

# NH<sub>4</sub>F Modified Al-SBA-15 Materials for Esterification of Valeric Acid to Alkyl Valerates <sup>†</sup>

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**Abstract:** Al-SBA-15 materials were functionalized by ball milling with several niobium loadings (0.25–1 wt.%) and/or with several F<sup>-</sup> loadings, using NH<sub>4</sub>F as a precursor. The catalysts synthesized in this study were characterised by X-ray diffraction (XRD), N<sub>2</sub> porosimetry, and diffuse reflection infrared spectroscopy (DRIFT) among others. The prepared materials shown, form moderate to high catalytic activities in the microwave-assisted transformation of valeric acid to ethyl valerate via esterification. The incorporation of fluoride anions either into Al-SBA-15 or on Nb1%/Al-SBA-15 led to a linear increase in valeric acid conversion with the F<sup>-</sup> content. Thus, F<sup>-</sup> modified mesoporous aluminosilicates efficiently catalyze the transformation of valeric acid into alkyl valerate esters as renewable fuels.

**Keywords:** heterogeneous catalysts; mesoporous materials; biomass valorisation; esterification; alkyl valerates

## 1. Introduction

The continuous increase in energy demand, together with a growing environmental concern have prompted research on alternative feedstocks for the production of chemicals and energy. In this context, lignocellulosic biomass appears to be an attractive alternative to petroleum as source for fuels and chemicals. Among the main advantages of using lignocellulosic biomass as feedstock, its accessibility, low price, and their minimal impact on the environment can be mentioned [1].

Initially, the production of the first biofuel generation employed feedstock such as starch, sunflower seeds, and sugar cane [2] as raw material, which directly competed with their utilization for alimentary purposes thus leading to an ethical problem [3]. To address such ethical problems, second-generation biofuels were produced from non-edible raw materials such as agriculture and forest residues, and grass, among others.

Biofuel production through transesterification reactions between short chain alcohol and a triacylglyceride [4] is a widely followed methodology, using raw materials derived from biomasses such valeric acid, which can be obtained through successive hydrogenation reactions from levulinic acid [1]. The esterification between valeric acid and a short chain alcohol lead to valerate esters, whose utilization as fuels is fully compatible with engines currently in use [5].

Such esterification reactions have been traditionally homogeneously catalyzed using inorganic acids, such as HCl, HNO<sub>3</sub>, HSO<sub>4</sub>, or organic acids such as p-toluenesulfonic acid [6]. However, the

use of these homogeneous catalysts results in contamination problems due to their corrosiveness and toxicity, in addition to other drawbacks such as difficulty separating them from the reaction mixture, difficulties in the handling, and the increase in the production costs [6]. To overcome the previously mentioned problems, heterogeneous catalysts were designed and employed in esterification reactions for the production of biofuels, including sulfonic resins [7], zeolites [8], and others based on zirconium oxide [9] and niobic acid [10]. Alternatively, this esterification reaction can be performed enzymatically under mild conditions [11,12].

The modification of mesoporous SBA-15 silicates with niobium following conventional protocols leads to efficient catalysts in the esterification of acids, including propanoic [13] and ricinoleic acids [14]. Thus, it is possible to perform analogous chemistries such as the esterification of valeric acid to obtain alkyl valerate fuels. Additionally, the modification of catalysts containing aluminum with ammonium fluoride boosts acidic properties [15] due to the formation of  $\text{Si}(\text{O}_2\text{F})\text{OH}$  species near the aluminum atoms domain [16].

In this work we report the modification of SBA-15 aluminosilicates with niobium and/or with ammonium fluoride following different methodologies, and their effect in the microwave-assisted esterification of valeric acid, either with methanol or ethanol leading to the formation of valerate fuels.

## 2. Materials and Methods

### 2.1. Materials Preparation

Aluminosilicate material used as support were synthesized according to a protocol previously reported by Bonardet et al. [17]. For the preparation of the Al-SBA-15 materials, 8 g of Pluronic P123 were dissolved in 300 mL of HCl (pH = 1.5) for two hours, then 18 mL of tetraethyl ortosilicate were dropwise added, subsequently the required amount of aluminum isopropoxide was added to achieve a Si/Al molar ratio of 20. The mixture was kept under continuous stirring at 35 °C for 24 h, and submitted to hydrothermal treatment for 24 h. Finally, the sample was filtered and calcined at 600 °C for 8 h. The material obtained was named Al-SBA-15.

Al-SBA-15 material was modified with several Nb loadings (0.25, 0.5, and 1 wt.%) using ammonium niobate oxalate as a precursor, following a mechanochemical approach previously optimized by our research group [18]. The niobium-loaded material were prepared in a Retsch PM-100 mill using a stainless-steel container, in which the Al-SBA-15 support and the metal salt precursor were ground together at 350 r.p.m. for 10 min. The material obtained was calcined at 400 °C for 4 h and named NbX%/Al-SBA-15, where X is the theoretical metal loading.

F-modified materials were obtained by wet impregnation. The materials Nb1%/Al-SBA-15 and Al-SBA-15 were impregnated with different amounts of  $\text{NH}_4\text{F}$  to achieve fluoride loadings of 3 and 10 wt.% for each material. Finally, the materials were calcined at 400 °C for hours, to obtain the materials F3%-Nb1%/Al-SBA-15, F10%-Nb1%/Al-SBA-15, F3%/Al-SBA-15, and F10%/Al-SBA-15.

### 2.2. Characterization Techniques

The textural properties of the synthesised materials were evaluated through the use of an ASAP 2000 instrument. Prior to analysis, samples were outgassed for 12 h at 130 °C. The specific surface area was evaluated using the linear part of the Brunauer, Emmet and Teller (BET) equation in the interval  $0.05 < P_0 < 0.22$ . The pore size distribution was calculated from the adsorption branch and using the Barrett, Joyner and Halenda (BJH) equation.

The X-ray diffractograms (XRD) of the catalysts synthesised were acquired in a Bruker D8D Discover (40 kV, 40 mA) diffractometer, the radiation employed was the line  $\text{Cu K}\alpha$  ( $\lambda = 1.54 \text{ \AA}$ ). The goniometer speed was  $0.5^\circ/\text{min}$  in the interval  $0.5^\circ < 2\theta < 5^\circ$ .

Diffuse reflection infrared spectroscopy (DRIFT) spectra were acquired using an ABB MB3000 spectrometer fitted with an environmental chamber (Diffus IR™ Pike Technologies). The spectra were recorded with a resolution of  $8 \text{ cm}^{-1}$  in the interval  $600\text{--}4000 \text{ cm}^{-1}$ .

Acidic properties were evaluated by a chromatographic titration method using pyridine and 2,6-dimethylpyridine as probe molecules, for total and Brønsted acidity, respectively, following a methodology similar to the one previously reported by our research group [18].

### 2.3. Catalytic Activity

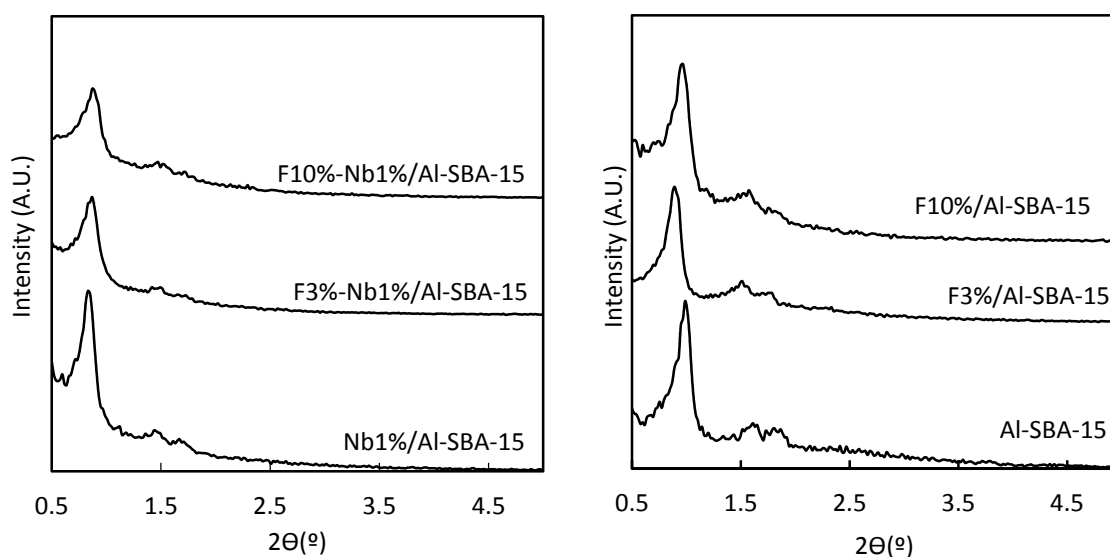
The catalytic activity of the materials was evaluated in the microwave-assisted esterification of valeric acid with ethanol. For a typical reaction, 50 mg of catalyst, 2 mL of ethanol, 0.1 mL of valeric acid were employed and submitted to 300 W microwave irradiation power for 15 min, reaching pressures in the reaction vessel below 50 PSI.

The reaction mixture was analysed using an Agilent 7890 GC fitted with a Petrocol capilar column (100 m  $\times$  0.25 mm  $\times$  0.5  $\mu$ m) and a FID detector.

## 3. Results and Discussion

### 3.1. X-ray Diffraction

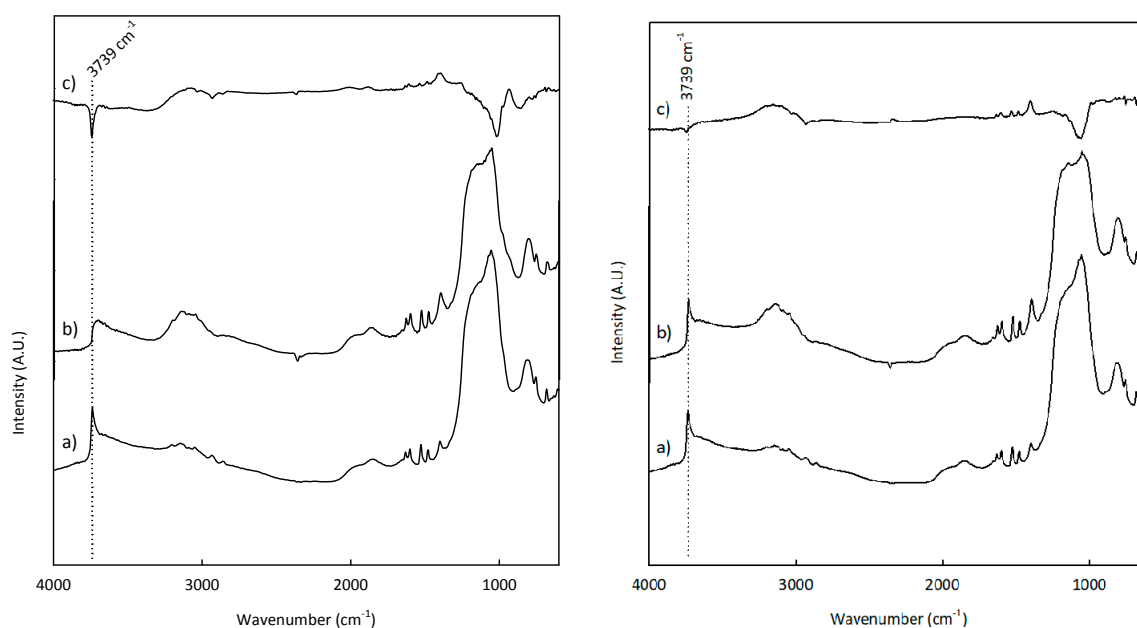
Structure and arrangement of the synthesized materials were evaluated by X-ray diffraction. Figure 1 shows typical reflections at (100), (110), and (200), corresponding with the ordered hexagonal arrangement (P6 mm symmetry group) characteristic of material with the SBA-15 structure. Materials with higher F content showed similar reflections, with a broadening and lower intensity of (100) compared with the parent Al-SBA-15, indicative of a partial deterioration of the structure.



**Figure 1.** Low-angle X-ray diffractograms for the materials synthesized after modification with  $\text{NH}_4\text{F}$  over Nb-modified materials (left side image) and over Al-SBA-15.

### 3.2. DRIFT Spectra

The DRIFT spectra in the region of -OH groups vibration for the Al-SBA-15 support, and the samples containing Nb, and after further modification with F were acquired following thermal treatment at 300 °C and one hour under  $\text{N}_2$  flow. The characteristic bands at 3739  $\text{cm}^{-1}$  corresponding to the stretching mode of the hydroxyl groups can be observed in Figure 2. In addition, there is a broad band at 3580  $\text{cm}^{-1}$  corresponding to the surface hydroxyl groups perturbed by hydrogen bridge bonds. The differential spectra show a negative band at 3939  $\text{cm}^{-1}$  due to the incorporation of Nb and F, which interact and replace -OH groups from Si-OH as well as Al-OH. Thus, the results show that after the incorporation of Nb and F the number of hydroxyl groups decreased, however, there was a part of the -OH groups still present. Such remaining -OH groups behave as strong protonic centers able to protonate 2,6-dimethyl pyridine.



**Figure 2.** DRIFT spectra of the materials, left side image: (a) Al-SBA-15; (b) F10%-Nb1%/Al-SBA-15; and (c) differential spectrum. Right side image: (a) Al-SBA-15; (b) Nb1%/Al-SBA-15; and (c) differential spectrum.

### 3.3. Textural Properties

Textural properties were evaluated by nitrogen adsorption/desorption measurements. Isotherm plots (not shown) obtained were type IV, according to the International Union of Pure and Applied Chemistry (IUPAC) classification, characteristic for mesoporous materials. Table 1 summarizes the textural properties (surface area, pore volume, and pore diameter). The specific surface area decreased after the incorporation of Nb and F, such decrease was more intense for the samples treated with a higher amount of  $\text{NH}_4\text{F}$ . Therefore, these data together with those obtained from the X-ray analysis indicate that the treatment with high loading of ammonium fluoride led to a deterioration in the structure of the materials. In addition, an increase in pore size together with a decrease in pore volume were observed in the materials with a 10 wt.% of F. This has been previously reported by Luque et al. [15], whose work obtained a similar result using the mesoporous material Al-SBA-15, and by Xu et al. [16] who reported that treatment with high loadings of ammonium fluoride damage the mesoporous structure of the material. Finally, it is noteworthy that Nb may partially block the pores of the support causing a decrease in the specific surface area and pore volume [14,19].

**Table 1.** Textural and surface acidic properties of the material employed in this work.

Materials	$S_{\text{BET}}$ ( $\text{m}^2\text{g}^{-1}$ )	D (nm)	$V_{\text{BJH}}$ ( $\text{cm}^3\text{g}^{-1}$ )	Total Acidity ( $\mu\text{mol Py/g}$ )	Brönsted Acidity ( $\mu\text{mol}$ DMPy/g)	Lewis Acidity ( $\mu\text{mol/g}$ )
Al-SBA-15	812	8.1	1.85	129	55	74
F3%/Al-SBA-15	555	8.8	0.88	115	58	57
F10%/Al-SBA-15	291	10.1	0.89	133	74	59
Nb1%/Al-SBA-15	685	8.0	0.82	120	61	59
F3%-Nb1%/Al-SBA-15	382	8.8	0.64	95	43	52
F10%-Nb1%/Al-SBA-15	322	9.0	0.64	129	55	74

### 3.4. Acidic Properties

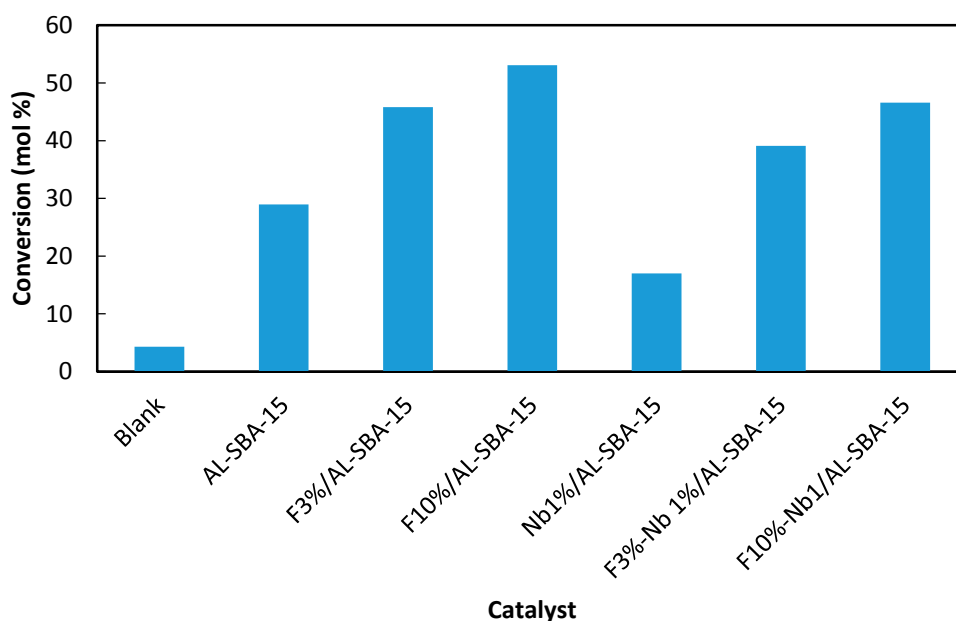
The results of surface acidity measured using pyridine and 2,6-dimethylpyridine as probe molecules are shown on Table 1. Generally, Brönsted acidity decreased after the incorporation either

of Nb or F. However, there were no noticeable differences that, initially, may have led to a significantly different catalytic activity.

### 3.5. Catalytic Activity

The catalytic activity of the synthesised materials was evaluated in the esterification of valeric acid with ethanol. Figure 3 summarizes the most remarkable results in the conversion of valeric acid by the different catalysts studied. No additional products were detected other than ethyl valerate, except for water that is normally produced in the esterification reaction. On the contrary to what was expected, the incorporation of Nb over the SBA-15 aluminosilicates had a negative effect on the conversion of valeric acid. The incorporation of Nb was going to produce, mainly, Lewis acid sites with a negligible increase in Brønsted acidity, which at some point can be blocked leading to reduced conversions for the materials containing Nb, compared with the parent Al-SBA-15.

On the contrary, the materials treated with  $\text{NH}_4\text{F}$ , either Al-SBA-15 or Nb1%/Al-SBA-15, led to materials with a higher catalytic activity in the esterification of valeric acid. Such increase in the conversion of valeric acid was going to be higher as the F loading increased. Therefore, the interaction of fluor with aluminum, despite not causing an increase in the number of acid sites, intensified acidity strength. These results correlate well with those reported by Luque et al. [15], who reported a change in the Al coordination from tetrahedral to octahedral after treatment with ammonium fluoride.



**Figure 3.** Conversion of valeric acid in its esterification reaction with ethanol with different catalysts studied in this work. Reaction conditions: 50 mg of catalyst, 2 mL of ethanol, 0.1 mL of valeric acid, microwave irradiation at 300 W for 15 min.

## 4. Conclusions

Mesoporous SBA-15 aluminosilicates have been modified with Nb and F following different methodologies, ball milling and wet impregnation, respectively. After incorporating both Nb and F, the materials preserve the most characteristic structural and textural properties of the SBA-15, except for the materials treated with a higher amount of ammonium fluoride where a certain degree of deterioration can be observed.

The catalytic activity of the materials was analyzed in the microwave-assisted esterification of valeric acid with ethanol. While the incorporation of Nb had a negative effect on the conversion of valeric acid, the materials treated with ammonium fluoride showed increased catalytic activity in the

esterification of valeric acid, as compared with analogous materials without F. This positive effect of F on the materials can be attributed to an increase in the strength of acid sites in the materials.

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**Conflicts of Interest:** The authors declare no conflicts of interest.

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