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Ketonization of hexanoic acid to diesel-blendable 6-undecanone on the stable zirconia aerogel catalyst

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Graphical abstract



Highlights

- Highly active ketonization of hexanoic acid.
- Stable zirconia aerogel catalysts exhibited the high activity.
- Mesopores improved the catalytic activity.

Abstract

The ketonization of hexanoic acid, which can be prepared by the fermentation of sugars, was performed in an effort to obtain the diesel-blendable high-carbon-number ketone 6-undecanone in this study. Based on observations of the leaching of highly active base catalysts, magnesium oxide and manganese oxide, the stable amphoteric solid catalyst zirconia was selected for the acid-rich reaction environment. A high-surface-area zirconia aerogel was prepared, which successfully ketonized hexanoic acid to 6-undecanone with high conversion, 72.3%, and high selectivity, 92.6%. The further optimization of the porous structures of zirconia led to possibly improved mass transfer with approximately 35 nm of pores, which improved the catalytic activity of zirconia.

Keywords: ketonization; hexanoic acid; zirconia; aerogel.

1. Introduction

Abundant amounts of carboxylic acids are produced during the thermolysis of biomass [1-3] and the anaerobic fermentation of sugars [4, 5] for the preparation of drop-in fuels. Although the carboxylic acid contains only two oxygen atoms in each molecule allowing to be converted to paraffins and olefins, its acidity must be reduced to produce petroleum-blendable hydrocarbons. The simple processes including decarboyxlation, decarbonylation, and deoxygenation can convert carboxylic acids, particularly fatty acids from the plant oil, to deoxygenated hydrocarbons without a significant loss of carbons although the high pressure hydrogen gas at the high reaction temperatures of 250 - 450 °C are required for the efficient processes [6]. Another method to convert the carboxylic acids is the ketonization which dimerizes two carboxylic acid molecules to one ketone molecule with the removal of one water and one carbon dioxide [7-9]. A gas-phase reaction using solid-base catalysts has been performed for the ketonization of small molecular weight organic acids [10-15].

In addition to the thermolysis and the anaerobic fermentation, biological processes which can be used to prepare carboxylic acids with higher carbon numbers, including butyric acid [16, 17] and hexanoic acid [18, 19], have been studied in the hope of preparing alternative fuels which blend better with gasoline and diesel. Although these carboxylic acids and their corresponding alcohols are promising as high-energy-density fuels, fuels with higher carbon numbers and with lower oxygen-to-carbon ratios can be better blended with gasoline and diesel, and the production of fuels with higher carbon numbers via a completely biological process have been developed [20]. However, the biological processes may not be efficient to produce these chemicals because of their

low productivity.

The goal of this study is to develop a heterogeneous catalyst for the efficient production of the higher-energy-density C11 ketone from biologically produced hexanoic acid [18, 19]. Attempts were made to avoid the possible leaching of base catalysts, and a stable amphoteric catalyst was developed for a feasible continuous flow reaction under an acid-rich environment. The optimization of the porous aerogel catalyst was also performed to find the ketonization descriptor.

(Fig. 1)

2. Experimental

2.1. Preparation of catalysts

Silica-alumina (Si_xAl_yO), alumina (Al₂O₃), titania (TiO₂), zirconia (ZrO₂), ceria (CeO₂), manganese oxide (MnO_x), zirconium butoxide (Zr(OC₄H₉)₄, 80% in butanol), methanol (99.5%), hexanoic acid (HA, 99%), 6-undeanone (6-UDO, 98%), hexanoic anhydride (HAn, 98%), and chloroform (99%) were purchased from Aldrich (Milwaukee, WI, USA). Magnesium oxide (MgO) was purchased from Yakuri (Kyoto, Japan). An aqueous nitric acid solution (61%) and an aqueous ammonia solution (28%) were purchased from Junsei (Tokyo, Japan). Zirconia xerogel and aerogel were prepared using a sol-gel method. A mixture of zirconium butoxide dissolved in butanol (80%, 22.8 mL,), methanol (51.2 mL), DI water (3.6 mL), and aqueous nitric acid (61%, 3.6 mL) was stirred at room temperature for 1 h. An aqueous ammonia solution (28%, 0.516 mL) was added to

the mixture, which was further stirred for 1 h. The mixture was aged for 6 h at 60 °C and dried by means of supercritical CO_2 drying (aerogel) or non-supercritical drying (xerogel). For the supercritical CO_2 drying process, the aged alcogel was placed in a chamber and liquid CO_2 was supplied to the chamber to be pressurized to 137 bar at room temperature. The chamber was kept at 30 °C for 5 h to exchange methanol and water with CO_2 and then kept at 70 °C and 137 bar for 3 h. CO_2 was released and the reactor was depressurized to ambient pressure, after which the chamber was cooled to room temperature. The prepared aerogel was collected and calcined under an air flow at 500 °C for 6 h. For the non-supercritical drying process used to prepare the xerogel, the prepared alcogel was dried at 120 °C for 12 h and calcined under an air flow at 700 °C for 6 h.

2.2. Characterizations of catalysts

X-ray diffraction (XRD) was performed using a D/MAX-2500 diffractometer (Rigaku) with CuK α_1 ($\lambda = 1.54056$ Å). N₂-physisroption was performed using an ASAP 2020 (Micromeritics). The samples for N₂-physisorption were degassed in a vacuum at 120 °C for 12 h prior to the measurement. CO₂- and NH₃ temperature-programmed desorption (TPD) measurements were performed using a BELCAT chemisorption analyzer (BEL Japan) equipped with a thermal conductivity detector (TCD) and a mass spectrometer. For the CO₂-TPD, the catalyst (~500 mg) was heated under a He flow (30 mL/min) at 500 °C for 1 h and a CO₂ flow (50 mL/min) was introduced at 100 °C for 1 h prior to the measurement. For the NH₃-TPD, the catalyst (~500 mg) was heated under a He flow (30 mL/min) at 500 °C for 1 h and a NH₃ flow (30 mL/min) was introduced at 100 °C for 1 h prior to the measurement.

2.3. Fixed-bed reaction

The catalyst (0.2 g) was placed on quartz wool in a stainless steel fixed-bed reactor and pretreated at 500 °C under a N₂ flow for 4 h. HA (0.8 g/h) was fed using an LC pump and mixed with a N₂ flow (40 mL/min) before being supplied to the reactor. The weight-hourly space velocity (WHSV) was adjusted to 4 h⁻¹ by manipulating the amount of catalyst. The obtained mixture of gas products was cooled to -2 °C and the liquid products were collected using a 20-cm-long 15-mL separator. The collected liquid products were mixed with 2-propanol (internal standard) and diluted with chloroform, which were quantified using a GC-FID (Hewlett-Packard 5890 series gas chromatograph equipped with 60 m 0.25 m HP-5 capillary column).

3. Results and Discussion

3.1. Ketonization of hexanoic acid on the metal oxide catalysts

The ketonization of hexanoic acid was performed using several metal oxide catalysts at 360 °C (Table 1). As reported for the ketonization of carboxylic acids with lower carbon numbers [12], solid bases of MgO and MnO exhibited the highest conversion of hexanoic acid (HA) with the highest selectivity to 6-undecanone (6-UDO), and other solid acids and weak bases exhibited lower catalytic ketonization activity. A significantly large amount of hexanoic anhydride (HAn) was obtained by the intermolecular dehydration of two HA molecules formed on poor catalysts, including Si_xAl_yO, Al₂O₃, TiO₂, ZrO₂, and CeO₂.

(Table 1)

While the high catalytic ketonization activity of MgO and MnO_x is attributed to the basicity in the literature [21], we further investigated the origin of the catalytic activity using certain characterization methods. The most active MgO and MnO_x, with very low BET surface areas and negligible pore volumes (Table 2), excluding the beneficial effects of highly dispersed MgO and MnO_x particles on the catalytic activity, exhibited the higher basicity (by CO₂-TPD) compared to TiO₂, ZrO₂, and CeO₂ (Table 2 and Fig. S1). The less active Si_xAl_yO and Al₂O₃ exhibited the unusually large quantities of desorbed CO₂ in the CO₂-TPD results, which can be attributed to their high surface areas.

(Table 2)

In addition to the basicity, the high activity of MgO and MnO_x, despite their low BET surface areas, is attributed to the homogenous reaction which took place on the dissolved MgO and MnO_x. During the continuous flow reaction, we frequently observed plugging or a significant pressure drop for the highly active MgO and MnO_x, most likely because of the leaching of the catalysts. The catalyst powder exhibited physical changes, including the formation of gel-like sticky pastes, and a change of the color was observed during the continuous reaction for 90 – 200 h (Figs. S2 and S3). To predict the possible leaching or reconstruction of these solid-base catalysts as they interacted with hexanoic acid, leading to homogeneous catalysis, the liquid products were observed using ICP-AES and the spent catalysts were observed using XRD and TG. When observed with ICP-AES, 4.33 and 5.34 g/h of Mg and Mn, respectively, dissolved in the liquid

products were observed during the first 25 h of operation, which indicates that MgO and MnO_x were deformed and leached during the continuous flow reaction, and a homogeneous reaction using dissolved metal oxides occurred. The leaching of catalysts was further confirmed by performing batch reactions at 360 °C for 6 h (Table S1), which exhibited the almost complete leaching of Mg and Mn confirming the homogenous catalysis on MgO and MnO_x.

The leaching of MgO and MnO_x was further confirmed with XRD (Fig. S4). MnO_x exhibited a major transformation of face-centered cubic manganosite (MnO) [22] to other manganese oxides, indicating that MnO_x was partially dissolved in hexanoic acid and reconstructed. Although the leaching and deforming of MgO was observed, both fresh and spent MgO exhibited a face-centered cubic periclase structure [23] possibly because the ambient-pressure-stable periclase formed even after the reconstruction of MgO in the acid-rich environment. Although MgO did not exhibit significant changes in the XRD analysis, catalysis using MgO was forced to stop at 90 h because of the significant pressure drop and plugging caused by the dissolution and re-agglomeration of the MgO powder. These observations indicate that MgO and MnO_x are not appropriate for the heterogeneous catalytic ketonization of hexanoic acid in spite of their high catalytic activity.

3.2 Ketonization of hexanoic acid on zirconia

To avoid the homogeneous reaction by leached solid catalysts, zirconia was selected as a possible stable ketonization catalyst because its amphoteric nature may resist the leaching under the acidic conditions. Assuming that the observed poor activity of bulk zirconia powder could be attributed to its low surface area (Table 2), a highly dispersed aerogel, a less dispersed xerogel, commercially

available zirconia, and sulfated zirconia were prepared or purchased for catalysis, and their activities were measured as described at the experimental section (Table 3). Although the commercially available zirconia (m-ZrO₂) exhibited very poor activity and low BET surface area, the sulfated zirconia and aerogel (ZrO_x(A500)) exhibited higher conversions of HA and higher yields of 6-UDO. Interestingly, the preferred formation of HAn was observed for the less active m-ZrO₂ and xerogel (ZrO_x(X)), which exhibited lower conversion of HA.

(Table 3)

In order to find the descriptor to determine the catalytic activity of zirconia for the improved catalysts, the crystal structures, pore structures, and acid-base properties of the catalysts were observed. The XRD results of zirconia exhibited monoclinic ZrO_2 for m- ZrO_2 , tetragonal ZrO_2 for S- ZrO_2 , and a mixture of monoclinic (minor) and tetragonal (major) ZrO_2 for $ZrO_x(X)$, and $ZrO_x(A500)$ (Fig. S5). The formation of tetragonal ZrO_2 in chemically treated zirconia and the aerogels has been reported in the literature [24]. Although the formation of tetragonal ZrO_2 has been attributed to the improved catalytic activity of zirconia in the literature [25], it is not clear whether the crystal structure determined the catalytic activity in this study. Other than the crystal structure, the pore structures of the zirconia catalysts were measured by means of N₂-physisorption (Table 4 and Fig. S6). S- ZrO_2 and $ZrO_x(A500)$ exhibited higher BET surface areas, while m- ZrO_2 and $ZrO_x(X)$ exhibited negligible BET surface areas and pore volumes. These observations indicate that the surface area did not clearly determine the catalytic activity because S- ZrO_2 with its higher surface area did not exhibit better activity compared to $ZrO_2(A500)$.

(Table 4)

Along with the crystal structures and porosity, the basicity and acidity of the zirconia catalysts were observed with CO₂- and NH₃-TPD measurements, respectively (Fig. S7 and Table 5), indicating that the basicity was a good descriptor for the ketonization of zirconia. While the less active S-ZrO₂ exhibited the highest acidity because of its sulfate functionalities, the most active ZrO_x(A500) exhibited the highest basicity and high acidity. When the yield of 6-UDO, representing the catalytic ketonization activity, was plotted on the BET surface area, CO₂-desorption, and NH₃-desorption, it was clear that the basicity as measured by CO₂-TPD determined the ketonization activity, although zirconia exhibited both acidity and basicity (Fig. 2). Although the basicity more clearly improved the ketonization activity, the synergistic effects of acids and bases can be expected. By the possible reaction pathway (Fig. S8) [9, 26, 27], acid sites on the catalysts also appear to contribute to the conversion of carboxylic acid to ketone.

(Fig. 2)

Along with the basicity-improved catalytic activity, the stability of $ZrO_x(A500)$ was confirmed with an extended reaction (Fig. S9). While the selectivity to 6-UDO did not change significantly, exhibiting results of 90 – 92%, the conversion of HA continuously decreased over time, indicating that the deactivation of $ZrO_x(A500)$ occurred. The XRD measurements did not exhibit any changes in the crystal structures of zirconia (Fig. S10); however, the TG of spent $ZrO_x(A500)$ exhibited the deposition of carbon on the catalyst surface (Fig. S11). Because of the carbon deposition process, the BET surface area (82.2 to 75.1 m²/g) and the pore volume (0.59 to 0.49 cm³/g) of $ZrO_x(A500)$

decreased slightly, although the pore width did not significantly change. These observations indicate that the structure of $ZrO_x(A500)$ was very stable during the extended continuous flow reaction and that deactivation occurred as a result of the carbon deposition, not because of the leaching or deformation of the catalyst. The ICP-AES of liquid products confirmed the excellent stability of $ZrO_x(A500)$, exhibiting negligible Zr (less than the detection limit of 10 ppm in the liquid products collected for 25 h) dissolved in the liquid products, in contrast to the observations of MgO and MnO_x. The batch reaction using $ZrO_x(A500)$ also confirmed the negligible leaching of zirconia (Table S1).

Note that the ketonization of HA on zirconia aerogel catalysts was not significantly affected by the existence of CO₂ under ambient pressure although the pressurized CO₂ was reported to inhibit the ketonization [28]. When HA was condensed to 6-UDO on $ZrO_x(A500)$ at 330 °C with co-fed CO₂ ([CO₂]/[HA] = 7.7 (mol/mol)), the conversion of HA and the yield of 6-UDO were 32.5 and 30.5% at WHSV = 4 h⁻¹, respectively, which are not significantly different from those observed without co-fed CO₂, 29.8% conversion of HA and 27.9% yield of 6-UDO.

3.3 Ketonization on the zirconia aerogels with different pore structures.

While $ZrO_x(A500)$ exhibited high stability and basicity-improved activity for ketonization, its optimization was further attempted by the thermal modification of its pore structures. Because aerogel catalysts will give the benefit of better mass transfer during the reaction, it is important to understand the relationship between the pore structure and the catalytic activity. Although the adjustment of calcination temperature controlled the pore structure, the acidity per BET surface

area was similar to one another exhibiting $5.1 - 7.0 \ \mu mol/m^2$ (calculated by NH₃-TPD results and BET surface areas) for all zirconia except the one calcined at 1200 °C (ZrO_x(A1200)) which exhibited the negligible BET surface area (Figs. S13, S14, and Table S2). The XRD measurement of zirconia aerogels exhibited more monoclinic and less tetragonal structures while the monoclinic structure became more distinct at the higher calcination temperature (Fig. S15).

By manipulating the calcination temperature during the preparation of the aerogels, the zirconia aerogel calcined at 500 °C (ZrO_x(A500)), with the largest BET surface area and the smallest pore width, exhibited the highest ketonization activity while those calcined at 1200 °C ($ZrO_x(A1200)$), with the smallest BET surface area and the smallest pore volume, exhibited the lowest activity (Table 6 and Fig. 3). Because the acidity per BET surface area was not significantly different, the catalytic activity was expected to be proportional to the BET surface area. When the yield of 6-UDO was plotted on the BET surface area, the deviation from linearity was observed for $ZrO_x(A800)$ and $ZrO_x(A600)$ (Fig. 4). The BJH desorption pore size distribution indicated that $ZrO_x(A500)$ and $ZrO_x(A600)$ exhibited similar pore structures, while $ZrO_x(A1000)$ and $ZrO_x(A1200)$ exhibited thermally destroyed pores. $ZrO_x(A800)$ was different from the others in that it exhibited mesopores of approximately 35 nm, which are larger than those of $ZrO_x(A500)$ and $ZrO_x(A600)$. It is reasonable to expect better gas-phase catalytic activity with larger pores, which improve the mass transfer. Pores of zirconia aerogels in this study are mesopores exhibiting the Knudsen diffusion whose diffusion coefficient is proportional to the pore width [29]. Although the pores of zirconia catalysts are not uniform, we can expect the mass transfer on ZrO_x(A800) with pores of 35 nm is approximately 1.6 times faster than those on $ZrO_x(A500)$ and $ZrO_x(A600)$ whose peak pores are approximately 20 nm. The rates of formation of 6-UDO per base site were

13 h⁻¹ for ZrO_x(A800) and 5.9 – 6.9 h⁻¹ for the others except ZrO_x(A1200), which may indicate the beneficial effects of mass transfer. Therefore, the positive deviation of the catalytic activity of ZrO_x(A800) could be attributed to the better superficial catalytic activity which is obtained by the better mass transfer through the larger pores. The slight positive deviation of ZrO_x(A600) was likely caused by the same process, although the pore size was slightly larger than that of ZrO_x(A500).

(Table 6)

(**Fig. 3**)

(**Fig. 4**)

4. Conclusions

Although the basic catalysts MgO and MnO_x exhibited high catalytic activity for the ketonization of hexanoic acid, their leaching in an acid-rich environment may not be feasible for a long-term continuous flow reaction. High-surface-area zirconia aerogels exhibited high stability and excellent catalytic activity under a flow of a hexanoic acid reactant, which must be appropriate for a continuous process. With nearly identical base properties, the activity of the zirconia aerogel was proportional to the BET surface area, although the better mass transfer with larger pores appears to improve the catalytic activity.

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Appendix A.

Supplementary data are available at

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0 || ↓ H₂O + CO₂

Fig. 1. Ketonization of hexanoic acid to 6-undecanone.



Fig. 2. Effects of the (a) surface area, (b) basicity, and (c) acidity of zirconia catalysts on the yields of 6-UDO.



Fig. 3. N₂-physisorption isotherms and BJH desorption pore size distributions of zirconia aerogel catalysts prepared with different calcination temperatures.



Fig. 4. Yield of 6-UDO depending on the BET surface area.

	Reaction	HA			
Catalust	4		6-UDO	6-UDO yield	HAn
Catalyst	temperature	conversion	selectivity (%)	(%)	selectivity (%)
	(°C)	(%)	selectivity (70)	(70)	selectivity (70)
Si _x Al _y O	360	15.6	63.9	10.0	31.4
Al ₂ O ₃	360	7.9	22.4	1.8	76.6
TiO ₂	360	14.9	28.3	4.2	66.9
ZrO ₂	360	9.8	20.8	2.0	78.0
CeO ₂	360	14.7	37.2	4.9	64.7
MgO	360	61.9	87.5	54.1	1.5
MnO _x	360	75.8	90.3	68.4	0.9

Table 1. Catalysis results using metal oxides at 360 °C.

Catalysts	S_{BET} (m ² /g)	V_p (cm ³ /g)	Amount of CO_2 desorbed (µmol/g)
Si _x Al _y O	569	0.75	150
Al ₂ O ₃	62.7	0.18	120
TiO ₂	5.7	0.012	3
ZrO_2	4.5	0.011	7
CeO ₂	3.6	0.009	5
MgO	6.1	0.015	44
MnO _x	8.3	0.029	15

 Table 2. N₂-physisorption and CO₂-TPD results of the metal oxide catalysts.

	Reaction	НА	6-UDO	6-UDO vield	HAn
Catalysts	temperature	conversion	selectivity	(%)	selectivity
	(°C)	(%)	(%)	(/0)	(%)
m-ZrO ₂	360	9.8	20.8	2.0	78.0
S-ZrO ₂	360	32.9	85.0	28.0	5.6
$ZrO_x(X)$	360	11.6	11.4	1.3	87.5
ZrO _x (A500)	360	74.5	92.6	68.9	0.5

Table 3. Catalysis activity of zirconia at	360 °C	•
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Catalyst	$S_{\text{DET}}(m^2/q)$	V_{a} (cm ³ /g)	S _{Micropore} measured by <i>t</i> -		
	SBEI (III /g)	v _p (cm/g)	plot (m^2/g)		
m-ZrO ₂	4.6	0.011	3.1		
S-ZrO ₂	126.0	0.12	36.7		
$ZrO_x(X)$	1.8	0.004	0.9		
ZrO _x (A500)	82.2	0.59	9.6		

 Table 4. N2-physisorption results of the zirconia catalysts.

Catalyst	Amount of desorbed CO ₂ (µmol/g)	Amount of desorbed NH ₃ (µmol/g)
<i>m</i> -ZrO ₂	7	26
S-ZrO ₂	77	589
$ZrO_x(X)$	4	11
ZrO _x (A500)	172	480

Table 5. Basic and acidic properties of zirconia catalysts according to a TPD analysis.

Catalyst	Sbet (m²/g)	V _p (cm ³ /g)	S _{Micropore} by <i>t</i> -plot (m ² /g)	Reaction temperat ure (°C)	HA conversio n (%) ^a	6-UDO selectivit y (%)	6-UDO yield (%) ^a	HAn selectivit y (%)	6-UDO formation per base site (h ⁻¹)
ZrO _x (A500)	103.3	0.55	4.8	360	72.3	92.6	66.9	0.7	5.9
ZrO _x (A600)	69.2	0.46	12.4	360	58.7	93.4	54.9	1.1	6.9
ZrO _x (A800)	28.2	0.27	9.9	360	48.3	93.2	45.0	1.5	13
ZrO _x (A1000)	13.0	0.11	6.0	360	14.3	63.7	9.1	35.1	6.6
ZrO _x (A1200)	1.7	0.01	1.0	360	6.2	11.2	0.7	88.0	2.6

Table 6. Ketonization results on zirconia aerogel catalysts at 360 °C.

^aThe error ranges: $\pm 1.9\%$ for the HA conversion and $\pm 1.7\%$ for the 6-UDO yield.