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

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KEYWORDS

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ABSTRACT

Branched fatty acids are of great interest in the oleochemical industry for many high-end applications due to their interesting physicochemical properties. In the last decades, research focuses mainly on the use of Ferrierite (FER) as catalyst for the isomerization of fatty acids into these branched fatty acids. With the use of FER, high yields of branched fatty acids can be obtained. FER is however expensive and additives are necessary to obtain a high selectivity towards branched fatty acids. In this letter, we focus on the use of ZSM-5 - a much cheaper zeolite - which has been extensively studied in the past for other reactions. Five commercial ZSM-5 samples and one hierarchical ZSM-5 sample were tested for the isomerization of fatty acids into branched fatty acids. The results clearly show that the accessibility of Brønsted acid sites is of utmost importance for their catalytic activity. Thanks to the introduction of mesopores in the zeolite crystals of ZSM-5, creating a hierarchical zeolite, a superior catalyst was obtained with a multifold activity increase without compromising in branched fatty acid selectivity, capable of competing against the state-of-the-art FER zeolite.

INTRODUCTION

Saturated branched chain fatty acids (i.e. fatty acids containing a methyl or ethyl group on the aliphatic chain, usually isostearic acids) have shown to be of great interest for many applications like cosmetics, detergents, surfactants, fuel additives and lubricants. As such, they can act as a substitute for compounds originating from petroleum sources. Their potential can be attributed to their interesting physicochemical properties, as they show a low pour point and cloud point, good spreadability, oxidative, hydrolytic stability and biodegradability, and a high viscosity index. Nowadays, branched fatty acids are produced industrially, typically in low yields of around 20 %, as a side product of the dimerization of unsaturated fatty acids using acid clays such as Bentonite or Montmorillonite.[1–5]

In the last 25 years, efforts have been made to increase the yield of branched fatty acids, focusing mainly on using zeolites as catalysts in the so-called isomerization reaction of unsaturated fatty acids into unsaturated branched chain fatty acids. After a subsequent hydrogenation step, saturated branched chain fatty acids are obtained. Thanks to the zeolites' microporous character, oligomerization is retarded, leading to a higher selectivity towards the branched fatty acids. Different zeolite topologies have been tested so far (*e.g.* MOR, MFI, *BEA), but the last years research focusses mainly on Ferrierite (FER). This zeolite has shown to be a very promising candidate, with reported yields of >70 %. However, additives like water and triphenylphosphine (TPP) were required to obtain these results.[3,6,7]

More extensive research with FER by Wiedemann *et al*. has shown that the isomerization of fatty acids likely occurs via pore mouth catalysis, in analogy with the hydroisomerization of n-alkanes with zeolites.[8,9] Therefore, when purely microporous zeolites are applied, a large amount of the catalytically active sites are not accessible and thus inactive during the catalytic reaction. The presence of mesopores in the zeolite structure can partially overcome this problem by creating more pore mouths available for catalysis. This beneficial effect of the mesopores was already demonstrated by Zhang *et al*., who showed that Beta zeolites containing mesopores were more active during the isomerization of fatty acids to branched fatty acids.[10] Nevertheless, these mesoporous Beta were significantly less active than FER and researchers have merely been focusing on microporous zeolites ever since.

Hierarchical zeolites are zeolites that contain, on top of and interconnecting with a microporous network, an additional network consisting of meso- and/or macropores. They can be engineered using two main strategies, *i.e.* via (I) top-down methods which consist of creating mesopores by etching away parts of an already synthesized zeolite using acids (dealumination) or bases (desilication), and (II) bottom-up methods that allow the creation of the hierarchical system during zeolite synthesis. Here, the synthesis conditions need to be controlled precisely in order to obtain the desired hierarchical zeolite.[11–17] Very recently, Bolshakov *et al.* used a bottom-up technique to obtain a hierarchical FER and used it for the reaction discussed in this work. They showed that a more active catalyst was obtained without losing selectivity, clearly indicating the potential of hierarchical zeolites.[18]

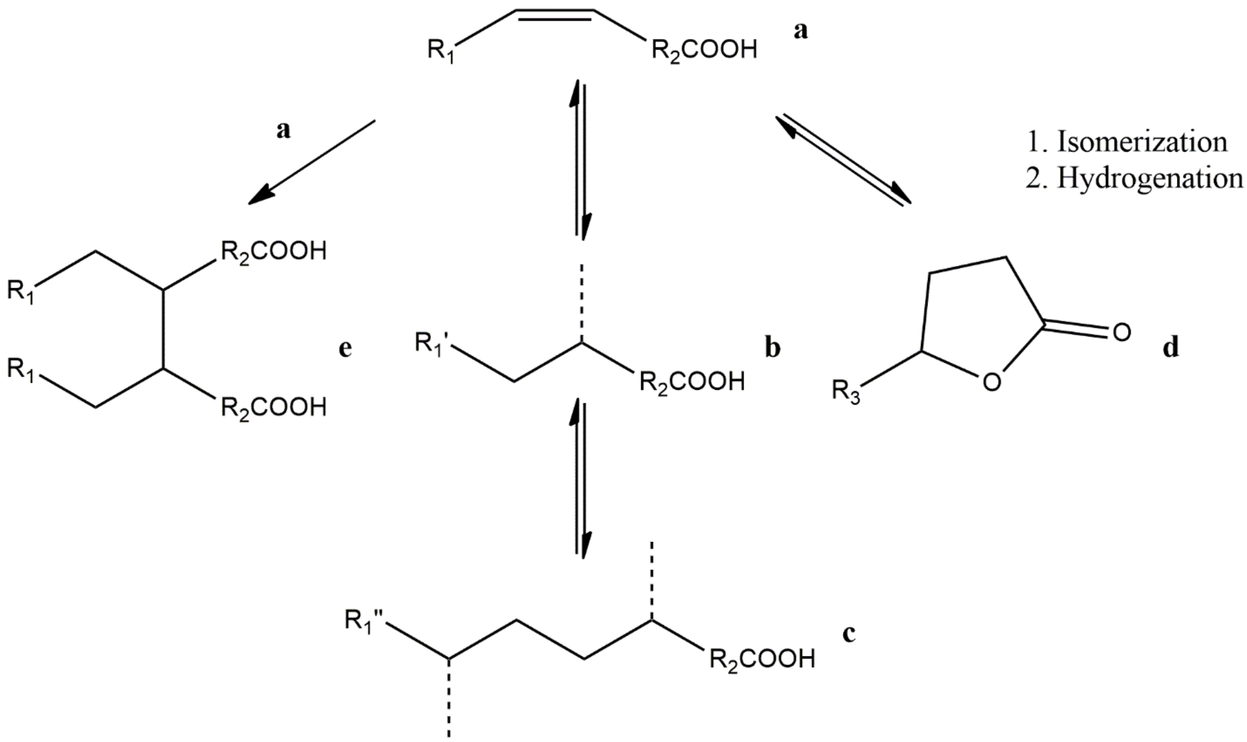
ZSM-5 (MFI topology) is a zeolite with intersecting straight (0.53 x 0.56 nm) and zig-zag (0.51 x 0.55 nm) 10-membered ring channels.[19] Thanks to its hydrothermal stability, unique pore structure and controlled (high) acidity, it is one of the most studied zeolites. Industrial scale applications include alkylation, isomerization, and cracking reactions.[20,21] On top of that, ZSM-5 has shown great potential in different biomass conversion reactions, is much cheaper compared to FER and available on a larger scale on the industrial market,[22–32] which makes it interesting from an economical point of view for the replacement of FER. Sarker *et al*. already used ZSM-5 as a catalyst for the isomerization of unsaturated fatty acids to unsaturated branched chain fatty acids, but found a lower activity and selectivity than FER.[7]

In this letter, the potential of ZSM-5 as a catalyst for the solventless isomerization of unsaturated fatty acids (here oleic acid) into unsaturated branched chain fatty acids will be investigated, thereby looking for an economically more attractive alternative for the current state-of-the-art system using FER in combination with additives. In addition, efforts were made to gain more insights in those zeolite characteristics responsible for the catalytic activity of the zeolite system.

RESULTS AND DISCUSSION

Five commercial ZSM-5 samples with different Si/Al ratios were tested as catalysts for the isomerization of unsaturated fatty acids into unsaturated branched chain fatty acids and compared with a commercial FER, used as reference material. The zeolites are denoted as H-ZSM-5-X and H-FER-X, with X the Si/Al ratio provided by the supplier. Characterization details of these samples can be found in **Table 1.** Experimental details can be found in the Supporting Information (SI). One commercial ZSM-5 sample was subjected to a series of post-synthetic treatments to obtain a hierarchical ZSM-5. Both its activity and selectivity are compared to those of the parent material. Thanks to a comprehensive product analysis using GC and GPC, as well as some typical parameters (*i.e.*, acid value (AV), saponification value (SV), iodine value (IV)), it is for the first time possible to study the effect of the hierarchization of the zeolite (*i.e.* the introduction of mesopores in the zeolite crystal via post-synthetic treatments) on the selectivity concerning both desired (b and c in **Scheme** 1) and undesired products (d and e in **Scheme 1**) in this type of reaction (at full mass balance). A simplified reaction scheme is given in **Scheme 1**.

Scheme 1 Proposed reaction scheme for the isomerization (and hydrogenation) of unsaturated fatty acids (a) to both desired (b and c) and undesired products (d and e) in the presence of a Brønsted acid zeolite. The dashed lines indicate a possible position of the methyl branch on the carbon chain.



a = unsaturated fatty acid; b = monobranched fatty acid; c = polybranched fatty acid; d = γ-lactone; e = oligomeric fatty acid.

Table 1 Characterization of ZSM-5 and FER samples.

Catalyst	Si/ Al	Acid sites at 150°C (µmol g^{-1})			L_{BAS}/ P_{BAS}	Surface area (m^2 g^{-1})		Pore volume (cm^3 g^{-1})		ASVF^b (mmol m^2 cm^3 g^{-3})	k (h^{-1})^b
		P_{BAS}	P_{LAS}	L_{BAS}		BET	S_{meso}	V_{micro}	V_{meso}		
H-ZSM-5-12	12	539	60	186	0.35	415	43	0.15	0.04	0.83	0.061
H-ZSM-5-15	15	272	111	n.m.	-	423	64	0.15	0.07	1.15	0.060
H-ZSM-5-25	25	275	43	n.m.	-	440	50	0.17	0.07	1.01	0.054
H-ZSM-5-40	40	177	40	n.m.	-	478	82	0.17	0.08	1.15	0.053
H-ZSM-5-140	140	53	7	n.m.	-	427	46	0.18	0.04	0.10	0.008
H-ZSM-5-AT-AW	9^a	326	111	306	0.94	473	110	0.15	0.16	5.71	0.325
H-FER-9	9	107	18	74	0.69	375	17	0.14	0.02	0.040	0.241

ASVF = Acid-Surface-Volume Factor, defined as the product of P_{BAS} with S_{meso} and V_{meso}. 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] Si/Al ratio measured with ICP. [b] Observed (pseudo-)first order rate constant, see SI and **Figure S4** in SI for more details on calculations.

Figure 1A and **Figure S1** (SI) show the results obtained during a 6 hours batch reaction performed at 250 °C at a stirring speed of 600 rpm with 2.5 wt% of catalyst (relative to the substrate) in the absence of solvent and additives. The reaction is considered to take place without any external diffusion limitations, as increasing the stirring from 600 rpm to 900 rpm does not affect the conversion rate (**Table** S1). Samples were taken during the reaction to monitor the reaction characteristics as a function of time. After 6 hours reaction, all commercial ZSM-5 samples, except H-ZSM-5-140, show a similar activity (≈ 40 % conversion) and selectivity (≈ 50 % towards branched fatty acids). More analytical details regarding the composition of the crude product after 6 hours are given in **Table S1** (SI). The low branching selectivity obtained with ZSM-5 can be explained by the large amount of side-products present in the crude reaction mixture. More specifically, the amount of oligomers is high, but also a significant amount of lactones (both linear and branched) is formed. Interestingly, these zeolites all show a similar selectivity regarding both the desired and undesired products, which is also reflected in the AV, SV and IV. In contrast, H-ZSM-5-140 is considerably less active than the other commercial samples. No lactones were detected, but still more than 6 wt% of oligomers were found in the crude reaction product. The AV, a measure for the amount of carboxylic acids present in the sample, is also significantly higher for this sample. This indicates that the more active ZSM-5 samples enabled more cracking to smaller alkanes and fatty acids than H-ZSM-5-140. When the reaction temperature is decreased or increased, the activity of the zeolite is affected as expected (**Table S1**). The higher the reaction temperature, the more of the substrate is converted in agreement with Arrhenius, and the more branched fatty acids and lactones are formed. Moreover, the AV is lower for higher reaction temperatures, which is indicative of slightly more carbon skeleton cracking. In contrast to all commercial ZSM-5 samples, FER has shown to be more than twice as active per amount of catalyst, with a similar selectivity to branched fatty acids at a similar conversion, and lower formation of oligomers. As such, yields of branched fatty acids up to three times higher were obtained compared to those obtained with ZSM-5 (for the same 6 hours reaction time). The observed yields for ZSM-5 are even lower than the ones reported in literature for Beta and Mordenite. Comparison with previous literature is however difficult and has to be done with care as often different reaction conditions and/or additives were used.[5,7,33,34]

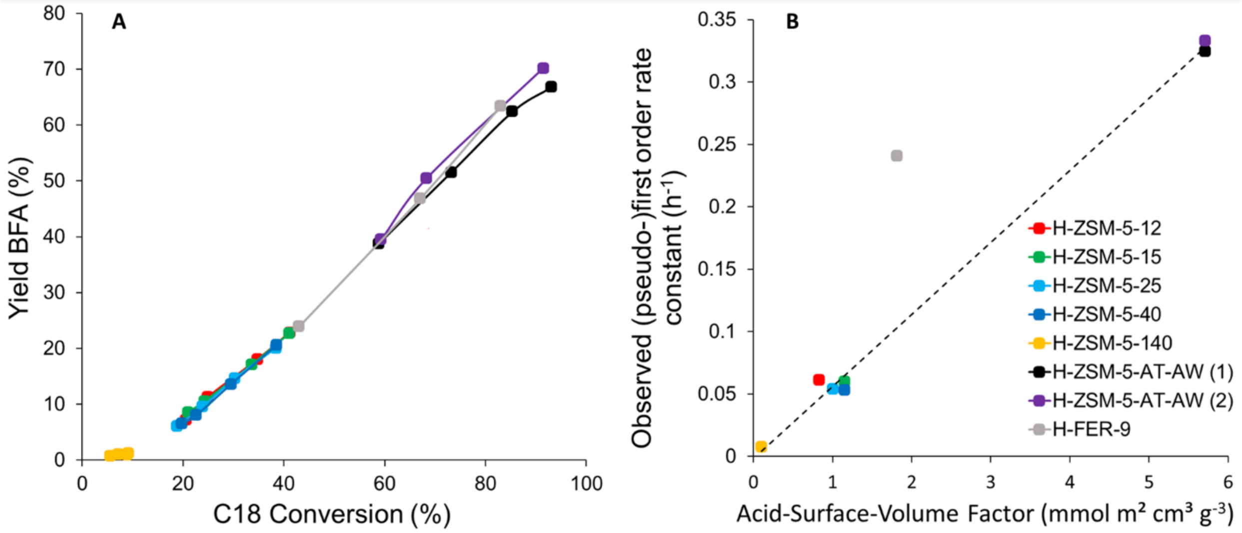


Figure 1 a) Yield of branched fatty acids as a function of the unsaturated C18 conversion (based on contact time changes). Reactions were performed at 250 °C in a batch reactor. Oleic acid was used as substrate, and 2.5 wt% of zeolite (relative to the substrate) was added as a catalyst to the reaction mixture. The reaction with H-ZSM-5-AT-AW (2) is a duplicate of the reaction with H-ZSM-5-AT-AW (1). An example of a GC and GPC chromatogram used to calculate the conversion and yield can be found in the SI (**Figure S2** and **Figure S3**). b) The observed (pseudo-)first order rate constant as a function of the Acid-Surface-Volume Factor ASVF. A guide to the eye for the ZSM-5 catalysts is added for clarity.

To interpret the obtained results properly and identify the zeolite characteristics responsible for its activity, a basic kinetic study was performed on the obtained results. A (pseudo-)first order reaction is considered here, as it can be rationalized based on the reaction mechanism (**Scheme 1**). One can see clearly from this scheme that the different products are formed in multiple parallel reactions. Monomer and oligomer compounds are formed during monomolecular and bimolecular reactions, respectively. The former dominantly takes place, as oligomers only account for about 10 wt% of the final reaction mixture. A linearization of the obtained data was made (see

Experimental section in SI for details) so that an observed (pseudo-)first order rate constant k (units: h^{-1}), which is a measure for the activity of the zeolite, could be defined for each commercial zeolite (**Figure S4** (SI) and **Table 1**). All commercial samples, except H-ZSM-5-140, have a similar observed rate constant, which is about five-fold lower than the one obtained with FER.

The similar results obtained with the commercial ZSM-5 samples, except H-ZSM-5-140, might be surprising as the Si/Al ratios and the Brønsted acidity, measured with pyridine FT-IR, are significantly different. Moreover, as the Brønsted acidity follows a more logical trend, *i.e.* the P_{BAS} is the highest for the lowest Si/Al ratio and vice versa, one would expect that the activity follows a similar trend. The Brønsted acid sites (BAS) are accordingly the catalytically active sites during the isomerization reaction. The only exception here is again H-ZSM-5-140, which has a low amount of P_{BAS} that is indeed reflected in a low activity of the zeolite.

To explain the observed lack in activity difference, a closer look is taken at the porosity characteristics of the different zeolites, measured with N_2-physisorption (**Table 1**). All commercial samples, except H-ZSM-5-12 and H-ZSM-5-140, show a similar mesoporosity. H-ZSM-5-12 and H-ZSM-5-140 are less mesoporous. It is expected that the accessibility of the BAS plays a key role during the reaction. Due to the reagent's bulkiness, there is expected that a significant amount of the P_{BAS} is not accessible for the reagent. The presence of mesopores can help here, as they facilitate the diffusion of reagents and products to and from the acid sites. Moreover, by introducing mesoporosity in a zeolite crystal, the more outer surface is present, and thus more accessible BAS. To test this hypothesis, a top-down hierarchization method, based on the research performed by Verboekend *et al.*,[35] was performed on H-ZSM-5-12 (selected for its high Brønsted acidity; see SI for experimental details). The hierarchical zeolite is denoted as H-ZSM-5-AT-AW and its characterization details can be found in **Table 1**. Powder-XRD was measured both on the parent and the hierarchical zeolite (**Figure S5**), showing that the ZSM-5 crystal structure is largely retained during hierarchization.

It is clear from **Table 1** that during hierarchization, a significant amount of P_{BAS} was lost, which was linked to the removal of both terminal and framework Al-OH species (**Figure S6** in SI). At the same time, an increase in external silanols was detected, while the amount of extra-framework Al (EFAl) remained unchanged. The mesoporosity increased strongly, yielding a zeolite with a four times larger mesopore surface area than its parent zeolite, without a major loss in microporosity.

H-ZSM-5-AT-AW was subsequently tested twice in the same way as the five commercial ZSM-5 samples (**Figure 1A**, **Figure S1**, and **Table S1**). H-ZSM-5-AT-AW is clearly more active than its parent zeolite, as, after 1 hour reaction, three times more conversion was achieved. After 6 hours, a conversion of >90 % was observed. Interestingly, the observed activity is even higher than the one observed with the state-of-the-art FER catalyst. This is also reflected in the calculated (pseudo-)first order rate constant (**Table 1**), which is more than five times higher than the one of H-ZSM-5-12 and about 1.3 times higher than the one of H-FER-9. The yield of branched fatty acids after 1 hour is almost double the yield of branched fatty acids obtained with the parent zeolite after 6 hours. At the end of the reaction, an average yield of branched fatty acids of almost 69 % was detected, slightly higher than the one obtained with FER.

The presence of mesopores might harm the reaction's selectivity as the mesopores are large enough to accommodate oligomerization if any catalytically active sites are present. FT-IR has shown that for H-ZSM-5-AT-AW not only the framework and terminal Al-OH species are the predominant acid sites, as is the case for H-ZSM-5-12, but also external silanols and EFAl take on this role (**Figure S7**). This might explain the higher amount of oligomers formed with this sample

(**Table S1**). Also, AV is somewhat lower indicative for slightly more extensive cracking. In contrast, the amount of lactones (branched and non-branched) is lower, making the branched fatty acid product more attractive towards high-end applications such as cosmetics. Nevertheless, a selectivity towards branched fatty acids of >70 % is reached at a conversion of >90 %. In general, the branched fatty acid selectivity is unaltered, as can also be depicted in **Figure 1A** and **Figure S1**. Thus, it is clear that by performing a top-down method on one of the commercial zeolites, a superior hierarchical zeolite was obtained, which stands out in activity without loss of selectivity towards the branched fatty acids. This is despite a material loss of about 60 wt% during the hierarchization procedure, which can be compensated thanks to the much lower cost price of ZSM-5. Moreover, characterization of the spent and regenerated H-ZSM-5-AT-AW (**Figure S5** and **Table S2**, see Experimental section in SI for details on zeolite regeneration) has shown that the zeolite is stable during reaction. The zeolite structure remains intact and only a limited amount of crystallinity is lost during regeneration, as is clear from XRD measurements (**Figure S5**). A significant amount of cokes is formed (12.9 wt% as measured with TGA), causing a large amount of the pores of the zeolite to get blocked (**Table S2**). Regeneration of the catalyst for 5 hours at 500 °C under O_2 removes most of cokes, and as such, a large amount of the initial pore volume and surface area is recovered. The amount of acid sites is slightly lower after regeneration when compared to the fresh catalyst, which can be explained by some minor dealumination and the presence of a small amount of cokes after regeneration. Still, the relative amount of accessible sites remains very high, indicating that the zeolite has great potential for re-use.

To rationalize the observed phenomena and thus check the before mentioned hypothesis that the accessibility of the acid sites is a key parameter in the investigated reaction, a closer look is first taken at the correlation between the observed (pseudo-)first order rate constant and the

Brønsted acidity multiplied with one or more mesoporosity characteristics (**Figure 1B**, **Figure S8** and **Figure S9**). By plotting the observed (pseudo-)first order rate constant against the Brønsted acidity multiplied with only V_{meso} (**Figure S8**) or S_{meso} (**Figure S9**), a positive trend already is visible, which is more pronounced when the Brønsted acidity is multiplied with V_{meso}. However, there is no perfect fit, indicating that these combinations of zeolite characteristics aren't sufficient to perfectly rationalize the similar activity of the different non post-synthetically treated ZSM-5 samples (except H-ZSM-5-140). The best correlation is obtained when the Brønsted acidity is multiplied with both S_{meso} and V_{meso} (**Figure 1B**), clearly indicating the importance of the mesoporous character of the zeolites. The higher S_{meso}, the more pore mouths at the external surface and as such the more catalytically active sites are available. The higher V_{meso}, the lower the intracrystalline diffusion limitations creating a more efficient intracrystalline molecular transport system for reagents and products. The result of this multiplication is defined as a new parameter, the 'Acid-Surface-Volume Factor' (ASVF), and can be found in **Table 1**. Using the ASVF, the hypothesis proposing that the activity of a zeolite not only depends on the amount of BAS, but also on their accessibility, gets a first confirmation. All commercial samples, except H-ZSM-5-140, have a similar ASVF, which results in a similar activity. However, the best example in this paper is H-ZSM-5-AT-AW, which doesn't show the highest amount of BAS, but is by far the most active one. As this zeolite is the most mesoporous of the ones tested, it has the highest ASVF indicating it probably has the most accessible BAS. Lutidine FT-IR measurements indeed confirmed this hypothesis (L_{BAS} in **Table 1**). From all acid sites of H-ZSM-5-12 measured with pyridine FT-IR, only 35 % are reached by lutidine. In contrast, this is the case for 94 % of the BAS of H-ZSM-5-AT-AW measured with pyridine FT-IR, indicating that hierarchization led to a three-fold increase in accessible acid sites. When comparing to FER, we see that this zeolite also contains a high amount of accessible BAS (69 %, **Table 1**). This relatively high amount of accessible acid sites might explain its high activity. Nevertheless, FER contains in absolute numbers far less BAS when compared to the ZSM-5 samples. Further research is necessary to explain the activity difference of the BAS between these different zeolite topologies. Most likely, ZSM-5 contains a lot of cokes, blocking a lot of acid sites, and therefore is deactivated more pronouncedly when compared to FER, although differences in adsorption enthalpies of the sites cannot be ruled out.

CONCLUSIONS

In summary, five commercial ZSM-5 catalysts and one hierarchical ZSM-5 catalyst were tested for their suitability in the isomerization of unsaturated fatty acids into unsaturated branched chain fatty acids (solvent and additives free) and compared with FER. Our data have shown that ZSM-5 is, next to FER, a promising catalyst. However, hierarchization is necessary to boost the activity of ZSM-5, creating a superior catalyst without loss of selectivity towards the branched fatty acids which on top of that remains stable during reaction. Hierarchization via top-down methods involves a loss of material. The much lower cost price of ZSM-5 can compensate for this material loss, causing it to compete against the more expensive FER, while fewer lactones have been formed. By comparing multiple ZSM-5 samples via the Acid-Surface-Volume Factor ASVF and lutidine FT-IR measurements, it is clear that accessibility of the catalytically active Brønsted acid sites is a key factor in this type of catalysis due to the bulkiness of the reagent. By introducing extra mesoporosity in the zeolite crystal via hierarchization, more Brønsted acid sites were made accessible for the reagent by increasing the accessible surface containing micropores and better diffusion of reagents and products via the mesopores to these micropores. As such, the activity of the zeolite was strongly improved. The next step in future research for this isomerization type should focus on selective post-synthetic treatments with less material loss and reducing oligomerization.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge.

Supporting information: Fast and selective solvent-free branching of unsaturated fatty acids with hierarchical ZSM-5_SI (PDF)

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SYNOPSIS

This letter discusses the solvent and additives free, high-selective valorization of fatty acids using cheap post-synthetically treated zeolites, yielding a high-end oleochemical product.

TABLE OF CONTENTS