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PERSPECTIVE
Darya Radziuk and Helmuth Möhwald
Ultrasonically treated liquid interfaces for progress in cleaning and separation processes

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1 **One-step hydroprocessing of fatty acids into renewable aromatic**

2 **hydrocarbons over Ni/HZSM-5: Insight into the major reaction**

3 **pathways**

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15 **Abstract.** For high caloricity and stability in bio-aviation fuels, a certain content of aromatic

16 hydrocarbons (AHCs, 8–25 wt%) is crucial. Fatty acids, obtained from waste or inedible oils, are a

17 renewable and economic feedstock for AHC production. Considerable amounts of AHCs, up to

18 64.61 wt%, were produced through the one-step hydroprocessing of fatty acids over Ni/HZSM-5

19 catalysts. Hydrogenation, hydrocracking, and aromatization constituted the principal AHC

20 formation processes. At a lower temperature, fatty acids were first hydrosaturated and then

21 hydrodeoxygenated at metal sites to form long-chain hydrocarbons. Alternatively, the unsaturated

22 fatty acids could be directly deoxygenated at acid sites without first being saturated. The

23 long-chain hydrocarbons were cracked into gases such as ethane, propane, and C_6–C_8 olefins over

24 the catalysts' Brønsted acid sites; these underwent Diels-Alder reactions on the catalysts' Lewis

25 acid sites to form the AHCs. The C_6–C_8 olefins were determined as critical intermediates for AHC

26 formation. As the Ni content in the catalyst increased, the Brønsted-acid site density was reduced

27 due to coverage by the metal nanoparticles. Good performance was achieved with a loading of 10

28 wt% Ni, where the Ni nanoparticles exhibited a polyhedral morphology which exposed more

29 active sites for aromatization.

1 Introduction

The rapid, steady consumption of commercial transportation fuels such as aviation fuel, commonly produced by petroleum refining [1], has placed substantial burdens on the natural environment through the excessive emission of greenhouse gases. The development of aviation fuels derived from renewable and sustainable feedstocks has shown great potential because of their ability to reduce the total carbon footprint by ~80% over their full life-cycle [2], and has attracted increasing interest in recent years [3, 4]. Specifically designed for use in aircraft, aviation fuels must meet stringent specifications such as high caloricity and low boiling points for safe, high-altitude flight. Aromatic hydrocarbons (AHCs) are indispensable components of aviation fuels because of their higher densities and volumetric heating values, in contrast to straight-chain and iso-alkanes. More importantly, the presence of AHCs is necessary to ensure the shrinkage of aged elastomer seals and prevent the leakage of aviation fuels [5]. Therefore, for safe application, current aviation fuels must contain 8–25% AHCs.

Because of their plentiful supply, ready accessibility, and low cost, biomass-derived feedstocks for AHC synthesis are primarily composed of raw lignocellulosic materials such as cellulose, hemicellulose, and lignin, and lipidic materials such as lipids and fatty acids [6-9]. Several researchers have investigated the synthesis of AHCs from biomass derivatives such as furans (e.g., 2,5-dimethylfuran (DMF) or 2-methylfuran (MF)) and ethylene or propylene via Diels-Alder cycloadditions and subsequent dehydration reactions [10-14]. For example, toluene, a typical AHC, could be synthesized through two principal steps: the Diels-Alder cycloaddition between MF and ethylene, and the dehydrogenation of the cyclic intermediate to produce toluene [15]. Unfortunately, several side reactions also occurred during the Diels-Alder cycloaddition of MF and ethylene, which made it difficult to achieve a high AHC yield and selectivity [10]. Similarly, *p*-xylene could be successfully synthesized from DMF and ethylene [11, 16]. However, for the conversion of lignocellulose into AHCs, several pretreatment steps are needed, including the hydrolysis of hemicellulose to xylose; the dehydration of xylose to furfural; and the hydrodeoxygenation of furfural to 2-methylfuran.

Compared to lignocellulosic biomass, fatty acids require less pretreatment. Lipidic feedstocks are abundantly available in waste or inedible oils, and are significantly renewable and sustainable. More importantly, fatty acids share structurally similar characteristics with petroleum substrates

60   and should undergo hydroprocessing without additional pretreatments. Many studies have

61   extensively addressed the hydroprocessing of waste oils or fatty acids into renewable fuel-like

62   hydrocarbons, but the products are mainly either isomerized C_8–C_{16} alkanes, or diesel-like

63   hydrocarbons, such as long-chain C17 and C18 alkanes, rather than AHCs [17-20]. In our group, other

64   researchers have conducted the study of hydro-converting fatty acid methyl esters into renewable

65   alkane fuels with considerable isomerized ratios in the presence of solvent hexane and the

66   conversion routines were investigated [21, 22]. The main transformation routines included (i) the

67   hydrosaturation of unsaturated feedstocks, (ii) the hydrodeoxygenation of the saturated oils or

68   fatty acids into long-chain alkanes via dehydration, decarbonylation, and decarboxylation

69   reactions, and (iii) the partial hydrocracking and isomerization of long-chain alkanes into products

70   with the required carbon numbers and properties [9, 23]. Due to the challenge of obtaining highly

71   isomerized products in the third step to improve low-temperature fluidity, a number of studies

72   have concentrated on tuning the fatty acid hydroconversion process by employing advanced

73   metal-supported acidic zeolite catalysts [21, 23, 24].

74   However, these synthesized alkanes have not been able to meet the application specifications

75   and must be blended with conventional aviation fuel [25] due to the absence of AHCs. Some recent

76   works have reported the production of AHCs in the hydroprocessing of waste oils and fatty acids.

77   Li T. et al. [26] investigated the hydroprocessing of waste oil into jet biofuel using three types of

78   zeolites (*meso*-Y, SAPO-34, and HY) loaded with nickel. Their results indicated that meso-Y

79   exhibited a high jet-range alkane selectivity of 53% and an AHC selectivity of 13.4% in the liquid

80   fuel products. Rabaev M. et al. [27] found that a certain level of polyunsaturated fatty acids is

81   required to produce relatively high aromatics contents. Despite having structural similarity with

82   petroleum-based substrates, the hydroprocessing of fatty acids is considered to be quite different

83   from current petroleum refinery methods. Conventional methods for AHC synthesis employ the

84   catalytic reforming of oxygen-free naphtha into AHC-enriched reformate. However, a new

85   catalytic reaction system is required for the hydroprocessing of these oxygenated lipidic

86   feedstocks, because more complex reactions (e.g., hydrodeoxygenation) are involved. By

87   inference, hydrodeoxygenation should play an important role throughout the whole transformation

88   process, but that conclusion remains unsubstantiated at present. Hence, it is of prime importance

89   to clarify the conversion routes and catalytic mechanisms for AHC formation during the

90   hydroprocessing of fatty acids.

91   In this work, under solvent-free conditions, we employed the Ni-impregnated HZSM-5 catalyst

92   for one-step hydroprocessing of fatty acids and successfully obtained considerable amounts of

93   AHCs. The main catalytic reaction pathways were analyzed in detail on the basis of detected

94   intermediates. The catalytic roles of the loaded Ni metal and catalyst acid sites were

95   well-determined combining the catalyst characterization through scanning electron microscopy

96   (SEM), transmission electron microscopy (TEM), and pyridine-adsorbed infrared spectroscopy

97   (Py-IR), etc. The overall catalytic conversion routes for AHC formation were proposed and

98   discussed. The advantage of this work was that it provided a new facile, effective approach for the

99   mass production of renewable AHCs. Further, the major reaction pathways for AHCs formation

100   were first proposed and the catalytic mechanisms were investigated into deep as well.

101   **2 Materials and methods**

102   **2.1 Materials**

103   The fatty acids feedstock was purchased from Tianjin Damao Chemical Reagent Factory, China,

104   and its specific composition is shown in Table 1. Nickel nitrate hexahydrate [$Ni(NO_3)_2 \cdot 6H_2O$]

105   (98%, Reagent Plus) was purchased from Tianjin Fuchen Chemical Factory. The HZSM-5

106   supports with Si/Al ratios of 25, 80, 120, 150, and 200 were obtained from Nankai Catalysts

107   Industry, China. Cyclohexane (AR) was purchased from Aladdin, China. All materials were used

108   as received.

109   Table 1. Feedstock composition

Fatty acid	Fatty acid structure	Formula	Composition (wt%)
Palmitic acid	C16:0	$C_{16}H_{32}O_2$	8.36
Stearic acid	C18:0	$C_{18}H_{36}O_2$	3.59
Oleic acid	C18:1	$C_{18}H_{34}O_2$	67.20
Linoleic acid	C18:2	$C_{18}H_{32}O_2$	13.67
Linolenic acid	C18:3	$C_{18}H_{30}O_2$	2.87
Eicosenoic acid	C20:1	$C_{20}H_{38}O_2$	4.31

110   **2.2 Catalyst preparation and characterization**

111   Ni/HZSM-5 catalysts with different wt% nickel contents (5 wt%, 10 wt%, 12.5 wt% and 15

wt%) were prepared by the impregnation of the HZSM-5 supports in aqueous solutions of

$Ni(NO_3)_2 \cdot 6H_2O$. The Si/Al ratios of used HZSM-5 were 25, 80, 120, 150 and 200. The mixture

was stirred at 150 rpm for 6 h at ambient temperature, dried at 110°C for 12 h, and calcined at a

rate of 10°C/min from ambient temperature to 550°C and maintained for 8 h. After reduction

under H_2 atmosphere at 500°C for 2 h, Ni/HZSM-5 was finally obtained. For comparison, a Ni

metal catalyst was prepared by the calcination of $Ni(NO_3)_2 \cdot 6H_2O$ followed by H_2 reduction under

similar conditions. XRD measurements were carried out using an X'Pert PRO MPD

diffractometer (PANalytical) operated at 40 kV and 40 mA with Cu Kα ($\lambda = 0.15406$ nm) radiation.

SEM was performed on a Hitachi S-4800 instrument operated at 10 kV. Before the SEM

experiment, samples were placed under an E1010 ion-sputtering instrument to improve

conductivity. TEM studies were carried out on a Hitachi H-7560 electron microscope with an

accelerating voltage of 100 kV. An X-ray fluorescence spectrometer (XRF, model: AxiosmAX

Petro, PANalytical B.V.) was used to identify the Ni contents of the prepared catalysts. The type of

acid sites on the catalysts was determined by recording infrared spectra of the substrates after the

adsorption of pyridine (Py-IR) using a Nicolet 6700 spectrometer.

2.3 Hydroprocessing of fatty acids and product analysis

The one-step hydroprocessing of fatty acids was conducted in a high-pressure autoclave with a

volume of 150 mL as shown in Figure S1. About 10 g feedstock and 0.6 g catalyst were added into

the reactor. After charging and discharging with hydrogen (99.999%) several times to remove

oxygen, the reaction system was pressurized to 4MPa with hydrogen. The H_2/oil mol ratio was

calculated as 7.13. After 8 h reaction at a designated temperature (280°C, 320°C, 340°C, 360°C, and

380°C) with agitator stirring speed of 200 rpm, the reactor was immediately removed and cooled

with ambient-temperature water. The reactor pressure during the hydroconversion process was

monitored with a paperless recorder (Model VX5304R, Hangzhou Pangu Ltd., China). Gaseous

products were collected into a gas sampling bag, and the liquid products were sampled after

filtration through a 0.22 μm organic nylon 66 membrane (Tianjing Jinteng Ltd., China).

The gaseous products (CH_4, CO, CO_2, and C_2–C_6 hydrocarbons) were quantified with an

Agilent 7890A gas chromatograph (GC) equipped with a capillary column (GS-GASPRO, 60 m ×

0.32 mm), a thermal conductivity detector (TCD), and a flame-ionization detector (FID). The

composition of the liquid products was analyzed with a GC-mass spectrometry instrument

142   (GC/MS, Agilent 7890A-5975C) equipped with an Agilent HP-5MS column (5% phenyl methyl

143   silox, 30 m × 0.25 mm × 0.25 μm). Before being tested, the liquid products were diluted with

144   cyclohexane at a ratio of 1:100. The GC-MS test parameters were as follows. The diluted sample

145   (1 μL) was injected with a split ratio of 1:10 at 280°C. The initial column temperature of 60°C

146   was increased at 10°C/min to 300°C over 28.67 min. The major chemical constituents were

147   identified using the NIST 2014 Mass Spectral Library. The FID response was linear for each

148   component over the concentration ranges used, and the content analyses of the products generated

149   are summarized in terms of peak area %.

150   **3 Results and discussion**

151   **3.1 Products distribution**

152   The overall products distribution of the hydroprocessed fatty acids as a function of reaction time

153   is shown in Figure 1, and the yields of the produced AHCs are listed in Table 2. GC/MS analysis

154   of the liquid products shows that a large number of AHCs is produced, including toluene, o-xylene,

155   p-xylene, and propylbenzene (Figure 1(a)). Toluene, o-xylene, and 1-ethyl-2-methylbenzene are

156   the main AHC components. The total AHC content increases with reaction time, reaching 64.61

157   wt% after 12 h, as shown in Table 3. Other products such as alkanes, olefins, and cyclic

158   hydrocarbons are also formed, and their yields are shown in Table 3. After 2 h, the yields of

159   alkanes, olefins, cyclic hydrocarbons, and AHCs are 55.57, 7.48, 8.50, and 19.00 wt%,

160   respectively. With increasing reaction time, the alkane yield sharply decreases while that of the

161   AHCs greatly increases, suggesting that the AHCs are formed mainly from the transformation of

162   alkanes. Gases such as CO, CO_2, CH_4, C_2H_6, C_3H_8, and C_3H_6 are increasingly produced over time,

163   as illustrated in Figure 1(b), during the one-step hydroprocessing of the fatty acids.
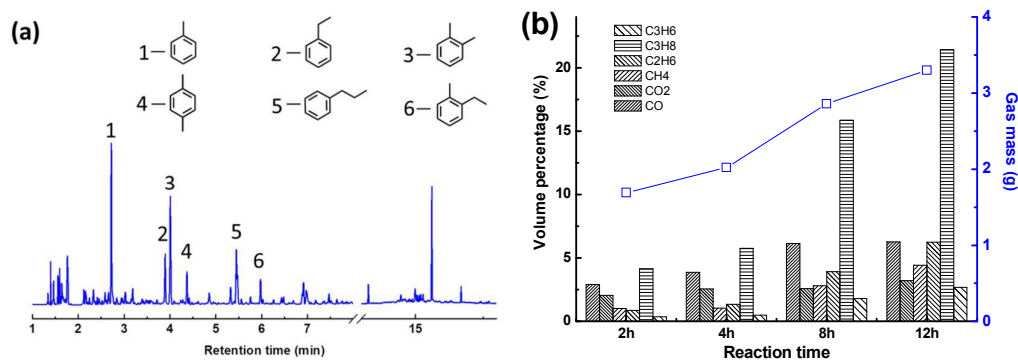
164

165   Figure 1. GC spectra for liquid products (a) and gas products distributions (b). The compounds in

166　　(a) were as follows: (1) toluene, (2) ethylbenzene, (3) *o*-xylene, (4) *p*-xylene, (5) propylbenzene,

167　　(6) 1-ethyl-2-methyl-benzene. Reaction conditions: 360°C, 4 MPa H_2, 10 g fatty acids, 0.6 g 10 wt%

168　　　　　　　　　　　　　　　　Ni/HZSM-5.

169　　Table 2. AHC distribution as a function of reaction time (wt%)[a]

AHC products	Toluene	Ethylbenzene	*o*-Xylene	*p*-Xylene	Propyl benzene	1-Ethyl-2-methylbenzene	Other[b]
2 h	6.53	2.20	5.12	0.75	0	3.09	1.31
4 h	9.90	3.07	7.10	0.77	0.87	4.31	4.63
8 h	15.61	4.51	12.17	2.84	1.48	7.50	9.85
12 h	16.87	5.38	13.81	2.59	1.47	9.18	15.31

170　　[a]Reaction conditions: 10 g fatty acids, 0.6 g 10 wt% Ni/HZSM-5, 360°C, 4 MPa H_2. [b]Other

171　　products represent those containing one benzene ring and several methyl branches, as shown in

172　　Figure S2.

173　　Table 3. Liquid products distribution as a function of reaction time (wt%)[a]

| Products	Alkanes	Olefins	Cyclic hydrocarbons	AHCs	Fatty acids	Other[b]
2 h	57.57	7.48	6.50	19.00	5.16	6.55
4 h	39.94	14.98	5.21	30.65	1.26	4.30
8 h	28.18	7.33	5.06	53.96	0	0
12 h	14.07	4.33	4.59	64.61	0	0

174　　[a]Reaction conditions: 10 g fatty acids, 0.6 g 10 wt% Ni/HZSM-5, 360°C, 4 MPa H_2. [b]Other

175　　products represent oxygen-containing compounds such as octadecanol and octadecanal.

176　　**3.2 Major reaction pathways in the one-step hydroprocessing of fatty acids**

177　　**3.2.1 Hydrodeoxygenation**

178　　　A variety of complex reactions, including hydrodeoxygenation, hydrocracking, and

179　　aromatization, occur during the one-step hydroprocessing of fatty acids for AHC formation.

180　　GC/MS spectra showing the intermediate product distributions during the heating period are

181　　presented in Figure 2. Note that the fatty acids feedstock consists mostly of monounsaturated oleic

182　　acid and polyunsaturated linoleic acid. Clearly, the yield of stearic acid increases as the reaction

183　　temperature is elevated from 200 to 260°C. This reveals that unsaturated acids such as oleic acid

184 undergo hydrosaturation to form stearic acid, as shown by reaction ① in Figure 3. Jovanovic [28]

185 and Gabrovska [29] employed various nickel catalysts for the hydrogenation of unsaturated oils to

186 produce vegetable tallows and fats in the temperature range of 145–190°C. They reported high

187 selectivity in the hydrogenation of C18:3 (linolenic) into C18:2 (linoleic), C18:2 (linoleic) into

188 C18:1 (oleic), and C18:1 (oleic) into C18:0 (stearic), respectively, but did not observe stearic acid

189 as a major product. In this study, the further increase in the reaction temperature apparently

190 promotes the hydrogenation of all the unsaturated C18 acids to stearic acid [30, 31].
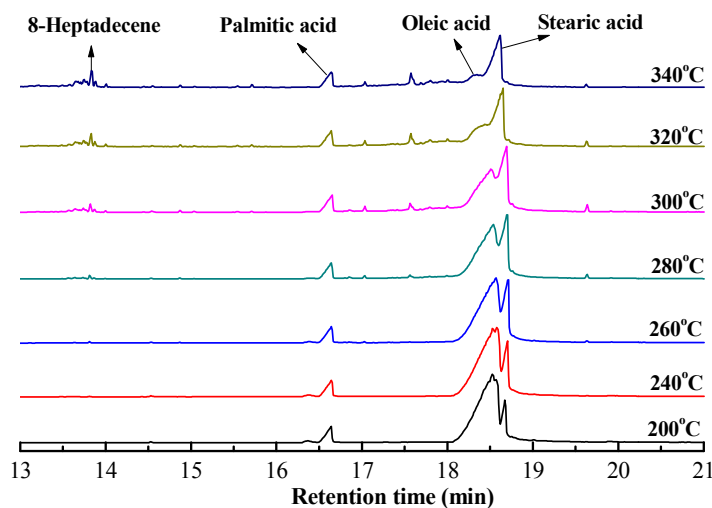
191

192 Figure 2. GC/MS spectra obtained after heating at various temperatures. Reaction conditions: 10 g

193 fatty acids, 0.6 g 10 wt% Ni/HZSM-5 (Si/Al = 25), 4 MPa H_2, 10°C/min heating rate.
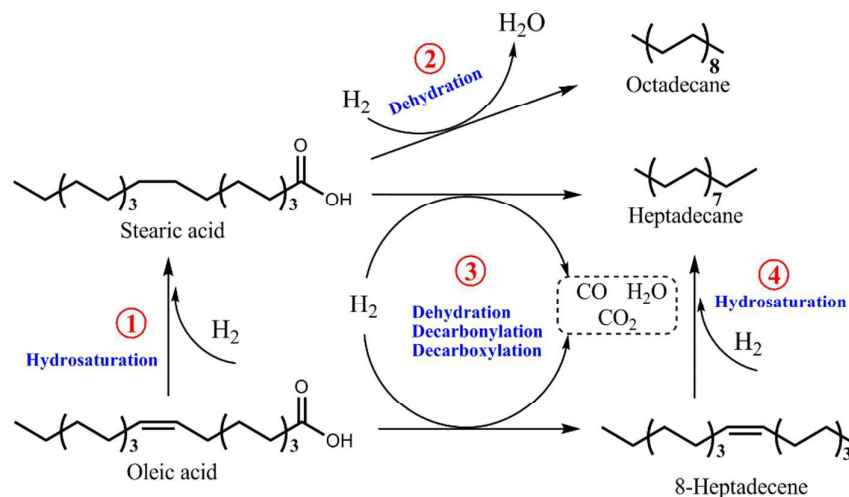

194

195 Figure 3. Pathways for the hydrosaturation and hydrodeoxygenation of fatty acids, using oleic acid

196 as an example and including reactions ①–④.

197 Subsequently, the saturated stearic acid is converted into long-chain hydrocarbons by

198   dehydration, decarbonylation, and decarboxylation reactions. Figure 4 shows the intermediate

199   products distribution after the fatty acids are hydroprocessed for various reaction times at 320°C.

200   Stearic acid is mostly transformed with increasing reaction time. Octadecane ($C_{18}H_{38}$) is found

201   among the liquid products, suggesting the dehydration of stearic acid via reaction ② in Figure 3.

202   The formation of heptadecane, CO, and CO_2 products (Figure 1(b)) indicates the dehydration,

203   decarbonylation, and decarboxylation reactions of stearic acid, as depicted in reaction ③ of Figure

204   3. Pentadecane ($C_{15}H_{34}$) is produced from palmitic acid via reaction ③. The partial enlargement of

205   Figure 4(a) shows the presence of 8-heptadecene after 1 and 2 h reaction, suggesting that oleic

206   acid can be directly deoxygenated without first being saturated, via reaction ③. After 4 h, the

207   8-heptadecene is nearly completely consumed, most likely via hydrogenation to heptadecane

208   (reaction ④). The relative percentages of C_{15} and C_{17} hydrocarbons after 1 h and 12 h reaction are

209   both higher than those of C_{16} and C_{18} hydrocarbons, as shown in Figure 4(b), which suggested that

210   the decarbonylation and decarboxylation reactions proceeded preferentially than the dehydration

211   reaction during the whole process [32].
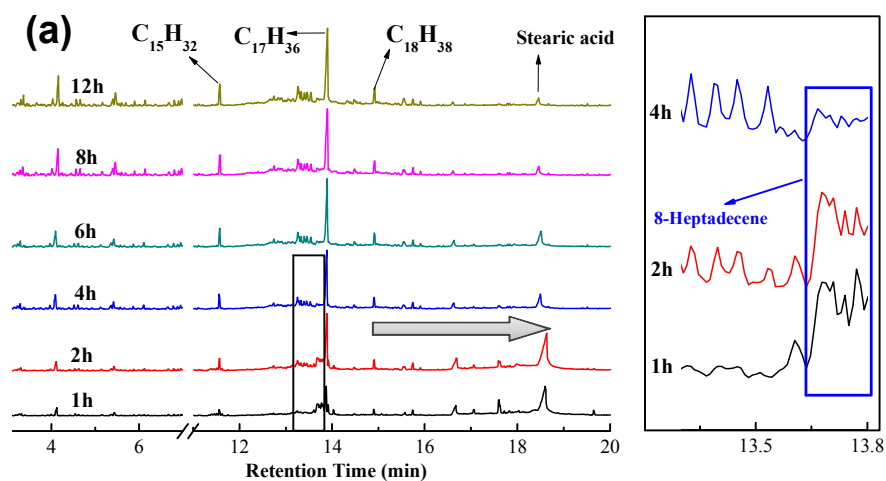
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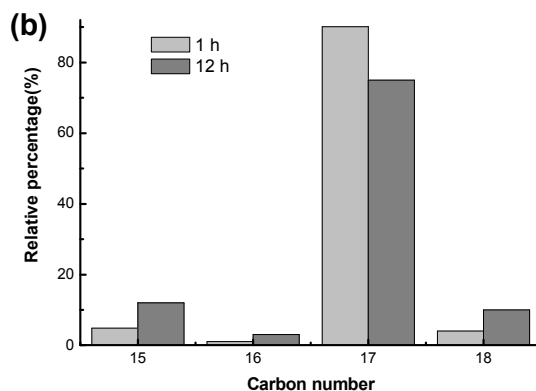
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214   Figure 4. (a) GC/MS spectra of fatty acid products after hydroprocessing for various reaction

215   times. (b) Relative percentages of C_{15}–C_{18} hydrocarbons after 1 h and 12 h reaction. Reaction

216   conditions: 10 g fatty acids, 0.6 g 10 wt% Ni/HZSM-5 (Si/Al = 25), 320°C, 4 MPa H_2.

217   **3.2.2 Hydrocracking**

218   Long-chain hydrocarbons produced in the hydrodeoxygenation stage can be further cracked into

219   C_6–C_8 olefins and gases such as CH_4, C_2H_6, and C_3H_8 through a series of hydrocracking reactions.

220   Figure 5(a) shows the results after 8 h at temperatures of 280–380°C. The conversion ratio is

221   36.90 wt% at 280°C, and reaches 100 wt% at 340°C, demonstrating the significance of the

222   reaction temperature for the high conversion of fatty acids. The yield of alkanes is 15.90 wt% at

223   280°C, increases to a maximum value of 52.08 wt% at 340°C, and sharply drops to 25.18 wt% at

224   360°C. Although only minor amounts of olefins are produced at 320°C, this fraction increases to

225   9.5 wt% at 340°C and remains stable even at 380°C. The yields of cracked low-molecular-weight

226   gases increase at higher reaction temperatures, as shown in Figure 5(b). C_2H_6, and C_3H_8 are

227   mainly produced by thermal cracking and catalytic cracking processes [33-35], respectively. However,

228   the yield of C_3H_8 is about three times higher than that of C_2H_6, suggesting that catalytic

229   hydrocracking is the main cracking process.

230   Figure 5(c) shows the hydroprocessing results with various reaction times at 360°C. The fatty

231   acids are mostly converted during the initial 2 h reaction period. At this stage, the alkanes yield is

232   the highest, up to 55.57 wt%, and the olefins yield is low (7.48 wt%). After 4 h, the yield of

233   alkanes decreases to 39.94 wt%, while the amount of olefins increases to 14.98 wt%. Details of

234   the alkane and short-chain olefin (C_6–C_8) structures are shown in Table 4. Straight-chain alkanes

235   with different carbon numbers are present in the liquid products, and a variety of C_6–C_8 olefins

236   such as 2-methyl-1-pentene, (*Z*)-3-methyl-2-pentene, and 2,4-dimethyl-1-pentene are produced.

237   Katikaneni and co-workers [36, 37] conducted the catalytic conversion of canola oil over

238   potassium-impregnated HZSM-5, and obtained short-chain olefins. They believed that the

239   amorphous, non-shape-selective characteristics of the catalyst and severe thermal effects at

240   reaction temperatures of 400–500°C enhanced the subsequent secondary cracking of long-chain

241   hydrocarbons into lighter molecules.

242   For the alkane cracking process, two mechanisms have been previously proposed: a

243   monomolecular mechanism and a bimolecular mechanism. In the former, an acidic catalyst such

244   as a zeolite protonates an alkane to form a five-coordinate-carbon transition state [38, 39]. This

245   carbonium ion may undergo cracking to produce an alkane and an alkene, regenerating the catalyst

246   by the loss of protons [40]. The cracking products include dihydrogen, methane, and ethane. In the

247   bimolecular mechanism, an alkane is activated by hydride transfer between the alkane and an

248   adsorbed alkoxide species [18, 41]. This reaction may be followed by β-scission or isomerization. Due

249   to dimerization, oligomerization, isomerization, and β-scission reactions, the resulting product

250   distribution is complicated. The sophisticated cracking products obtained in this study, which

251   include methane, ethane, propane, and C_6–C_8 olefins, suggest that both these mechanisms are

252   operative in the transformation of the long-chain alkanes. As the reaction time increases, the yields

253   of long-chain alkanes decrease, indicating that hydrocracking reactions proceed concurrently.

254   Moreover, the olefin yields also decrease after longer reaction times, suggesting that the produced

255   C_6–C_8 olefins are not accumulated, but rather, are quickly converted.

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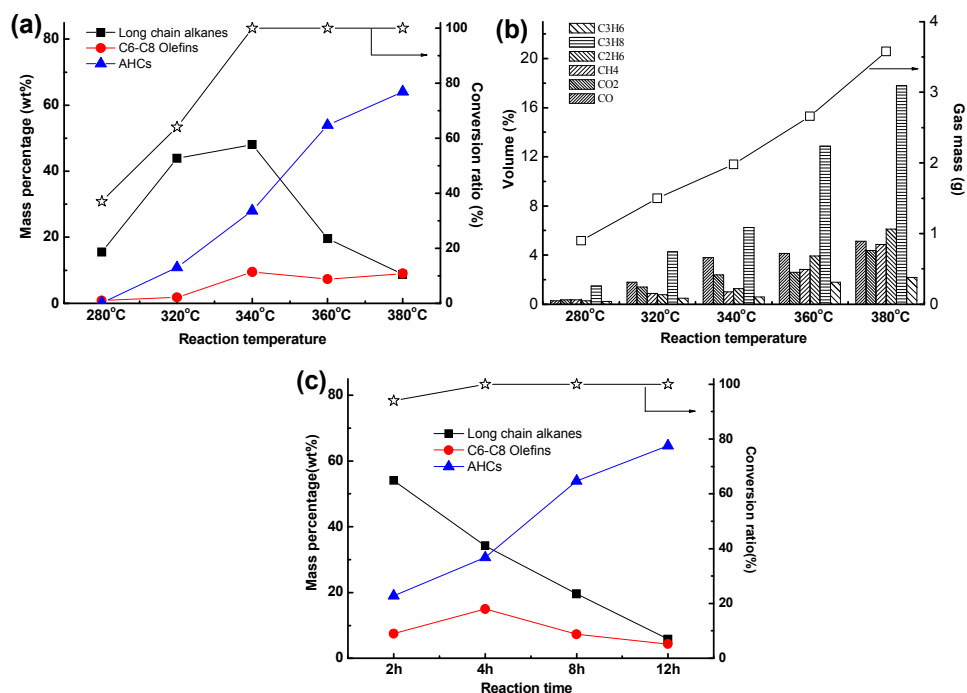
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258   Figure 5. Conversion ratios and yields of long-chain alkanes, C_6–C_8 olefins, and AHCs as a

259   function of reaction temperature (a) and time (c). Gas yields at various reaction temperatures (b).
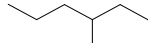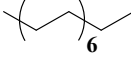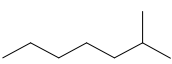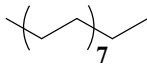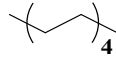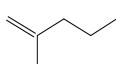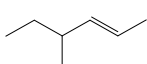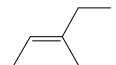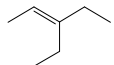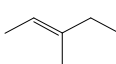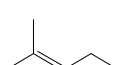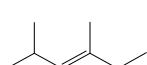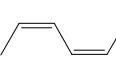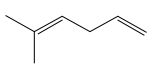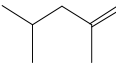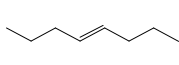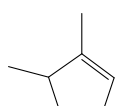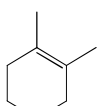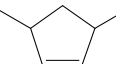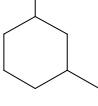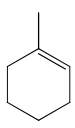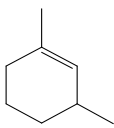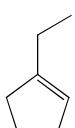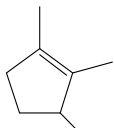
260   Reaction conditions: (a) and (b) 10 g fatty acids, 0.6 g 10 wt% Ni/HZSM-5 (Si/Al = 25), 4 MPa

261   H_2, 8 h, and (c) 10 g fatty acids, 0.6 g 10 wt% Ni/HZSM-5 (Si/Al = 25), 360°C, 4 MPa H_2.

262

263   Table 4. Structures of alkanes, short-chain olefins (C_6–C_8), and cyclic hydrocarbons after 4 h at

264   360°C

Retention time(min)	Compound name	Structure	Retention time(min)	Compound name	Structure
Alkanes					
1.34	Butane		9.19	Dodecane	
1.97	3-Methylhexane		13.26	Pentadecane	
2.1	Heptane		15.01	Hexadecane	
2.67	2-Methylheptane		15.61	Heptadecane	
4.42	Decane		16.70	Octadecane	
Short-chain olefins (C$_6$–C$_8$)					
1.62	2-Methyl-1-pentene		2.16	(E)-4-Methyl-2-hexene	
1.67	(Z)-3-Methyl-2-pentene		2.20	3-Ethyl-2-pentene	
1.72	3-Methyl-2-pentene		2.23	3,4-Dimethyl-(Z)-2-pentene	
1.77	2-Methyl-2-pentene		2.48	2,4-Dimethyl-3-hexene (c,t)	
1.87	(Z),(Z)-2,4-Hexadiene		2.58	5-Methyl-1,4-hexadiene	
2.03	2,4-Dimethyl-1-pentene		3.03	(E)-4-Octene	
Cyclic hydrocarbons					
2.12	1.5-Dimethylcyclopentene		2.54	1,2-Dimethylcyclohexene	
2.24	3,5-Dimethylcyclopentene		2.84	1,3-Dimethylcyclohexane	
2.30	1-Methylcyclohexene		3.06	1,3-Dimethyl-1-cyclohexene	
2.41	1-Ethylcyclopentene		3.19	1,2,3-Trimethyl cyclopentene	

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266   **3.2.3 Aromatization**

267   The produced C_6–C_8 olefins and small alkane molecules can cyclize and, by means of

268   aromatization, be converted into various types of AHCs. As shown in Figure 5(a), more AHCs are

269   produced at higher reaction temperatures, whereas the olefin yields remain stable at 9.5 wt%

270   without accumulation. Figure 5(c) shows a decreasing yield of the C_6–C_8 olefins with reaction

271   time, which suggests that these compounds are crucial intermediates for AHC formation. A variety

272   of cyclic hydrocarbons, amounting to ~5 wt%, were identified in the liquid product mixture, as

273   shown in Table 4. The cyclic hydrocarbons are mainly five- and six-membered ring compounds

274   such as 1,5-dimethylcyclopentene and 1-methylcyclohexene, respectively.

275   At a rather high temperature (380°C), substantial changes in the reaction pressure are observed

276   (see Figure S3). The distributions of the gaseous products CH_4, C_2H_6, and C_3H_8 obtained from

277   alkane hydrocracking in this process are shown in Figure 6. The slope (k) of each line segment in

278   Figure 6 signifies the change in a product's formation rate. Higher k values in Table 5 indicate that

279   more alkanes are cracked into gases, and *vice versa*. For better comparison, it was assumed that

280   the increased yield of every type of produced gas was proportional to the decreased amount of the

281   total alkanes. To characterize the relative changes, parameter n (defined as the absolute value of

282   the ratio of k (produced gas) vs. k (alkanes)) was used to eliminate the effect of the decreasing

283   alkane content on the equilibrium of the cracking reactions. The lower n value (see Table 5) from

284   n_{2-4} to n_{4-8} for C_3H_8 signifies that C_3H_8 is consumed during the 4–8 h reaction time. In comparison,

285   the higher n values of CH_4 and C_2H_6 suggest that these products are generated via other routes in

286   addition to alkane hydrocracking. H_2 is consumed in the hydrodeoxygenation and alkane

287   hydrocracking processes. The n value for H_2 is lower during the 4–8 h reaction period compared

288   to 2–4 h, suggesting that there are additional sources of H_2 production in this process. Here, it is

289   considered that the consumed C_3H_8 is transformed to AHCs, and in this process, CH_4, C_2H_6, and

290   H_2 are produced simultaneously.
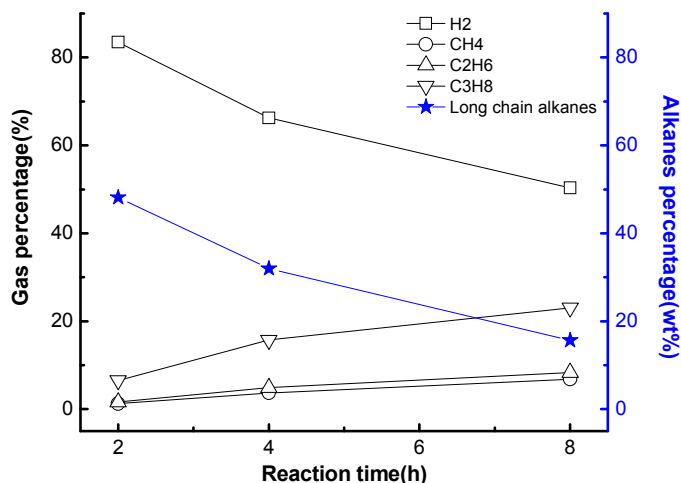
Figure 6. Gas and alkane percentages after different reaction times at 380°C.

Table 5. Changes in product formation rate over time.

k	Alkanes	CH_4	C_2H_6	C_3H_8	H_2
$k_{2\text{-}4}$ [a]	−8.09	1.23	1.65	4.60	−8.62
$k_{4\text{-}8}$ [a]	−4.08	0.78	0.86	1.82	−3.98
$n_{2\text{-}4}$ [b]	-	0.15	0.20	0.57	1.07
$n_{4\text{-}8}$ [b]	-	0.19	0.21	0.45	0.98

[a] k was the slope value of line segment 2-4 and 4-8

[b] n was defined as the absolute value of the ratio of k (produced gas) vs. k (alkanes). For

instance, $(n_{2-4})_{CH_4} = \left| \frac{(k_{2-4})_{CH_4}}{(k_{2-4})_{Alkanes}} \right| = \left| \frac{1.23}{-8.09} \right| = 0.15$.

In recent publications, aromatics were proposed to be formed by the Diels-Alder reactions of

olefins [10, 42]. Depeyre et al. [43] examined the steam cracking of *n*-hexadecane at 750–850°C in a

quartz flow reactor, with the aim of maximizing alkene production. They found that aromatics

were increasingly formed at the expense of liquid olefin compounds with increasing temperature

and reaction time. Cheng and Huber [13] studied the co-feeding of olefins (ethylene and propene)

with a series of furanoid compounds over a ZSM-5 catalyst. They found that co-feeding propene

with furan (a C_4 diene) and 2-methylfuran (a C_5 diene), respectively, increased the selectivity for

toluene and xylenes, which clearly suggested Diels-Alder cycloaddition reactions between the

olefins and furans. Similar cases were also reported by Williams [44] and Nikbin [14]. Ethylene has

also been frequently used as a substrate for aromatics production with biomass-derived furans [11].

307   As shown in Figure 6, many small alkanes such as ethane and propane are produced in this

308   process, and they can be directly dehydrogenated into ethylene and propene, respectively. In

309   addition, various types of C_6–C_8 olefins are produced. It is therefore suggested that Diels-Alder

310   reactions between these olefins can account for the produced AHCs.

311   Four pathways are presented in Figure 7 to illustrate the possible reactions involved in AHC

312   formation. First, a molecule of propane is dehydrogenated to propene, which can be combined

313   with a C_6 olefin such as 3-methyl-2-pentene to form a C_7 molecule with a five-membered ring.

314   Through ring expansion [45, 46], the five-membered carbocycle is reformed to a six-membered ring.

315   Subsequently, after the removal of hydrogen, this is transformed into toluene, as shown in

316   pathway (1). In the second case, a six-membered hydrocarbon ring such as

317   1-ethyl-6-methylcyclohexene is directly formed through cyclization, as shown in pathway (2).

318   Dehydrogenation then affords 1-ethyl-6-methylbenzene. Alternatively, as shown in pathway (3),

319   the six-membered ring hydrocarbon, after demethanization, can be converted into

320   1,6-dimethylcyclohexene, which forms o-xylene after dehydrogenation. C_6–C_8 olefins such as

321   5-methyl-1,4-hexadiene, through self-cyclization [47], can form five- or six-membered ring

322   hydrocarbons, as shown in pathway (4). A small number of higher-molecular-weight AHCs [48] with

323   9 or more carbon atoms (e.g., 1,2,4-trimethylbenzene, 1-ethyl-2,4-dimethylbenzene, and

324   1-methyl-3-propylbenzene, as shown in the Figure S2) may be formed through direct cyclization

325   and dehydrogenation reactions between two C_6–C_8 olefins.

326

327
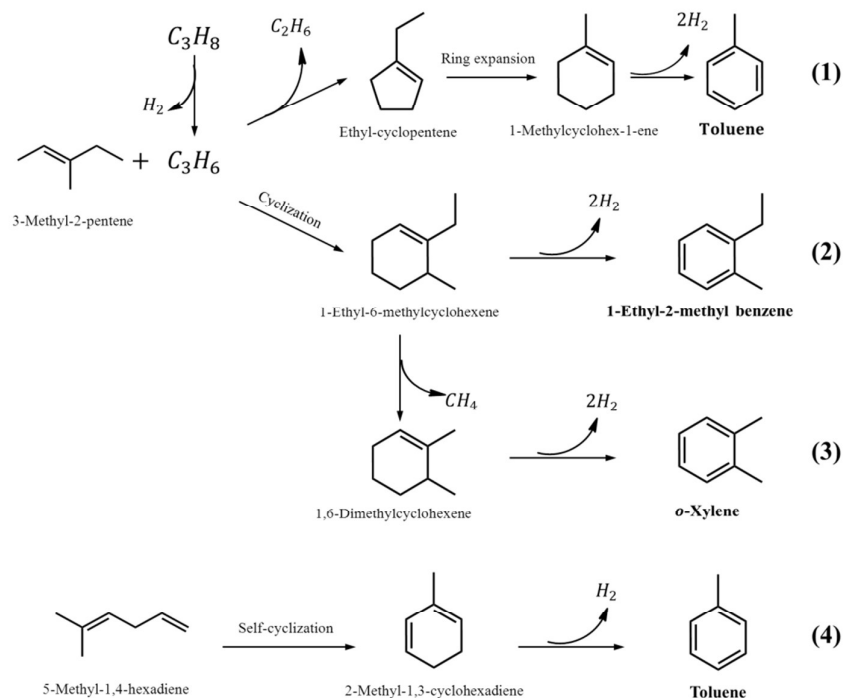
328   Figure 7. Possible pathways for AHC formation.

329   **3.3 Catalysis mechanisms**

330   According to the foregoing results, conversion routes for the one-step hydroprocessing of fatty

331   acids are proposed in Figure 8; these mainly consist of hydrodeoxygenation [19, 20, 31, 49, 50],

332   hydrocracking, and aromatization processes. The first step is the hydrodeoxygenation of the fatty

333   acids into long-chain hydrocarbons, including the hydrosaturation of oleic and linoleic acids into

334   stearic acid at a low reaction temperature [28, 29]. Subsequently, the long-chain hydrocarbon products

335   are transformed into short-chain compounds by thermal and catalytic hydrocracking reactions.

336   These cracking products include: the gases methane, ethane, and propane; abundant C_6–C_8 olefins

337   such as 2-methyl-1-pentene, (*Z*)-3-methyl-2-pentene, and (*Z*),(*Z*)-2,4-hexadiene (with two C=C

338   bonds); a few types of short-chain alkanes such as butane, 3-methylhexane, and heptane; and

339   long-chain alkanes, including pentadecane. After the C_6–C_8 olefins and propene undergo

340   Diels-Alder reactions, cyclic hydrocarbons with five- or six-membered rings containing C=C

341   bond(s) are formed. The five-membered hydrocarbon rings can be converted into six-membered

342   hydrocarbon rings through ring-expansion reactions. Eventually, these six-membered ring

343   hydrocarbons are transformed into AHCs by dehydrogenation.

344   When pure Ni metal (see XRD patterns in Figure S4) was used as the catalyst for the one-step

345 hydroprocessing of the fatty acids, the vast majority of the products (~93 wt%) consisted of

346 long-chain alkanes (Figure 9). Thus, Ni metal perfectly facilitates the hydrodeoxygenation

347 reactions but has almost no effect on the hydrocracking of long-chain alkanes. In contrast, as little

348 as 25.18 wt% alkanes remain when using the 10 wt% Ni/HZSM-5 catalyst, indicating the

349 enhanced hydrocracking with HZSM-5. This zeolite has abundant nano-holes with size of 0.55 nm

350 [22], which are much smaller than the size of the long-chain alkane molecules. This suggests that the

351 surface properties of the catalyst are quite critical for the hydroconversion process, particularly the

352 acid sites [51].
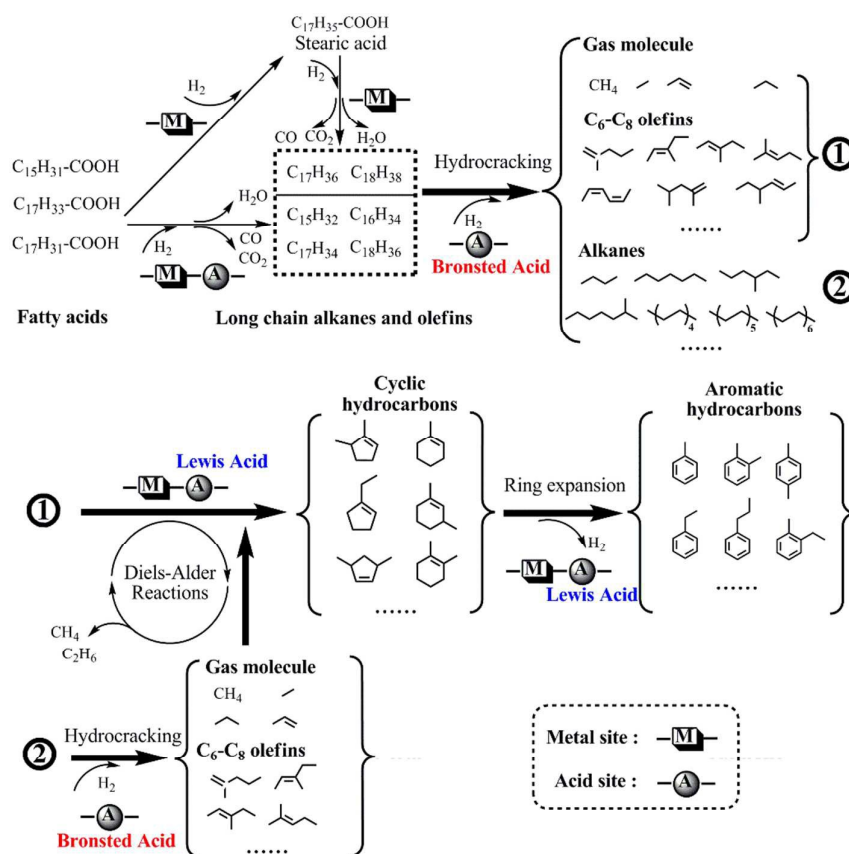
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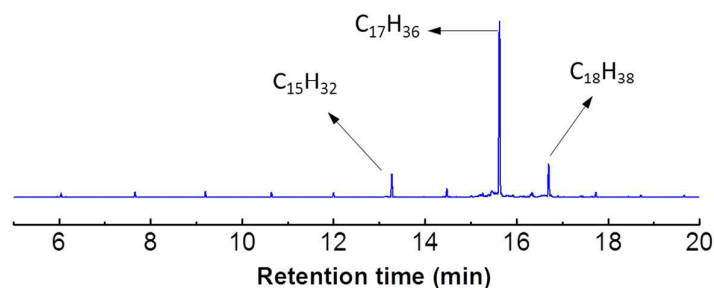354 Figure 8. Proposed conversion routes for AHC formation in the one-step hydroprocessing of fatty

355   acids.

356

357

358   Figure 9. GC/MS spectra of products from the hydroprocessing of fatty acids using Ni metal

359   catalyst. Reaction conditions: 10 g fatty acids, 0.6 g Ni metal, 360°C, 4 MPa H_2, 8h.

360   The Si/Al ratios of the catalyst have a significant impact on the catalytic performance and the

361   product distribution. It is remarkable that, with increasing Si/Al ratios, the yield of long-chain

362   alkanes begins to increase and they become the major products, affording as much as 85.04 wt%

363   at Si/Al = 200 (Figure 10(a)). This suggests the inhibition of the hydrocracking of the long-chain

364   hydrocarbons. Note that the olefin yield increases to 15.36 wt% at Si/Al = 120 compared to Si/Al

365   = 80, but then decreases to 5.61 wt% at Si/Al = 200. It was reported that the cracking and

366   dehydrogenation of alkanes to form olefins take place at the Brønsted acid sites [48]. The Py-IR

367   results in Table 6 show the highest density of Brønsted acid sites (0.12 mmol/g) for Si/Al = 25, but

368   this decreases sharply to 0.01 mmol/g at Si/Al = 200. Obviously, the decrease in the density of

369   Brønsted acid sites results in fewer long-chain alkanes being cracked. Moreover, the increase in

370   the recovery of C_6–C_8 olefins in the Si/Al range of 25–120 signifies the high cracking degree of

371   long-chain alkanes when the density of Brønsted acid sites exceeds 0.06 mmol/g. Thus, a high

372   number of Brønsted acid sites in the catalyst can effectively facilitate the hydrocracking of

373   long-chain alkanes.

374   According to previous investigations, the Diels-Alder reaction relies, to a great extent, on the

375   Lewis acidity of the catalyst [52-54]. Recently, it was shown that the Lewis-acidic catalyst plays a

376   significant role in the production of renewable aromatics by the tandem Diels-Alder cycloaddition

377   and dehydration reactions of biomass-derived dimethylfuran and ethylene [12, 15, 55]. In those studies,

378   the high selectivity for toluene by the Lewis-acidic catalysts was mainly attributed to their ability

379   to accelerate the cycloaddition of dimethylfuran and ethylene and retard side reactions such as

380   oligomerization and alkylation. In the case of Brønsted-acidic zeolites, the side reactions were

381   significantly enhanced, resulting in lower selectivity for AHCs. As shown in Table 6, the highest

yield of AHCs, up to 53.96 wt%, is obtained at Si/Al = 25, at which the catalyst has a high Lewis

acid content of 0.06 mmol/g. However, the yield decreases quickly to 4.39 wt% at Si/Al = 200,

with only 0.02 mmol/g Lewis acid sites, suggesting the restriction of the Diels-Alder reactions

necessary for AHC formation.

It is noteworthy that the yield of C_6–C_8 olefins over catalysts with different Si/Al ratios is

determined by the degrees of both the hydrocracking of long-chain alkanes at the Brønsted acid

sites and the Diels-Alder reactions for AHC formation at the Lewis acid sites. For Si/Al = 25, the

low yield (25.18 wt%) of long-chain alkanes suggests a high degree of the hydrocracking reaction

on the Brønsted acid sites to produce C_6–C_8 olefins. However, the yield of C_6–C_8 olefins could be

as low as 7.33 wt%, which signifies that these olefins are ultimately transformed into AHCs on the

Lewis acid sites. When the catalyst Si/Al ratio is 120, the hydrocracking of the long-chain alkanes

still occurs to a significant extent due to the relatively adequate amount of Brønsted acid sites.

However, the insufficient number of Lewis acid sites inhibits the Diels-Alder reactions for AHC

formation, which leads to the increased yields of C_6–C_8 olefins. For Si/Al = 200, the high yield of

long-chain alkanes indicates a reduction in the extent of hydrocracking, which directly leads to

decreased yields of both the C_6–C_8 olefins and AHCs. It can be thus concluded that the Brønsted

and Lewis acid sites of the catalyst both influence the formation of AHCs.
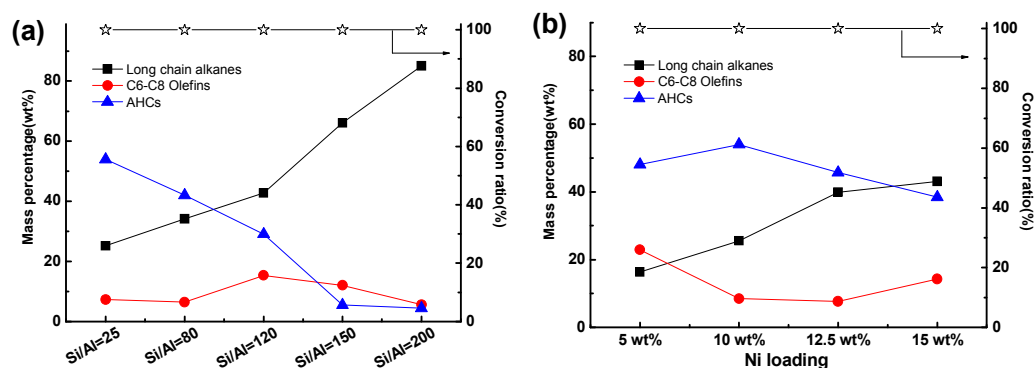
Figure 10. Conversion ratios and productions of alkanes, C_6–C_8 olefins, and AHC products for

various Si/Al ratios and different Ni loadings. Reaction conditions: (a) 10 g fatty acids, 0.6 g 10 wt%

Ni/HZSM-5, 4 MPa H_2, 8 h, 360°C and (b) 10 g fatty acids, 0.6 g Ni/HZSM-5 (Si/Al = 25), 360°C,

4 MPa H_2, 8 h.

406 Table 6. Acid site densities of the prepared catalysts with different Si/Al ratios, determined by

407 Py-IR

Si/Al ratio	Ni content (wt%)	Acid site contents (mmol/g)			AHC yield
		Brønsted	Lewis	Total	(wt%)
25	10 (9.89)[a]	0.12	0.06	0.18	53.96
80	10 (9.91)[a]	0.08	0.04	0.12	41.99
120	10 (9.94)[a]	0.06	0.03	0.09	29.05
150	10 (9.90)[a]	0.03	0.03	0.06	5.47
200	10 (9.96)[a]	0.01	0.02	0.03	4.39

408 [a]Actual Ni loading content (in the bracket) determined by XRF.

409 Table 7. Acid site densities of the prepared catalysts with different Ni contents, determined by

410 Py-IR

Si/Al ratio	Ni content (wt%)	Acid site contents (mmol/g)			AHC yield
		Brønsted	Lewis	Total	(wt%)
25	5 (4.92)[a]	0.14	0.08	0.24	48.09
25	10 (9.91)[a]	0.12	0.06	0.18	53.96
25	12.5 (12.43)[a]	0.11	0.06	0.17	45.73
25	15 (14.95)[a]	0.10	0.06	0.16	38.43
-	100[b]	0	0.005	0.005	0

411 [a]Actual Ni loading content (in the bracket) determined by XRF. [b]Ni metal catalyst without

412 HZSM-5.

413   As mentioned above, pure Ni metal has almost no acid sites. We attempted to tune the catalyst

414 acid properties through the coverage of its acid sites by loading different amounts of Ni metal (5,

415 10, 12.5, and 15 wt%). The Py-IR results (Table 7) support the successful reduction in the

416 densities of Brønsted-acid sites with increasing Ni loads, and accordingly, the alkane yields were

417 projected to increase and the AHC yields to decrease. However, the phenomena observed in

418 Figure 10(b) do not agree with these conjectures. Even the AHC yield exhibits a tendency to

419 decrease, on the whole, with the increasing Ni contents. However, the highest AHC yield of 53.96

420 wt% was obtained for a Ni content of 10 wt%. Note that the olefin yields obtained with 10 and

421 12.5 wt% Ni are lower than those achieved for 5 and 15 wt% Ni, as shown in Figure 9(b).

422   In view of these results, these four catalysts were characterized in detail by XRD, SEM, and

423 TEM. The catalyst XRD patterns in Figure S5 in the SI show that Ni metal was successfully

424 loaded on the HZSM-5. The SEM and TEM results illustrated in Figure 11 reveal that the Ni

425   particle size increases with increased Ni loading. Moreover, it is interesting to note that the

426   morphology of the loaded Ni nanoparticles exhibits polyhedral shapes for the 10 wt% Ni content,

427   such as the tetrahedron example shown in Figure 11(b), whereas round shapes are observed for 5

428   and 15 wt% Ni. When the Ni content is 12.5 wt%, both polyhedral and round Ni nanoparticles are

429   evident (Figure 11(c)). Notably, more round than polyhedral particles are observed, suggesting the

430   disappearance of the polyhedrons. Previous studies have demonstrated that the morphology of a

431   metal catalyst substantially influences its catalytic activity [25, 56-58], and irregularly shaped metal

432   centers provided abundant surface defects as active sites, which exhibit high catalytic activity [59, 60].

433   Recently, Qiao and Yang [61, 62] successfully obtained a single-atom catalyst which exhibited

434   extremely high catalytic activity, suggesting that catalysts based on single-atom dispersions would

435   be highly desirable to maximize atom efficiency. Based on these results, the polyhedral

436   morphology of the Ni nanoparticles in our catalysts may expose more surface defects, and the Ni

437   loading of 10 wt% may increase the number of accessible surface metal atoms, which would both

438   facilitate the Diels-Alder reactions and lead to higher AHC production.
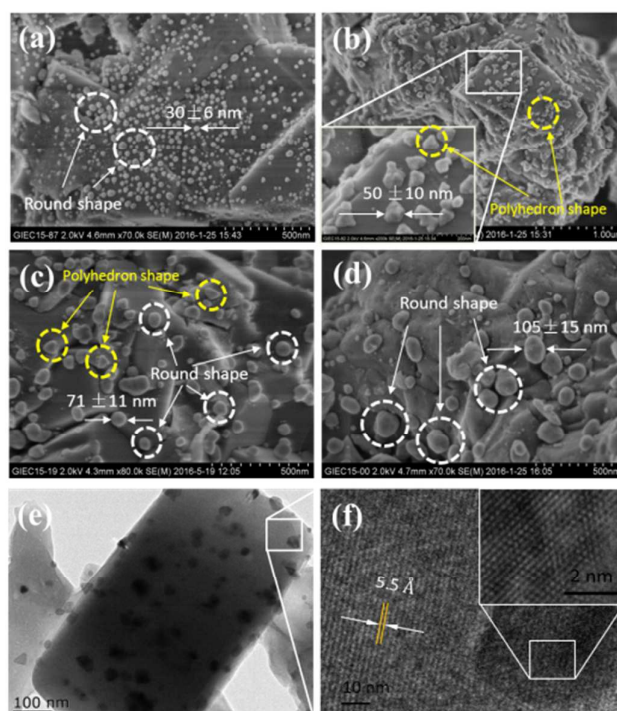
439

440   Figure 11. Microstructural images of the prepared catalysts (Si/Al = 25): SEM images of HZSM-5

441   with different Ni loadings: (a) 5.0, (b) 10, (c) 12.5, and (d) 15 wt%; (e) TEM and (f) HRTEM

442   images of HZSM-5 with 10 wt% Ni loading. The loaded Ni particles showed round morphology in

443   (a), (c) and (d) whereas polyhedron morphology in (b).

444   **4 Conclusions**

445   The one-step hydroprocessing of fatty acids for the sustainable production of aromatic

446   hydrocarbons was conducted over Ni/HZSM-5 catalysts. A yield of ~64% AHCs was obtained by

447   hydroprocessing 10 g fatty acids in the presence of 0.6 g catalyst comprising 10 wt% Ni/HZSM-5

448   with a Si/Al ratio of 25 for 12 h at 360°C and 4 MPa H_2. The major reaction pathways involved in

449   the one-step transformation consisted of hydrodeoxygenation, hydrocracking, and aromatization

450   reactions. During the hydrodeoxygenation process, the unsaturated oleic and linoleic acids in the

451   feedstock were hydrosaturated to stearic acid at a low reaction temperature. Subsequently, the

452   stearic acid was transformed into the long-chain hydrocarbons octadecane and heptadecane

453   through a series of dehydration, decarbonylation, and decarboxylation reactions. Conversely,

454   unsaturated acids could be directly hydrodeoxygenated to long-chain olefins, as in the conversion

455   of oleic acid to 8-heptadecene. These pathways could be well performed on metal sites. However,

456   the hydrocracking of the long-chain hydrocarbons was performed on the catalyst acid sites rather

457   than metal sites. Through thermal and catalytic cracking reactions, the long-chain hydrocarbons

458   were transformed into gaseous products such as methane, ethane, propane, C_6–C_8 olefins, and a

459   fraction of alkanes. Subsequently, these cracked small molecules cyclized to form cyclic

460   hydrocarbons with five- or six-membered rings that could be transformed into the AHCs after

461   ring-expansion and dehydrogenation reactions. The C_6–C_8 olefins were determined to be crucial

462   intermediates for AHC formation. Lower numbers of catalytic Brønsted and Lewis acid sites

463   restricted the hydrocracking and aromatization reactions, respectively, and both led to a decrease

464   in AHC production. Additional Ni loading led to a decrease in the Brønsted acid site contents. A

465   polyhedral morphology was found for the loaded Ni nanoparticles at a Ni content of 10 wt%,

466   which may have exposed more metal defects and accessible surface metal atoms to promote AHC

467   formation. This work provides a simple, effective approach for the mass production of renewable

468   AHCs and will be helpful in ultilizating such oxygenous-rich substrates in large scales for the

469   effective synthesis of renewable transportation fuels to release the atmosphere warming

470   deterioration.

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