



# Article Balance between Catalyst Acidity and Hydrophilicity in Biofuel Production from Fatty Acid Esterification over Al-SBA-15

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Abstract: A collection of Al-SBA-15 mesoporous catalysts (Si/Al = 13-174) was investigated to overcome typical accessibility constraints of microporous solids. <sup>27</sup>Al MAS NMR confirmed the existence of tetrahedrally coordinated Al in the catalyst's framework, and the fraction of such species increased as the Si/Al ratio decreased. Brønsted acidity followed the same pattern found using *n*-propylamine thermodecomposition. Mesoporous catalysts with lower Si/Al ratios exhibited a higher affinity to water as quantitatively determined using water adsorption experiments. Those surface properties were correlated to the catalytic performance on oleic acid esterification. The introduction of Al into the SBA-15 framework significantly improved esterification activity, leading to conversions ranging from 70 to 93%. This was explained by the acidity engendered upon Si substitution by Al. However, a turning point from which activity started dropping was registered and it was proposed to be associated with catalyst hydrophilicity. The balance between acidity and hydrophilicity was unveiled to be of paramount importance to accomplish the best catalytic efficiency and uppermost biofuel yield. Catalyst activity was also assessed for the esterification of stearic and linoleic acids. Higher conversion rates were accomplished with unsaturated fatty acids (oleic acid > linoleic acid > stearic acid) due to the higher reactivity of the carboxylic acid moieties as a consequence of the polarity of the double bonds in the carbon chain.

Keywords: oleic acid; aluminosilicate; SBA-15; biofuel; bioenergy; biomass; green chemistry

# 1. Introduction

Acid esterification is an industrially important reaction as it is involved in a wide variety of applications, such as surfactants, emollients, moisturizers, emulsifiers, plasticizers, solvents, explosives, flavoring agents, lubricants, fuel and oil additives. Indeed, chemicals, food, automotive and aviation, marine, textiles, cosmetics and personal care products are the main end-use industries of esters. Their global market is under expansive growth particularly due to the use of esters in the energy industry as biofuels and lubricants [1], and the alkyl esters of fatty acids are the major chemicals for such applications. It is well known, however, that most biofuels are produced from vegetable oils' basic transesterification, but the search for cheaper alternative waste feedstocks, such as waste cooking oils, has been encouraged to increase the effectiveness of the process. Though cheaper, cheaper alternative waste feedstocks are more acidic due to the high content of free fatty acids and are, as a consequence, more difficult to efficiently convert with basic transesterification catalysts, leading to a high loss of yield due to soap formation during the reaction. A prior



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). acid esterification step, at which free fatty acids are firstly converted, is a feasible process approach and fits the need for the establishment of a bio-based circular economy.

Generally, homogeneous acid catalysts, such as  $H_2SO_4$ , HCl and *p*-toluene sulfonic acid, are used in the esterification of fatty acids [2,3]. However, these catalysts are corrosive, toxic, environmentally aggressive and difficult to separate from the reaction medium, demanding much effort in downstream processing and generating substantial residues [2]. Several studies have been carried out using heterogeneous catalysts, mostly hybrid organic–inorganic catalysts, zeolites and mesoporous molecular sieves.

Zeolites have been widely studied in fatty acid esterification reactions [4–7]. Some of these materials have adequate acidity; however, they usually show low esterification activity, which is attributed to pore-size limitations due to the intrinsic zeolite microporosity [8]. Additionally, recent studies with ZSM-5 at different Si/Al molar ratios have shown that an increase in the Brønsted acidity (low Si/Al) is accompanied by a decrease in the conversion of fatty acids, which was not expected [9,10]. Such behavior can be explained by the intensification of the catalyst's hydrophilic character at a higher Al content. The water produced in the reaction (Scheme 1) is more likely to be adsorbed on the surface of a hydrophilic catalyst, hindering the access of the reactants to the zeolite acidic sites. Consistently higher conversion values have been accomplished over more hydrophobic zeolites [9,10]. Nonetheless, it is highlighted that no systematic quantitative study has addressed this issue so far.

$$\begin{array}{c} O \\ R_1 \\ fatty acids \end{array} + R_2 - OH \underbrace{\overset{acidic}{\overbrace{catalyst}}}_{catalyst} R_1 \\ fatty acids \\ alkyl esters \end{array} + H_2O$$

Scheme 1. Fatty acid esterification reaction.

Mesoporous silicas have been found to overcome accessibility constraints due to their high surface area, large pore size (2–50 nm) and thermal stability. Although these materials do not hold relevant intrinsic acidity, Brønsted and Lewis acid sites can be created by modifying the mesoporous silica surface with functional organic groups [11]. Indeed, some studies have been carried out on fatty acid esterification over such hybrid mesoporous catalysts [12–14]. The results revealed that high conversion levels (ranging from 85% to almost 100%) can be achieved by adjusting the amount of Brønsted acid groups grafted on the surface of mesoporous silicas [15]. Nonetheless, this class of hybrid mesoporous catalysts may suffer from low stability due to leaching of functional groups, leading to an irreversible catalyst deactivation despite some controversial reports [16,17].

Alternatively, isomorphic substitution using transition elements can be applied to develop acidity on mesoporous molecular sieves [18]. These modified solids can overcome the low chemical stability of hybrid silicas while providing a large framework for fatty acid bulky diffusion. Oddly, this approach has rarely been pursued concerning esterification of long-chain fatty acids [19–22]. Carmo et al. firstly investigated palmitic acid esterification over Al-MCM-41 with different Si/Al molar ratios (8, 16 and 32) at 130 °C and a 60:1 alcohol:fatty acid ratio [19]. The authors claimed that higher conversion rates were reached for catalysts with lower Si/Al due to the higher Brønsted acidity generated by higher Al contents. This conclusion was corroborated later by a study on lauric acid esterification carried out by Talha et al. using Al-SBA-15 catalysts, despite the different range of Si/Al molar ratios used (50, 75 and 100) [20]. These findings contrasted with the results reported for zeolite catalysts previously discussed [9,10]. However, it should also be pointed out that the high amount of alcohol used by Carmo et al. [19] have favored the reaction, clouding the result of the catalyst activity.

The activity of Al-MCM-41 (Si/Al = 14) synthesized with bentonite as alternative Si and Al sources was also recently reported by Sahel et al. on the esterification of lauric

acid [21]. This catalyst reached 82% conversion under specific conditions (65 °C, 7 wt.% catalyst, 1 h). The authors also studied the performance of Al-SBA-15 under the same conditions, reporting a lauric acid conversion of 70%. Nevertheless, the Al content in that SBA-15 sample was very low indeed (0.02 wt.%, Si/Al = 1614) and no data on surface acidity were reported, raising some concern about the catalyst's effectiveness. It is important to outline that no blank run without a solid catalyst was reported either. These sorts of data are, however, quite relevant for esterification reactions as evidenced by Cabrera-Munguia et al., who also investigated modified M-SBA-15 catalysts (M = Al or Ti) [22]. These authors showed that Al-SBA-15 (Si/Al = 33) presented no catalytic activity for oleic acid esterification, since the conversion reached over the mesoporous catalyst was comparable to the blank run, with 33% and 30% conversions at 140 °C and 2 h of reaction, respectively. This contradictory result was not discussed deeply by the authors, and we speculate that it might be related to the low efficiency of the Al substitute to create Brønsted acidity in their samples, as suggested by the infrared spectra presented by the authors [22].

This literature review indicates that the generation of Brønsted acid sites on mesoporous silica using isomorphic substitution can be a potential strategy to obtain an active catalyst for fatty acid esterification. It also allowed us to identify that the chemical environment of the heteroatom in the silica structure, the balance between the quantity and quality of the Brønsted acid sites and the hydrophilicity/hydrophobicity character tuned using the introduction of Al in the catalyst framework must all be considered. However, these issues have rarely been discussed together, and whenever they have, contradictory conclusions were reached. This present work aims then at filling the gap in this discussion, bringing some contribution to the design of mesoporous catalysts for the production of biofuels. This contribution specifically aims to provide a systematic quantitative study on the impact of water adsorption on oleic acid catalytic esterification, and its relation with surface acidity generated through the replacement of Si atoms with Al in the SBA-15 framework.

### 2. Results and Discussion

#### 2.1. Catalyst Characterization

The formation of the SBA-15 structure was monitored using SA-XRD. The diffraction patterns (Figure S1) revealed the presence of the typical three well-resolved peaks associated with the (100), (110) and (200) planes, confirming the formation of the hexagonal (P6mm) structure of SBA-15 [23].

The porosity of the synthesized samples was assessed using N<sub>2</sub> adsorption–desorption isotherms as presented in Figure S2. All solids presented a type IVa isotherm characteristic of SBA-15 mesoporous materials, and a type H1 hysteresis associated with the existence of cylindrical pore channels [24]. The surface area (S<sub>BET</sub>) varied within 567–944 m<sup>2</sup> g<sup>-1</sup> as summarized in Table 1, in line with the typical range reported in the literature for similar materials [25,26]. It was observed that the surface area tended to increase as the Al loading decreased, i.e., a higher Si/Al ratio would generally lead to higher S<sub>BET</sub> values, which is a similar behavior to that reported elsewhere [27,28]. This is usually ascribed to the loss of existing micropores by adding Al [27]. However, an opposite behavior was observed regarding the pore volume (V<sub>p</sub>) and average pore diameter (D<sub>p</sub>), which increased with the content of Al in the samples, which was in close agreement with the literature [27].

Chemical analyses performed using ICP-OES allowed the determination of the Al content in all samples and the results are also shown in Table 1. The presence of Al was confirmed in Al-SBA-15 samples and its content ranged from 0.3 wt.% to 3.4 wt.%, corresponding to Si/Al ratios from 13 to 174. These findings show that the synthesis protocol successfully produced a suitable assortment of samples that allowed a systematic study on the impact of mesoporous catalyst properties on fatty acid esterification.

Catalyst	Si/Al	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>p</sub> (cm <sup>3</sup> g <sup>-1</sup> )	D <sub>p</sub> (nm)	Al <sub>Td</sub> (%)	Al <sub>Oct</sub> (%)	BAS (μmol g <sup>-1</sup> )	H <sub>2</sub> O Adsorbed (μmol g <sup>-1</sup> )
SBA-15	-	944	0.96	4.2	-	-	11	315
Al-SBA-15(13)	13	699	1.08	5.6	48	35	195	842
Al-SBA-15(19)	19	567	0.88	5.9	50	29	136	784
Al-SBA-15(33)	33	824	1.16	5.2	n.d.	n.d.	165	693
Al-SBA-15(70)	70	744	0.90	4.6	32	48	71	390
Al-SBA-15(174)	174	740	0.55	3.6	27	59	45	333

**Table 1.** Si/Al ratio, surface area ( $S_{BET}$ ), pore volume ( $V_p$ ), average pore diameter ( $D_p$ ), concentration of Brønsted acid sites (BAS) and amount of adsorbed water of SBA-15 and Al-SBA-15 catalysts.

n.d. not determined.

The Si chemical environment was examined using <sup>29</sup>Si CP/MAS NMR spectroscopy. The spectra (Figure S3) revealed the presence of a small narrow resonance signal at approximately -90 ppm related to Q<sub>2</sub> (Si(OSi)<sub>2</sub>(OH)<sub>2</sub>) species, and a narrow and well-resolved signal due to Q<sub>3</sub> species (Si(OSi)<sub>2</sub>(OAl)(OH)) at -100 ppm. Furthermore, Q<sub>4</sub> sites ascribed to non-substituted siloxanes (Si(OSi)<sub>4</sub>) were observed at approximately -110 ppm [25,29].

<sup>27</sup>Al MAS NMR spectra were also collected for the isomorphically substituted samples (Figure 1). They mainly presented two resonances, one at around 52 ppm and the other around 0 ppm, which were associated with tetrahedrally and octahedrally coordinated Al, respectively [26,29–31]. The occurrence of tetrahedral Al species confirmed the heteroatom's incorporation into the SBA-15 framework. These species are in the genesis of Brønsted acidity due to the formation of bridging Si-(OH)-Al sites, where protons act as balancing cations. The presence of octahedral sites, on the other hand, is usually assigned either to extra-framework Al or to partially extra-framework Al species linked to two water molecules [30]. Finally, a small signal at approximately 30 ppm was also detected in some samples and it was ascribed to five-coordinate Al species [32,33].

Deconvolution of  $^{27}$ Al MAS NMR spectra allowed an estimation of the proportion of tetrahedral (Al<sub>Td</sub>) and octahedral (Al<sub>Oct</sub>) Al sites and it was seen that the fraction of tetrahedral sites increased as the Si/Al ratio decreased (Table 1), revealing that Al incorporation into the SiO<sub>2</sub> framework was accomplished even at high Al contents. However, it should be outlined that the insertion of Al into tetrahedral sites was unexpectedly more difficult at very low Al content (high Si/Al) as they only accounted for approximately 30% of the Al-SBA-15(70) and Al-SBA-15(174) samples. The rest of the Al species, which varied within 14–21%, were associated with the five-coordinate Al species, as previously described.

It was, thus, expected that Brønsted acidity in Al-SBA-15 catalysts increased as the Si/Al ratio decreased, since these samples not only presented higher amounts of Al, but also higher amounts of tetrahedrally coordinated Al species (Table 1), which are responsible for the generation of this type of acid site [34,35].

It is well known that Al-SBA-15 catalysts possess both Lewis and Brønsted acid sites. However, it is also reckoned that Lewis acid sites are much less active in esterification reactions compared to Brønsted centers. Therefore, only Brønsted acid sites were assessed in this paper. The occurrence and amount of Brønsted acid sites were determined using the temperature-programmed decomposition of *n*-propylamine. This reaction is known to selectively occur on Brønsted acid sites via the Hofmann elimination mechanism, leading to the equimolar formation of propene and ammonia [36], and has been used to assess Brønsted acidity, particularly in refining catalysts [37,38].



Figure 1. <sup>27</sup>Al MAS NMR spectra of all synthesized mesoporous catalysts.

The profiles of propene formation shown in Figure 2a exhibited only one peak at approximately 440 °C, which was in good agreement with the values already reported by other authors with similar mesoporous solids [36,39].

The formation of propene over all catalysts evidenced the generation of Brønsted acidity through the introduction of Al, as shown by the <sup>27</sup>Al MAS NMR results. The unmodified SBA-15 sample was also analyzed as a reference and, as expected, it did not show a significant concentration of acid sites (Table 1). These results, along with those collected from the <sup>27</sup>Al MAS NMR spectra, disclosed that the concentration of Brønsted acid sites increased as a function of the population of tetrahedral Al species in Al-SBA-15 catalysts. The same trend was observed in previous reports [23,26].



**Figure 2.** (a) Temperature-programmed decomposition profiles of *n*-propylamine and (b) temperature-programmed water desorption profiles of all synthesized mesoporous catalysts.

The hydrophobicity/hydrophilicity of these catalysts was estimated using the tempe rature-programmed desorption of water. The desorption profiles are presented in Figure 2b.

It can be noticed that unmodified SBA-15 presented two peaks, one at approximately 118 °C and the other at 305 °C, which could be related to the desorption of water molecules and dehydroxylation of silanol groups, respectively [40]. The same pattern was observed for the Al-SBA-15 samples. Nevertheless, the intensity of the first peak consistently increased as the Al content increased, disclosing that the catalysts with lower Si/Al ratios had a higher affinity to water. Unmodified SBA-15 presented the lowest amount of adsorbed water (Table 1), and this was attributed to the much larger number of silanol groups (Si-OH) on the surface. These species poorly interact with water molecules [20,41], rendering a more hydrophobic surface. As Al was introduced into the SBA-15 framework, the amount of water adsorbed during the experiment increased (Table 1), verifying that samples with a higher Al content possess a more hydrophilic behavior [20].

# 2.2. Catalyst Performance

Al-SBA-15 mesoporous catalysts were evaluated in oleic acid esterification and the results are shown in Figure 3. A reaction run with non-acidic SBA-15 and a blank experiment (without catalyst) were also carried out as control experiments. All these reactions were performed within a 2-h timeframe so that the catalyst activity could be distinguished as observed in preliminary experiments (Figure S4). A longer reaction time can increase fatty acid conversion and may alter the catalyst's behavior, which might lead to a deceptive conclusion.



**Figure 3.** Oleic acid esterification over SBA-15 and Al-SBA-15 catalysts. Reaction conditions:  $T = 150 \degree C$ ,  $P = 20 \text{ bar} (N_2)$ , methanol:oleic acid 30:1, 2 h and 10% of catalyst.

In both control experiments, an oleic acid conversion of ~28% was achieved, establishing the contribution from a thermal catalyzed reaction (blank) and the expected negligible activity of non-acidic SBA-15. The introduction of Al into the SBA-15 framework, on the other hand, significantly improved the esterification activity, leading to conversions ranging from 70 to 93%, and reliably revealed the different performance of all catalysts. This result can be explained by the acidity engendered upon Si isomorphic substitution by Al, as indicated by the previous characterization results. These findings were in line with some reports on the behavior of Al-modified mesoporous silicas in the esterification of palmitic (C16:0) and lauric (C12:0) acids over Al-MCM-41 and Al-SBA-15, respectively [19–21]. An overall comparison between the results obtained in this study and those reported in the literature over mesoporous catalysts is shown in Table S1.

Nevertheless, some contradictory results can also be found in the literature, as Al-SBA-15 was claimed not to be active for oleic acid (C18) esterification and the blank (no catalyst) run reached similar conversion levels [22]. The authors found a very low concentration of Brønsted acid sites on the synthesized Al-SBA-15 compared to figures from other reports in the literature [23,26]. It can only be speculated that the introduction of Al to the SBA-15 framework was unsuccessful because the chemical environment of Al species was not assessed [22]. As disclosed hereinbefore, all Al-SBA-15 catalysts synthesized in this work exhibited tetrahedral Al sites, confirming the addition of Al into the SBA-15 framework and generation of Brønsted acid sites, well reckoned to be the active sites for esterification, supporting their high catalytic activity.

By comparing the overall activity of all six synthesized samples (Figure 3), it could be noticed that Al-SBA-15(13) was the least active among them, reaching 70% conversion of oleic acid. This is odd at first sight as this is the catalyst holding the highest amount of Al and, therefore, the highest concentration of Brønsted acid sites (Table 1). Decreasing the aluminum content seemed to increase activity, but it is not a straightforward correlation, as can be inferred from Figure 3. Indeed, the pattern suggested a turning point from which activity started dropping. It revealed that esterification activity is not simply related to the concentration of Brønsted acid sites and that other properties also play a role. Some other arguments, besides the quantitative acidity, have to be stressed at this point of the discussion, particularly the quality of those Brønsted acid sites and the impact of introducing Al on the catalyst surface hydrophilicity.

Some authors have indeed claimed enhanced catalytic activity in oleic (C18:1) and linoleic (C18:2) acid esterification at high acid-strength zeolites with low Si/Al ratios [42,43]. The strength of Brønsted acid sites is known to increase with decreasing Al content, as the Al(OH)Si bridging hydroxyl possesses higher ionic character and, therefore, a stronger acidity [44,45]. This could lead one to consider that lower Brønsted strength rules activity, but still, it cannot explain the non-linear trend observed in Figure 3 either. Furthermore, the results from *n*-propylamine thermodecomposition (Figure 2a) suggested that the synthesized Al-SBA-15 catalysts had a similar acid strength or at least that the range of Al content in these samples did not enforce any assessable difference. Besides this contribution from the limited amount of Al, it might be a framework-related effect, since unlike zeolites, the mesoporous silicas used in this study are amorphous materials with less strained bond angles and, consequently, an overall weaker acidity [44].

Catalyst hydrophobicity/hydrophilicity is also an important chemical property, as water is formed along with esters during esterification reactions and, thus, its competitive interaction with the catalyst surface must be considered. Water molecules can interact with a more hydrophilic catalyst surface, hindering hydrophobic fatty acid molecules to adsorb and, therefore, leading to a lower catalytic activity. Introducing Al into silica makes it transition from an electrically neutral hydrophobic framework to a more hydrophilic material [44]. The higher the aluminum content (lower Si/Al), the more hydrophilic the catalyst. Notwithstanding this expected influence, the impact of catalyst hydrophilicity on esterification activity has been neglected in some studies, which were mostly based on the acidity–activity relation arising from the Si/Al ratio [19,21,22,46]. On the other hand, catalytic activity disturbance promoted by water, either in reactions at which water is formed or in reactions carried out in water or water/organic solvents, has been reported [8–10,20,33,42,43,47], but a straightforward quantitative correlation has hardly ever been provided. In one case, Talha et al. did analyze water adsorption on Al-SBA-15 materials through adsorption–desorption isotherms [20]. In a qualitative way, the authors mentioned that water adsorption decreased as Si/Al ratio decreased. In fact, when the authors estimated the water adsorption potential, they found that the value calculated for Al-SBA-15 containing a Si/Al ratio of 75 was lower than Al-SBA-15 with a Si/Al ratio of 100 (0.49 and 0.58 kJ mol<sup>-1</sup>, respectively). The lower the value for the adsorption potential, the more hydrophobic the material is. This trend was the opposite of what was expected and conflicted with the results reported herein, since water adsorption increased as Si/Al ratio decreased, i.e., Al content increased (Table 1). One should bear in mind, however, that only two Al-containing molecular sieve catalysts were evaluated in Talha et al.'s previous work [20] and, therefore, it was not possible to reach a general conclusion in this regard. In this contentious scenario, contradictory conclusions on the impact of Si/Al ratio on esterification activity can easily be noted. While fatty acid esterification activity has been seen to decrease over high Si/Al catalysts [20,48,49], an increase in activity has also been reported [42,43,50].

In this present contribution, the catalyst hydrophilicity was assessed using water thermodesorption experiments (Figure 2b and Table 1) and its influence on oleic acid esterification was examined along with the catalyst acidity as depicted in Figure 4.

At a high Si/Al ratio range at which the acidity is low and the catalyst is more hydrophobic, conversion was found to progressively increase as the Si/Al ratio decreased, corroborating the conclusion that activity indeed improves as Brønsted acidity increases. Nonetheless, from some point at which the Si/Al ratio is much lower, oleic acid conversion drops significantly, despite the steady increase in acidity. In this chemical composition region, it is proposed that the catalyst hydrophilicity takes over, allowing the adsorption onto the catalyst surface of water molecules produced in the reaction and spoiling the access of both more hydrophobic fatty acid molecules and the less polar methanol.





The rather similar trend obtained by correlating either catalyst acidity or hydrophilicity with oleic acid conversion unveils that a balance between such properties is of paramount importance to accomplish the best catalytic efficiency and uppermost biofuel yield. It is suggested that this interdependence disclosed in this work might be responsible for some divergent conclusions in the literature regarding the performance of aluminosilicate-based catalysts as it would depend on the range of Si/Al ratios studied, which tailors both the acidity and hydrophilicity.

Catalyst recyclability was evaluated using Al-SBA-15(19) in four consecutive cycles. The results depicted in Figure 5 revealed that the mesoporous catalyst was robust and stable, since only a very slight conversion drop was observed in the fourth reaction run.



**Figure 5.** Oleic acid esterification over Al-SBA-15(19). Reaction conditions:  $T = 150 \degree C$ , P = 20 bar (N<sub>2</sub>), methanol:oleic acid 30:1, 2 h and 10% of catalyst.

Finally, the activity of the Al-SBA-15 mesoporous catalyst was also assessed for the esterification of different C18 fatty acids with different unsaturation numbers, namely, stearic acid (C18:0), oleic acid (C18:1) and linoleic acid (C18:2). Figure 6 shows that the catalyst was active for all those fatty acids, but higher conversion was reached with unsaturated ones (oleic acid > linoleic acid > stearic acid). A similar behavior has indeed been reported by other authors in the literature [51–53]. This trend may be ascribed to the polarity of the double bonds in the carbon chain leading to a higher reactivity of the carboxylic acid group [53–55].



**Figure 6.** Fatty acid esterification over Al-SBA-15(19). Reaction conditions:  $T = 150 \degree C$ , P = 20 bar (N<sub>2</sub>), methanol:fatty acid 30:1, 2 h and 10% of catalyst.

The results reported herein showed that modified mesoporous silicas are suitable catalysts for the esterification of fatty acids. Their large structure associated with the possibility of tuning the surface acidity and hydrophilic character brings them some technical advantages compared to the more traditionally used zeolites. A disclosure of the interplay between acidity and hydrophilicity could contribute to a better understanding of new catalysts' behavior, supporting the development of more suitable processes to produce biofuels from biomass-derived molecules.

## 3. Materials and Methods

## 3.1. Materials

Poly(ethyleneglycol)-block-poly(propyleneglycol)-block-poly(ethylene glycol) 20:70:20 (Pluronic<sup>®</sup> P-123—Mn  $\approx$  5800), tetraethyl ortosilicate (TEOS— $\geq$ 99%) and aluminum isopropoxide (Al(iPrO)<sub>3</sub>—98%) purchased from Sigma Aldrich, and hydrochloric acid (HCl—37% solution) purchased from Neon were used to synthesize SBA-15 and Al-SBA-15 catalysts. For the fatty acid esterification, oleic acid (90%), stearic acid (95%), linoleic acid (95%) and methanol (P.A) were all purchased from Sigma Aldrich and used without any prior purification.

### 3.2. Synthesis of SBA-15 and Isomorphically Substituted Al-SBA-15 Catalysts

SBA-15 was synthesized following a method previously described by Zhao et al. [56]. Firstly, 9.0 g of Pluronic<sup>®</sup> P123 was dissolved in 337.5 mL of HCl aqueous solution (pH = 1.5) and stirred at 30 °C for 3 h. In parallel, 20.7 mL of TEOS was dissolved in 22.5 mL of HCl aqueous solution (pH = 1.5) and stirred at 30 °C for 3 h. Afterwards, the first solution was

heated to 40 °C and TEOS solution was added into it dropwise. The resulting solution was aged under stirring at 40 °C for 20 h and then transferred to an autoclave for a hydrothermal treatment at 100 °C for 24 h. The final suspension was filtered and washed with distilled water until constant pH was attained and the white powder obtained was dried at 100 °C for 24 h. SBA-15 was obtained after calcination at 500 °C in air flow (50 mL min<sup>-1</sup>), with a heating rate of 1 °C min<sup>-1</sup> for 5 h.

Al-SBA-15 catalysts were prepared following a method adapted from Perez et al. [23]. Initially, 9 g of Pluronic<sup>®</sup> P123 was dissolved in 337.5 mL of a HCl aqueous solution (pH = 1.5) under stirring for 3 h. At the same time, 20.7 mL of TEOS was dissolved in 22.5 mL of HCl aqueous solution (pH = 1.5) along with Al(iPrO)<sub>3</sub> under stirring for 3 h. The amount of Al(iPrO)<sub>3</sub> was adjusted to obtain the desired Si/Al ratio. After that, TEOS and Al(iPrO)<sub>3</sub> solution was added dropwise to the Pluronic<sup>®</sup> P123 suspension and aged at 40 °C for 20 h. From that point, the same procedure used to synthesize the mesoporous SBA-15 was followed. The samples were named Al-SBA-15(X), where X is the experimental Si/Al ratio.

## 3.3. Catalyst Characterization

Chemical composition of all samples was determined using inductively coupled plasma-optical emission spectrometry (ICP-OES) in a Varian Vista MXP. Previous to the analysis, the samples were heated at 900 °C for 6 h, with a heating rate of 10 °C min<sup>-1</sup>. Afterwards, the samples were dissolved in 4 mL of HNO<sub>3</sub> (65%) and 4 mL of HF (40%) in a DGT 100 Plus Digester (Provecto Analitica, Jundiaí, Brazil). The resulting solutions were adequately diluted prior to ICP measurement. Standard deviations found for Al content analyses ranged from 0.1 to 0.4 ppm.

The catalysts' mesostructured formation was assessed using small-angle X-ray powder diffraction (SA-XRD). The analyses were performed in a Bruker D8 Discover with diffractometer equipped with a Lynxeye position sensitive detector and a CuK $\alpha$  radiation source at 40 kV and 40 mA. The diffractograms were collected in Bragg small-angles from 0.5° to 5° with an incremental step increase of 0.01°.

The porosity of the catalysts was determined using nitrogen adsorption–desorption isotherms at -196 °C in a Micromeritics ASAP 2020. Before analyses, samples were dried at 100 °C for 24 h and outgassed at 150 °C. The specific surface areas (S<sub>BET</sub>) were obtained according to the Brunauer–Emmet–Teller (BET) equation. The pore size distribution and average pore size were determined using the Barrett–Joyner–Halenda (BJH) method, considering the desorption isotherm branch.

NMR spectra were acquired at room temperature (~22 °C) using an Agilent DD2 400 spectrometer equipped with a 9.4 T wide-bore magnet operating at Larmor frequencies of 79.21 MHz for <sup>29</sup>Si and 103.89 MHz for <sup>27</sup>Al. Powdered SBA-15-based samples were packed into 4 mm ZrO<sub>2</sub> with Kel-F cap rotors and rotated at magic angle spinning (MAS) rate of 10 KHz, using a triple channel 4 mm HXY probe for the <sup>27</sup>Al MAS experiments. <sup>27</sup>Al MAS spectra were acquired using radio frequency field strength of ~110 KHz, recycle interval of 2.0 s, spectral window of 100 KHz, pulse length of 0.4  $\mu$ s ( $\pi/12$ ), acquisition time of 16 ms and 5000 to 20,000 scans. As for <sup>29</sup>Si NMR spectra, powdered SBA-15 based samples were packed into 7.5 mm ZrO2 with Kel-F cap rotors and rotated at MAS rate of 5 KHz, using a double channel 7.5 mm HX probe for the <sup>29</sup>Si cross polarization CP/MAS experiments. <sup>29</sup>Si CP/MAS spectra were acquired using radio frequency field strength of ~80 KHz, recycle interval of 4.0 s, spectral window of 50 KHz, acquisition time of 20 ms and 4096 scans. A ramp CP pulse sequence was used, with a contact time of 2.5 ms and highpower <sup>1</sup>H decoupling (TPPM, ~90 KHz) during acquisition. The spectra were obtained using Fourier transform and 50 Hz line broadening of the free induction decays, and they were externally referenced using tetramethylsilane (TMS), with a 1.02 M Al(NO<sub>3</sub>)<sub>3</sub> solution (0.0 ppm for <sup>27</sup>Al MAS) and kaolin (-91.5 ppm for <sup>29</sup>Si CP/MAS) as secondary references.

Concentration of Brønsted acid sites in all catalysts was determined using *n*-propylamine temperature-programmed decomposition (TPD-*n*PA). Analyses were performed in a mul-

tipurpose unit coupled to a Pfeiffer Vacuum model TC110 mass spectrometer used to monitor the *n*-propylamine desorption products signals, both propene (m/z = 41) and NH<sub>3</sub> (m/z = 17). Initially, samples were pretreated at 500 °C for 30 min, at a heating rate of 20 °C min<sup>-1</sup> under He flow (30 mL min<sup>-1</sup>). Thereafter, the solids were submitted to a stream of 30 mL min<sup>-1</sup> of *n*-propylamine/He (13–15% *n*-C<sub>3</sub>H<sub>9</sub>N) for 30 min at 40 °C. The remaining *n*-propylamine was purged at 150 °C for 1 h in He flow (30 mL min<sup>-1</sup>). Desorption was performed by heating the samples from 150 to 500 °C, at a heating rate of 20 °C min<sup>-1</sup>. All samples were analyzed as triplicates and the error was ~7%.

Temperature-programmed desorption of water (TPD-H<sub>2</sub>O) was performed to assess the hydrophilicity of the catalysts in the same multipurpose unit used for TPD-*n*PA experiments. Prior to analysis, samples were pretreated in situ at 400 °C, with a heating rate of 20 °C min<sup>-1</sup> under He flow (30 mL min<sup>-1</sup>) for 15 min. After, they were cooled down to 40 °C and a flow of 3%vol. water/He (30 mL min<sup>-1</sup>) was admitted into the reactor for 1 h. After purging the reactor for 1 h under He flow (30 mL min<sup>-1</sup>), water desorption was carried out by heating up the samples to 300 °C under He flow (30 mL min<sup>-1</sup>), following a heating rate of 15 °C min<sup>-1</sup>, and kept at 300 °C for 15 min. An error of ~12% was estimated for the triplicates.

## 3.4. Catalytic Activity

Fatty acid esterification with methanol was carried out in a batch Parr reactor. In each run, 50 mL, 11.62 g of fatty acid and 10 wt.% of catalyst (1.162 g) were maintained at 150 °C, 20 bar of  $N_2$  and under mechanical stirring of 600 rpm. Such reaction conditions were set based on extensive reports evidencing the main impact of temperature and alcohol:fatty acid ratio in this endothermic equilibrium reaction that is usually performed under conditions to push equilibrium to the product [9,57–59]. A high methanol:fatty acid ratio (30:1) was used due to experimental set up limitations and to avoid mass transfer problems since the mesoporous catalyst studied herein is not very dense.

At the end of the reaction, samples were filtered, washed with chloroform and dried in a rotary evaporator until complete water and solvent removal was achieved. A portion of 0.1 g of the oil phase was diluted in 100 mL of a solvent mixture (2 mL water:98 mL anhydrous isopropanol:100 mL toluene) and titrated using a 0.1 mol  $L^{-1}$  alcoholic solution of potassium hydroxide. Fatty acid conversion was calculated by determining initial and final total acidity number (TAN) through potentiometric titration using the ASTM D664 procedure in a Methrom model 848 Titrino Plus titrator (Equation (1)). Only methyl oleate (ester product) was formed (100% selectivity).

$$X = \frac{\left[TAN_i - TAN_f\right]}{\left[TAN_i\right]} \tag{1}$$

Reactions were performed in triplicate and presented data are average values with corresponding standard deviations.

After oleic acid esterification reactions, Al-SBA-15(19) was recovered through centrifugation, washed with 50 mL of methanol, dried at 80 °C overnight and then used again in consecutive catalytic runs, which were carried out under the same conditions in order to investigate the catalyst's recyclability.

#### 4. Conclusions

Al-SBA-15 mesoporous catalysts were shown to be effective to promote the esterification of oleic acid, leading to conversions ranging from 70 to 93%. This was explained by the acidity engendered upon Si substitution by Al, as disclosed through <sup>27</sup>Al MAS NMR and *n*-propylamine thermodecomposition. However, a turning point from which activity started dropping was registered and it was proposed to be associated with catalyst hydrophilicity, as determined using quantitative measurements of water adsorption. The catalytic activity was then shown to be determined by both the catalyst's acidity and hydrophilicity, and that an appropriate balance between those properties is demanded so the catalyst's efficiency can be higher. It was proposed that on hydrophobic surfaces, acidity plays a major role and activity increases along with it. Such protagonism fades when the catalyst surface turns more hydrophilic through the introduction of high amounts of aluminum. Activity is then seen to drop due to the competitive interaction of water molecules. Tailoring the amount of aluminum sitting in the silica framework is, thus, the key point to tuning the esterification activity. The mesoporous catalysts were also active for the esterification of stearic and linoleic acids.

**Supplementary Materials:** The following supporting information can be downloaded at https: //www.mdpi.com/article/10.3390/catal13050827/s1: Figure S1: SA-XRD diffractograms of the synthesized mesoporous SBA-15, Al-SBA-15(13), Al-SBA-15(19), Al-SBA-15(33), Al-SBA-15(70) and Al-SBA-15(174); Figure S2: N<sub>2</sub> adsorption–desorption isotherms of the synthesized mesoporous SBA-15, Al-SBA-15(13), Al-SBA-15(19), Al-SBA-15(33), Al-SBA-15(70) and Al-SBA-15(174); Figure S3: <sup>29</sup>Si CP/MAS NMR spectra of Al-SBA-15(13), Al-SBA-15(19), Al-SBA-15(70) and Al-SBA-15(174); Figure S4: Oleic acid esterification over Al-SBA-15(19) at different reaction times. Reaction conditions: T = 150 °C, P = 20 bar (N<sub>2</sub>), methanol:oleic acid 30:1 and 10% of catalyst; Table S1: Comparison of reaction conditions and catalyst performance for different silicate-based catalysts in the esterfification of fatty acids.

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## References

- 1. Esters Market-Global Industry Analysis, Size, Share, Growth, Trends and Forecast, 2020–2030, TMR. Available online: https://www.transparencymarketresearch.com/esters-market.html (accessed on 20 March 2021).
- Blanco-Sánchez, M.; Franco, A.; Pineda, A.; Balu, A.; Romero, A.; Luque, R. NH<sub>4</sub>F Modified Al-SBA-15 Materials for Esterification of Valeric Acid to Alkyl Valerates. *Proceedings* 2019, 3, 4.
- do Nascimento, L.A.S.; Tito, L.M.Z.; Angélica, R.S.; da Costa, C.E.F.; Zamian, J.R.; da Rocha Filho, G.N. Esterification of oleic acid over solid acid catalysts prepared from Amazon flint kaolin. *Appl. Catal. B Environ.* 2011, 101, 495–503. [CrossRef]
- Mostafa Marzouk, N.; Abo El Naga, A.O.; Younis, S.A.; Shaban, S.A.; EL Torgoman, A.M.; EL Kady, F.Y. Process optimization of biodiesel production via esterification of oleic acid using sulfonated hierarchical mesoporous ZSM-5 as an efficient heterogeneous catalyst. J. Environ. Chem. Eng. 2021, 9, 105035. [CrossRef]
- Dal Pozzo, D.M.; dos Santos, J.A.; Júnior, E.S.; Santos, R.F.; Feiden, A.; de Souza, S.N. Free fatty acids esterification catalyzed by acid Faujasite type zeolite. RSC Adv. 2019, 9, 4900–4907. [CrossRef] [PubMed]
- 6. Sahu, P.; Sakthivel, A. Zeolite-β based molecular sieves: A potential catalyst for esterification of biomass derived model compound levulinic acid. *Mater. Sci. Energy Technol.* **2021**, *4*, 307–316. [CrossRef]
- Gomes, G.J.; Costa, M.B.; Bittencourt, P.R.S.; Zalazar, M.F.; Arroyo, P.A. Catalytic improvement of biomass conversion: Effect of adding mesoporosity on MOR zeolite for esterification with oleic acid. *Renew. Energy* 2021, 178, 1–12. [CrossRef]
- Prinsen, P.; Luque, R.; González-Arellano, C. Zeolite catalyzed palmitic acid esterification. *Microporous Mesoporous Mater.* 2018, 262, 133–139. [CrossRef]
- Fawaz, E.G.; Salam, D.A.; Daou, T.J. Esterification of linoleic acid using HZSM-5 zeolites with different Si/Al ratios. *Microporous Mesoporous Mater.* 2020, 294, 109855. [CrossRef]
- 10. Mohebbi, S.; Rostamizadeh, M.; Kahforoushan, D. Efficient sulfated high silica ZSM-5 nanocatalyst for esterification of oleic acid with methanol. *Microporous Mesoporous Mater.* **2020**, *294*, 109845. [CrossRef]

- Canhaci, S.J.; Perez, R.F.; Borges, L.E.P.; Fraga, M.A. Direct conversion of xylose to furfuryl alcohol on single organic–inorganic hybrid mesoporous silica-supported catalysts. *Appl. Catal. B Environ.* 2017, 207, 279–285. [CrossRef]
- 12. Tututi-Ríos, E.; González, H.; Cabrera-Munguia, D.A.; Gutiérrez-Alejandre, A.; Rico, J.L. Acid properties of Sn-SBA-15 and Sn-SBA-15-PrSO<sub>3</sub>H materials and their role on the esterification of oleic acid. *Catal. Today* **2022**, *394*, 235–246. [CrossRef]
- Yu, Z.; Chen, X.; Zhang, Y.; Tu, H.; Pan, P.; Li, S. Phosphotungstic acid and propylsulfonic acid bifunctionalized ordered mesoporous silica: A highly efficient and reusable catalysts for esterification of oleic acid. *Chem. Eng. J.* 2022, 430, 133059. [CrossRef]
- 14. Zhang, P.; Wu, H.; Fan, M.; Sun, W.; Jiang, P.; Dong, Y. Direct and postsynthesis of tin-incorporated SBA-15 functionalized with sulfonic acid for efficient biodiesel production. *Fuel* **2019**, *235*, 426–432. [CrossRef]
- Mbaraka, I.K.; Radu, D.R.; Lin, V.S.Y.; Shanks, B.H. Organosulfonic acid-functionalized mesoporous silicas for the esterification of fatty acid. J. Catal. 2003, 219, 329–336. [CrossRef]
- Pečar, D.; Goršek, A. Synthesis and characterization of sulfonic acid functionalized mesoporous SBA-15: Application in esterification reaction. React. Kinet. *Mechan. Catal.* 2019, 128, 991–1003. [CrossRef]
- Wang, Y.; You, J.; Liu, B. Preparation of mesoporous silica supported sulfonic acid and evaluation of the catalyst in esterification reactions. React. Kinet. *Mechan. Catal.* 2019, 128, 493–505.
- Tuel, A. Modification of mesoporous silicas by incorporation of heteroelements in the framework. *Microporous Mesoporous Mater*. 1999, 27, 151–169. [CrossRef]
- 19. Carmo, A.C.; de Souza, L.K.C.; da Costa, C.E.F.; Longo, E.; Zamian, J.R.; da Rocha Filho, G.N. Production of biodiesel by esterification of palmitic acid over mesoporous aluminosilicate Al-MCM-41. *Fuel* **2009**, *88*, 461–468. [CrossRef]
- 20. Talha, Z.; Bachir, C.; Ziri, S.; Bellahouel, S.; Bengueddach, A.; Villièras, F. Al-Rich Ordered Mesoporous Silica SBA-15 Materials: Synthesis, Surface Characterization and Acid Properties. *Catal. Lett.* **2017**, *147*, 2116–2126. [CrossRef]
- Sahel, F.; Sebih, F.; Bellahouel, S.; Bengueddach, A.; Hamacha, R. Synthesis and characterization of highly ordered mesoporous nanomaterials Al-MCM-41 and Al-SBA-15 from bentonite as efficient catalysts for the production of biodiesel MELA and EELA. *Res. Chem. Intermed.* 2020, 46, 133–148. [CrossRef]
- Cabrera-Munguia, D.A.; González, H.; Tututi-Ríos, E.; Gutiérrez-Alejandre, A.; Rico, J.L. Acid properties of M-SBA-15 and M-SBA-15-SO<sub>3</sub>H (M = Al, Ti) materials and their role on esterification of oleic acid. *J. Mater. Res.* 2018, 33, 3634–3645. [CrossRef]
- 23. Perez, R.F.; Albuquerque, E.M.; Borges, L.E.P.; Hardacre, C.; Fraga, M.A. Aqueous-phase tandem catalytic conversion of xylose to furfuryl alcohol over [Al]-SBA-15 molecular sieves. *Catal. Sci. Technol.* **2019**, *9*, 5350–5358. [CrossRef]
- 24. Thommes, M.; Kaneko, K.; Neimark, A.; Olivier, J.P.; Rodriguez-Reinoso, F.; Rouquerol, J. Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report). *Pure Appl. Chem.* **2015**, *87*, 1051–1069. [CrossRef]
- Benamor, T.; Vidal, L.; Lebeau, B.; Marichal, C. Influence of synthesis parameters on the physico-chemical characteristics of SBA-15 type ordered mesoporous silica. *Microporous Mesoporous Mater.* 2012, 153, 100–114. [CrossRef]
- Gallo, J.M.R.; Bisio, C.; Gatti, G.; Marchese, L.; Pastore, H.O. Physicochemical Characterization and Surface Acid Properties of Mesoporous [Al]-SBA-15 Obtained by Direct Synthesis. *Langmuir* 2010, 26, 5791–5800. [CrossRef]
- Xing, S.; Lv, P.; Fu, J.; Wang, J.; Fan, P.; Yang, L. Direct synthesis and characterization of pore-broadened Al-SBA-15. *Microporous Mesoporous Mater.* 2017, 239, 316–327. [CrossRef]
- Liu, J.; Zhang, X.; Han, Y.; Xiao, F.S. Direct Observation of Nanorange Ordered Microporosity within Mesoporous Molecular Sieves. Chem. Mater. 2002, 14, 2536–2540. [CrossRef]
- 29. Bhange, P.; Bhange, D.S.; Pradhan, S.; Ramaswamy, V. Direct synthesis of well-ordered mesoporous Al-SBA-15 and its correlation with the catalytic activity. *Appl. Catal. A Gen.* **2011**, 400, 176–184. [CrossRef]
- Hu, W.; Luo, Q.; Su, Y.; Chen, L.; Yue, Y.; Ye, C. Acid sites in mesoporous Al-SBA-15 material as revealed by solid-state NMR spectroscopy. *Microporous Mesoporous Mater.* 2006, 92, 22–30. [CrossRef]
- Luan, Z.; Cheng, C.F.; Zhou, W.; Klinowski, J. Mesopore Molecular Sieve MCM-41 Containing Framework Aluminum. J. Phys. Chem. 1995, 99, 1018–1024. [CrossRef]
- Ravi, M.; Sushkevich, V.L.; van Bokhoven, J.A. Towards a better understanding of Lewis acidic aluminium in zeolites. *Nat. Mater.* 2020, 19, 1047–1056. [CrossRef] [PubMed]
- Campos, G.P.; Albuquerque, E.M.; Fraga, M.A.; Pastore, H.O. Continuous Cellobiose Hydrolysis over Lamellar Aluminosilicates— Unveiling [Al]-magadiite Water-Tolerant Acid Sites. *Ind. Eng. Chem. Res.* 2021, 60, 4794–4805. [CrossRef]
- 34. Busca, G. Acidity and basicity of zeolites: A fundamental approach. Microporous Mesoporous Mater. 2017, 254, 3–16. [CrossRef]
- Sandoval-Díaz, L.E.; González-Amaya, J.A.; Trujillo, C.A. General aspects of zeolite acidity characterization. *Microporous Mesoporous Mater.* 2015, 215, 229–243. [CrossRef]
- 36. Socci, J.; Saraeian, A.; Stefanidis, S.D.; Banks, S.W.; Shanks, B.H.; Bridgwater, T. The role of catalyst acidity and shape selectivity on products from the catalytic fast pyrolysis of beech wood. *J. Anal. Appl. Pyrolysis* **2022**, *162*, 104710. [CrossRef]
- 37. Milina, M.; Mitchell, S.; Michels, N.L.; Kenvin, J.; Pérez-Ramírez, J. Interdependence between porosity, acidity, and catalytic performance in hierarchical ZSM-5 zeolites prepared by post-synthetic modification. *J. Catal.* **2013**, *308*, 398–407. [CrossRef]
- Kresnawahjuesa, O.; Gorte, R.J.; de Oliveira, D.; Lau, L.Y. A Simple, Inexpensive, and Reliable Method for Measuring Brønsted-Acid Site Densities in Solid Acids. *Catal. Lett.* 2002, 82, 155–160. [CrossRef]

- Socci, J.; Osatiashtiani, A.; Kyriakou, G.; Bridgwater, T. The catalytic cracking of sterically challenging plastic feedstocks over high acid density Al-SBA-15 catalysts. *Appl. Catal. A Gen.* 2019, 570, 218–227. [CrossRef]
- 40. Serrano, D.P.; Calleja, G.; Botas, J.A.; Gutierrez, F.J. Adsorption and Hydrophobic Properties of Mesostructured MCM-41 and SBA-15 Materials for Volatile Organic Compound Removal. *Ind. Eng. Chem. Res.* **2004**, *43*, 7010–7018. [CrossRef]
- Gounder, R. Hydrophobic microporous and mesoporous oxides as Brønsted and Lewis acid catalysts for biomass conversion in liquid water. *Catal. Sci. Technol.* 2014, *4*, 2877–2886. [CrossRef]
- Doyle, A.M.; Albayati, T.M.; Abbas, A.S.; Alismaeel, Z.T. Biodiesel production by esterification of oleic acid over zeolite Y prepared from kaolin. *Renew. Energy* 2016, 97, 19–23. [CrossRef]
- Tarach, K.A.; Góra-Marek, K.; Martinez-Triguero, J.; Melián-Cabrera, I. Acidity and accessibility studies of desilicated ZSM-5 zeolites in terms of their effectiveness as catalysts in acid-catalyzed cracking processes. *Catal. Sci. Technol.* 2017, 7, 858–873. [CrossRef]
- 44. Palčić, A.; Valtchev, V. Analysis and control of acid sites in zeolites. Appl. Catal. A Gen. 2020, 606, 117795. [CrossRef]
- 45. Barthomeuf, D. Framework induced basicity in zeolites. Microporous Mesoporous Mater. 2003, 66, 1–14. [CrossRef]
- Rade, L.L.; Lemos, C.O.T.; Barrozo, M.A.S.; Ribas, R.M.; Monteiro, R.S.; Hori, C.E. Optimization of continuous esterification of oleic acid with ethanol over niobic acid. *Renew. Energy* 2018, 115, 208–216. [CrossRef]
- 47. Liu, F.; Huang, K.; Zheng, A.; Xiao, F.S.; Dai, S. Hydrophobic Solid Acids and Their Catalytic Applications in Green and Sustainable Chemistry. *ACS Catal.* **2018**, *8*, 372–391. [CrossRef]
- Chung, K.H.; Chang, D.R.; Park, B.G. Removal of free fatty acid in waste frying oil by esterification with methanol on zeolite catalysts. *Bioresour. Technol.* 2008, 99, 7438–7443. [CrossRef]
- 49. Chung, K.H.; Park, B.G. Esterification of oleic acid in soybean oil on zeolite catalysts with different acidity. *J. Ind. Eng. Chem.* 2009, 15, 388–392. [CrossRef]
- Sun, K.; Lu, J.; Ma, L.; Han, Y.; Fu, Z.; Ding, J. A comparative study on the catalytic performance of different types of zeolites for biodiesel production. *Fuel* 2015, 158, 848–854. [CrossRef]
- Hawash, S.A.; Ebrahiem, E.E.; Farag, H.A. Kinetics of esterification of oleic and linoleic free fatty acids. J. Adv. Eng. Trends 2020, 39, 25–36. [CrossRef]
- Hawash, S.A.; Ebrahiem, E.E.; Farag, H.A. Kinetic study of the esterification of unsaturated free fatty acids. *Proc. Inst. Civ. Eng.* —*Energy* 2019, 172, 105–114. [CrossRef]
- 53. Joelianingsih, J.; Tambunan, A.H.; Nabetani, H. Reactivity of Palm Fatty Acids for the Non-catalytic Esterification in a Bubble Column Reactor at Atmospheric Pressure. *Procedia Chem.* **2014**, *9*, 182–193. [CrossRef]
- 54. Kusdiana, D.; Saka, S. Methyl Esterification of Free Fatty Acids of Rapeseed Oil as Treated in Supercritical Methanol. *J. Chem. Eng. Japan* **2001**, *34*, 383–387. [CrossRef]
- 55. Aranda, D.A.G.; Santos, R.T.P.; Tapanes, N.C.O.; Ramos, A.L.D.; Antunes, O.A.C. Acid-Catalyzed Homogeneous Esterification Reaction for Biodiesel Production from Palm Fatty Acids. *Catal. Lett.* **2008**, *122*, 20–25. [CrossRef]
- Zhao, D.; Feng, J.; Huo, Q.; Melosh, N.; Fredrickson, G.H.; Chmelka, B.F. Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores. *Science* 1998, 279, 548–552. [CrossRef] [PubMed]
- 57. Rattanaphra, D.; Harvey, A.P.; Thanapimmetha, A.; Srinophakun, P. Kinetic of myristic acid esterification with methanol in the presence of triglycerides over sulfated zirconia. *Renew. Energy* **2011**, *36*, 2679–2686. [CrossRef]
- Lapuerta, M.; Rodríguez-Fernández, J.; Armas, O. Correlation for the estimation of the density of fatty acid esters fuels and its implications. A proposed Biodiesel Cetane Index. *Chem. Phys. Lipids* 2010, 163, 720–727. [CrossRef] [PubMed]
- 59. Gan, S.; Ng, H.K.; Chan, P.H.; Leong, F.L. Heterogeneous free fatty acids esterification in waste cooking oil using ion-exchange resins. *Fuel Proc. Technol.* 2012, 102, 67–72. [CrossRef]

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