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Skeletal isomerization of unsaturated fatty acids: the role of mesopores in HBeta zeolites

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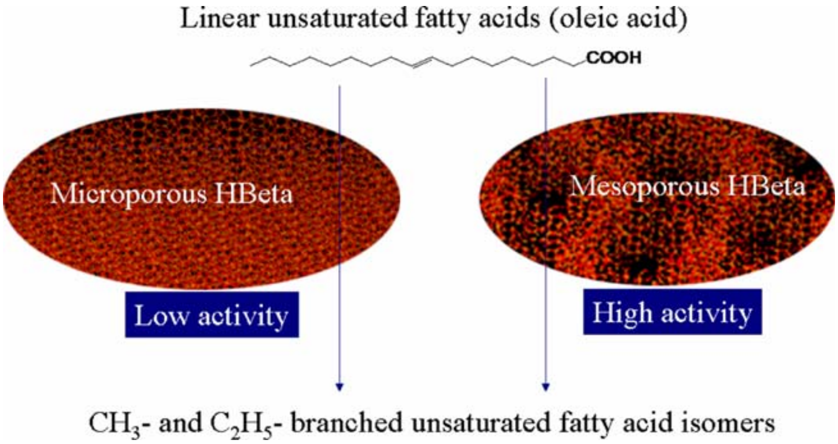
Fatty acids are an important class of feedstock for the production of many chemicals, such as surfactants, lubricants, biodiesel, etc. Fatty acids derived from vegetable oils and animal fats typically have linear aliphatic chain, and are therefore called linear fatty acids. Products based on branched fatty acids offer many attractive properties over those based on linear ones, e.g. low melting points and low viscosity. Catalytic skeletal isomerization of linear fatty acids to branched ones is particularly important for industrial production of branched fatty acids. This paper for the first time reveals the key properties of the most active zeolite catalysts for this reaction. Among many solid acid catalysts studied, acidic Beta zeolites were found to stand out in their performance for the reaction. In this work, several acidic Beta zeolites (HBeta) from commercial sources were evaluated for their performance in fatty acid skeletal isomerization. The activities of these zeolites under identical test conditions were found to vary in a wide range, even with similar silica to alumina molar ratios (SAR). A combination of characterization techniques was used to systematically investigate the most critical property of the zeolites responsible for the observed superior activity. All the HBeta zeolites in this study have high crystallinity. Pore size distribution of the zeolites was identified to be the most important factor that unambiguously correlates the catalyst activity to the amount of mesopores in the HBeta zeolites.



KEY WORDS: isomerization; fatty acid; branched; zeolite; acidity; mesopore.

1. Introduction

Fatty acids are aliphatic carboxylic acids of typically straight hydrocarbon chains having an even number of carbons, most commonly with 12–24 carbons. The degree of unsaturation and the carbon chain length of a fatty acid are dependent on the triglyceride source from which it is derived.

Linear fatty acids have been widely used as a raw material for surfactant and detergent applications. Mono-alkyl esters of fatty acids are particularly important derivatives of fatty acids. Fatty acid methyl ester (FAME), for example, is a well known

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economically competitive biodiesel as an alternative fuel [1].

In general, the intrinsic chemical and physical properties of fatty acids or their esters are inherited in the final products. A critical chemical property is their stability against aerial oxidation at ambient conditions, which is directly linked to product shelf life. Saturated fatty chains are stable while unsaturated fatty chains are prone to oxidation in air. On the other hand, a critical physical property for products of fatty molecules is their melting points. Saturated molecules have considerably higher melting points than those unsaturated ones. Therefore, for commercial applications, product formulation has often been practiced to balance between the desired chemical stability and the desired physical properties [2]. But the formulation approach is limited and often a sacrifice has to be made in the performance characteristics of the final products.

For biodiesel applications, the aliphatic structure of fatty esters determines the fuel properties, e.g. oxidative stability, viscosity, cetane number, cold flow properties, etc. In addition to poor oxidative stability, unsaturation in biodiesel fatty chain causes dramatic decrease in cetane numbers, which is a prime indicator of fuel quality in the realm of diesel engines. On the other hand, the cold flow properties are also an important measure of biodiesel applicability. They are associated with cloud points and pour points [3]. Cloud point is defined as the temperature at which a liquid fatty material becomes cloudy due to the formation of crystals and solidification of saturates. Pour point is defined as the lowest temperature at which the liquid material still flows. Biodiesel comprised of saturated fatty chains has typically poor cold flow properties [1].

A highly promising solution for fatty acids and derivatives, including biodiesel, to resist oxidation by air and to maintain the desired liquidity relies on the fact that saturated branched fatty acids or esters have considerably lower melting point and higher oxidative stability than do the corresponding straight chain acids or esters [4].

Although branched fatty acids can be found in nature, they do not exist in appreciable quantities and are thus not a common raw material for either surfactant or biodiesel production. Natural branched fatty acids are commonly short chain isomers [5]. A few branched long chain fatty acids, 14-methyl-6(*Z*)-pentadecenoic acid, 16-methyl-6(*Z*)-heptadecenoic acid, 16-methyl-8(*Z*)-heptadecenoic acid, were recently identified in several marine organisms [6, 7]. Biosynthesis of iso-fatty acids from a few branched chain amino acids was also reported [8].

The current available branched monomeric fatty acids are limited to byproducts of the dimer acid production process starting from unsaturated fatty acids [9]. Acidic clays are used as catalysts in the acid dimerization process [10–12]. With the clay catalysts operated at 240–260 °C, the yield of the monomeric branched byproduct is near or below 20%. The branched-chain acids have the same number of carbon atoms as the parent acids in the feed. From tall oil fatty acids, methyl branching predominates with a branch methyl group to acid ratio of about 1.3 [13].

Direct catalytic isomerization of fatty acids or esters represents an emerging technology that converts linear fatty molecules to branched ones. Although it has been a common practice in the petrochemical industry to isomerize straight chain hydrocarbons to branched ones for octane number improvement, the task of converting straight chain fatty acids or corresponding alkyl esters to branched ones has turned out to be much more challenging. This observation is not surprising because carboxylic acids have been recognized as a poison in the isomerization of hydrocarbons [14]. Therefore, published work on the skeletal isomerization of linear fatty acids and esters has so far appeared only in a few patent literature [15, 16].

In a previous publication, we reported the superior performance of an acidic Beta zeolite over that of several other common types of zeolites, including HZSM-5 and HMor [4]. A combination of the large pore diameter and the three dimensional structure of Beta is believed to be the major reason. This paper, for the first time in the literature, reports results obtained with HBeta zeolites for the skeletal isomerization of unsaturated fatty acids, and elucidates the decisive structural factor of HBeta zeolites responsible for the skeletal isomerization of unsaturated fatty acids. Comparison to other types of zeolites, which have been found to be less active than HBeta, is outside the scope of this paper.

2. Experimental section

An oleic acid obtained from Uniqema (Priolene 6204) was used as a fatty acid feed. It contains a typical mixture of fatty acids with about 80 wt% unsaturated C_{18} carboxylic acid (n-$C_{18}{}^{1}$) and the rest includes stearic acid (saturated C_{18} acid) and other fatty acids of 12, 14, 16 and 20 carbons in the aliphatic chains.

Commercial Beta zeolite powder catalysts received from Sinopec, Sud-Chemie, TOSOH, Tricat, and Zeolyst in NH_4^+ or H^+ form, all with low Na^+ content, were calcined at 550 °C in air for 5 h before catalytic evaluation in a high throughput batch reactor system having individual magnetic stirring. The calcination removes impurities, such as organic residues and moisture from the samples and converts NH_4^+ form Beta into H^+ form Beta (HBeta). The reactors are glass vials circularly fixed into an aluminum block inside a conventional autoclave. In each vial, 0.03 g of catalyst and 1 g of oleic acid were loaded. The reaction was conducted under a 100 psig N_2 headspace. The reactors were heated to 250 °C with stirring within 30 min and maintained for 5 h. Since the oleic acid has a boiling point of 360 °C at atmospheric pressure, vaporization of the feed under the reaction conditions is dismissible. Very little condensation of product was observed after reaction, indicating cross contamination of products from different vials was trivial. Liquid product from each reactor was separated from the catalyst by filtration and mixed with a fatty acid analysis reagent, METH-PREP I from Alltech (5% (*m*-trifluoromethylphenyl)-trimethylammonium hydroxide in H_2O) for analysis with GC. Gas phase after reaction was directly injected into GC for analysis. The GC was equipped with a FID detector and a 30 m DB-1 capillary column.

Isomerization mentioned in this work all refers to skeletal isomerization and double bond migration is not considered as a contribution to the conversion of the linear $C_{18}{}^1$ acid. Decarboxylation and cracking were not significant under the reaction conditions. In the gas phase, trace amount (<0.1 wt%) of carbon monoxide was the major product. Hydrocarbons in the liquid product from cracking were less than 1 wt%. As to polymerization, it should be noted that the GC analysis could not detect heavy compounds in the liquid product, such as dimer and trimer acids which were usually the bottom cut of a vacuum distillation. For the cases discussed here, the total weight of such oligermers was less than 3 wt% of the total product. Therefore, the absence of the oligomers from GC analysis does not affect the measured distribution of the fatty acid products. Due to the limited amount of byproducts (mainly lactone), the isomerization selectivity from GC analysis is in the range of 55–80% and generally increases with conversion, but an accurate number can only be obtained from the analysis of distilled products.

To simplify the reactivity measurement with GC method, the following equations are used to define conversion, isomerization selectivity to branched fatty acid (i-$C_{18}{}^1$) and yield of branched isomers:

$$n-\mathrm{C}_{18}^{1}\text{conversion (wt\%)} = \frac{\mathrm{n}-C_{18}^{1}(\text{in feed})-n-\mathrm{C}_{18}^{1}(\text{in product})}{n-\mathrm{C}_{18}^{1}(\text{in feed})}\times 100$$

$$i-\mathrm{C}_{18}^{1}\text{selectivity (wt\%)} = \frac{i-\mathrm{C}_{18}^{1}(\text{in product})-i-\mathrm{C}_{18}^{1}(\text{in feed})}{n-\mathrm{C}_{18}^{1}(\text{in feed})-n-\mathrm{C}_{18}^{1}(\text{in product})}\times 100$$

$$i-\mathrm{C}_{18}^{1}\text{yield (wt\%)} = n-\mathrm{C}_{18}^{1}\text{conversion}\times i-\mathrm{C}_{18}^{1}\text{selectivity}\times 100$$

The acidic catalysts used for oleic acid isomerization do little to the saturated fatty acid under the reaction conditions. Therefore, saturated acids did not appear in the equations above.

A highly ordered crystalline hexagonal mesoporous aluminosilicate (MAS-5) was synthesized in this laboratory following a procedure similar to that described by Xiao and colleagues [17]. A proton form MAS-5 (HMAS-5) was prepared by ion exchange of Na^+ for $NH_4{}^+$ from the Na^+-MAS-5 mesoporous zeolite, followed by drying and calcination in air at 500 °C for 2 h. This HMAS-5 (SAR 50) was tested in a conventional 135 mL autoclave reactor with mechanical stirring. Due to its high SAR, a relatively large amount of the catalyst was used: (oleic acid)/HMAS-5 weight ratio = 10/1. The performance of this catalyst was compared with that of a commercial HBeta zeolite in the same reactor under identical conditions.

XRD patterns were recorded at 20 °C on an X-ray diffractometer (Philips, PW-1700) with a scintillation counter and a graphite mono-chromator attachment, utilizing Ni-filtered CuKα radiation (30 kV, 15 mA) with a scanning speed of 1 ° (2θ)/min. The morphology of the crystalline phase was examined using a scanning electron microscope (Hitachi, X-650) after coating with an Au-Pd evaporated film.

Temperature programmed desorption (TPD) of ammonia was used for acidity measurement. The measurement was conducted on a Micromeritics Autochem 2910 system. A pretreatment was done on all samples by calcination at 500 °C for 1 h in a helium flow of 50 mL/min. Adsorption of ammonia was carried out at 100 °C for 1 h followed by purging under a helium flow of 50 mL/min for 1 h at the same temperature. Desorption started from room temperature with a temperature ramp of 10 °C/min to 700 °C. Desorbed species were monitored with a calibrated thermoconductivity detector (TCD) as well as a mass spectrometer.

Nitrogen adsorption for pore size distribution measurement was done on a Micromeritics ASAP 2010. All samples were calcined at 500 °C under vacuum before measurement.

3. Results

3.1. *Catalytic activities of different HBeta catalysts for oleic acid isomerization*

The HBeta catalysts studied in this work are grouped according to their silica/alumina ratio (SAR). Typically a lower SAR value is associated with a higher acid site density in a zeolite. The first group of four HBeta catalysts has a SAR value of near 25. They are denoted as HB-22, HB-25, HB-27, and HB-28 and their activities are shown in figure 1. In the rest of this paper, HB-value is used where HB stands for a HBeta zeolite and the value correspond to a SAR value. For example, HB-27 stands for HBeta zeolite with a SAR value of 27. The second group consists of three catalysts with higher SAR values at 37, 45, and 50 and they are denoted as HB-37, HB-45, and HB-50, respectively (figure 1).

As shown in figure 1, the HB-27 stands out with the highest catalytic activity among all catalysts, presenting an n-$C_{18}{}^1$ conversion of 40%. Although with a very similar SAR, the HB-28 has the lowest activity in the

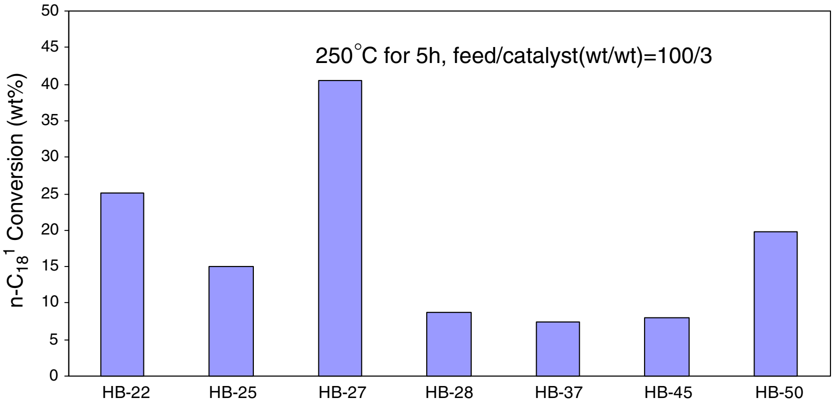

Figure 1. High throughput testing of HBeta from different sources.

first group. The conversion of n-C_{18}^{1} fatty acid on the HB-27 is about 5 times that on the HB-28. The HB-22 is the second most active catalyst among this group. Overall, there is no apparent correlation between the catalyst activities and their SAR values in this group.

The HB-50 is the most active one in the second group, and is even more active than the two catalysts, HB-25 and HB-28, in the first group. The activities of the HB-37 and HB-45 are similar and close to that of the HB-28 in the first group. The activities of these catalysts were confirmed for the same reaction in a conventional autoclave reactor (135 mL); the trend among these catalysts was consistent with the results from the high throughput reactors.

Separately, the catalytic performance of a mesoporous Beta zeolite, HMAS-5, of SAR 50 was tested in a 135 ml autoclave reactor. The results are shown in table 1 and compared with the performance results of HB-22 that was tested under the identical conditions. The conditions were controlled so that the conversions are above 50% with the fresh catalysts to make assessment of regenerated catalyst meaningful. As shown in the table 1, the fresh HMAS-5 is slightly more active than the HB-22, although its theoretical acid site density is less than half of that of the HB-22. Prior to the evaluation of the activity of a used catalyst, the used catalyst after filtration from the first use was washed with acetone and subsequently dried at 110 °C. It was then loaded into the reactor for evaluation again with a fresh feed under the same conditions as for the fresh catalyst. After the first use and the acetone wash, the HMAS-5 lost about 27% of its original activity, while the HB-22 lost 61% (table 1). Evidently, the mesoporous zeolite deactivated much less than the HB-22.

Table 1
Comparison of HMAS-5 and HB-22

Catalyst	C_{18}^{1} conversion (wt%)	
	Fresh catalyst	Used catalyst, washed
HMAS-5 (SAR 50)	60	44
HB-22	54	21

Reaction conditions: 250 °C, 5 h, feed/catalyst(wt/wt) = 10/1.

3.2. Catalyst characterization

Several catalyst samples were selected to represent those in the two groups for full characterizations. They were pure zeolite powder without binder and other support.

3.3. SEM characterization

SEM images of the HB-27 (a highly active catalyst) and the HB-28 (a poor catalyst) from the first group of zeolites are shown in figure 2A and B. Both samples consisted of irregular shape of zeolite grains with size from 0.5 μm to 2 μm. These grains appear to be aggregates of 100 nm zeolite crystals. No distinction in particle size could be concluded from the SEM characterization between these two samples.

3.4. XRD analysis of the HB-27 and the HB-28

These two catalysts from the first group were also characterized with XRD for their crystallinity. Both samples showed characteristics of typical Beta [18]. Little difference could be found between their XRD patterns (figure 3), indicating that they have similar crystallinity.

3.5. Ammonia TPD

From NH_3-TPD, only ammonia and water were observed as desorbed species. Since the samples were treated at 500 °C in helium flow before ammonia adsorption at 100 °C, the amount of water coming off the sample during desorption was so small that no attempt was made to correct the NH_3 desorption profile by taking into account of the water signal from the TCD response. The TCD signals for five samples were plotted again desorption temperature in figure 4. Two major

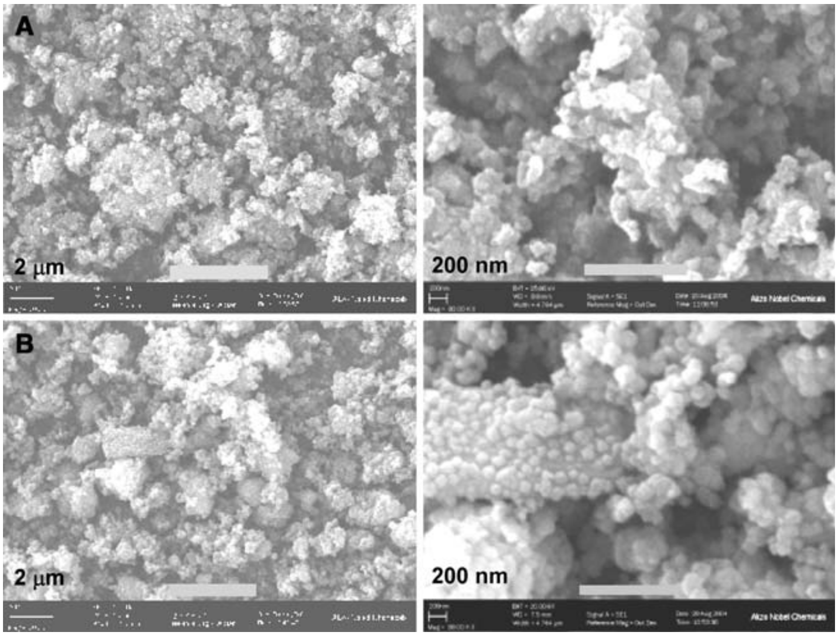

Figure 2. (A) SEM images of the HB-27 and (B) SEM images of the HB-28.

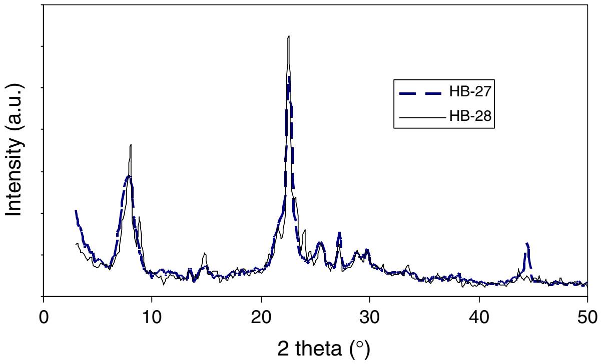

Figure 3. XRD patterns of HBeta-T(SAR 27) and HBeta-R(SAR 28).

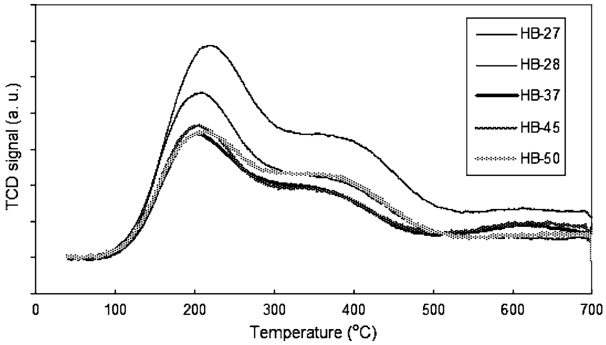

Figure 4. NH_3-TPD of different Beta zeolites.

broad peaks were observed with maximal intensity at temperatures of about 215 °C and 380 °C, respectively. The amounts of desorbed ammonia from these five samples, as shown in table 2, are in the following order: HB-27 $\gg$ HB-28 > HB-50 > HB-45 $\cong$ HB-37. For the HB-50 and the HB-45, a small broad peak above 600 °C was observed. Signal from mass spectrometer (MS) indicated that it was from water desorption, which may be formed from the dehydroxylation of hydroxyl groups from the zeolite at the high temperature. The theoretical amount of acid sites in table 2 was calculated based on their SAR values. The effect of the de-hydroxylation on the calculation of ammonia desorption was corrected by selecting a right baseline end point during area integration. The numbers in Table 2 were obtained after the correction.

Table 2
Total amount of ammonia desorbed from different Beta during NH_3-TPD

Catalyst	Total NH_3 desorbed mL/g STP	Total acid sites mmol/g	Theoretical amount of acid sites (mmol/g)
HB-27	42.18	1.88	1.15
HB-28	29.73	1.33	1.11
HB-37	25.29	1.13	0.85
HB-45	25.96	1.16	0.71
HB-50	27.14	1.21	0.64

3.6. *Pore size measurement with nitrogen adsorption*

Nitrogen adsorption experiments showed that the four selected samples in figure 5 contained a large amount of micropores with diameter less than 10 Å. This is typical for Beta type zeolites. The figure also reveals that there are significantly more mesopores in the HB-27 and the HB-50 than in the HB-28 and HB-37.

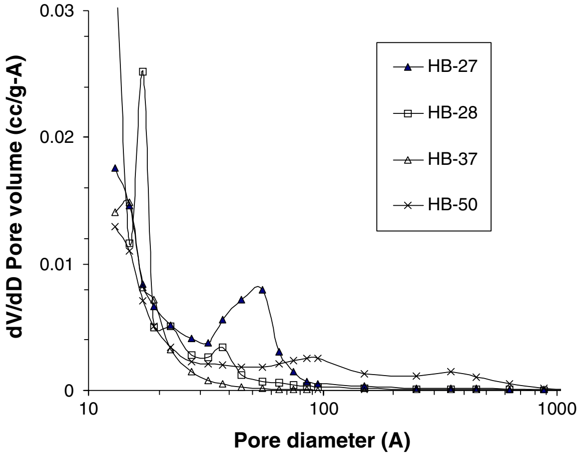

Figure 5. Pore volume plots of different Beta zeolites.

The mesopores in the HB-27 have diameters around 50 Å. The pore size distribution for the mesopore in the HB-50 is broad. The synthesized HMAS-5 zeolite (SAR 50) contained both micropores and mesopores. Most strikingly, these mesopores are narrowly distributed at about 25 Å, as shown in figure 6.

The volumes for pores with diameters larger than 20 Å and the BET surface areas of the four Beta zeolites and the HMAS-5 are listed in table 3. Not only does the HMAS-5 have the highest surface area, but also it has the largest pore volume. The pore volumes of the four Beta zeolites have the following order: HB-50 > HB-27 > HB-28 > HB-37.

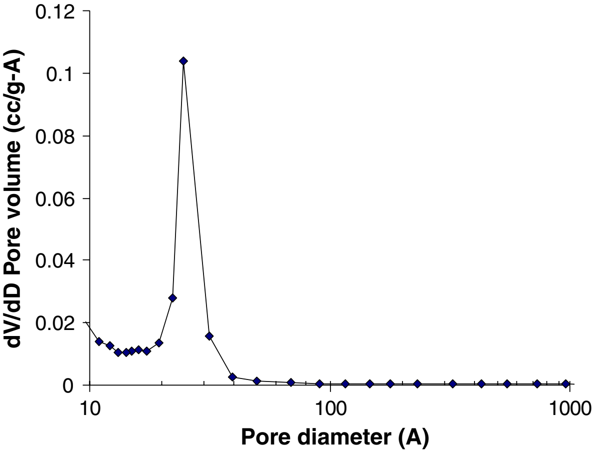

Figure 6. Pore volume plot of synthetic mesoporous zeolite HMAS-5.

Table 3
Total volume of pores with diameter larger than 20 Å

Catalyst	Pore volume for pore $d > 20$ Å mL/g	BET surface area m^2/g
HB-27	0.46	618
HB- 28	0.18	479
HB- 37	0.05	552
HB- 50	0.89	635
HMAS-5(SAR 50)	1.14	907

4. Discussion

While the skeletal isomerization of linear alkanes to branched ones readily takes place over many solid acid catalysts [19–21], the isomerization of fatty acids or esters was found to be particularly challenging [4]. Most solid acids failed to produce branched products from fatty acid feed because of the strong inhibiting effect of the carboxylate group that weakens the acidity of most encountered catalyst surfaces. Acidic clays have been used for the conversion of fatty acids, but mainly to produce dimer acids as an additive for resin applications [9]. Only a few patent literatures are available that discloses the use of zeolites of intermediate pore/channel size for the isomerization of unsaturated fatty acids. It is likely that the zeolites surface, due to their hydrophobicity, favors the aliphatic part of a fatty acid molecule over the carboxylic acid group. The strong hydrophobocity could eliminate or ease the poisoning effect of carboxylic effect to acid sites. In a previous study, we found that zeolite HBeta was a particularly effective catalyst for this reaction among several types of zeolites, including HZSM-5, HMor, and HY. The results in this study reveal the essential properties of a single type of zeolite, HBeta, but with structural differences.

The difference in catalytic performance among the HBeta zeolites of similar SARs for the isomerization of fatty acids and fatty esters was dramatically large. Several properties, particle or crystal size, crystallinity, acidity, and porosity of the zeolites were studied to identify the dominant one responsible for the observed difference in catalytic activity. The results of SEM and XRD characterizations indicate that the particle size and crystallinity of these zeolites are not distinguishable. The discussion is therefore mainly focused on the effect of acidity and porosity of the acidic zeolites.

The isomerization of unsaturated fatty acid, such as oleic acid, is a fundamentally Brönsted acid catalyzed reaction and follows the conventional carbenium ion mechanism. Brönsted acid sites in zeolite provide protons to form carbenium ions from adsorbed fatty acids that contain unsaturated $C=C$ bonds. Double bond migration can also readily take place under the reaction conditions, resulting in various carbocation intermediates with positive charge at different locations along the alkyl chain. Double bond migration followed by a ring closure reaction also produced γ-lactones as byproducts. Lewis acid sites on zeolites could play a role in the isomerization too. Commercial fatty acid feed typically contain some water, which can turn strong Lewis acids to Brönsted acids. In addition, the fatty acid itself has a proton that could be released as a Brönsted acid once the carboxylic group is adsorbed on the Lewis acid site.

The use of ammonia and other amines in TPD experiments for zeolite acidity study has been well reviewed by Farneth and Gorte [22]. Assuming that all physically adsorbed ammonia was removed after adsorption, the desorbed ammonia from NH_3-TPD measurement could yield the total amount of acid sites (both Brönsted and Lewis acids) on a sample. Comparing the amount of acid sites obtained from NH_3-TPD and the one from a calculation based on SAR, the amount of NH_3 desorbed was more than the theoretical amount calculated based on the SiO_2/Al_2O_3 ratio, indicating that the physically adsorbed ammonia was not completely removed.

Neither the amount of NH_3 desorbed from TPD measurement of all zeolites, as shown in figure 4 and table 2, nor the theoretical acid amount (table 2) correlates with the measured activity trend shown in figure 1. It is particularly evident that there is a large discrepancy in the measured acidity and the catalytic activity, especially when the HB-27 and HB-28 are compared. The HB-27 has the highest activity and the largest amount of acid sites. The HB-28 has the second largest amount of acid sites, but it is almost the least active one. Among the second group of zeolite catalysts, the fatty acid conversion on the HB-50 more than doubled that on the HB-37 or HB-45, but they all have similar amount of acid sites. The temperature profiles in figure 4 show that these zeolites had similar acid strength. Because the fatty acids in the feed are considerably larger molecules than ammonia, it is not surprising that the acid sites in the micropores of zeolites accessible to ammonia are not available to oleic acid molecules for the isomerization reaction. It follows that the acidity of the zeolites measured by ammonia does not provide a good correlation to catalysis involving molecules as large as long chain fatty acids.

For fatty acids, the most accessible acid sites can be expected to be located inside the mesopores of the zeolites. In deed, the HBeta zeolites which showed high activities all have a large amount of mesopores, as demonstrated in figure 5. The SAR value is an important parameter for isomerization reaction since it correlates with the number of acid sites in the zeolite. However, to be an active catalyst for fatty acid conversion, the acid site density and their accessibility to the feed, oleic acid in this case, are two important parameters. Neither a zeolite with a high acid site density limited to micropores nor a zeolite with large pores but having a low acid site density can have high activity. Those inactive catalysts in figure 1 belong to the former category. Zeolite Beta is known to have structural defects and mesopores depending on the manufacturing processes. The crucial role of the mesoporosity of the acidic Beta zeolites was further confirmed by the superior performance of the mesoporous zeolite HMAS-5, even though it has a lower acid site density. The remarkably narrow distribution of the HMAS-5 mesopores at 25 Å accounts for the high accessibility of the acid sites in this synthetic zeolite for oleic acid.

The importance of the accessibility of acid sites in Beta type zeolites to the conversion of other molecules has also been reported in the literature. In the acylation of toluene, the use of nanocrystalline Beta zeolites improved the accessibility to the acid sites through increased surface area [23]. In the alkylation of toluene with 1-heptene and 1-dodecene in HBeta [24], the activity for toluene alkylation with 1-dodecene was much lower than that with 1-heptene even over small zeolite crystallites. For the isopropylation of benzene over HBeta, it was reported that pore volume accessibility to benzene was more important than the percentage of the zeolite crystallinity [25]. In the isomerization of alpha-pinene, the main activity was limited to the HBeta zeolites that have mesopores [26]. Attempt to introduce other metal ions, such as B, Ti, and V, into the zeolite framework did not lead to an active catalyst, also suggesting that pore site accessibility is crucial for the reaction [27]. Even for the isomerization of *n*-heptane over zeolites Y and Beta, it was found that the zeolite acidity was a parameter less important than the zeolite porosity [28]. In the present study, oleic acid is a considerably large molecule than the molecules as discussed above [17, 24–28]. Therefore, the mesoporosity of acid zeolites is critically important for the isomerization of fatty acids when zeolites with similar SARs are compared.

In conclusion, fatty acid skeletal isomerization can be effectively catalyzed by Beta zeolites that have both high acid site density and accessible mesoporosity to the feed. Most acid sites accessible to probe molecules, such as ammonia, are not easily accessible for reactions involving large molecules, for example, fatty acids. The activity difference of the acidic commercial Beta zeolites in oleic acid isomerization is mainly due to their difference in mesoporosity. The lab generated mesopore zeolite with Beta type structure has the highest activity and stability against coking during oleic acid isomerization.

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