation was, however, unavoidable on top of the catalyst bed during long-term operation.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00226-021-01333-2>.

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Authors' contributions IC was involved in methodology, experiment, analysis, investigation, visualization, and writing—original draft. HL contributed to experiment, formal analysis, investigation and visualization. KH was involved in conceptualization, supervision, project administration and writing—review and editing.

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Data availability Datasets used during this study are openly available, and the data citation in the main article has the full URL.

Declarations

Conflicts of interest The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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