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Zeolite-catalyzed isomerization of oleic acid to branched-chain isomers*

Branched-chain (bc) saturated fatty acids (SFA) have potential as oleochemical intermediates since they have better oxidative stability than linear unsaturated fatty acids (UFA) and have better low-temperature properties than linear SFA. Previous studies in converting UFA to bc-FA using clay catalysts have resulted in only modest yields and conversions. Recent reports, however, have suggested that certain zeolites can be effective catalysts for converting UFA to bc-FA in higher yields and conversions. In this work, we examined the scope and potential of the zeolite-catalyzed synthesis of bc-FA starting from readily available monounsaturated linear FA. Our results show that common UFA such as oleic acid can be converted to bc-isomers using modified Ferrierite zeolite catalysts with high conversions (98%) and high selectivity (85%) and that the zeolite catalysts are reusable for at least three cycles. The positions of branching (methyl) on the FA chain were determined from the GC-MS spectra of the picolinyl esters of the bc-FA.

Keywords: Branched-chain fatty acids, dimer acids, ferrierites, isostearic acid, zeolite.

1 Introduction

Saturated branched-chain fatty acids (bc-SFA), which are commonly referred to as isostearic acids, are important intermediates in the production of biodegradable lubricants, emollients, and hydraulic fluids. bc-SFA and their simple alkyl esters have the advantages over common fatty acids (FA) in that they have better oxidative stability than unsaturated FA (UFA) and typically have lower melting points and cloud points than comparable linear SFA. Several research groups have reported that UFA such as oleic acid (OA) can be converted to bc-isomers in the presence of clay catalysts such as bentonite and montmorillonite. In 1983, Foglia *et al*. [1] reported that OA could be converted to a mixture of methyl bc-FA at up to 50% conversion when using a bentonite clay and dichloroethane as a co-catalyst [1, 2]. In 1994, Neuss *et al*. [3] reported that, with a montmorillonite clay catalyst in combination with an active carbon, sunflower oil FA/esters could be converted to bc-isomers in yields between 30 and 40%. Although bc-acids can be synthesized using clay catalysts [4], there are several drawbacks to using them. First, conversion of the linear UFA is modest at best and, secondly, the clay catalysts give primarily oligomeric byproducts (mainly dimers and trimers) and thus have a rather low selectivity to bc-FA. Finally, no work has been carried out to demonstrate that the clay catalyst can be reused [5].

Recent research by several groups has shown that OA can be isomerized to bc-isomers using zeolites such as ZSM-5, mordenite, beta, and zeolite L [6–11]. Zeolites are aluminosilicates that have small internal cavities interconnected by small channels with dimensions typically on the order of several Angstroms. Interestingly, the four types of zeolites referenced above all have uni-dimensional channels. The rigid aluminosilicate networks are made up of tetrahedral SiO_4 and AlO_4 molecules and possess negative charges in the framework wherever the tetravalent Si is replaced by the trivalent Al. In order to balance the charges, zeolites typically contain counter ions such as Na^+, K^+, Ca^{2+}, NH_4^+ and H^+ inside the cavities and channels [12]. The electronegative aluminum centers can act as catalysts for a variety of petrochemical processes while on the other hand the cations play an important role in ion exchange processes. In some instances, the cations within these channels and cavities can act as Brönsted acid catalysts. Such zeolite structures are thought to be typically large enough for an FA to diffuse through and to allow skeletal isomerization to bc-FA, but small enough to limit the formation of oligomeric products (dimer and trimer FA).

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In 1996, Hodgson *et al*. [6] reported that H-mordenite and zeolite L solid acid catalysts can isomerize OA to bc-isomers in yields up to 51%, which after hydrogenation gave the desired bc-SFA. They showed that the ratio of SiO_2/Al_2O_3 greatly influenced the conversion of OA and the yields of bc-FA. They also observed that lower Si/Al ratios resulted in higher catalyst activity and selectivity [6]. In 1997, Tomifuji *et al*. [7] showed that the addition of small amounts of water or methanol to the H-mordenite-catalyzed isomerization of OA increased the conversion to isostearic acid to ~70%. It is thought that the water or methanol increased the acidity of the zeolite, which in turn improved the activity and selectivity of the catalyst [7, 8]. More recently, Zhang *et al*. [9] disclosed further details on this skeletal isomerization reaction of linear-chain UFA. They used both microporous and mesoporous zeolites to isomerize OA. The isomerization of OA with microporous H-beta zeolite gave 45% bc-SFA, 5.9% stearic acid, 14% γ-stearolactone and ~20% unreacted OA (presumably a mixture of *cis* and *trans* positional isomers). In comparison, MAS-5 zeolite, a highly ordered hexagonal mesoporous aluminosilicate with an acid strength higher than that of pure silicate (MCM-41), gave a lower conversion of OA (~65%) and selectivity for bc-SFA (~30% after hydrogenation). MAS-5 zeolite also gave 4% stearic acid and 16% lactone [10, 11].

The above patent disclosures [6–10] illustrate the potential of solid acid catalysts for the skeletal isomerization of UFA. It was speculated that the Brönsted acids within the channels of these zeolitic materials are the active sites in catalyzing these isomerization reactions. In spite of the potential shown by these zeolite catalysts, the conversion and selectivity of the isomerization reactions reported need to be improved before they can become practically useful for the production of bc-SFA from linear UFA.

In this regard, it was our intention to carry out a systematic study to improve the production of bc-FA from UFA using these solid acid-catalysts. This work focused on establishing the experimental protocols for solid acid-catalyzed skeletal isomerization of UFA. OA was converted to bc-UFA isomers with up to 85% yield (after hydrogenation to bc-SFA) in the presence of modified Ferrierite zeolites (after Pd-catalyzed hydrogenation). The formation of dimer and trimer byproducts was greatly suppressed when Ferrierite zeolites were used as catalysts. The solid Ferrierite zeolite catalyst was characterized by powder X-ray diffraction (PXRD), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), nitrogen adsorption measurements, and scanning electron microscopy (SEM), while the organic products were characterized by gas chromatography (GC), gas chromatography/mass spectroscopy (GC/MS), and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF). We also determined the branching positions of the methyl group from the GC-MS spectra of the picolinyl ester of the bc-acids.

2 Materials and methods

2.1 Materials

OA (~90 wt-%) was purchased from Aldrich Chemical (Milwaukee, WI, USA). Methyl oleate (>99%) was from NuCheck Prep (Elysian, MN, USA). Mordenite (HSZ-640HOA, H^+, 17.5–19.5 mol/mol SiO_4/AlO_4) and Ferrierite (HSZ-720KOA, K^+, 17.5 mol/mol SiO_4/AlO_4) were purchased from Tosoh Co. (Tokyo, Japan). Ferrierite (CP914C, NH_4^+, 20 mol/mol SiO_4/AlO_4) and Ferrierite (CP914, NH_4^+, 55 mol/mol SiO_4/AlO_4) were purchased from Zeolyst Int. (Valley Forge, PA, USA). All other reagents used were of the highest purity available as obtainable from commercial suppliers.

2.2 Instrumentation

GC analysis of bc-fatty acid methyl ester (FAME) products was carried out with a Hewlett Packard HP 5890 instrument (Agilent, Wilmington, DE, USA) equipped with a capillary inlet (on-column mode) and an FID detector. The GC capillary columns used were a HP DB-1HT column (15 m × 0.25 mm × 0.25 μm) and a HP DB-5HT column (15 m × 0.25 mm × 0.25 μm) with the He carrier gas set at a linear velocity of 22 cm/s at 100 °C. The oven temperature profile was: initial temperature 50 °C, hold 1 min; ramp at 15 °C/min to 160 °C; ramp at 7 °C/min to 230 °C; ramp at 30 °C/min to 370 °C, hold 10 min.

GC/MS characterization of bc-FAME was carried out with an HP 5890 instrument (Agilent, Wilmington, DE, USA) with a capillary inlet (split mode) and an HP Model 5972 mass detector set to scan from 40 to 550 *m/z* at a rate of 1.5 scans/s. The capillary column used was a HP DB-5 column (30 m × 0.25 mm × 0.25 μm) with the He carrier gas set at a linear velocity of 22 cm/s at 100 °C. The injector and detector transfer line temperatures were set at 250 and 280 °C, respectively. The oven temperature profile was: initial temperature 100 °C; ramp at 10 °C/min to 250 °C, hold for 5 min; ramp at 10 °C/min to 300 °C, hold for 5 min.

GC/MS characterization of picolinyl fatty ester products was carried out on a Supelco SP-2340 capillary column (60 m × 0.25 mm × 0.20 μm) with the He carrier gas set at a linear velocity of 26.9 cm/s at 130 °C. The injector and detector transfer line temperatures were set both at

250 °C, respectively. The oven temperature profile was: initial temperature 130 °C; ramp at 2 °C/min to 180 °C, hold 8 min; ramp at 2 °C/min to 230 °C, hold 5 min; ramp at 2 °C/min to 250 °C, hold 20 min.

MALDI-TOF mass spectra were acquired with a 4700 Proteomics Analyzer (Applied Biosystems, Framingham, MA, USA) mass spectrometer set to operate in the positive reflectron mode with a 200-Hz Nd-YAG 355 nm laser. Spectra were obtained by averaging 1000 acquired spectra in the MS mode. Conversion of time of flight to mass (Da) for the monoisotopic ions $[M+Na]^+$ was based on calibration of the instrument with standards. Dimer acids in the isomerized OA products were characterized by dissolving the crude product in methanol (1 mg/mL in methanol) and mixing 40 μL of this solution with 60 μL meso-tetrakis(pentafluorophenyl)porphyrin (F20TPP; Sigma-Aldrich-Fluka, St. Louis, MO, USA) (10 mg/mL in chloroform) and 10 μL sodium acetate in methanol (1 mg/mL). Approximately 0.5–0.7 μL of this solution was spotted on a MALDI plate [13].

^{1}H NMR spectra were recorded at room temperature (RT) in $CDCl_3$ on a Varian Inova 400-MHz (Palo Alto, CA, USA) spectrometer. Operating parameters were: cycle time (D1) = 1.0 s; acquisition time (at) = 3.7 s; transmitter power (tpwr) = 57 Hz; pulse width (pw) = 90°.

2.3 Zeolite treatments

Ferrierite CP914C (30 g, 20 mol/mol SiO_4/AlO_4) containing NH_4^+ ions was treated with 100 mL 1 N HCl in deionized water. The suspension was allowed to stir at 55 °C for 24 h. The suspension was centrifuged at 15,000 rpm for 0.5 h. The fine powdered solid was washed with deionized water (3 × 100 mL) and dried at RT in air for 3–4 days before use. Approximately 40 g of H^+-exchanged Ferrierite was obtained and this catalyst is referred to as H-Ferr-NH_4. ^{1}H NMR was used to determine the extent of NH_4^+ removed from the zeolite.

A Ferrierite HSZ (30 g, 17.5 mol/mol SiO_4/AlO_4) containing K^+ ions was similarly treated with 100 mL 1 N HCl in deionized water. The suspension was allowed to stir at 55 °C for 24 h, centrifuged at 15,000 rpm for 0.5 h, and the fine powdered solid was washed with deionized water (3 × 100 mL). The solid H^+-exchanged catalyst was air-dried for 3 days at RT before use. Approximately 45 g of H^+-exchanged catalyst was obtained and is referred to as H-Ferr-K.

Alternatively, Ferrierite CP914C (20 g, 20 mol/mol SiO_4/AlO_4) containing NH_4^+ was calcined in air at 500 °C for 5 h. The zeolite went from light brown to white and ~20 g of solid was obtained, and this catalyst is referred to as H-Ferr-NH_4-500. In addition, Ferrierite CP914 (20 g, 55 mol/mol SiO_4/AlO_4) containing NH_4^+ was calcined under similar conditions to give an H^+ Ferrierite (~20 g, white solid), and this catalyst is referred to as H-Ferr-55-NH_4-500.

2.4 Isomerization of UFA

OA [50 g, 0.17 mol, 91.2 wt-% (stearic acid 2.7 wt-%, linolenic acid 6.1 wt-%)], 1.25 g (2.5 wt-%) modified Ferrierite H-Ferr-K (17.5 mol/mol SiO_4/AlO_4), and deionized water (1.0 mL, 0.055 mol) were placed into a 600-mL high-pressure stainless-steel vessel (Parr Instrument, Moline, IL, USA) equipped with a mechanical stirrer and an electric heating mantle equipped with a temperature controller. The vessel was sealed and purged with 40 psi N_2 (3 × for 15 min each). The reactor was filled with N_2 to ~20 psi and then heated to 250 °C for 6 h. The reaction mixture was cooled to RT, the catalyst was separated from the crude product by filtration through a 60-mm fritted funnel, and the catalyst residue was washed with acetone (~50 mL). The filtrate was dried over $MgSO_4$ for ~0.5 h and the solvent removed under reduced pressure to give the crude bc-UFA as a yellow liquid (~50 g).

2.5 Catalyst reuse experiments

The catalyst recovered from the above experiment was used in the catalyst reuse experiments. The residual brown solid catalyst was washed with acetone (~30 mL), deionized water (~50 mL), and then calcined in air at 500 °C for 24 h. The recovered catalyst went from brown to white in color. The freshly calcined catalyst (5 wt-% of OA), OA and deionized water were then recharged for a subsequent isomerization reaction. This process was repeated for three cycles.

2.6 Product characterization

The crude bc-UFA (45 g, 0.16 mol) were transferred to a 300-mL high-pressure heavy-wall glass reactor along with 5% Pd on activated carbon (2 g, 0.94 mmol) and ~50 mL methanol. The reactor was quickly attached to a hydrogenation apparatus (Parr Instrument), purged with H_2 three times at ~45 psi, charged with H_2 to 45 psi, and allowed to shake at RT for 12 h. Excess H_2 was discharged from the reactor, and the reaction mixture was filtered through Celite to remove the Pd catalyst, and the methanol was removed under reduced pressure. The residue was dissolved in ~150 mL hexane, and the solution was placed in a –3 °C freezer for 24 h. The crystallized solid (stearic acid, 4.5 g) was suction-filtered and rinsed with cold hexane, and the solvent was removed from the

filtrate under reduced pressure to give the bc-SFA as a light yellow oil (40.5 g). The bc-SFA was recrystallized once more from hexane at 0 °C and the final bc-SFA yield was 39 g (87%).

The bc-SFA (39 g, 0.14 mol) was transferred to a 500-mL 1-neck round-bottom flask, and methanol (200 mL) containing conc. sulfuric acid (~5 mL) was added to the flask. The mixture was heated to reflux for ~2 h and then cooled to RT [14]. The mixture was quenched with saturated Na_2CO_3 solution (100 mL), extracted with ethyl acetate (2 × 200 mL), and the combined ethyl acetate extracts were washed with water (400 mL). The organic layer was dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The recovery of bc-FAME was quantitative (41 g, 0.14 mol). The bc-FAME can be distilled under vacuum (0.25 mmHg) at high temperature (140–165 °C) to give bc-FAME of a purity ranging between 95 and 99%. ^{1}H NMR of bc-FAME (clear liquid) ($CDCl_3$, 400 MHz, RT): δ 3.66 (s, -CO_2CH_3, 3H), 2.35 (m, -$CH_2CO_2CH_3$, 2H), 1.26 (m, 24H), 1.09 (m, -$CHCH_3$, 1H), 0.87 (t, -CH_2CH_3, 2H), 0.84 (m, -$CHCH_3$, 3H). GC/MS of the bc-FAME showed multiple peaks with retention times ranging between 14 and 15.1 min and gave an $[M]^+$ of *m/z* 298 (*m/z* = 298 *calcd.* for isostearic acid methyl ester). Dimer FAME, minor co-products formed in the isomerization process and present in the crude bc-FAME, were identified by MALDI-TOF MS. The dimer esters gave $[M+Na]^+$ ions at *m/z* 615 and 617 (calc., $[M+Na]^+$ for an unsaturated dimer product is *m/z* 615 and for a saturated dimer product is *m/z* 617).

GC/MS was used to characterize the crude product distribution and determine the yields of these products as well as the conversion of OA to products. The crude bc-SFA mixtures were hydrogenated and then methylated, but not subjected to a recrystallization step for this gross product characterization. GC/MS was also used to determine the ratio between monomer fatty methyl esters (bc-FAME and methyl stearate), dimer, and trimer FAME in the crude bc-FAME.

2.7 Preparation of picolinyl esters

bc-SFA (100 mg, 0.35 mmol) was placed into a 25-mL 2-neck round-bottom flask equipped with a reflux condenser, and dichloromethane (DMC) (3 mL) was added. A solution of 1,1'-carbonyldiimidazole (500 mg, 3.1 mmol) in DMC (3 mL) was added, the mixture was stirred at RT for 1 min, and a solution containing 3-(hydroxymethyl)pyridine (250 μL, 2.6 mmol) in 2.5 mL of DMC and 2.5 mL of triethylamine was added. The resulting mixture was heated to reflux for 1 h, quenched with 1 N HCl (50 mL), and extracted with DMC (50 mL) [15]. The DMC layer was washed with water (2 × 120 mL) and the solvent was removed under reduced pressure. The residue was redissolved in ethyl acetate (50 mL) and washed with water (100 mL). The organic phase was dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure to give a quantitative yield of the picolinyl esters. GC/MS of the picolinyl esters gave multiple peaks at retention times ranging between 65.5 and 72 min that gave an $[M]^+$ of *m/z* 375 (*m/z* = 375 *calcd.* for picolinyl methyl-heptadecanoate) (Fig. 3). ^{1}H NMR of bc-SFA picolinyl esters (light brown oil ($CDCl_3$, 200 MHz): δ 8.59 (m, -C*H*NC*H*, 2H), 7.69 (m, -C*H*CHNCH, 1H), 7.3 (m, -C*H*CHNCH, 1H), 5.13 (s, -OCH_2CH, 2H), 2.36 (t, -COCH_2CH_2, 2H), 1.64 (m, -$COCH_2CH_2$, 2H), 1.26 (s, 25H), 0.85 (m, 6H).

3 Results and discussion

3.1 Modification of ferrierite catalysts

For the purposes of this study, we used a commercially available zeolite, Ferrierite, which has not been studied previously for the skeletal isomerization of FA. This catalyst has a two-dimensional aluminum-silica network structure with interconnecting channels between the 8-membered-ring (MR) and 10-MR structures [16]. The channels of commercially available Ferrierites typically contain an alkali metal (Na^+ or K^+) or ammonium (NH_4^+) cation. In this work, we examined three types of Ferrierite: a K^+-containing Ferrierite with a Si/Al molar ratio of 17.5; an NH_4^+-containing Ferrierite with a Si/Al molar ratio of 20; and an NH_4^+-containing Ferrierite with a Si/Al molar ratio of 55. The K^+ or NH_4^+ cations were exchanged with protons (H^+) by washing with 1 N HCl or by heating the NH_4^+-containing Ferrierite in air at 500 °C for 5 h to decompose the NH_4^+ groups to H^+. The unmodified and modified Ferrierite solids were characterized by PXRD, FTIR, TGA, and SEM. Surface areas for the modified Ferrierites were obtained by nitrogen adsorption measurements (BET). The proton-exchanged Ferrierites (H-Ferrierite) obtained were directly used in the skeletal isomerization reactions.

The exchange of K^+ or NH_4^+ cations in the Ferrierite framework by H^+ was evidenced in the FTIR spectra, which give a broad peak at 3610 cm^{-1} that is assignable to the terminal OH groups (*i.e.* the Brönsted acidic site) [17]. PXRD patterns of the Ferrierites before and after the exchange processes were similar (Fig. 1), which indicated that the ion exchange or thermal decomposition process did not destroy the Ferrierite crystalline framework. SEM images indicated that these materials comprised submicron to micron particle sizes comparable to the starting

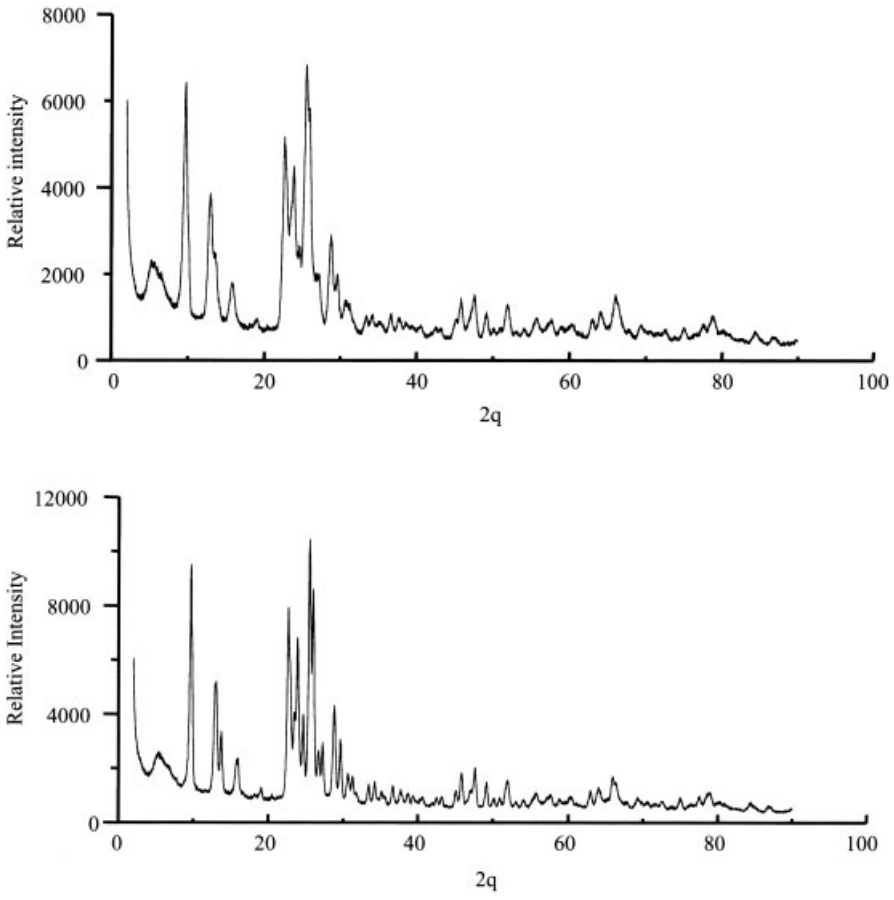

Fig. 1. Top: PXRD pattern of NH_4^+-containing Ferrierite. Bottom: PXRD pattern of H-Ferr-NH_4^+ (treated with 1 N HCl solution).

Ferrierites and with no significant morphological changes. TGA showed that the NH_4^+ ion-containing Ferrierite lost 6.4% of its weight when heated from RT to 160 °C while the proton-exchanged Ferrierite lost 8.2% of its weight over the same temperature range, which is consistent with the presence of more water in the latter as a result of the smaller size of the proton *vs.* the ammonium ion. Gas adsorption indicated that both the NH_4^+ ion- and proton-containing Ferrierites are highly porous with a Langmuir surface area of 489 and 510 m^2/g, respectively (Fig. 2). Again, a slightly higher surface area was observed for the H^+-containing Ferrierite, which is consistent with the smaller size of H^+ *vs.* NH_4^+ cations.

3.2 Ferrierite-catalyzed skeletal isomerization of OA

It was anticipated that the H^+ Ferr zeolites would be active catalysts for the skeletal isomerization of UFA such as OA because of their high surface areas and high density of Brönsted acid sites. In general, initial results showed that OA was converted to bc-isomers (isostearic acid isomers) in the presence of the modified Ferrierite zeolites (SiO_4/AlO_4 ratio 17.5–20) after 6 h of reaction at 250 °C. The total product from the isomerization reactions were hydrogenated and converted to methyl esters. GC analysis of this material showed the formation of bc-SFA isomers (isostearate isomers), FA dimers, methyl stearate, and other byproducts (primarily γ-stearolactone and hydroxy stearates (Fig. 3)). GC/MS of the mixture showed a very complicated ion spectrum, since the isostearate product is a complex mixture of isomers as a result of the location of the methyl group at various sites along the FA alkyl chain. MALDI-TOF was used to determine the mass of the dimer and trimer FA formed in the reaction. Detailed ^{1}H NMR, GC, GC/MS, and MALDI-TOF studies showed that isostearic acids (**1**) are the major products of these heterogeneously catalyzed isomerization reactions, along with linear FA (**2**), hydroxylated FA (**3**), lactone (**4**), and dimer acids (**5**) (Fig. 3). As shown in Tab. 1, without added co-catalyst, the H-Ferr-K catalyst isomerized OA to a product composed of 59% bc-FA (**1**), 23% linear FA (**2**), 14% **3** and **4**, and 3.7% dimer FA (**5**). This represents an 82% conversion of OA to products. This bc-FA yield is rather modest. Previous reports indicated that conversion

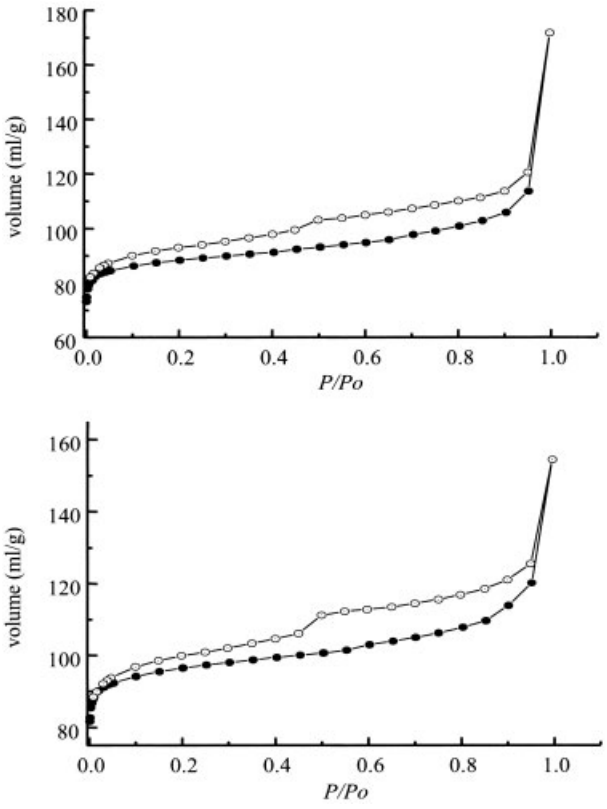

Fig. 2. N_2 adsorption isotherms for NH_4^+-containing Ferrierite (top: solid circles, adsorption; open circles, desorption) and H-Ferr-NH_4^+ (bottom: solid circles, adsorption; open circles, desorption).

and selectivity of the OA to bc-FA could be significantly improved by adding water or other co-solvents to the reaction [7, 8]. We have therefore preformed the isomerization reactions with H-Ferr-K in the presence of small amounts of different co-solvents. While the H-Ferr-K/deionized water combination catalyzed the isomerization of OA to bc-SFA (after hydrogenation) with 99% conversion of OA and 85% selectively for bc-FA selectivity, the H-Ferr-K/methanol combination and H-Ferr-K/isopropanol combination gave 96% conversion/85% selectivity and 87% conversion/70% selectivity, respectively. All the subsequent reactions were thus carried out with deionized water.

Of the solid acid catalysts prepared in this study (Tab. 2), the best result for skeletal isomerization of UFA to bc-FA was obtained when 2.5 wt-% H-Ferr-K solid catalyst was used in the presence of small amounts of deionized water. This is presumably a result of the higher number of active Brönsted acid sites in the H-Ferr-K solid since it has the lowest Si/Al molar ratio among the Ferrierite catalysts we have tested. As seen in Tab. 2, the H-Ferr-K/deionized water system (entry 6, Tab. 2) gave 99% conversion of OA with 82% selectivity to bc-FA. Under similar conditions (with 2.5 wt-% catalyst loading), the H-Ferr-NH_4 catalyst system (entry 8, Tab. 2) gave 91% conversion and 75% bc-FA selectivity whereas the H-Ferr-NH_4-500 system (entry 9, Tab. 2) gave 93% conversion and 74% selectivity to bc-FA. The high selectivity observed for the isomerization of UFA is undoubtedly a result of confinement effects of the porous solid catalysts. The channels are large enough for the passage (transport) of OA to undergo intra-molecular reaction, but the confined spaces minimize the chance of inter-molecular reactions between OA molecules.

Interestingly, when 5 wt-% of H-Ferr-K catalysts was used (entry 5, Tab. 2), the bc-FA (**1**) selectivity dropped and there was an increase in the formation of dimers (**5**).

Tab. 1. H^+ Ferrerite-catalyzed isomerization of OA in the presence of co-catalysts.[†]

Entry	Co-catalyst	Area [wt-%][‡]				Conversion [%][§]
		Methyl isostearates (**1**)	Methyl stearate (**2**)	**3** and **4**	Dimers (**5**)	
1	None	59	23	14	3.7	82
2	0.5 mL H_2O	77	9.2	8.5	5.7	96
3	1 mL H_2O	82	5.9	6.4	5.5	99
4	1 mL H_2O[#]	85	6.2	6.9	2.3	94
5	1 mL MeOH	77	9.9	7.2	5.7	96
6	1 mL MeOH[#]	85	7.2	5.9	2.0	95
7	1 mL isopropanol	70	18	6.6	5.6	87

[†] All reactions were performed at 250 °C for 6 h with OA (91.5% pure) and 2.5 wt-% zeolite loading.
[‡] GC data collected on the intact reaction product after hydrogenation and methylation using dodecane as internal standard.
[§] Conversion calculated as 94.3 – [(stearate – 5.74)]/94.3 × 100 (94.3% is the UFA).
[#] OA (99%) was used in these experiments.

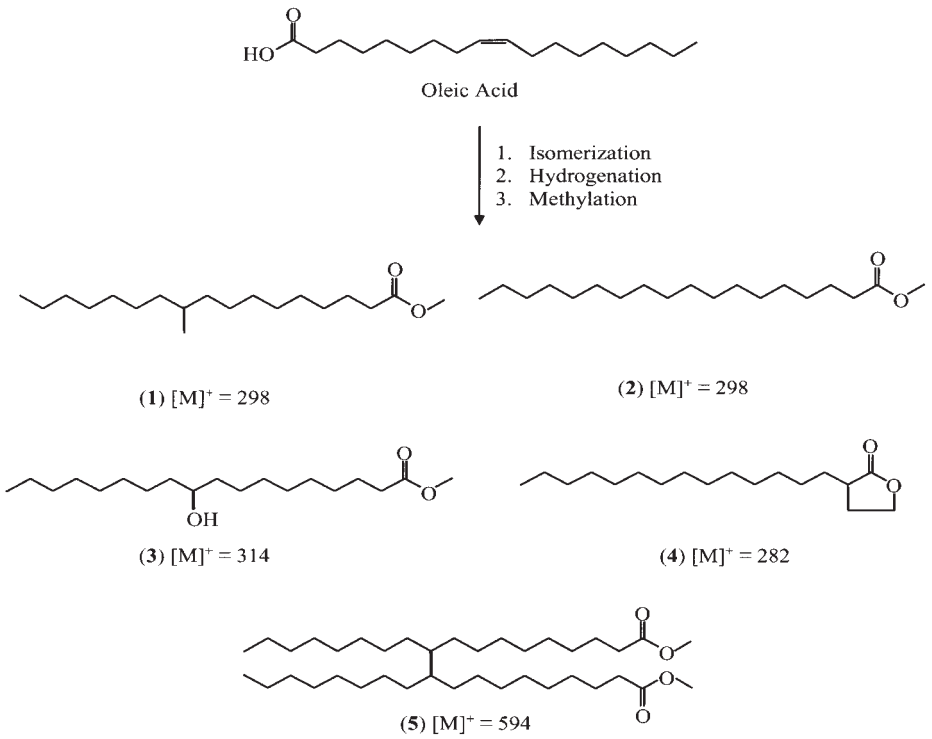

Fig. 3. Products produced from zeolite-catalyzed isomerization of oleic acid: **1**, isomeric methyl-methylheptadecanoates; **2**, methyl stearate; **3**, isomeric hydroxy-methyloctadecanoates; **4**, γ-stearolactone; **5**, isomeric C_{36}-dimer fatty methyl esters.

Tab. 2. OA isomerization with different catalysts.[†]

Entry	Catalyst [wt-%]	Area [wt-%][‡]				Conversion[§] [%]
		Methyl isostearates (**1**)	Methyl stearate (**2**)	**3** and **4**	Dimers (**5**)	
1	Clay (4.3)[#]	30	21	none	49	84
2	H-Mordenite (2.5)[††]	52	34	9.8	3.6	70
3	Ferrierite-NH_4 (10)	43	33	19	6.1	72
4	Ferrierite-K (2.5)	–	–	–	–	0
5	H-Ferr-K (5)[‡‡]	79	6.2	6.3	8.4	99
6	H-Ferr-K (2.5)[‡‡]	82	5.9	6.4	5.5	99
7	H-Ferr-K (2.5)[‡‡,§§]	85	6.2	6.9	2.3	94
8	H-Ferr-NH_4 (2.5)[‡‡]	75	14	7.7	3.6	91
9	H-Ferr-NH_4-500 (2.5)[##]	74	12	9.2	4.5	93
10	H-Ferr-NH_4-55-500 (2.5)[##]	38	41	13	7.3	58
11	H-Ferr-NH_4-500 (5)[##]	80	5.0	7.5	7.3	99
12	H-Ferr-NH_4-500 (5) 1st[†††]	75	12	8.7	4.8	94
13	H-Ferr-NH_4-500 (5) 2nd[†††]	61	21	13	5.3	83
14	H-Ferr-NH_4-500 (5) 3rd[†††]	53	30	11	6.3	74

[†] All reactions were performed at 250 °C for 6 h with OA (91.5% pure) and 1 mL deionized water.
[‡] GC data collected on the intact reaction product after hydrogenation and methylation using dodecane as internal standard.
[§] Conversion calculated as 94.3 – [(stearate – 5.74)]/94.3 × 100 (94.3% is the UFA).
[#] Reaction carried out at 250 °C for 2.5 h.
[††] H-Mordenite (17.5–19.5 mol/mol SiO_4/AlO_4) used in this experiment.
[‡‡] Catalysts were proton-exchanged with HCl before use.
[§§] OA (99%) was used in this experiment.
[##] Ferrierite NH_4^+ catalyst (55 mol/mol SiO_4/AlO_4) was activated by calcination at 500 °C for 5 h.
[†††] Entries 12–14 represent successive reuse of the 5 wt-% Ferr-NH_4^+ catalyst from entry 11. The catalyst was regenerated by heating at 500 °C for 12 h after each use.

This increase in dimer formation may be a result of the residual Brönsted acid sites on the external surface of the H-Ferr-K catalyst promoting the formation of the dimer or trimer products (resulting from intra-molecular reaction). Since higher catalyst loadings promoted the intra-molecular reactions, all subsequent reactions were carried out with a 2.5 wt-% catalyst loading.

We also carried out control experiments with the unmodified Ferrierite zeolites that contained either K^+ or NH_4^+ cations. The Ferrierite zeolite containing K^+ cations in combination with deionized water (entry 4, Tab. 2) did not show catalytic activity for the OA skeletal isomerization reactions, apparently due to the lack of Brönsted acid sites, but did promote isomerization of OA to elaidic acid. On the other hand, the combination of NH_4^+-containing Ferrierite and water (entry 3, Tab. 2) gave a 72% conversion of OA and 43% bc-FA selectivity. The activity observed with this catalyst may be a result of decomposition of NH_4^+ cations into H^+ at the reaction temperature (250 °C). This would substantiate that pretreatment of the zeolite is an important step for OA isomerization to attain high conversion and selectivity to bc-FA.

We also examined a previously studied zeolite catalyst, namely the H-mordenite zeolite with a Si/Al ratio of 17.5 and a surface area of 380 m^2/g. Although the Si/Al ratio for the H-mordenite catalyst is similar to that of the Ferrierite zeolites, the 2.5 wt-% H-mordenite/water combination (entry 2, Tab. 2) was an active catalyst for the isomerization of UFA to bc-SFA (after hydrogenation), but only at 70% conversion of OA and 52% selectivity for bc-FA. Other products formed in this reaction were: linear FA (**2**), 34%; **3** and **4**, 9.8%; and dimer acids (**5**), 3.6%. A much higher catalyst loading (15 wt-%) of H-mordenite zeolite in combination with water resulted in a 99% conversion of OA but only a 76% selectivity for bc-FA (along with 6.1% **1**; 5.4% **2**; and 12% **4**). It is clear that the modified H-Ferrierite zeolites perform better than previously studied zeolite catalysts, presumably because of the greater number of Brönsted acid sites within the channels of the Ferrierite zeolites.

3.3 Recycle and reuse of the ferrierite zeolite catalysts

The modified H-Ferr-NH_4^+ zeolites could be recycled and reused for at least three reaction cycles (Tab. 2). The catalyst, recovered from entry 11, Tab. 2, was regenerated by heating at 500 °C for 12 h, after which it was ready to be reused. Both the conversion and selectivity, however, decreased with increased reuse and dropped significantly after the third reuse (data not shown). Although the selectivity and activity of this catalyst decreased with reuse (entries 12–14, Tab. 2), the results were still better than those reported previously using clay and H-mordenite catalysts. Unfortunately, reuse of the H-Ferr-K catalyst could not be done since this catalyst lost activity after calcination. This may be a result of the acid treatment of the zeolite, which may have altered the zeolite structure making it fragile.

3.4 Characterization of bc-FA/FAME

The bc-SFA obtained using zeolite catalysts are typically a mixture of methyl-branched isomers, with the methyl group located at different positions on the alkyl chain as a result of the migration of the C=C bond during the isomerization process, as shown in the gas chromatogram of the hydrogenated bc-FAME (Fig. 4A). A more definitive analysis of the position of the methyl group on the FA chain was made by GC/MS after the hydrogenated bc-FA had been converted to picolinyl ester derivatives [15]. As shown in Fig. 4B, the gas chromatogram of the picolinyl esters gave a better separation of the methyl-branched isomers. From this spectrum (Fig. 4B), we determined that 8.3% of the picolinyl methyl-heptadecanoate derivatives (peak A) contain a methyl branch on the 2 to 7 position, 84.4% have the methyl branch on the 8 to 14 position (peaks 1–7), and 7.3% have the methyl branch on the 15 and 16 positions of the alkyl chain (peaks 8 and 9, respectively). This analysis was made from an interpretation of the ms fragmentation ions of the picolinyl esters as shown in Fig. 5 for the 11, 12, and 13 methyl-branched isomers, which correspond to peaks 4–6 in Fig. 4B. We have also compared this result with the isomerized products obtained with the clay catalyst. Interestingly, we found that the isomerized products obtained from the clay-catalyzed reactions gave a very different distribution of the methyl-branching products. Of the picolinyl methyl-heptadecanoate derivatives, 17.9% contain the methyl branch on the 2 to 7 position, 53.5% of them have the methyl branch on the 8 to 14 position, and 27% of them have the methyl branch on the 15 and 16 positions of the alkyl chain.

3.5 Properties of bc-FA/FAME

The iodine values (IV) [18], cloud points (CP), and pour points (PP) [19] for the bc-FA and esters prepared in this study are listed in Tab. 3. The IV of the crude methyl ester bc-SFA product was ~20. Distillation of the bc-SFA gave a product with an IV of ~6 (Tab. 3). The IV is higher for the crude product because of the presence of dimers and other presumably higher-molecular-weight byproducts.

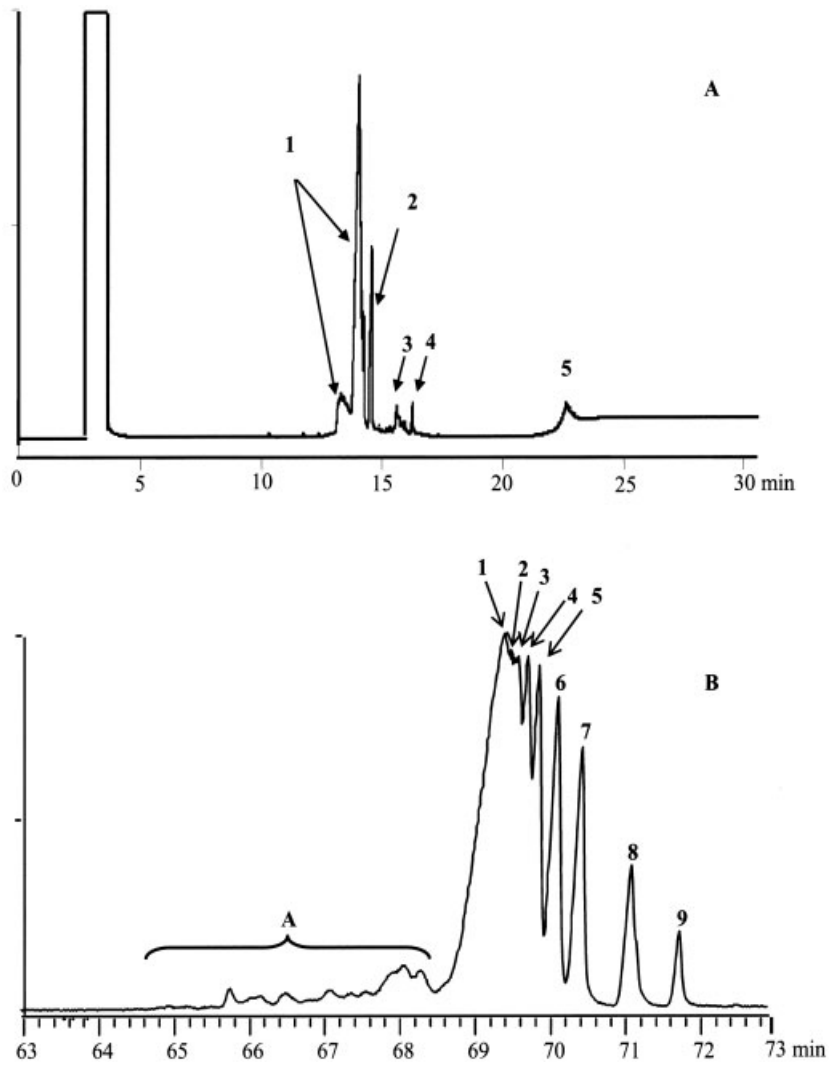

Fig. 4. (A) Gas chromatogram for the crude product mixture obtained from the zeolite-catalyzed isomerization of OA (after hydrogenation and methylation.): **1**, isomeric methyl-methylheptadecanotes; **2**, methyl stearate; **3**, isomeric hydroxy-methyloctadecanoates; **4**, γ-stearolactone; **5**, isomeric C_{36}-dimer fatty methyl esters. (B) GC trace of picolinyl methyl-heptadecanoates peak # (position of methyl branch on the alkyl chain): (A), 2–7; (1), 8; (2), 9; (3), 10; (4), 11; (5), 12; (6), 13; (7), 14; (8), 15; (9), 16.

Tab. 3. Physical properties of bc-FA and -FAME.[†]

Entry	Fatty ester (acid) (% purity)	Cloud point [°C]	Pour point [°C]	Iodine value
1	Oleic acid (91.5%)	12	10	92
2	Crude saturated branched-chain acids[‡]	−10	−15	26
3	Crude saturated branched-chain acids[§]	7	−13	23
4	Crude saturated branched-chain methyl esters[§,#]	−9	>−22	23
5	Saturated branched-chain methyl esters[††]	−13	>−22	6
6	Saturated branched-chain acids[‡‡]	3	0	5

[†] IV, PP and CP for the bc-FA and bc-FAME were measured following AOCS [18] and ASTM [19] methods, respectively.
[‡] Catalyzed by 15 wt-% H-mordenite.
[§] See Tab. 1, entry 5 for % composition.
[#] Methylated with concentrated sulfuric acid in methanol.
[††] Distilled at 145 °C under vacuum, from Tab. 3, entry 4.
[‡‡] See Tab. 1, entry 5 for % composition; product was hydrogenated, recrystallized, methylated, and hydrolyzed with 1 N KOH.

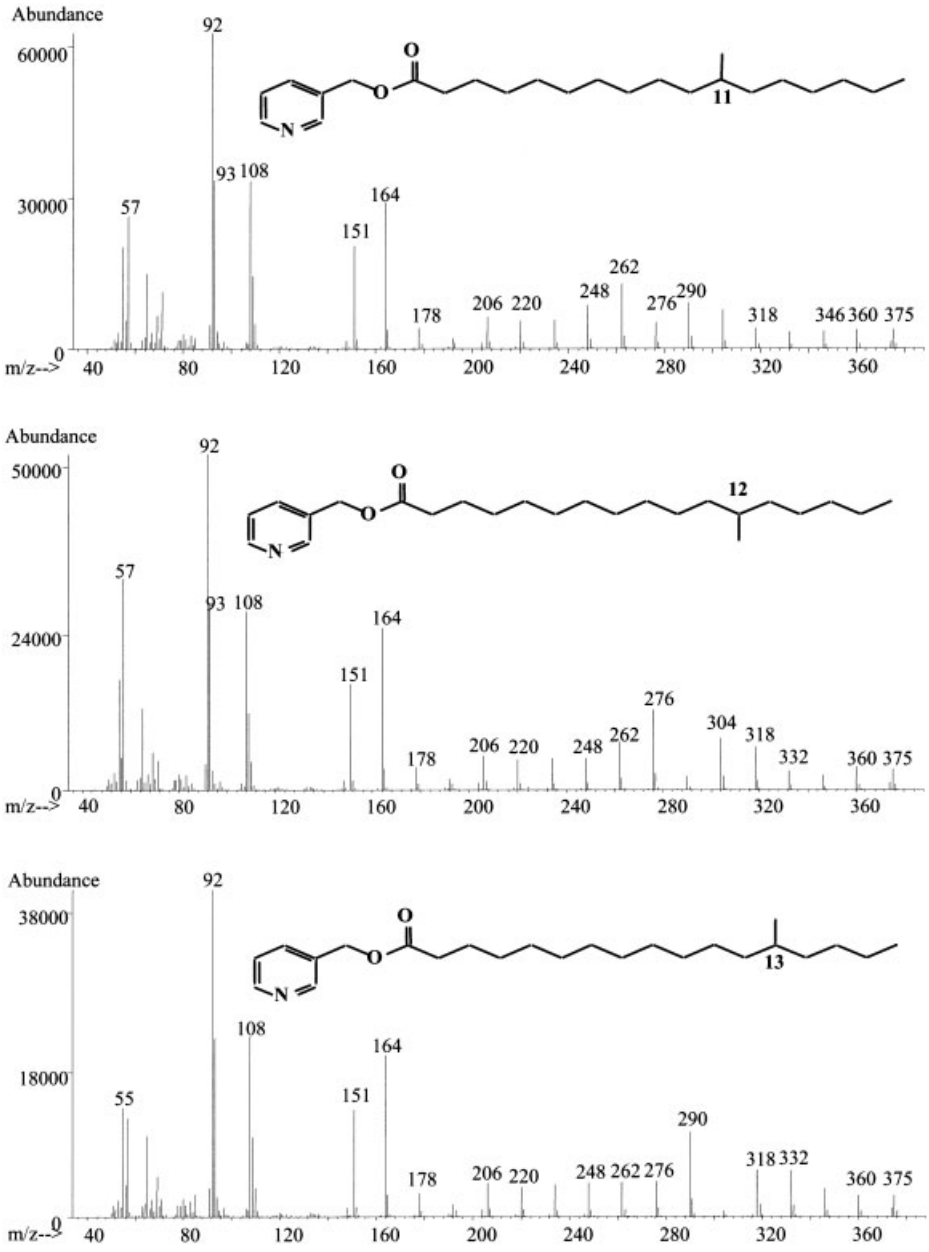

Fig. 5. Mass spectra of picolinyl methyl-heptadecanoates with the methyl branch at different positions along the alkyl chain. Top, 69.67–69.73 min: peak # 4, Fig. 4B; middle, 69.80–69.89 min: peak # 5, Fig. 4B; bottom, 70.05–70.11 min: peak # 6, Fig. 4B).

The isostearic acids, which are liquid at RT, have a CP of ~3 °C while the CP for the saturated bc-methyl ester is ~–13 °C. For comparison, the CP for OA (90%) is ~12 °C.

4 Conclusions

We have successfully demonstrated that OA can be isomerized to bc-FA using modified Ferrierite zeolites. Isomerization of OA over modified H-Ferr catalysts produces bc-SFA with quantitative conversion and >85% selectivity. This level of conversion and selectivity to bc-SFA is unprecedented and potentially opens the way for their large-scale production. The bc-SFA obtained from this process have physical characteristics that make them suitable for biodegradable lubricant production. Byproducts formed in the process include dimer FA (~2%) and minor amounts of lactones and hydroxy FA (~7%). The performance of the H-Ferr zeolites critically depends on the Si/Al ratio and how the zeolite is pretreated. The position of methyl branching in the bc-SFA was determined using GC-MS after conversion to their picolinyl esters. The results from the GC-MS studies indicated that 8.3% of the picolinyl methyl-heptadecanoate derivatives

contain the methyl branch on the 2 to 7 position, 84.4% of them have the methyl branch on the 8 to 14 position, and 7.3% of them have the methyl branches on the 15 and 16 positions of the alkyl chain. The methyl branching seen for bc-SFA obtained with modified Ferrierites is different from that of the bc-SFA obtained with clay catalysts.

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