Supporting Information

Fast and selective solvent-free branching of unsaturated fatty acids with hierarchical ZSM-5

Dorien Kerstens, ^a Hannes De Peuter, ^a Ibrahim Khalil, ^a Sofie Van Praet, ^a Joost Van Aelst, ^a

*and Bert F. Sels a**

a Center for Sustainable Catalysis and Engineering, KU Leuven, Celestijnenlaan 200f, 3001

Leuven, Belgium

*Corresponding author. E-mail address: bert.sels@kuleuven.be

Experimental section

Materials

ZSM-5 zeolites were from Zeolyst (CBV 2314 (H-ZSM-5-12); CBV 3024 (H-ZSM-5-15); CBV 5524G (H-ZSM-5-25); CBV 8014 (H-ZSM-5-40); CBV 28014 (H-ZSM-5-140)). Ferrierite zeolite was from Tosoh (HSZ-720 NHA (H-FER-9)). Oleic acid (technical grade, 89 %) was from Sigma Aldrich. Radiacid 0134 (oleic acid, 84 %) was from Oleon N.V. 5 wt% Pd on carbon, 14 % BF3 in methanol and tetrahydrofuran (with 250 ppm BHT as an inhibitor, >99.9 %) were from Sigma Aldrich. N-octane (>99 %), methanol (99.9 %), octanoic acid (99 %) and sodium chloride were from Acros Organics. Sodium hydroxide, hydrochloric acid (37 %), and ammonia nitrate (98 %) were from Fisher Scientific.

Calcination treatment

Prior to zeolite testing, the commercial zeolites were calcined in a static air environment to set them into the protonic form. A thin layer of the zeolite is put in a porcelain incineration boat and placed in a muffle oven. The commercial ZSM-5 samples were heated to 550 °C at 3 °C min⁻¹. After 5 hours at this temperature, the oven was cooled down to room temperature. The commercial Ferrierite sample was heated to 550 °C at 1 °C min⁻¹. After 5 hours at this temperature, the oven was cooled down to room temperature. The post-synthetically treated ZSM-5 sample was heated to 550 °C at 5 °C min⁻¹. After 5 hours at this temperature, the oven was cooled down to room temperature.

Post-synthetic treatment ZSM-5

ZSM-5-12 was post-synthetically treated in order to obtain a hierarchical ZSM-5 zeolite (H-ZSM-5-AT-AW). First, an alkaline treatment was carried out in a 0.8 M aqueous NaOH solution (33 g zeolite per liter of solution) at 65 \degree C under constant stirring at 450 rpm to induce desilication creating mesopores in the zeolite crystals. The zeolite was added to the aqueous NaOH solution after the treatment temperature was reached. After 30 minutes, the reaction was quenched by adding distilled water and the zeolite was filtered and washed three times with distilled water. The zeolite was dried overnight in an oven at 100 °C. Then, an acid wash was performed in a 0.02 M aqueous HCl solution (10 g zeolite per liter of solution) at 65 °C under constant stirring at 450 rpm to remove any Al debris, i.e. extra-framework Al (EFAl) formed during desilication. The zeolite was added to the aqueous HCl solution after the treatment temperature was reached. After 6 hours, the reaction was quenched by adding distilled water and the zeolite was filtered and washed three times with distilled water. The zeolite was dried overnight in an oven at 100 °C. Subsequently, the zeolite was converted to the NH₄⁺-form using a 0.1 M NH₄NO₃ solution (10 g zeolite per liter of solution) at room temperature three times overnight under constant stirring at 250 rpm. After each treatment, the zeolite was filtered and washed with distilled water. After the third treatment, the zeolite was dried overnight in an oven at 100 °C. Finally, the zeolite was calcined as described earlier. An overall solid yield of 41.5 wt% was obtained after the calcination was completed.

Characterization

X-ray powder diffraction (XRPD) measurements were performed on a STOE STADIP Combi diffractometer in transmission mode using CuKα radiation.

N2 isotherms were measured on a TriStar (Micromeritics) gas adsorption analysis instrument at -196 °C. Before analysis, the samples were pre-treated under a N₂ atmosphere at 300 °C for 16 hours using a SmartPrep degassing system (Micromeritics). The spent and washed, not regenerated, catalyst was pretreated at 200 °C to avoid the removal of any cokes from the zeolite. The surface area was calculated using the BET method according to Rouquerol *et al*. 1 The t-plot method was used to determine the micropore and mesopore volume.

The nature and density of the acid sites were determined by pyridine adsorption followed by Fourier-transform infrared spectroscopy (FT-IR) using a Nicolet 6700 Spectrometer equipped with a deuterated triglycine sulfate (DTGS) detector. In addition, the accessibility of the Brønsted acid sites (BAS) was estimated by comparing the ratio BAS detected by 2,6-dimethylpyridine adsorption (lutidine, diameter $= 0.67$ nm) to those quantified with pyridine (diameter $= 0.57$ nm).^{2,3} Prior to analysis, samples were pressed (10⁷ Pa) into precisely weighted selfsupported wafers of 5-10 mg cm⁻², and degassed in-situ for 1 hour at 400 °C (5 °C min⁻¹) under vacuum $\ll 1$ mbar). After cooling to 150 °C, spectra of the materials were recorded as a reference with an accumulation of 128 scans at a resolution of 2 cm^{-1} . Note that the graphical resolution is greater than the spectral resolution and is close to 0.5 cm^{-1} and that all spectra were normalized to a constant disc mass of 5 mg cm⁻² of dry catalyst.

For pyridine adsorption measurements, the samples were subjected to 25 mbar pyridine until saturation at 50 °C. Once saturation was reached, vacuum-thermal desorption was performed for 20 minutes at 150 °C (and optionally at 250 °C and 350 °C), and spectra were recorded at 150 °C after each desorption step. The amount of Brønsted (BAS) and Lewis (LAS) acid sites were determined by integrating the area of the characteristic bands: ν8a of the pyridinium ions (PyH⁺) at 1545 cm⁻¹ and v19b of the coordinated pyridine species (PyL) at ~1445 cm⁻¹, and using their corresponding molar absorption coefficients: $\epsilon(PyH^+) = 1.67$ cm μ mol⁻¹ and $\epsilon(PyL)$ $= 2.22$ cm μ mol⁻¹, respectively.⁴

The accessibility of BAS was measured by gas-phase lutidine adsorption at 50 °C. Small doses of almost 3 mbar lutidine were added onto the samples after activation until saturation. A spectrum was recorded after each dose with 2 minutes delay to give time for the diffusion of lutidine molecules inside the pores. Thermal desorption was first performed at 50 °C for 10 minutes under vacuum, in order to remove the excess-lutidine species from the surface of the catalyst, followed by a second desorption step of 20 minutes at 150 °C. The amount of lutidinetitrated BAS was estimated from the sum of the bands at 1643 and 1627 cm^{-1} (respectively, v8a and v8b vibrations) using the integrated molar absorption coefficient ε (Lut-H⁺) = 6.8 cm µmol⁻ ^{1.5} An accessibility ratio was determined by dividing the amount of lutidine-titrated BAS over the amount of pyridine-titrated BAS.

Thermogravimetric analysis (TGA) was performed on a TGA Q500 Instrument (TA Instruments) using platina pans to determine the amount of cokes present in the catalyst. Samples were heated from room temperature to 800 $^{\circ}$ C at 10 $^{\circ}$ C min⁻¹ under a flow of O₂. The amount of cokes present in the catalyst was calculated based on the weight loss between 200 $\rm{^{\circ}C}$ and 800 $\rm{^{\circ}C}$.

Isomerization

The isomerization reaction was performed in a 50 ml batch Parr reactor (Parr 5500 series compact reactor) equipped with a sampling tube and under 7 bar of N_2 (measured at room temperature). The reactor was loaded with 35 g of oleic acid and 0.875 g of catalyst (2.5 wt%) relative to the substrate) and flushed three times with $7 \text{ bar } N_2$ for 1.5 minutes prior heating. The oleic acid provided by Sigma Aldrich was used for the experiments with the ZSM-5 zeolites. The oleic acid provided by Oleon N.V. was used for the experiment with the FER zeolite. The reactor was heated up to 250 °C in 40 minutes and constantly stirred at 600 rpm. Samples were taken during the reaction using the sampling tube. During the reactions with ZSM-5, samples were taken after 1 hour, 2 hours, 4 hours and 6 hours at 250 °C. During the reaction with FER, samples were taken after 1 hour, 3 hours and 6 hours at 250 °C. After 6 hours at 250 °C, the reactor was cooled down to room temperature. The reaction with the postsynthetically treated ZSM-5 was performed twice (denoted as H-ZSM-5-AT-AW (1) and H-ZSM-5-AT-AW (2)). The catalyst used in both reactions were from the same batch and thus identical. During reaction H-ZSM-5-AT-AW (2), samples were taken at 1 hour, 2hours and 6 hours at 250 °C. The catalyst from this reaction was recovered and washed and regenerated as described below.

Hydrogenation

Prior to esterification, the fatty acids were hydrogenated to facilitate GC-analysis. 1 g of the crude reaction mixture without zeolite catalyst was dissolved in 3 ml tetrahydrofuran and loaded in a 10 ml high pressure reactor with 0.15 g Pd/C and a cruciform stirring bar. The reactor was flushed three times with 15 bar N_2 for 1 minute prior heating. The reactor was then loaded with 20 bar H₂, placed on a copper block, and heated to 80 °C while stirring at 600 rpm. After 6 hours, the reactor was cooled down and the product was centrifuged to remove the Pd/C.

Esterification of fatty acids

300 µl of the hydrogenated sample, 10 ml of 0.5 M NaOH in methanol and a stirring bar were put together in a 250 ml round bottom flask and connected to a reflux set-up. The mixture was refluxed for 10 minutes after which 8 ml BF3 in methanol was added via the reflux cooler. The mixture was refluxed for another 5 minutes after which 4 ml n-octane was added via the reflux cooler. The mixture was refluxed for one more minute and cooled down. 25 ml of a saturated NaCl solution was added, after which the upper organic layer was transferred to a GC-vial.

GC analysis

The fatty acid methyl esters (monomeric fraction of the crude reaction product) were analyzed on a Hewlett Packard HP 6890 gas chromatograph with a split injection system (split ratio 59:1) and H2 as carrier gas. A 100 m CP-Sil 88 column with an internal diameter of 0.25 mm and a film thickness of $0.2 \mu m$ was used for separation. Initially, the temperature was set at 60 °C after which the column was heated immediately to 120 °C at 8.8 °C min-1 . After 0.95 minutes, the column was further heated to 180 $^{\circ}$ C at 4.2 $^{\circ}$ C min⁻¹. This temperature was maintained for 1.05 minutes. Then, the column was heated to 220 °C at 6.2 °C min⁻¹. After 7.4 minutes at this temperature, the column was finally heated to 225 °C at 22.3 °C min⁻¹. This temperature was maintained for 23 minutes. The FID detector was kept at a constant temperature of 300 °C. Identification of the fatty acids was based on the retention time of standard compounds. Quantification was done based on the relative area of the different peaks.

GPC analysis

Gel permeation chromatography (GPC) was performed on the diluted hydrogenated sample to quantify the amount of oligomers in the crude reaction mixture. A Waters e2695 Separations Module and a Waters 2414 RI detector were used. The stationary phase consisted of a PL Gel Mixed column, which was kept at 40 °C. 5 μ l of the sample was injected and a flow of 1 μ l min⁻¹ was used. Octanoic acid was used as an external standard.

Acid value

The acid value is the amount of KOH (in mg) required to neutralize the free fatty acids in a 1 g sample. The acid value has been measured following official methods ISO 660 and AOCS Te 1a-64.^{6,7}

Saponification value

The saponification value is the amount of KOH (in mg) required to saponify the total amount of esterified and free fatty acids in a 1 g sample. The saponification value has been measured following official methods AOCS Cd 3-25, AOCS Tl 1a-64 and APAG/ISO 3657:1977. $8-10$

Iodine value

The iodine value measures the amount of double bonds in a sample expressed by the amount of iodine (in g) that reacts to a 100 g sample. The iodine value has been measured following the official method ISO 3961 ¹¹

Calculation of reaction characteristics

The C18 conversion was followed as a function of time and was calculated as:

$$
C18 Conversion = \frac{(C_{OA, substr} + C_{LA, substr}) - (C_{SA, yh} - C_{SA, 0h})}{(C_{OA, substr} + C_{LA, substr})} [\%]
$$
 Eq. S1

The selectivity to branched fatty acids was followed as a function of time and was calculated as:

$$
BFASelectivity = \frac{C_{iSA,yh}}{(C_{OA,substr} + C_{LA,substr}) - (C_{SA,yh} - C_{SA,substr})}
$$
 [%) $Eq.S2$

The yield of branched fatty acids was followed as a function of time and was calculated as:

$$
BFAYield = \frac{C_{iSA,yh}}{(C_{OA,substr} + C_{LA,substr})} [\%]
$$
 Eq. S3

The (pseudo-)first order rate constant k (units: h^{-1}) was determined based on the procedure of following section or can be calculated as:

$$
k = \frac{\ln\left(\frac{C_{SA, yh}}{C_{SA, 0h}}\right)}{t} [h^{-1}]
$$
 Eq. S4

With $C_{x,substr}$ = the amount of compound x present in the substrate (wt%), $C_{x,yh}$ = the amount of compound x in the product after y hours at reaction temperature (wt%), $OA =$ oleic acid, LA $=$ linoleic acid, SA = stearic acid, iSA = isostearic acid, BFA = branched fatty acids, t = reaction time (hours).

Linearization procedure

A linearization of the obtained data was made so that an observed (pseudo-)first order rate constant k could be determined (**Figure S4**). A first order reaction is considered here, based on the type of reaction that is taking place (**Scheme 1** in main text). In this case, the natural logarithm of the saturated C18 linear fatty acid concentration was plotted against the time at reaction temperature. The slope of this curve represents the observed (pseudo-)first order rate constant k, with units h^{-1} .¹²

Regeneration of the spent catalyst

Before regeneration, the spent catalyst was washed with acetone to remove any remaining fatty acids and other weakly adsorbed compounds. This treatment was repeated until the acetone remained colorless after which the catalyst was dried under a N2-flow. The catalyst was subsequently pelletized in 250 µm to 500 µm pellets and transferred to a U-tube and placed in a tubular oven. The regeneration was performed at 500 °C for 5 hours (heating rate 1 °C min- $¹$) under a constant flow of O₂.</sup>

Extra figures

Figure S1 a) Conversion of C18 unsaturated fatty acids as a function of time (based on contact time changes). Reactions were performed at 250 °C in a batch reactor. Oleic acid was used as substrate and 2.5 wt% of zeolite (relative to the substrate) was added as a catalyst to the reaction mixture. b) Selectivity towards branched fatty acids as a function of the unsaturated C18 conversion (based on contact time changes). Reactions were performed at 250 °C in a batch reactor. Oleic acid was used as substrate and 2.5 wt% of zeolite (relative to the substrate) was added as a catalyst to the reaction mixture.

Figure S2 Gas chromatogram of the hydrogenated and esterified reaction product after 6 hours at 250 °C with 2.5 wt% H-ZSM-5-12 as catalyst (stirring speed 600 rpm). Details about the gas chromatographic analysis can be found in the Experimental section (SI). 1) Solvent peak (noctane). 2) Methylpalmitate. 3) Branched C18:0 fatty acids. 4) Methylstearate. 5) Branched C18:0 lactones. 6) C18:0 lactone.

Figure S3 GPC chromatogram of the hydrogenated reaction product after 6 hours at 250 °C with 2.5 wt% H-ZSM-5-12 as catalyst (stirring speed 600 rpm). Details about the gel permeation chromatographic analysis can be found in the Experimental section (SI). 1) Trimer acids (C54). 2) Dimer acids (C36). 3) Monomeric acids (C16-C18). 4) External standard (octanoic acid).

Figure S4 Linearization of the reaction data yielding an observed (pseudo-)first order rate constant k.

Figure S5 Powder X-ray diffractograms of H-ZSM-5-12, H-ZSM-5-AT-AW before reaction (H-ZSM-5-AT-AW), after reaction (H-ZSM-5-AT-AW (spent)) and after regeneration for 5 hours at 500 °C (H-ZSM-5-AT-AW (regenerated)).

Figure S6 FT-IR spectra in the OH vibrational region of H-FER-9, H-ZSM-5-12 and H-ZSM-5-AT-AW after activation at 400 °C under vacuum (spectra collected at 150 °C).

Figure S7 Difference spectra of H-FER-9, H-ZSM-5-12 and H-ZSM-5-AT-AW showing the superficial sites holding the strongly adsorbed lutidine species (difference spectrum = spectrum before lutidine adsorption minus spectrum after lutidine desorption at 150 °C).

Figure S8 The observed (pseudo-)first order rate constant as a function of the Brønsted acidity measured with pyridine at 150 °C multiplied with V_{meso}. A guide to the eye for the ZSM-5 catalysts is added for clarity.

Figure S9 The observed (pseudo-)first order rate constant as a function of the Brønsted acidity measured with pyridine at 150 °C multiplied with Smeso. A guide to the eye for the ZSM-5 catalysts is added for clarity.

Extra tables

Table S1 Details of product composition after a reaction time of 6 hours.

BFA = branched fatty acid; AV = acid value; SV = saponification value; IV = iodine value; n.d. = not detected. ^a Duplicate of reaction ^b, samples were taken at 1 hour, 2 hours and 6 hours at reaction temperature instead of at 1 hour, 2 hours, 4 hours and 6 hours at reaction temperature. The catalyst of this duplicate reaction was recovered after reaction, washed with acetone and regenerated at 500 °C for 5 hours in an O_2 environment as described in the Experimental section (SI).

Table S2 Characterization of H-ZSM-5-AT-AW after reaction.

 P_{BAS} = Brønsted acid sites from pyridine adsorption. P_{LAS} = Lewis acid sites from pyridine adsorption. L_{BAS} = Brønsted acid sites from lutidine adsorption. n.m. = not measured. ^a Measured with TGA as described in the Experimental section (SI). ^b Catalyst recovered after reaction and washed with acetone as described in the Experimental section (SI)^c Catalyst recovered after reaction, washed with acetone and regenerated at 500 °C for 5 hours in an O2 environment as described in the Experimental section (SI).

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