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NH_4F modified Al-SBA-15 materials for esterification of valeric acid to alkyl valerates. †

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Abstract: Al-SBA-15 material were functionalised by ball milling with several niobium loadings (0.25-1 wt.%) and/or with several F^-loadings, using NH_4F as precursor. The catalyst herein synthesised were characterised by XRD, N2 porosimetry and 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 on Al-SBA-15 or on Nb1%/Al-SBA-15 leads to a linear increase in valeric acid conversion with the F^- content. Thus, F^- modified mesoporous aluminosilicates efficiently catalyse 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 on the energy demand together with a growing concern about environment has prompt the research on alternative feedstocks for the production of chemicals and energy. In this sense, lignocellulosic biomass appears as an attractive alternative to petroleum as source for fuels and chemicals. Among the main advantages of the utilization of lignocellulosic biomass as feedstock, its accessibility, low price and the minimization of their impact in the environment can be mentioned [1].

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

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

Such esterification reactions have been traditionally homogeneously catalyzed by inorganic acids such as HCl, HNO3, HSO4 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 drawback such as their difficult separation from the reaction mixture, difficulties in the handling and the increase in the production cost [6]. To overcome the previously mentioned problems, heterogeneous catalysts were employed were designed and employed in esterification reactions for the production of biofuels including sulfonic resins [7], zeolites [8] and other 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 could be possible perform analogous chemistries such us the esterification of valeric acid to obtain alkyl valerate fuels. Additionally, the modification of the catalysts containing aluminum with ammonium fluoride boost acidic properties [15] due to the formation of Si(O2F)OH species near aluminum atoms domain [16].

Thus, in this work is going to be reported the modification of SBA-15 aluminosilicates with niobioum 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

The aluminosilate material used as support were synthesized accordingly with a protocol already 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 of tetraethyl ortosilicate were dropwise added and, subsequently the required amount of aluminum isopropoxide to achieve a Si/Al molar ratio of 20. The mixture was kept under continuous stirring at 35 ºC for 24 hours and submitted to hydrothermal treatment for 24 hours. Finally, the sample was filtered out and calcined at 600 ºC for 8 hours. The material herein obtained was named Al-SBA-15.

Al-SBA-15 material was modified with several Nb loadings (0.25, 0.5, 1 wt.%) using ammonium niobate oxalate as 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 minutes. The material obtained was calcined at 400 ºC for 4 hours 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 NH_4F to achieve fluoride loadings of 3 and 10 wt. %. Finally, the materials were calcined at 400 ºC for hours obtaining in this way the materials F3%-Nb1%/Al-SBA-15, F10%-Nb1%/Al-SBA-15, F3%/Al-SBA-15 y 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 the analysis, samples were outgassed for 12 hours at 130 ºC. The specific surface area was evaluated using the linear part of the BET equation in the interval $0,05 < P_o < 0,22$. The pore size distribution was calculated from the adsorption branch and using the BJH equation.

The XRD of the catalysts synthesised were acquired in a Bruker D8D Discover (40 kV,40 mA) diffractometer, the radiation employed has been the line Cu Kα (λ=1,54 Å). The goniometer speed was 0.5 º/min in the interval $0,5° < 2\theta < 5°$.

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

Acidic properties were evaluated by a chromatographic titration method using pyridine and 2,6-dimethylpiridine as probe molecules, for total and Brönsted 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 minutes, 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 x 0,25 nm x 0,5 μm) and a FID detector.

3. Results and discussion

3.1. X-Ray diffraction.

The structure and arrangement in the sunthesised materials wereevaluated by X-Ray diffraction. Figure 1 shows typical refections at (100), (110) y (200), corresponding with ordered hexagonal arrangement (P6mm simmetry group) characteristic for material with SBA-15 structure. Even, those materials with higher F content, show these refelction with a broadening and lower intensity for (100) as compared with the parent Al-SBA-15 as indicative of a partial deterioration of the sturcture.

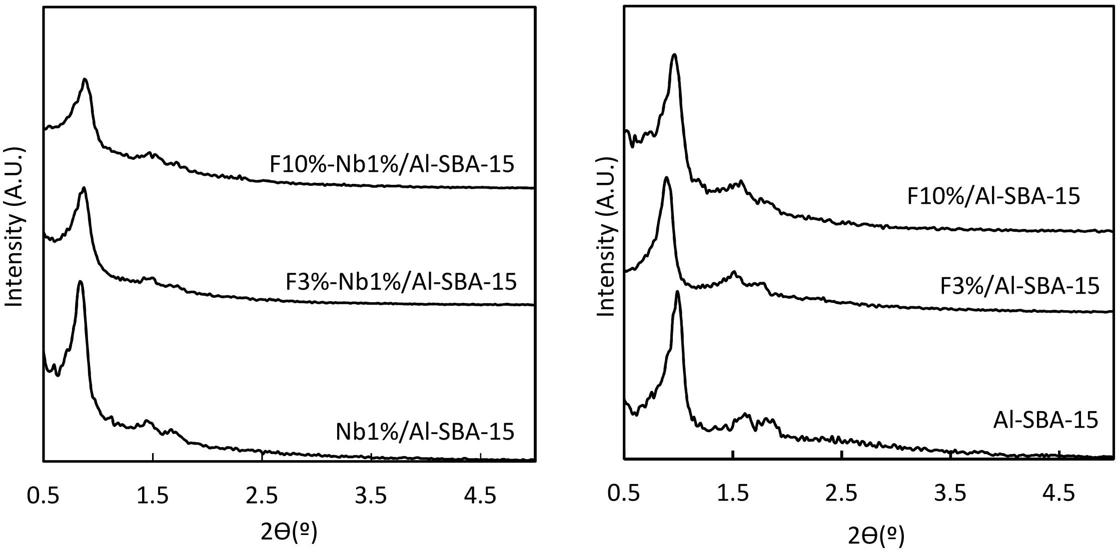

Figure 1. Low-angle X-ray diffractograms for the materials synthesized after modification with NH_4F over Nb modified materials (left side image) and over Al-SBA-15.

3.2. DRIFT spectra.

The DRIFT spectra in the region of the vibration of -OH groups for the Al-SBA-15 support and the samples containing Nb and after further modification with F were acquired after thermal treatment 300 ºC after one hour under N_2 flow. The characteristics bands at 3739 $^{-1}$corresponding with the stretching mode of the hydroxyl groups can be observed in Figure 2. In addition, a broad band at 3580 cm^{-1} corresponding with surface hydroxyl groups perturbed by hydrogen bridge bonds. The differential spectra show a negative band at 3939 cm^{-1} due to the incorporation of Nb and F, which interact and replace -OH groups from Si-OH as well as from Al-OH. Thus, the results are showing that after the incorporation of Nb and F the number of hydroxyl groups decrease, however there is a part of the -OH groups still present. Such remaing -OH groups behave as strong protonic centers able to protonate 2,6-dimethyl pyridine.

3.3. Textural properties.

Textural properties were evaluated by nitrogen adsorption/desorption measurements. Isotherm plots (not shown) obtained were type IV, according with IUPAC classification, characteristic for mesoporous materials. Table 1 summarises the textural properties (surface area, pore volume and pore diameter). The specific surface area decreases after the incorporation of Nb and F, such decrease it is more intense for the samples treated with a higher ammount of NH_4F. Therefore, these data together with those obtained from X-ray point out that the treatment with high loading of ammonium fluoride lead to a deterioration in the structure of the materials. In addition, an increase in the pore size together with a decrease in pore volume are observed in the materials with a 10 wt.% of F. This has been previously reported by Luque et al. [15] in whose work obtained a similar result using the mesoporous material Al-SBA-15 and by Xu et al. [16] who reported that the treatment with high loadings of ammonium fluoride damage the mesoporous structure of the material. Finally, it is wothy to mention 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_{BET} (m^2g^{-1})	D (nm)	V_{BJH} (cm^3g^{-1})	Total acidity (μmol Py/g)	Brönsted acidity (μmol DMPy/g)	Lewis acidity (μmol /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

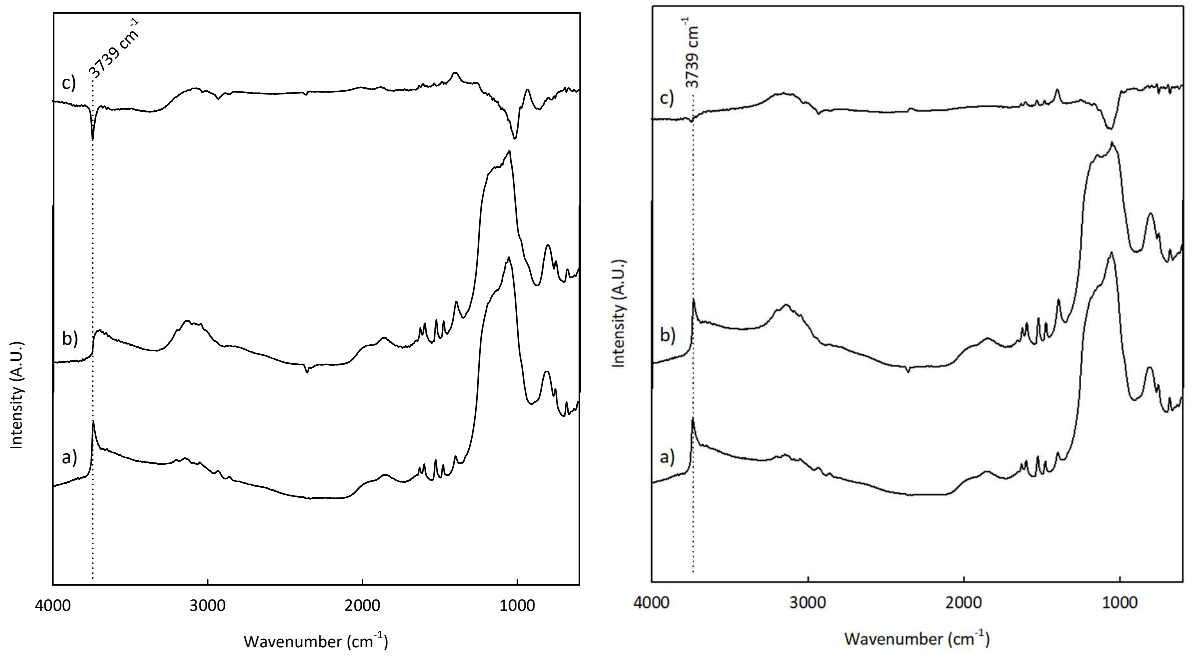

Figure 2. DRIFT spectra of the materials, left side image: a) Al-SBA-15, b) F10%-Nb1%/Al-SBA-15 and c) differential spectrum, right side image: a) Al-SBA-15, b) Nb1%/Al-SBA-15 and c) differential spectrum.

3.4. Acidic properties.

The results of surface acidity measured using pyridine and 2,6-dimethylpiridine as probe molecules are shown on Table 1. Generally, Brönsted acidity is decreased after the incorporation either of Nb or F. However, there are not noticeable differences that, initially, may lead to a significative 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 summarises the most remarkable results in the conversion of valeric acid by the different catalysts studied. There was not detected any other additional product to ethyl valerate, except for water that is normally produced in the esterification reaction. On the contrary of what it could be expected, the incorporation of Nb over the SBA-15 aluminosilicates has a negative effect on the conversion of valeric acid. The incorporation of Nb is going to produce, mainly, Lewis acid sites with a negligible increase in Brönsted acidity, that at some point can be blocked leading to reduced conversions for the materials containing Nb as compared with the parent Al-SBA-15.

On the contrary, the materials treated with NH_4F, either Al-SBA-15 or Nb1%/Al-SBA-15, lead to materials with a higher catalytic activity in the esterification of valeric acid. Such increase in the conversion of valeric acid is going to be higher as higher is the F loading. Therefore, the interaction of fluor with aluminum, despite of not cause an increase in the number of acid sites, intensify 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 the treatment with ammonium fluoride.

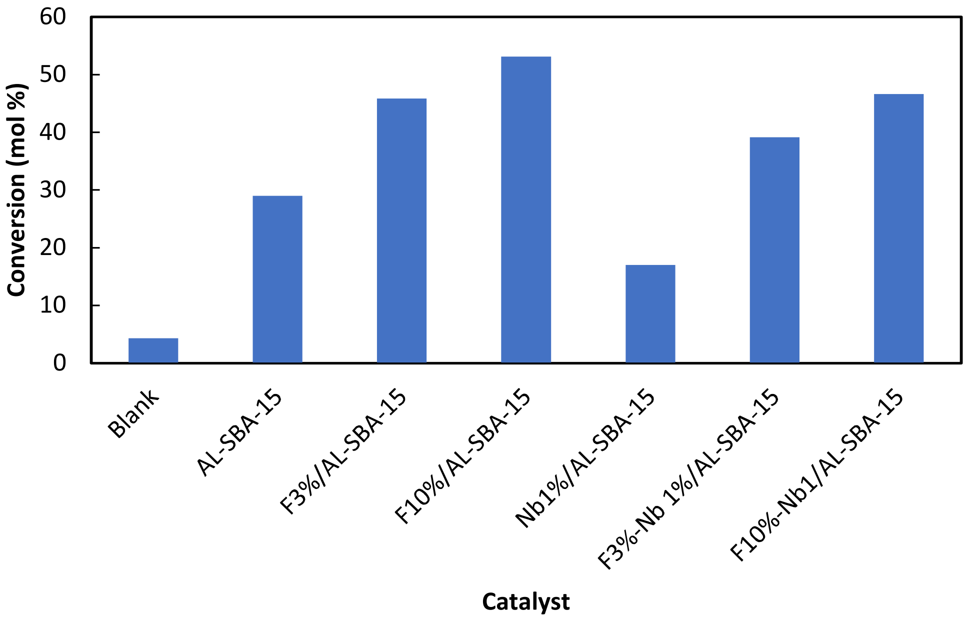

Figure 3. Conversion of valeric acid in its esterification reaction with ethanol with different catalysts studied in this work. Reaction conditions: 50 mg of catalyst, 2 mL of ethanol, 0.1 mL of valeric acid, Microwave irradiation: 300 W, 15 minutes.

4. Conclusions.

Mesoporous SBA-15 aluminosilicates have been modified with Nb and F following different methodologies, ball milling and wet impregnation, respectively. After the incorporation of 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 has a negative effect on the conversion of valeric acid, the materials treated with ammonium fluoride shown 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 explaining to an increase in the strength of the acid sites in the materials.

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Conflicts of Interest: "The authors declare no conflict of interest."

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