

Ketonization of carboxylic acids over CeO₂-based composite oxides

Osamu Nagashima, Satoshi Sato*, Ryoji Takahashi, Toshiaki Sodesawa

Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoi, Inage, Chiba 263-8522, Japan

Received 3 September 2004; received in revised form 26 October 2004; accepted 28 October 2004

Available online 10 December 2004

Abstract

The ketonization of propanoic acid to form 3-pentanone over CeO₂-based composite oxides at temperatures of 300–425 °C was investigated. A CeO₂-based solid solution, CeO₂–Mn₂O₃, was effective for the ketonization. The citrate process was the most appropriate method for preparing a well-dispersed solid solution. In the ketonization of propanoic acid with another linear carboxylic acid, an asymmetric ketone together with two symmetric ketones was formed, and the ketone composition was approximated by a binomial distribution. The reactivity of the carboxylic acid was slightly decreased as its chain length was increased. In contrast to linear aliphatic acids, branched acids were less reactive. Methyl group substituents at the α - and β -positions of carboxylic acids decreased their reactivities in both homo- and cross-ketonization. The lack of an α -hydrogen or the increase in steric hindrance was surmised to be the cause of the decrease in reactivity.

© 2004 Elsevier B.V. All rights reserved.

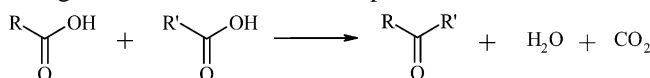
Keywords: Ketonization; Carboxylic acid; CeO₂; Mn₂O₃; Symmetric and asymmetric ketones

1. Introduction

CeO₂ is a significant component of automobile exhaust catalysts [1,2], working as a promoter in the three-way catalysis due to its oxygen storage capacity [2]. CeO₂ also functions as a catalyst in the *ortho*-selective alkylation of phenol with primary alcohols [3–5]. We have recently found that pure CeO₂ catalyzes the dehydration of 1,3-diols into allylic alcohols [6,7] and of 1,4-butanediol into 3-buten-1-ol [8].

The synthesis of ketones from carboxylic acids in the vapor phase is called ketonization. A number of articles on the ketonization of carboxylic acids are available: several oxides, such as Cr₂O₃ [9,10], Al₂O₃ [11,12], PbO₂ [12], TiO₂ [13–16], ZrO₂ [14,17–19], CeO₂ [19–24], iron oxide [14,15,25–27], and manganese oxide [12,19,20,22,28], as well as Mg/Al hydrotalcites [29] catalyze the ketonization of carboxylic acids. Many other catalysts have been found since the 19th century: BaCO₃, MgO, ThO₂, UO₂, CdO, ZnO, NiO, Bi₂O₃, and SnO₂ have been introduced in references [12,30].

Two molecules of carboxylic acids are required to form a ketone via ketonization, producing carbon dioxide and water. The general reaction scheme is expressed as follows:



In the above reaction, RCOOH reacts with R'COOH via cross-ketonization; on the other hand, two symmetric ketones of RCOR and R'COR' can be formed via homo-ketonization, namely, two different carboxylic acids produce three different ketones. Cross-ketonization has been reported [12,22–24].

Alcohols, aldehydes, and esters are also converted into ketones through dimerization in the presence of CeO₂ and ZrO₂ [5,31–37]. In our previous study [35], 1-propanol, propanal and propyl propanoate were converted into 3-pentanone in the presence of CeO₂–Fe₂O₃ catalysts. The intramolecular condensation of 1,6-hexanediol to form cyclopentanone also proceeds over CeO₂–Mn₂O₃ [36]. It has been proved that a solid solution containing CeO₂ is effective for ketone formation [35,36]. Therefore, we focused on the utility of CeO₂-based solid solutions in producing ketones from carboxylic acids.

* Corresponding author. Tel.: +81 43 290 3376; fax: +81 43 290 3401.
E-mail address: satoshi@faculty.chiba-u.jp (S. Sato).

In this study, we investigated the effective CeO₂-based catalysts and the reaction conditions for the ketonization of propanoic acid to form 3-pentanone as a model of ketonization. Then, we examined the cross-ketonization of propanoic acid with several carboxylic acids, and discussed the reactivity of the carboxylic acids in the ketonization.

2. Experimental

2.1. Catalyst preparation

All reagents were purchased from Wako Pure Chemical Industries (Japan). CeO₂-based catalysts were prepared by three methods: co-precipitation, citrate process, and impregnation.

The first group of CeO₂-based composite oxides was prepared by the co-precipitation method. Ce(NO₃)₃·6H₂O and Mn(NO₃)₂·6H₂O at the prescribed molar ratio were dissolved in water to prepare a 10 wt.% solution. The solution was added into 200 ml of 5 mol dm⁻³ aqueous ammonia with stirring. After precipitation and filtration, the precipitates were washed with water and dried at 50 °C for 24 h, followed by drying at 110 °C for 6 h. Then, the precipitates were calcined at 550 °C for 2 h.

The second group of catalysts was prepared by the citrate process, using corresponding metal nitrates and citric acid anhydride. The procedure is essentially the same as that for an amorphous citrate process [38], and the details have been described elsewhere [4]. After the precursor of mixed citrates had been heated in air at 170 °C for 2 h, it was calcined at 550 °C for 2 h.

The third group of catalysts was prepared by impregnation. CeO₂ and Mn₂O₃ prepared by the citrate process mentioned above were used as support. Either CeO₂ or Mn₂O₃ was immersed in a solution of Mn(NO₃)₂·6H₂O or Ce(NO₃)₃·6H₂O, respectively, and the water was evaporated by irradiating with an infrared lamp. The samples were finally calcined at 550 °C for 2 h.

2.2. Catalytic reaction

The ketonization of carboxylic acid was carried out in a conventional fixed bed flow reactor under the atmospheric pressure of N₂ at the flow rate of 40 cm³ min⁻¹ and temperatures of 300–425 °C. Prior to the reaction, a catalyst sample (0.30 g) was preheated in the N₂ flow at the reaction temperature for 1 h. Either propanoic acid alone or a mixture of propanoic acid with another carboxylic acid was fed into the reactor at the total liquid flow rate of 2.00 cm³ h⁻¹ by mean of a micro feed pump. The effluent collected in an ice trap every hour was subjected to analysis by FID-GC with a capillary column (TC-WAX, 30 m, GL Sciences, Japan) at temperatures ranging from 60 to 200 °C and the heating rate of 10 K min⁻¹. The gaseous product was only CO₂, as analyzed with both FID-GC with a packed column of PEG-HT (0.5 m)

at 110 °C and TCD-GC with a column of activated carbon (1.0 m) at 25 °C. Catalytic activity was evaluated in terms of the average conversion of carboxylic acid over a 5 h period. The conversion of propanoic acid is defined as the fraction of reacted propanoic acid. Selectivity to 3-pentanone, S_{3p}, is expressed by the following equation: $S_{3p} = 2 \times C_{3p} / (C_a - C_{pa})$, where C_a, C_{pa} and C_{3p} are the concentrations of fed propanoic acid, unreacted propanoic acid, and produced 3-pentanone, respectively.

2.3. Characterization

The specific surface area of the samples was calculated by the BET method using a nitrogen adsorption isotherm at -196 °C. The XRD patterns of the samples were recorded on an M18XHF (Mac Science, Japan) using Cu Kα radiation.

3. Results

3.1. Ketonization of propanoic acid over CeO₂-MO_x

Table 1 lists the results of the ketonization of propanoic acid at 350 °C over CeO₂-MO_x prepared by citrate process, where M is the second metal component having the content of 10 mol%. CeO₂-MO_x catalysts with M = Mg, Mn and Cu show higher conversion of propanoic acid than pure CeO₂, whereas the addition of Cr almost completely deactivates the catalytic activity of CeO₂. Except for Cr- and Co-modified CeO₂, CeO₂ catalysts modified with Mg, Al, Mn, Fe, Ni, Cu, and Zr show higher than 95 mol% selectivity to 3-pentanone, which is higher than that of pure CeO₂. The introduction of Mg, Mn, Fe, Ni, Cu, and Zr into CeO₂ decreases the selectivity to such by-products as butanone and 2-methyl-3-pentanone. The highest propanoic acid conversion and selectivity to 3-pentanone are observed when Mn-added CeO₂, i.e., CeO₂-Mn₂O₃, is used as the catalyst. Table 1 also lists the

Table 1
Catalytic performance over CeO₂-MO_x at 350 °C^a

Additive, M ^b (10 mol%)	Conv. (%)	Selec. (mol%)	SA (m ² g ⁻¹)
None	51.0	93.8	40.1
Mg	66.8	96.7	34.6
Al	49.6	96.1	46.5
Cr	2.6	15.5	40.9
Mn	73.9	97.4	38.4
Fe	53.5	95.6	24.3
Co	55.0	92.8	28.1
Ni	54.5	96.2	42.9
Cu	65.8	96.2	35.9
Zr	54.5	95.9	44.9

^a Propanoic acid was fed into the reactor at the liquid flow rate of 2.00 cm³ h⁻¹. The activity is an average value for the initial 5 h. Conv., conversion of propanoic acid; Selec., selectivity to 3-pentanone; SA, specific surface area calculated by the BET method.

^b Catalysts were prepared by the citrate process.

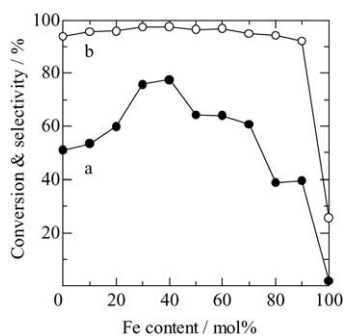


Fig. 1. Catalytic activity of $\text{CeO}_2\text{-Fe}_2\text{O}_3$ in the ketonization of propanoic acid at 350°C : (a) conversion of propanoic acid and (b) selectivity to 3-pentanone.

specific surface area of the catalysts. There is no correlation between specific surface area and conversion or selectivity.

In our previous papers [33,35], we reported that $\text{CeO}_2\text{-Fe}_2\text{O}_3$ was an effective catalyst for ketone formation from 1-propanol. Here, we investigated the ketonization of propanoic acid over $\text{CeO}_2\text{-Fe}_2\text{O}_3$ (Fig. 1). Fe content affects the catalytic activity: the highest conversion and selectivity are observed at the Fe content of 40 mol%. The reaction proceeds even at the Fe content of 90 mol%, whereas pure Fe_2O_3 has little catalytic activity for the ketonization.

In addition, the catalytic activity of pure Fe_2O_3 for the ketonization of propanoic acid is enhanced in H_2 flow: the conversion of 11.4% and the selectivity to 3-pentanone of 78.7% are attained in H_2 , whereas the conversion and the selectivity in N_2 are 1.8 and 25.6% (Fig. 1), respectively. The enhancement of the catalytic activity by H_2 is limited to the case of pure Fe_2O_3 : no enhancement is observed in the presence of pure CeO_2 or Mn_2O_3 .

The highest catalytic activity of the $\text{CeO}_2\text{-Fe}_2\text{O}_3$ (Fe content, 40 mol%) is similar to that of $\text{CeO}_2\text{-Mn}_2\text{O}_3$ (Mn,

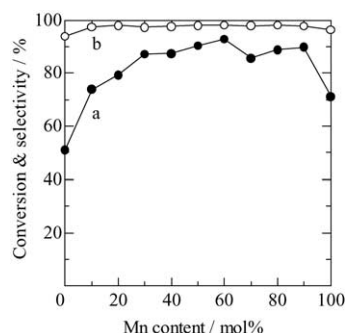


Fig. 2. Catalytic activity of $\text{CeO}_2\text{-Mn}_2\text{O}_3$ in the ketonization of propanoic acid at 350°C : (a) conversion of propanoic acid and (b) selectivity to 3-pentanone.

10 mol%, Table 1). Hereafter, we investigated the ketonization over $\text{CeO}_2\text{-Mn}_2\text{O}_3$ in detail.

3.2. Ketonization of propanoic acid over $\text{CeO}_2\text{-Mn}_2\text{O}_3$ and its structural property

Fig. 2 shows the catalytic activity of $\text{CeO}_2\text{-Mn}_2\text{O}_3$ prepared by the citrate process in the ketonization of propanoic acid to form 3-pentanone. The catalytic activity of pure Mn_2O_3 is higher than that of pure CeO_2 . However, the addition of only 10 mol% Mn to CeO_2 enhances the catalytic activity, and $\text{CeO}_2\text{-Mn}_2\text{O}_3$ has higher activity than pure Mn_2O_3 at all the Mn contents. The highest conversion and selectivity are observed at the Mn content of 60 mol%.

Table 2 lists the catalytic performance of $\text{CeO}_2\text{-Mn}_2\text{O}_3$ prepared with the three methods, namely, citrate process, co-precipitation, and impregnation. The addition of a small amount of Mn to CeO_2 enhances the catalytic performance. The $\text{CeO}_2\text{-Mn}_2\text{O}_3$ catalysts are more active than either pure CeO_2 or Mn_2O_3 . In each preparation method, the Mn_2O_3 -

Table 2
Effects of Mn content on catalytic performance over $\text{CeO}_2\text{-Mn}_2\text{O}_3$ ^a

Mn content (mol%) ^b	Citrate process			Co-precipitation		
	SA ($\text{m}^2 \text{g}^{-1}$)	Conv. (%)	Selec. (mol%)	SA ($\text{m}^2 \text{g}^{-1}$)	Conv. (%)	Selec. (mol%)
0	40.1	51.0	93.8	46.3	39.6	92.2
10	38.4	73.9	97.4	65.4	69.3	96.4
10 ^c				14.2	54.9	94.3
20	51.9	79.3	98.0	88.0	66.4	96.7
40	49.3	87.4	97.7	98.2	86.7	97.4
60	43.8	92.8	98.1	75.7	81.9	97.7
60 ^d				100.0	86.3	97.7
80	46.8	88.8	98.1	72.6	84.4	97.3
90	49.6	89.8	97.8	45.8	81.2	97.2
90 ^e				25.1	75.3	96.3
100	17.0	71.2	96.4	12.3	64.3	96.7

^a Propanoic acid was fed into the reactor at the liquid flow rate of $2.00 \text{ cm}^3 \text{ h}^{-1}$. The activity is the average value obtained at 350°C for the initial 5 h. SA, specific surface area; Conv., conversion of propanoic acid; Selec., selectivity to 3-pentanone.

^b Calcined at 550°C .

^c Prepared by impregnating $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution on pure CeO_2 prepared by the citrate process.

^d Calcined at 500°C .

^e Prepared by impregnating $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ solution on pure Mn_2O_3 prepared by the citrate process.

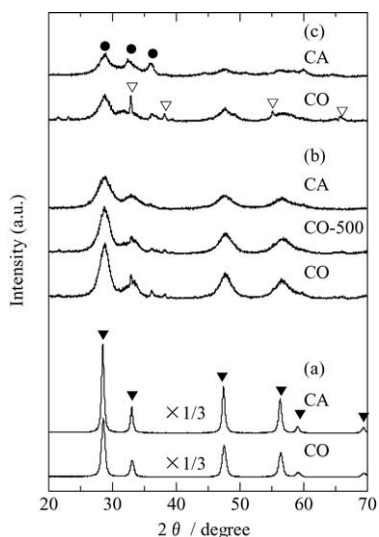


Fig. 3. XRD profiles for: (a) pure CeO₂, (b) CeO₂-Mn₂O₃ (Mn 60 mol%) and (c) CeO₂-Mn₂O₃ (Mn 80 mol%). CA means a sample prepared by the citrate process and CO by co-precipitation. Samples were calcined at 550 °C except for sample CO-500, which was calcined at 500 °C: (▼) CeO₂, (▽) α-Mn₂O₃ and (●) γ-Mn₂O₃.

rich catalysts are superior to the CeO₂-rich ones in producing 3-pentanone. However, modification methods influence the catalytic activity even at the same composition. The order of decreasing ketonization activity of the catalysts depending on the preparation method is as follows: citrate process > co-precipitation > impregnation. Calcination temperature also affects the catalytic activity: CeO₂-Mn₂O₃ calcined at 500 °C has higher activity than that calcined at 550 °C.

All catalysts show high selectivity to 3-pentanone, particularly at the Mn content of 20–80 mol% (Table 2). The addition of Mn to CeO₂ increases the selectivity to 3-pentanone. Over pure CeO₂, the selectivity is low, and butanone and 2-methyl-3-pentanone are observed. The specific surface areas of CeO₂-Mn₂O₃ catalysts are higher than those of pure CeO₂ and Mn₂O₃. In addition, the catalysts prepared by co-precipitation have specific surface areas larger than those by the citrate process.

Fig. 3 shows the XRD patterns for CeO₂ and CeO₂-Mn₂O₃ catalysts. The diffraction peaks of CeO₂ are observed at $2\theta = 28.1^\circ, 33.1^\circ, 47.5^\circ, 56.5^\circ, 59.1^\circ,$ and 67.5° in all the samples. Although the diffraction peaks of CeO₂ decrease in intensity and broaden with increasing Mn content, the peaks are observed even at the Mn content of 80 mol%. The diffraction peaks assigned to γ-Mn₂O₃ are observed at $2\theta = 29.1^\circ, 32.4^\circ,$ and 36.1° in the CeO₂-Mn₂O₃ catalyst prepared by the citrate process at the Mn content of 80 mol%. CeO₂-Mn₂O₃ prepared by co-precipitation at the Mn content of 80 mol% shows α-Mn₂O₃ peaks at $2\theta = 32.9^\circ, 36.1^\circ, 55.1^\circ,$ and 65.7° . Calcination temperature affects the sharpness of the peaks of the CeO₂-Mn₂O₃ catalyst (Mn 60 mol%) prepared by co-precipitation. The diffraction peaks of γ-Mn₂O₃ and α-Mn₂O₃ calcined at 550 °C are sharper than those at 500 °C. However, the catalyst prepared by the citrate

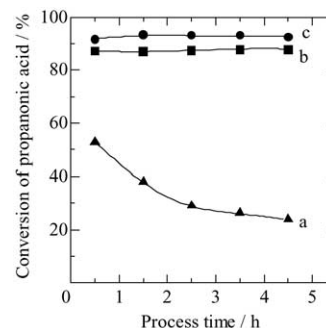


Fig. 4. Time dependence of propanoic acid conversion over Mn60 prepared by the citrate process. Reacted at: (a) 300 °C, (b) 325 °C and (c) 350 °C.

rate process has only broad peaks of γ-Mn₂O₃, even at the calcination temperature of 550 °C.

Fig. 4 depicts the conversion of propanoic acid with reaction time over CeO₂-Mn₂O₃ prepared by the citrate process at the Mn content of 60 mol% (hereafter called ‘Mn60’), at different reaction temperatures. At 325 and 350 °C, no decay is observed in the conversion, whereas the conversion is rapidly decreased at 300 °C.

Fig. 5 shows the temperature dependence of the catalytic activity of CeO₂-Mn₂O₃ prepared by the citrate process. Over pure CeO₂, the conversion of propanoic acid is increased with increasing reaction temperature, whereas the selectivity to 3-pentanone is maximized at 375 °C. The major by-products over pure CeO₂ at >375 °C are butanone and 2-methyl-3-pentanone. Over pure Mn₂O₃, the selectivity to

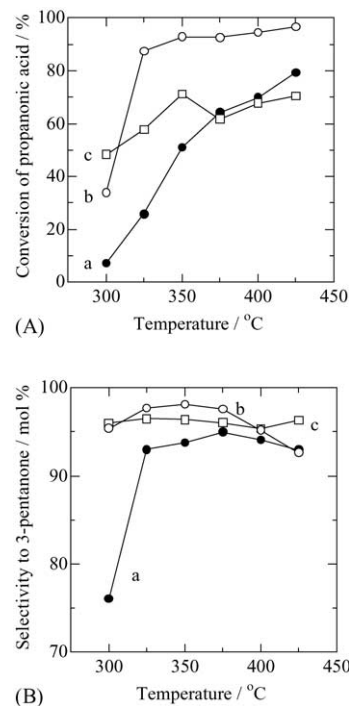

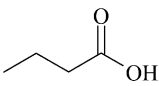
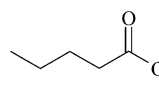
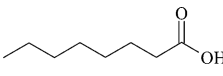


Fig. 5. Temperature dependence of catalytic activity. (A) Conversion of propanoic acid and (B) selectivity to 3-pentanone: (a) pure CeO₂; (b) Mn60; (c) pure Mn₂O₃. Samples were prepared by the citrate process.

Table 3
Composition (molar ratio) in the reaction of propanoic acid with *n*-carboxylic acid^a

Carboxylic acid	3-Pentanone	Asymmetric ketone ^b	Symmetric ketone ^c	Unreacted propanoic acid	Unreacted counter acid	Others
Acetic acid 	1.00	2.53 ^d	1.10 ^e	0.45	0.03	0.09
<i>n</i> -Butanoic acid 	1.00	2.00 ^f	0.86 ^g	0.15	0.41	0.21
<i>n</i> -Pentanoic acid 	1.00	1.92 ^h	0.86 ⁱ	0.19	0.51	0.20
<i>n</i> -Octanoic acid 	1.00	2.27 ^j	0.93 ^k	0.24	0.31	0.45

^a Composition of reactant was propanoic acid:carboxylic acid = 1:1. The reactant mixture was fed over Mn60 catalyst at the liquid flow rate of 2.00 ml h⁻¹ at 375 °C.

^b Cross-ketonization product of propanoic acid and another carboxylic acid.

^c Homo-ketonization product of another carboxylic acid.

^d Butanone.

^e Propanone.

^f 3-Hexanone.

^g 4-Heptanone.

^h 3-Heptanone.

ⁱ 5-Nonanone.

^j 3-Decanone.

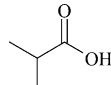
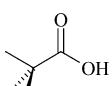
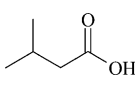
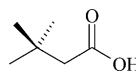
^k 8-Pentadecanone.

3-pentanone remains high regardless of the temperature. On the other hand, Mn60 exhibits high conversion at 325 °C, and the conversion is slightly increased with increasing temperature. The selectivity over Mn60 is the highest among the three catalysts, and is maximized at ca. 350 °C.

3.3. Cross-ketonization between propanoic acid with other carboxylic acids

In the following reactions, an equimolar mixture of propanoic acid and another carboxylic acid was used as the

Table 4
Composition (molar ratio) in the reaction of propanoic acid with branched carboxylic acid^a

Carboxylic acid	3-Pentanone	Asymmetric ketone	Symmetric ketone	Unreacted propanoic acid	Unreacted counter acid	Others
2-Methylpropanoic acid 	1.00	0.97 ^b	0.10 ^c	0.09	1.30	0.12
2,2-Dimethylpropanoic acid 	1.00	0.03 ^d	0.00 ^e	0.34	2.16	0.09
3-Methylbutanoic acid 	1.00	1.58 ^f	0.25 ^g	0.11	1.58	0.34
3,3-Dimethylbutanoic acid 	1.00	0.26 ^h	0.00 ⁱ	0.30	2.10	0.14

^a Composition of reactant was propanoic acid:carboxylic acid = 1:1. The reactant mixture was fed over Mn60 catalyst at the liquid flow rate of 2.00 ml h⁻¹ at 375 °C.

^b 2-Methyl-3-pentanone.

^c 2,4-Dimethyl-3-pentanone.

^d 2,2-Dimethyl-3-pentanone.

^e 2,2,4,4-Tetramethyl-3-pentanone.

^f 5-Methyl-3-hexanone.

^g 2,6-Dimethyl-4-heptanone.

^h 5,5-Dimethyl-3-hexanone.

ⁱ 2,2,6,6-Tetramethyl-4-heptanone.

reactants at 375 °C over Mn60, which showed the highest conversion of propanoic acid into 3-pentanone.

Table 3 summarizes the composition in the reaction effluent in the cross-ketonization of propanoic acid with another linear carboxylic acid. In each reaction, three ketones are observed: 3-pentanone and another symmetric ketone, which is denoted as ‘symmetric ketone’ in Table 3, are produced via the homo-ketonization of carboxylic acids, and an asymmetric ketone is produced by the cross-ketonization between propanoic acid and another carboxylic acid. An approximate binomial distribution is observed: the composition of the produced ketones is ca. 1:2:1 for 3-pentanone, asymmetric ketone, and another symmetric ketone, respectively. The amount of propanone, which is produced via the homo-ketonization of acetic acid, is slightly larger than that of 3-pentanone. On the other hand, the amounts of 4-heptanone, 5-nonanone, and 8-pentadecanone are slightly smaller than that of 3-pentanone. In addition, the amounts of unreacted carboxylic acids are increased with increasing chain length of the acids, except for octanoic acid.

Table 4 lists the composition in the reaction of propanoic acid with branched carboxylic acids. In the reaction of propanoic acid with 2-methylpropanoic acid, the composition of 3-pentanone, 2-methyl-3-pentanone, and 2,4-dimethyl-3-pentanone is ca. 1:1:0.1, respectively. The selectivity to cross-ketonization between propanoic acid and 2-methylpropanoic acid is decreased, and that to homo-ketonization of 2-methylpropanoic acid is suppressed. In the reaction of propanoic acid with 2,2-dimethylpropanoic acid, cross-ketonization is restrained, and no homo-ketonization of 2,2-dimethylpropanoic acid to 2,2,4,4-tetramethyl-3-pentanone is observed. The amounts of unreacted acids are increased with increasing the number of substituted methyl groups.

In the reactions of propanoic acid with other branched acids, such as 3-methylbutanoic acid and 3,3-dimethylbutanoic acid, cross-ketonization produces asymmetric ketones such as 5-methyl-3-hexanone and 5,5-dimethyl-3-hexanone, respectively. The number of substituents affects the reactivity. 2,6-Dimethyl-4-heptanone is produced via the homo-ketonization of 3-methylbutanoic acid although its composition is considerably small compared to that of 3-pentanone. In a similar manner to 2,2-dimethylpropanoic acid, no homo-ketonization of 3,3-dimethylbutanoic acid is observed. In addition, the amounts of unreacted acids are considerably large.

4. Discussion

4.1. Ketonization over various metal oxides

Stubenrauch et al. studied the ketonization of acetic acid over the single crystal surface of CeO₂ [21]. A difference in the catalytic activity was found between the (1 1 1) and (1 0 0) planes of CeO₂: propanone is formed only on the CeO₂ (1 1 1) plane in the ketonization of acetic acid, whereas the CeO₂ (1 0 0) plane does not catalyze the ketonization, indicating that the catalytic activity depends on the crystal plane. Various metal oxides including CeO₂ are active catalysts for the ketonization [9–29]. Gliński et al. investigated 20 oxides supported on SiO₂, and reported that such supported catalysts as CeO₂, MnO₂, CdO, and La₂O₃ were the most active in the synthesis of propanone from acetic acid [20]. In this study, the combination of CeO₂ with MnO₂ was found to be the most active.

Most of the second metal components in CeO₂ improved the catalytic activity for the ketonization of propanoic acid (Table 1). Only the addition of Cr completely deactivated the catalyst, in which Cr probably acted as poison for CeO₂. The introduction of Mg, Mn, Fe, Ni, Cu, and Zr into the CeO₂ structure increased the selectivity to 3-pentanone because it decreased the selectivity to such by-products as butanone and 2-methyl-3-pentanone. The addition of Fe of up to 40 mol% increased both conversion and selectivity, whereas pure Fe₂O₃ was less active for the ketonization of propanoic acid (Fig. 1). At high Fe content, CeO₂–Fe₂O₃ solid solution dispersed in the Fe₂O₃ matrix catalyzed the formation of 3-pentanone from 1-propanol and propanal [35]. Fig. 1 also indicates that the solid solution dispersed in the Fe₂O₃ matrix catalyzes the ketonization.

Pestman et al. reported that pure Fe₂O₃ reduced at >400 °C with metallic iron is effective for the hydrogenation of acetic acid to aldehyde in hydrogen atmosphere, whereas pure Fe₂O₃ reduced at <400 °C is active for the ketonization of acetic acid in the presence of hydrogen [26]. In the latter case, the propanone formation was explained by the decomposition of iron acetate, Fe(CH₃COO)₂. The explanation, however, seems to contradict the present results. In our previous study that was conducted in the absence of hydrogen, pure Fe₂O₃ was found to be less active for the ketonization of propanoic acid but to be active for the ketone formation from propanal [35], suggesting the following mechanism: acetaldehyde formed in the hydrogenation of acetic acid reacts with another acetaldehyde to form

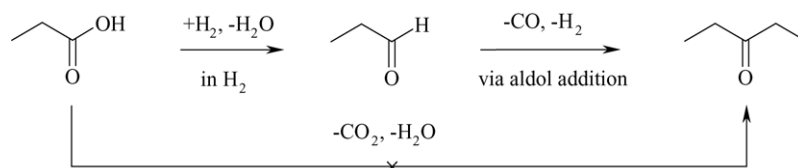


Fig. 6. Possible reaction route to ketone from carboxylic acid over pure Fe₂O₃.

propanone via aldol over pure Fe_2O_3 in the presence of H_2 . We confirmed that H_2 flow enhanced the catalytic activity of pure Fe_2O_3 for the ketonization of propanoic acid although no enhancement by H_2 was observed for both pure CeO_2 and Mn_2O_3 . The ketonization of carboxylic acid proceeds via aldehyde over Fe_2O_3 in the presence of H_2 , as shown in Fig. 6.

4.2. Effect of preparation method for CeO_2 – Mn_2O_3 catalysts

The catalytic activity of CeO_2 – Mn_2O_3 varies with the preparation method (Table 2). Judging from the specific surface area and the catalytic activity, it is obvious that CeO_2 – Mn_2O_3 prepared by the citrate process is superior to that prepared by co-precipitation. The difference in catalytic activity is attributable to the dispersion level of cerium and manganese ions. In our previous study [36], we reported that cerium–manganese composite oxide catalysts prepared by the citrate process consist of CeO_2 – Mn_2O_3 solid solution with a fluorite-type structure at the Mn content of 0–50 mol%. In the catalysts prepared by co-precipitation, however, α - Mn_2O_3 peaks are also observed even at the Mn content of 40 mol% (data not shown). As the solubility products between Ce^{3+} and OH^- and between Mn^{2+} and OH^- are not equal, their tendencies to generate hydroxide precipitates are different. Thus, in the co-precipitation method, CeO_2 -rich and Mn_2O_3 -rich phases precipitate locally, and both cerium and manganese hydroxides are mixed as precursors of CeO_2 and α - Mn_2O_3 . In contrast, a uniform precursor is formed by the citrate process. Because the homogeneous state of the precursor is maintained after calcination, CeO_2 – Mn_2O_3 solid solution is formed. In the catalysts prepared by impregnation, the second oxides dispersed on the support work individually as CeO_2 and Mn_2O_3 without forming solid solution. That is why the impregnation catalysts are as active as pure CeO_2 and Mn_2O_3 .

Manganese ions cannot substitute for cerium ions at Mn contents >50 mol%, because no more Mn^{3+} can enter the $\text{Ce}_{0.5}\text{Mn}_{0.5}\text{O}_{1.75}$ solid solution when the catalyst is prepared by the citrate process [36]. The catalysts at Mn contents >50 mol% consist of $\text{Ce}_{0.5}\text{Mn}_{0.5}\text{O}_{1.75}$ solid solution and γ - Mn_2O_3 phase, whereas only the α - Mn_2O_3 phase is observed in pure Mn_2O_3 . This indicates that the phase transition to α - Mn_2O_3 is inhibited by co-existing in the solid solution. We speculate that both $\text{Ce}_{0.5}\text{Mn}_{0.5}\text{O}_{1.75}$ solid solution and highly dispersed γ - Mn_2O_3 phase are effective for the reaction. As the catalysts prepared by co-precipitation have the α - Mn_2O_3 phase, the γ - Mn_2O_3 phase would be more effective for the reaction than the α - Mn_2O_3 phase. In addition, calcination at low temperature broadens the diffraction peaks and inhibits the phase transition from γ - Mn_2O_3 to α - Mn_2O_3 (Fig. 3), supporting the discussion mentioned above. Thus, the uniformity of the solid solution and the crystalline phase of Mn_2O_3 as well as the large specific surface area influence the catalytic activity.

4.3. Difference in reactivity of carboxylic acid for ketonization

In the reaction of an equimolar mixture of propanoic acid and acetic acid (Table 3), three ketones, propanone, butanone, and 3-pentanone, were observed at the molar ratio of ca. 1:2:1. In the ketonization of mixed acids, propanone is formed from two molecules of acetic acid; butanone, from propanoic acid and acetic acid; and 3-pentanone, from two propanoic acids. If there were no difference in the reactivity between the acids, the product distribution would be governed by statistics, namely, the composition of the produced ketones would be 3-pentanone:butanone:propanone = 1:2:1, according to a binomial theorem, when an equimolar mixture of propanoic acid and acetic acid is reacted with the same reactivity.

Binomial product distribution indicates that bimolecular reactions of homo- and cross-ketonization proceed at equal probability (Table 3). However, the reactivity between acetic acid and propanoic acid is slightly different: the reactivity of carboxylic acid is decreased with increasing chain length of the acid. This is consistent with the report of Gliński et al. on the homo-ketonization: a drop in ketone yield over $\text{MnO}_2/\text{Al}_2\text{O}_3$ was observed with increasing chain length of linear carboxylic acid [20]. They also reported that mixtures of propanoic acid and pentanoic acid at different molar ratios produced mixed ketones of 3-pentanone:3-heptanone:5-nonanone = 54:42:4 and 48:37:15 at the C3/C5 feed ratios of 3 and 2, respectively [22]. The compositions are roughly close to the ratios of 9:6:1 and 4:4:1, respectively. Because the binomial theorem governs the product distribution of ketones in the ketonization of linear carboxylic acid, this can be utilized for the effective production of a specific linear ketone while minimizing undesired ketones.

The cross-ketonization of acetic acid with branched carboxylic acids was found to proceed [12,23]. Branched carboxylic acids are less reactive than linear acids. Pestman et al. investigated the reaction of acetic acid with 2,2-dimethylpropanoic acid [12], and concluded that the abstraction of an α -hydrogen atom was required because propanone and 2,2-dimethyl-3-butanone were observed, but not 2,2,4,4-tetramethyl-3-pentanone via homo-ketonization. Their report is consistent with the present results (Table 4). Ketone composition in the reaction of propanoic acid with α -substituted carboxylic acids is far from the binomial distribution: the homo-ketonization of 2-methylpropanoic acid, which has an α -hydrogen atom, to form 2,4-dimethyl-3-pentanone proceeds whereas that of propanoic acid is 10 times faster. Cross-ketonization also depends on the number of α -hydrogen atoms: the amount of 2-methyl-3-pentanone produced is as much as that of 3-pentanone, whereas the amount of 2,2-dimethyl-3-pentanone is much less. Therefore, the decrease in α -hydrogen atom in the carboxylic acids depresses the homo-ketonization, and the lack of α -hydrogen atom suppresses the reaction. Thus, the reactivity is increased with increasing the number of α -hydrogen

atoms in the order of propanoic acid > 2-methylpropanoic acid > 2,2-dimethylpropanoic acid.

In a similar manner, β -substituents in carboxylic acids inhibit the ketonization (Table 4). In the reaction of β -substituted acids, both cross- and homo-ketonization became difficult to proceed as the number of methyl groups was increased, whereas the composition of 5-methyl-3-hexanone as a cross-ketonization product was similar to the binomial distribution. The methyl group(s) at the β -position would affect the interaction between α -hydrogen atom and the catalyst surface. The increase in steric hindrance probably causes the decrease in the reactivity.

4.4. Probable reaction pathway

In our previous study [35], we found that $\text{CeO}_2\text{-Fe}_2\text{O}_3$ catalysts were effective for 3-pentanone formation from different reactants, such as 1-propanol, propanal, and propyl propanoate. Each of those reactants could be converted into 3-pentanone. Propanal showed the highest reactivity among the reactants, the yield being ca. 57% at 400 °C. On the other hand, propanoic acid was converted into 3-pentanone with the yield of ca. 76% even at 350 °C over $\text{CeO}_2\text{-Fe}_2\text{O}_3$ (Fig. 1). Therefore, carboxylic acid is the most reactive and selective compound for ketone formation.

We speculate that the 3-pentanone formation from propanal proceeds via aldol addition of propanal over $\text{CeO}_2\text{-Fe}_2\text{O}_3$ [35]. If propanal is converted into 3-pentanone through propanoic acid, further oxidation is required in a non-oxidative atmosphere. Furthermore, pure Fe_2O_3 has the highest catalytic activity for producing 3-pentanone from propanal [35], although the ketonization of propanoic acid rarely proceeds over pure Fe_2O_3 in N_2 (Fig. 1). As mentioned in Section 4.1, the ketonization of acid over pure Fe_2O_3 may proceed via the aldol of an aldehyde in the presence of H_2 . It is therefore reasonable that the reaction pathway from propanoic acid to 3-pentanone over CeO_2 -based catalysts is different from that from propanal to ketone.

It has been reported that the ketonization of acetic acid involves the bimolecular condensation of adsorbed species via the Langmuir–Hinshelwood mechanism over Zn-Cr-Fe-O mixed oxide [39]. Pestman et al. studied the ketonization of labeled acids over TiO_2 [12], and negated a route via ketene, i.e., dehydration from acetic acid to ketene, followed by the addition of another acetic acid to the ketene to form propanone, as had been proposed by González et al. [40]. Thermal desorption [15] and IR [41] studies have revealed that acetic acid adsorbed on TiO_2 has a structure of a bidentate or a strongly adsorbed unidentate, and that it is removed as propanone and CO_2 at temperatures above 300 °C. Pestman et al. proposed that the ketonization proceeded via an intermediate of bidentate acetate that was oriented parallel to the surface, and that the α -hydrogen atom was abstracted to form an alkylidene group and a carbonate [12]. The alkylidene group could react with another carboxylate and a hydro-

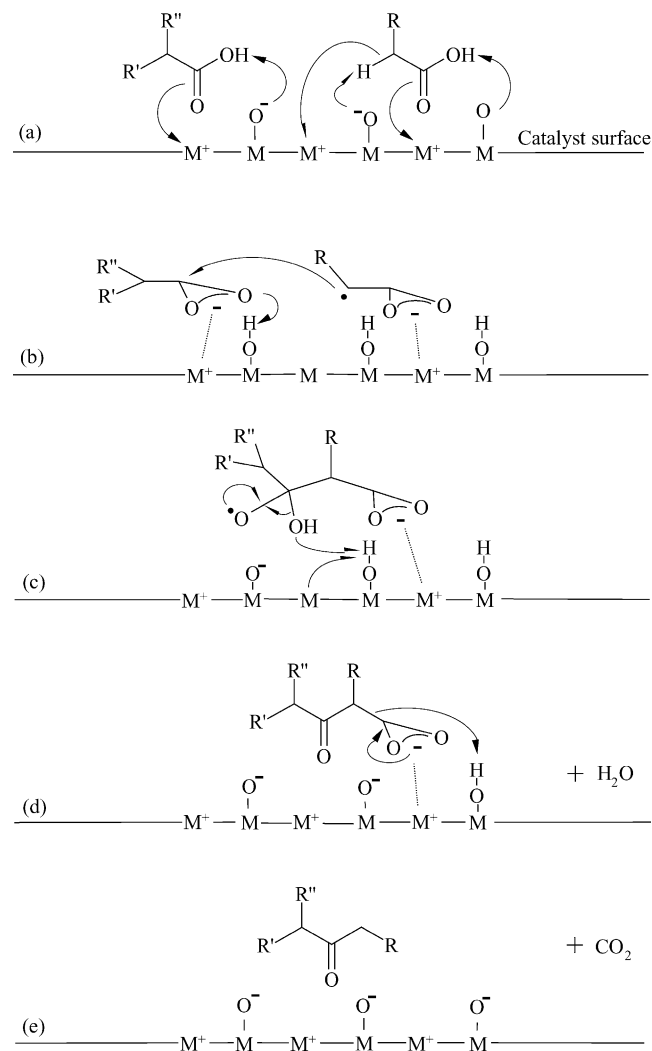


Fig. 7. Speculated reaction mechanism underlying the ketonization of carboxylic acid over $\text{CeO}_2\text{-Mn}_2\text{O}_3$.

gen atom to provide a ketone, and the remaining carbonate formed CO_2 .

However, it is not reasonable that abstraction of the α -hydrogen and the cleavage of the C–C bond to form the alkylidene group occur successively. If the alkylidene species is formed, it could have reacted with H_2O to form methanol as well as with acetic acid to form propanone. It is possible that the coupling with acetic acid proceeds at the same time as the cleavage or before it. If this is so, the route is the same as that via a β -keto acid such as acetoacetic acid, which was proposed by Plint et al. in a reaction of 1-butanol with oxygen over CeO_2/MgO [32]. Although they proposed that a bianionic species was formed from a carboxylate by abstracting a proton, an anion radical species was electronically plausible. Other reactions over CeO_2 were explained by mechanisms via radical species [5,7].

Here, we propose a modified reaction mechanism of ketonization (Fig. 7). First, surface carboxylates are formed, and an α -hydrogen atom is abstracted to form an anion radi-

cal (Fig. 7a and b), which is then added to another carboxylate to produce a β -keto acid (b and d), followed by decarboxylation to form a ketone (Fig. 7d and e). The surface metal of oxide may be reduced by an abstracted α -hydrogen atom (a and b) and re-oxidized by a hydroxyl radical that desorbed from the intermediate (c and d). The redox cycle is assumed to be a key step of the C–C bond formation. Both iron and manganese, being effective additives in CeO₂, probably work as the redox sites.

5. Conclusions

Both ketonization of propanoic acid and cross-ketonization of different carboxylic acids were investigated over CeO₂-based catalysts at 300–425 °C. CeO₂ catalysts modified with Mg, Al, Mn, Fe, Ni, Cu, and Zr are effective for the ketonization of propanoic acid to form 3-pentanone. CeO₂–Mn₂O₃ is the most efficient catalyst, and the citrate process is more appropriate than co-precipitation for preparing a solid solution of CeO₂–Mn₂O₃. The degree of mixing in a solid solution affects the catalytic activity for the ketonization.

In the reaction of propanoic acid with another linear carboxylic acid over CeO₂–Mn₂O₃ at 375 °C, the reactivity of the carboxylic acid is slightly decreased as its chain length is increased. Two kinds of symmetric ketones are formed via homo-ketonization, and one asymmetric ketone is formed via cross-ketonization. The composition of the produced ketones is governed by the binomial theorem. In contrast to linear carboxylic acids, branched acids are less reactive. In the cross-ketonization of propanoic acid with a branched acid, the composition of the resultant ketones is very different from the binomial distribution. Methyl group substituents at α - and β -positions in the acids, i.e., decreasing the number of α -hydrogen and increasing steric hindrance, decrease the reactivity of the acid for both homo- and cross-ketonization.

References

- [1] J.C. Summers, S.A. Ausen, *J. Catal.* 58 (1979) 131–143.
- [2] S. Matsumoto, *Catal. Today* 90 (2004) 183–190.
- [3] S. Sato, K. Koizumi, F. Nozaki, *Appl. Catal. A* 133 (1995) L7–L10.
- [4] S. Sato, K. Koizumi, F. Nozaki, *J. Catal.* 178 (1998) 264–274.
- [5] S. Sato, R. Takahashi, T. Sodesawa, K. Matsumoto, Y. Kamimura, *J. Catal.* 184 (1999) 180–188.
- [6] S. Sato, R. Takahashi, T. Sodesawa, N. Honda, H. Shimizu, *Catal. Commun.* 4 (2003) 77–81.
- [7] S. Sato, R. Takahashi, T. Sodesawa, N. Honda, *J. Mol. Catal. A* 221 (2004) 177–183.
- [8] S. Sato, R. Takahashi, T. Sodesawa, N. Yamamoto, *Catal. Commun.* 5 (2004) 397–400.
- [9] J.C. Kuriacose, R. Swaminathan, *J. Catal.* 14 (1969) 348–354.
- [10] R. Swaminathan, J.C. Kuriacose, *J. Catal.* 16 (1970) 357–362.
- [11] M. Jayamani, C.N. Pillai, *J. Catal.* 87 (1984) 93–97.
- [12] R. Pestman, R.M. Koster, A. van Duijne, J.A.Z. Pieterse, V. Ponec, *J. Catal.* 168 (1997) 265–272.
- [13] K.S. Kim, M.A. Barteau, *J. Catal.* 125 (1990) 353–375.
- [14] R. Pestman, A. van Duijne, J.A.Z. Pieterse, V. Ponec, *J. Mol. Catal. A* 103 (1995) 175–180.
- [15] R. Pestman, R.M. Koster, J.A.Z. Pieterse, V. Ponec, *J. Catal.* 168 (1997) 255–264.
- [16] R. Martinez, M.C. Huff, M.A. Barteau, *J. Catal.* 222 (2004) 404–409.
- [17] K. Okumura, Y. Iwasawa, *J. Catal.* 164 (1996) 440–448.
- [18] K. Parida, H.K. Mishra, *J. Mol. Catal. A* 139 (1999) 73–80.
- [19] M. Gliński, J. Kijeński, *Appl. Catal. A* 190 (2000) 87–91.
- [20] M. Gliński, J. Kijeński, A. Jakubowski, *Appl. Catal. A* 128 (1995) 209–217.
- [21] J. Stubenrauch, E. Broscha, J.M. Vohs, *Catal. Today* 28 (1996) 431–441.
- [22] M. Gliński, J. Kijeński, *React. Kinet. Catal. Lett.* 69 (2000) 123–128.
- [23] S.D. Randery, J.S. Warren, K.M. Dooley, *Appl. Catal. A* 226 (2002) 265–280.
- [24] T.S. Hendren, K.M. Dooley, *Catal. Today* 85 (2003) 333–351.
- [25] E.J. Grootendorst, R. Pestman, R.M. Koster, V. Ponec, *J. Catal.* 148 (1994) 261–269.
- [26] R. Pestman, R.M. Koster, E. Boellaard, A.M. van der Kraan, V. Ponec, *J. Catal.* 174 (1998) 142–152.
- [27] Y. Wang, B.H. Davis, *Appl. Catal. A* 180 (1999) 277–285.
- [28] K.M. Parida, A. Samal, N.N. Das, *Appl. Catal. A* 166 (1998) 201–205.
- [29] K. Parida, J. Das, *J. Mol. Catal. A* 151 (2000) 185–192.
- [30] V.I. Komarewsky, J.R. Coley, *Adv. Catal.* 8 (1956) 207–217.
- [31] H. Idriss, C. Diagne, J.P. Hindermann, A. Kiennemann, M.A. Barteau, *J. Catal.* 155 (1995) 219–237.
- [32] N. Plint, D. Ghavalas, T. Vally, V.D. Sokolovski, N.J. Coville, *Catal. Today* 49 (1999) 71–77.
- [33] Y. Kamimura, S. Sato, R. Takahashi, T. Sodesawa, M. Fukui, *Chem. Lett.* (2000) 232–233.
- [34] H. Teterycz, R. Klimkiewicz, B.W. Licznarski, *Appl. Catal. A* 214 (2001) 243–249.
- [35] Y. Kamimura, S. Sato, R. Takahashi, T. Sodesawa, T. Akashi, *Appl. Catal. A* 252 (2003) 399–411.
- [36] T. Akashi, S. Sato, R. Takahashi, T. Sodesawa, K. Inui, *Catal. Commun.* 4 (2003) 411–416.
- [37] H. Teterycz, R. Klimkiewicz, M. Łaniecki, *Appl. Catal. A* 249 (2003) 313–326.
- [38] C. Marcilly, P. Courty, B. Delmon, *J. Am. Ceram. Soc.* 53 (1970) 56–57.
- [39] S. Rajadurai, J.C. Kuriacose, *Mater. Chem. Phys.* 16 (1986) 17–29.
- [40] F. González, G. Munuera, J. Prieto, *J. Chem. Soc., Faraday Trans. 1* 74 (1978) 1517–1529.
- [41] Z.-F. Pei, V. Ponec, *Appl. Surf. Sci.* 103 (1996) 171–182.