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Isomerization and Arylation of Oleic Acid on Anion Modified Zirconia Catalysts

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Abstract The catalytic performance of anion modified zirconia catalysts, such as sulfated zirconia (SO_4/ZrO_2) and tungstated zirconia (WO_3/ZrO_2), was evaluated for the upgrading of oleic acid (OA). In the presence of an aromatic compound, two main reactions occurred on the catalysts: the skeletal isomerization of OA and the arylation of OA with aromatics. The activity of the SO_4/ZrO_2 was more than triple of that of the WO_3/ZrO_2. At 250 °C, $OA/(SO_4/ZrO_2)(wt/wt) = 5$, the OA conversion and the arylation selectivity reached their maximal values and the isomerization selectivity was the lowest when the toluene to OA (toluene/OA) molar ratio was about 6. When mesitylene was used instead of toluene, the OA conversion and the arylation selectivity decreased, probably because of a steric effect. An attempt to reuse the SO_4/ZrO_2 by solvent washing after a run was not so successful, while calcination at 630 °C in air recovered the activity completely.

Keywords Isomerization · Arylation · Fatty acid · Aromatic · Catalyst

1 Introduction

The properties of biodiesel and many household products like detergent, shampoo, and fabric softener are all linked to the aliphatic backbone of triglycerides derived from renewable resources. The physical properties of such end products are fundamentally determined by the structural features of the aliphatic chains. Besides chain length, the degree of unsaturation in the aliphatic chain is a crucial factor for the melting point, the color stability, viscosity, and formulation flexibility of the products.

Fatty acids are aliphatic carboxylic acids produced from the hydrolytic cleavage of triglycerides, producing glycerol as the by-product. When methanol is used in the process of triglyceride cleavage, the main product is methyl ester of fatty acids, also known as bio-diesel. Isomerization and arylation of the aliphatic chain are often desired processes to improve the end product rheological property for the target applications. In this work, upgrading OA, which has an unsaturated C=C bond at the 9, 10 position and is a major component in typical vegetable oil derived fatty acids, by isomerization and arylation on anion modified zirconia is reported.

Unsaturated fatty acids, such as OA, are usually liquid at room temperature and are desired in product formulation. However, the double bond(s) in unsaturated fatty acids is prone to air oxidation, especially in applications at elevated temperature such as lubrication. Saturated fatty acids are more stable and often considered in such applications, but they are usually solid at room temperature and hard to mix with other components. Branched saturated fatty acids have low melting point and are believed to be ideal in many applications involving lubrication, paint formulation, soap, metal salt, and corrosion inhibitor.

At present, branched fatty acids are available as a byproduct with a low yield below 20% from the dimmer acid production process [1], in which acidic clay is used as catalyst [2–4]. Recently, two approaches have been studied to synthesize branched saturated fatty acids as the main product: (1) direct isomerization of linear saturated fatty

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acids; (2) skeletal isomerization of unsaturated fatty acids followed by hydrogenation. Kenneally et al. took the first approach above and reported the isomerization of stearic acid on metal promoted Beta zeolite [5], but the yield of the desired products is quite low due to low conversion and selectivity. With the second approach, a relatively high yield of branched unsaturated fatty acids has been reported in several patents [6–14]. Various zeolites, such as Mordenite, zeolite L and/or zeolite Omega, Pentacyl, Beta and Ferrierite, all showed some activities.

Another way to synthesize branched saturated fatty acid is through a Frediel-Crafts reaction between an aromatic compound and an unsaturated fatty acid. Nakano and Foglia reported the use of strong Lewis acids, such as methanesulfonic acid and aluminum chloride as catalysts for the arylation of OA [15]. This homogeneous catalytic process has many disadvantages, such as catalyst consumption, hazarous gas generation, side reaction, and product separation. In another paper [16], Kohashi and Foglia showed that acidic bentonite clay catalyzed the reaction between phenol and OA to result in a yield of addition products as high as 96%. However, the catalyst hardly catalyzed the reaction of toluene with OA. Different types of clay catalysts (Montmorillonite K10, Clarion 470, and Clarion 550) were reported to be effective for arylation reactions between aromatic hydrocarbons and OA [17, 18], although a relative high clay to OA ratio, long reaction time and slow addition of OA were normally used to achieve a higher yield to the desired product.

Nafion, a perfluorinated resin treated with sulfonic acid from E. I. du Pont, was disclosed in a patent for reactions between toluene, xylene, phenol, and OA [19]. The heterogeneous superacid catalyst was very selective and presented a high yield of arylated fatty acid, but the amount of the catalyst used was almost the same as that of the OA. Due to the various disadvantages described above, there is no commercial process yet for the arylation of unsaturated fatty acids.

We recently reported the use of zeolite and anion modified zirconia catalysts for this reaction [20]. In the present work, the effects of reaction conditions on the activities of sulfated zirconia as well as tungstated zirconia, which are considered to be environmentally benign superacids and have been used in hydrocarbon isomerization and alkylation [21–24], were investigated for the addition reaction of aromatics and OA.

2 Experimental Section

An OA 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. Toluene (T) and mesitylene were purchased from Sigma-Aldrich.

Sulfated zirconium hydroxide (XZO1249/01, 7.5% SO_3) and tungstated zirconium hydroxide (XZO1251/02, 16% WO_3) in powder form were obtained from Magnesium Elektron Inc. These two samples were calcined in air for 3 h at 630 °C and 700 °C, respectively to convert them to sulfated zirconia and tungstated zirconia catalysts before use.

Catalytic testing was conducted in a 135 mL autoclave reactor. Specified amounts of aromatic and catalyst were loaded into the reactor, which was sealed and purged with nitrogen. With stirring at 1,000RPM, the mixture was heated up to reaction temperature within half an hour. While maintaining the reaction temperature, 10 g of OA was then injected into the reactor using a syringe pump in 2 h. Reaction time (RT) starts to count at this point ($RT = 0$). In one run, specified amounts of catalyst, OA and toluene were loaded into the reactor together; in another run in which no aromatic was used, a catalyst and the same amount of OA were loaded. For these last two runs, the point at which the mixtures reached the reaction temperature was considered to be $RT = 0$.

Reactions were terminated at desired RT by rapidly quenching the reactor with cold water to room temperature. Liquid product from the 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 on GC. Gas phase from the 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%. It should be noted that the GC analysis could not detect heavy compounds in the liquid product, such as dimer and trimer acids from OA polymerization, which were usually the bottom cut of a vacuum distillation. Heavy compounds may also include arylation products formed by one aromatic and two or more OA molecules. For the cases discussed here, the total weight of such compounds was usually less than 3 wt% of the total product, as indicated by mass balance from vacuum distillation. Therefore, the absence of these heavy compounds from GC analysis does not affect the measured distribution of the fatty acid products. To simplify the reactivity measurement with GC method, the following equations are used to define OA conversion, isomerization selectivity and arylation selectivity:

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

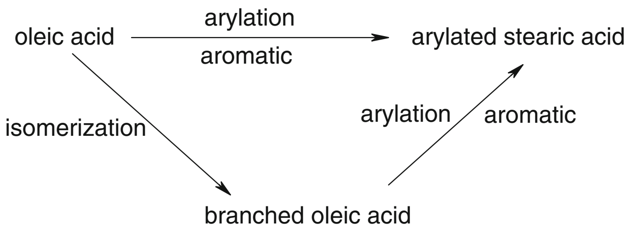
$$\text{Isomerization Selectivity(wt\%)} = \frac{i - \mathrm{C}_{18}^{1}(\text{in feed}) - i - \mathrm{C}_{18}^{1}(\text{in product})}{n - \mathrm{C}_{18}^{1}(\text{in feed}) - n - \mathrm{C}_{18}^{1}(\text{in product})} \times 100\%$$

$$\text{Arylation Selectivity(wt\%)} = \frac{\text{Arylated OA(in roduct)}}{n - \mathrm{C}_{18}^{1}(\text{in feed}) - n - \mathrm{C}_{18}^{1}(\text{in product})} \times 100\%$$

The acidic catalysts used here do little to the saturated fatty acid under the reaction conditions. Therefore, saturated acids did not appear in the equations above. Aromatics were used in excessive amount and their degree of conversion was not calculated here.

3 Results and Discussion

The isomerization and arylation may occur concurrently as two independent reactions to form branched OA and arylated stearic acid as the final products, respectively; arylation may also follow the isomerization of OA to convert the branched OA to arylated isostearic acids, as shown in Scheme 1. Certainly, the arylation of the branched OA could be difficult due to steric effect from the alkyl branch(es). A hydrogenation can easily convert the branched OA to isostearic acid which, like the arylated stearic acid, is also desired in many applications.



Scheme 1

3.1 SO_4/ZrO_2 and WO_3/ZrO_2 Catalysts

The catalytic activities of the two catalysts for the conversion of OA in the presence of toluene (T) are compared in Table 1. The surface area of the SO_4/ZrO_2 and WO_3/ZrO_2 was about 113.0 and 86.2 m^2/g, respectively. The surface area of the SO_4/ZrO_2 was 1.3 times of that of the WO_3/ZrO_2. The data in Table 1 shows that the OA conversion on the SO_4/ZrO_2 was more than three times as much as that on the WO_3/ZrO_2. Therefore, the SO_4/ZrO_2 was about 2.5 times as active as the WO_3/ZrO_2 in term of per surface area unit. It is known that the WO_3/ZrO_2 is of somewhat lower acid strength than SO_4/ZrO_2 based on acidity measurement using Hammett indicators [25, 26]. The difference on acid strength could be one of the factors contributing to difference in the activity.

On both catalysts, it was observed that the isomerization selectivity increased slightly with RT, while the arylation selectivity almost remained constant. The relatively stable selectivities means the ratio of the reaction rates of the isomerization and the arylation was almost the same during the runs. The SO_4/ZrO_2 also presented a much higher arylation selectivity than the WO_3/ZrO_2.

Since the SO_4/ZrO_2 was more active than the WO_3/ZrO_2, it was selected for the following studies.

3.2 Effect of Aromatic Size

At the same molar ratio of aromatic to OA, toluene, and mesitylene were used as reactants and compared (Fig. 1, (a) toluene and (b) mesitylene). With both aromatics, the conversions of OA increased with RT. The isomerization selectivity and the arylation selectivity with toluene varied little. With mesitylene, the isomerization selectivity increased while the arylation selectivity decreased steadily,

Table 1

250 °C, T/OA(molar ratio) = 10, OA/catalyst (wt/wt) = 5/1

Catalyst	RT (h)	OA conversion (wt%)	Isomerization selectivity (wt%)	Arylation selectivity (wt%)
SO_4/ZrO_2	1	60.3	44.7	36.2
	2	65.8	46.7	38.7
	4	73.3	48.5	38.4
	6	78.4	48.9	38.2
WO_3/ZrO_2	1	16.8	39.4	15.8
	2	18.3	40.5	16.4
	4	21.7	41.3	14.6
	6	24.3	42.4	14.9

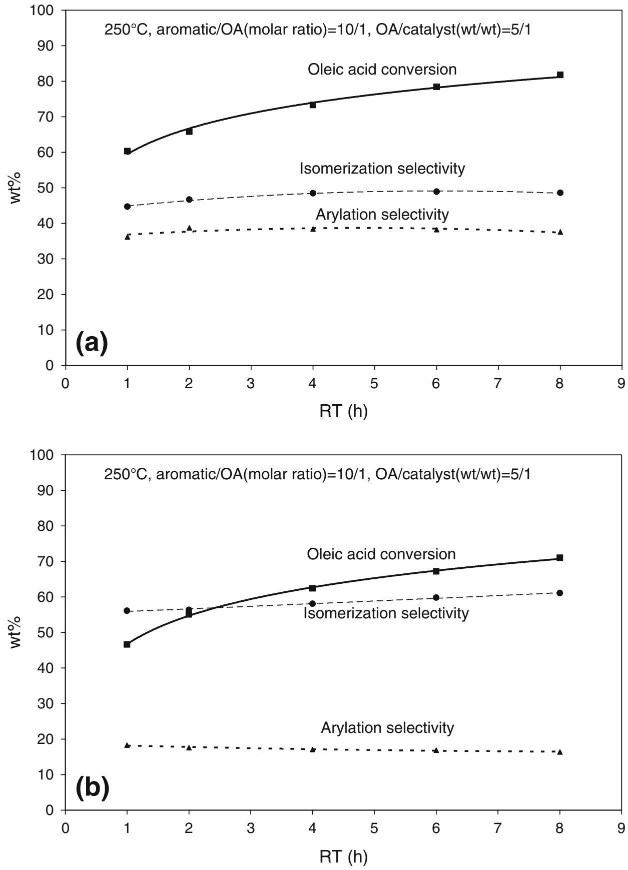


Fig. 1

indicating that the isomerization contributed more to the conversion of OA.

With mesitylene, both the conversion of OA and the arylation selectivity were lower and the isomerization was higher than the corresponding values with toluene. This is mainly attributed to the bulky size of mesitylene compared with toluene molecule. The steric effect was also shown by the high relative ratio of isomerization to arylation. The bulkier aromatic performs more like a solvent.

For both runs in Fig. 1, a large portion of OA was converted when RT = 1 h. For example, in the run using toluene (Fig. 1a), the conversion at RT = 1 h was 60.3 wt% and it only increased about 20 wt% to 81.8 wt% after another 7 h (RT = 8 h). The reaction rate seemed to decrease a lot with RT, probably due to catalyst deactivation and diffusion effect from the formation of bulkier branched OA and arylated OA. However, the decrease was actually not as significant as it appeared to be. As described in the third paragraph of the experimental section above, a gradual addition of OA was used for most runs. During the addition period (the 2 h before RT = 0), the reactions already started and the OA/catalyst ratio was much lower than 5/1. The carboxylic group of OA has been shown to have poisoning effect on catalytic sites. The (carboxylic group)/catalyst ratio steadily increased during the addition period and reached its maximal value at RT = 0 h when the addition ended and remained constant after that. Therefore, the reaction was very fast due to little poisoning effect and the OA conversion was significant before a sample was taken at RT = 1 h.

3.3 Reaction Temperature and Catalyst Loading

With other conditions the same (OA/catalyst = 5/1, T/OA molar ratio = 10, RT = 2 h), the reaction results at 180 °C and 250 °C are compared in Fig. 2. At 180 °C, the conversion of OA was 45.2 wt%, lower than 65.8 wt% at 250 °C, but the arylation selectivity (57.5 wt%) was much higher than that at 250 °C (38.7 wt%). The selectivity sum of isomerization and arylation was not 100% because there were other byproducts, such as lactones. The low conversion and isomerization selectivity of OA at 180 °C was probably because the skeletal rearrangement of the aliphatic chain was difficult at that temperature at which the weakening of the acidity (poisoning effect) due to the carboxylic group prevailed. The skeletal isomerization of an olefin should be easy on SO_4/ZrO_2 since Hino et al. [22, 23] has shown that the catalyst catalyzed butane isomerization at room temperature. In the absence of toluene, we observed little conversion of OA on the catalyst even at 220 °C. The addition of toluene could have alleviated the poisoning effect and improved the activity.

The last group of data in Fig. 2 was obtained with doubled catalyst loading. The OA conversion was about 90 wt%. The relatively high arylation selectivity was probably due to the arylation of branched OA from the isomerization.

3.4 Effect of Toluene Addition

The conversion of OA and arylation selectivity increased with the amount of toluene added and reached maximal

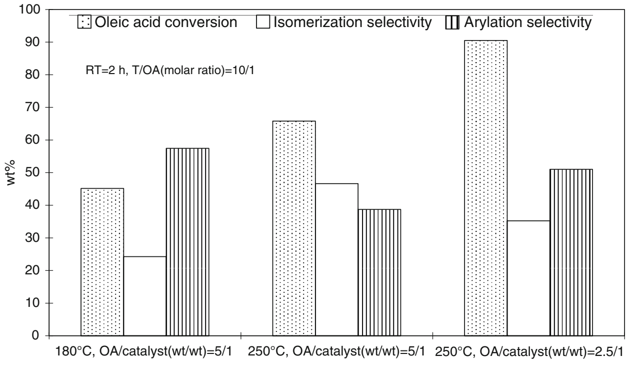


Fig. 2

values when the T/OA was around 6 (Fig. 3). Those open symbols in Fig. 3 (□, ◯, Δ) represent the OA conversion, isomerization selectivity and arylation selectivity, respectively when the OA, toluene, and SO_4/ZrO_2 were loaded into the reactor together (T/OA = 10). The conversion was about 47.5 wt%, higher than that with no toluene addition. However, the promoting effect of toluene was not as prominent as that when toluene was premixed with the catalyst and OA was added gradually. This observation could be explained by the stronger interaction between the carboxylic groups and the acid sites on the catalyst than that between toluene and the acid sites. Even though OA is soluble in toluene, the bonding of the carboxylic acid group to the acid site of the zeolite is the major cause for the observed poisoning effect in OA isomerization. Limiting the initial concentration of OA in the toluene solvent is therefore an effective approach to limit the adsorption of carboxylic acid onto the zeolite acid sites. Partition of OA in the toluene solvent is a desired driving force for a decreased poisoning effect, leading to high OA isomerization. Furthermore, the formation of arylated stearic acid as a result of acid catalyzed arylation reaction between OA and toluene, as will be discussed below, would increase the partitioning of the arylated product in the toluene phase due to increased solubility, thus reducing the poisonous interaction of carboxylic acid with the zeolite acid sites.

It should be noted that the reaction already effectively started as OA was added to the toluene solvent in the run with gradual addition and the T/OA was higher than 10 before the OA addition was finished. The actual RT was 2 h longer than the RT valve. Therefore, the results represented by open symbols in Fig. 3 should be compared with the results of SO_4/ZrO_2 in Table 1 with RT = 2 h.

The toluene was also a reactant in the arylation reaction. As the arylation is a bimolecular reaction, the reaction rate depends on the concentrations of toluene and OA. When the amount of toluene was in significant excess, the rate of OA consumption for arylation was mainly determined by the concentration of OA. At very high T/A ratio, the low concentration of OA resulted in a decreased arylation rate. As shown in Fig. 3, this happened as T/A approached 10.

The solvent effect of toluene was further demonstrated by the comparison of those reactions with toluene addition with the one without toluene addition (T/A = 0). In the absence of toluene, only a conversion of 27.6 wt% was achieved at 250 °C.

As a solvent, toluene may also play a negative role when its concentration was too high. Since the π electrons in toluene have a higher electron density than the double bond in OA, toluene absorbs stronger on an acid site than does the unsaturated aliphatic chain. In addition, the observed drop in OA conversion may also come from the excess partitioning of OA in the toluene phase versus onto the zeolite surface.

3.5 Catalyst Reuse and Regeneration

In most of the tests above, an OA/catalyst weight ratio of 5 was used, which is a significant decrease in catalyst loading compared with those employed in literature. Effort to reduce the amount of catalyst consumption was continued with an attempt to reuse the catalyst. The catalyst after a typical run was separated from the liquid product by filtration and washed with acetone followed by drying at 110 °C. It (labeled as Reused catalyst) was loaded with fresh feed for another run. In a separated case, the washed catalyst was calcined at 630 °C in air for 3 h after drying and was tested again (labeled as Regenerated catalyst). The results from the fresh, the reused and the regenerated catalysts are shown in Fig. 4. After the acetone wash, the used catalyst had an OA conversion of 45.0 wt%. This is about 42.7% of activity loss compared to the conversion on the fresh catalyst (78.4 wt%). It indicates a significant deactivation during the first use. After the calcination, the conversion (79.2 wt%) was basically the same as that on the fresh catalyst.

It is clear that a simple washing could not remove heavy molecules or coke from the used catalyst for full reuse,

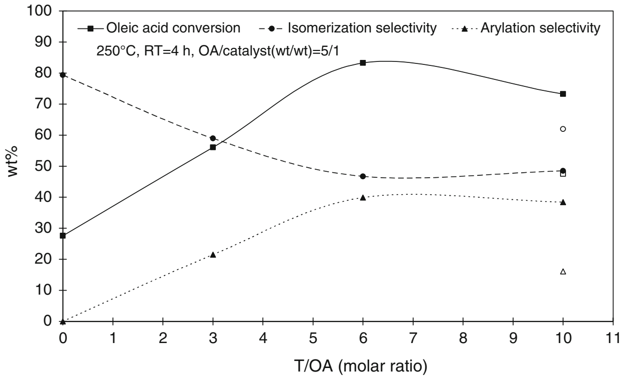


Fig. 3

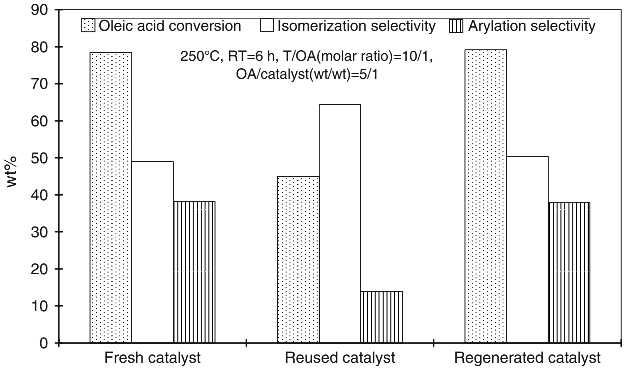


Fig. 4

while a calcination at high temperature is necessary to completely recover the catalytic activity. The results also suggest that no structure damage occurred to the catalyst during the reaction or regeneration.

4 Conclusions

Branched fatty acids have been synthesized through skeletal isomerization and arylation which occur simultaneously on SO_4/ZrO_2 and WO_3/ZrO_2 catalysts. The SO_4/ZrO_2 was much more active than the WO_3/ZrO_2. Reaction temperature, catalyst loading, molar ratio of aromatic to OA and the selection of aromatic can all be optimized to improve the conversion and to tune the selectivity to isomerization or arylation. The size of aromatic reactant affected the fatty acid conversion as well as product selectivities. With a bulkier aromatic, the conversion of OA was lower and isomerization was dominant over arylation. The activity of the used SO_4/ZrO_2 catalyst could be fully regenerated by calcination at 630 °C in the air.

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