New insights in the deactivation of sulfonic modified SBA-15 catalysts for biodiesel production from low-grade oleaginous feedstock.

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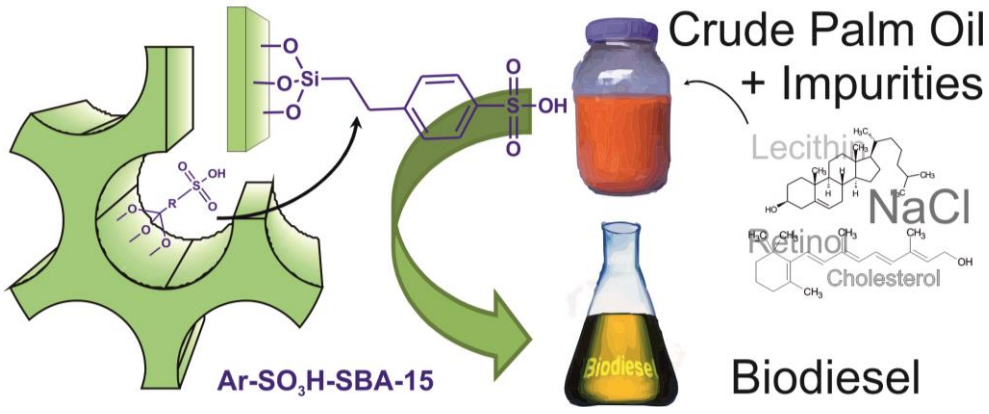
Abstract

Arenesulfonic-acid functionalized SBA-15 materials have been used in the production of biodiesel from low grade oleaginous feedstock. These materials display an outstanding catalytic activity, being able to promote the transformation of crude palm oil with methanol into fatty acid methyl esters with high yield (85%) under mild reaction conditions. However, high sensitivity of the catalyst against poisoning by different substances has also been detected. Thus, alkaline metal cations, such as sodium or potassium exert a negative influence on the catalytic activity of these materials, being necessary amounts around 500 ppm of sodium in the reaction media to decrease the catalytic activity of these materials to a half of its initial value in just two reaction runs. The deactivation of arenesulfonic acid functionalized SBA-15 materials seems to occur in this case by ion exchange of the acid protons at the sulfonic groups. Organic unsaponifiable compounds like lecithin or retinol also induce a negative influence in the catalytic activity of these sulfonic acid-based materials, though not so intense as in the case of alkaline metals. The deactivating mechanism associated to the influence of the organic compounds seems to be linked to the adsorption of such substances onto the catalytic acid sites as well as on the silica surface. The accumulation of lecithin in the surface of catalyst, observed by means of thermogravimetric analysis, suggest the creation of a strong interaction, probably by ion pair, between this compound and the sulfonic acid group.



Keywords

Biodiesel. Heterogeneous acid catalysts. Sulfonic acid catalysts. SBA-15. Low-grade feedstock. Second generation biodiesel.

1. Introduction

Oleaginous feedstock typically used in the production of first generation biodiesel are also edible substances (mainly refined vegetable oils) and thus, the interest of the different markets (food and biofuels) for the same feedstock has generated a competition for the raw materials, creating important problems and social concerns linked to increasing prices for these edible substances [1, 2]. Overcoming this important disadvantage has motivated scientist to focus their efforts in the development of new production technologies with higher profitability and environmental sustainability, being able to produce a second generation of biodiesel from less demanding non-edible feedstock, and thus numerous papers dealing with investigations devoted to the use of non-edible feedstocks for biodiesel production have been published. A whole collection of these substances has been reported, including non-refined natural feedstocks, like *Jatropha-curcas* oil or even waste oleaginous feedstocks, such as waste cooking oil, rendered animal fats and so on [3]. A proof of the importance of this trend is the promulgation of the EU Directive 2009/30/CE, establishing greenhouse emission reductions, which promotes the use of waste vegetable oils and animal fats because of higher reduction of greenhouse gasses emissions associated to the biodiesel obtained from these feedstock. Therefore, it is of major importance studying alternative non-edible waste feedstock for the sustainable production of biodiesel. However, this is not an easy task, since waste oils and fats usually contain a high number of impurities (free fatty acids, water, metals, unsaponifiable matter) which interfere in the chemical transformation step as well as in the quality of the final biodiesel. Regarding the influence of the impurities present in raw materials, most of the waste oleaginous substances cannot be processed by existing homogeneous base-catalyzed biodiesel processes. Furthermore, a significant amount of unsaponifiable matter and metals has a detrimental effect on the catalyst due to deactivation phenomena [4, 5].

During the last years, an important technological issue in the field of biodiesel production has been the design of novel heterogeneous catalysts [2, 6] since their use offers several advantages over their homogeneous counterparts (cheaper and easier separation processes, reusability, reduced water consumption and reduced capital and

energy costs). Thus, a wide collection of heterogeneous acid catalyst has been described in literature for biodiesel production [7]. Among these, the organosulfonic acid-functionalized mesoporous silicas have revealed to be highly active catalysts for biodiesel production [8], even in the transformation of low-grade oleaginous feedstock. However, the activity of these catalysts is strongly affected by the presence of several impurities and undesirable chemicals present in oleaginous feedstock, especially if these are wastes or recycled substances [9, 10], such as those above mentioned for the production of a second generation of biodiesel.

Typical impurities present in low grade oleaginous feedstock include alkaline metal cations, such as sodium –quite plenty in waste cooking oils because of the use of salt–, potassium, calcium or magnesium, coming from inorganic substances accompanying the lipid feedstock. Other impurities are phosphorus, nitrogen or sulphur-containing chemicals, which are more abundant in fats and oils extracted from animal organisms [11], due to the presence of phospholipids in animal membrane cells and nitrogen and sulfur in proteins [12]. Finally, unsaponifiable mater is usually considered as an impurity too. This includes all those constituents which cannot be saponified and thus, cannot be converted into biodiesel. Typical unsaponifiable compounds in lipid feedstock are sterols, terpenes, tocopherols, pigments, waxes, higher molecular weight alcohols... [13, 14].

Within the scope of this work, we present the follow up work with the aim to explore the effect of the impurities on the catalytic activity in order to correlate these effects on yield to fatty acid methyl esters. Special focus has been addressed to elucidate the interaction of impurities with sulfonic acid sites by means of X-ray Photoelectron Spectroscopy (XPS).

2. Experimental

2.1. Materials

Crude palm oil (CPO, Gran Velada) (see properties in Table 1) and methanol (ACS grade, Aldrich) were used as feedstock for fatty acid methyl ester production as received without further purification. Tetraethylorthosilicate (TEOS, 98 %, Aldrich) and 2-(4-cholorsulfonylphenyl)-ethyltrimethoxy silane (CSPTMS, ABCR) were used as silica and sulfonic acid groups precursors, respectively, for the synthesis of the arenesulfonic acid-functionalized SBA-15 material used as methanolysis catalyst. The tri-block copolymer Pluronic P-123 (PEO_{20}-PPO_{70}-PEO_{20}, Aldrich) was used as structure directing agent to template the mesoscopic porous structure of the catalyst.

2.2. Synthesis of Ar-SO_3H-SBA-15

Arenesulfonic acid-functionalized SBA-15 (Ar-SO_3H-SBA-15) was prepared from 2-(4-chlorosulfonylphenyl)-ethyltrimethoxy silane using a method described elsewhere [16]. In a typical synthesis, the surfactant (P123, 4 g) was dissolved at room temperature in 125 mL of a 1.9N aqueous solution of hydrochloric acid. The mixture was then warmed up to 40ºC and 7.67 g of TEOS were added. The resultant white suspension was then gently stirred for 45 min before adding dropwise 2.67 g of CSPTMS. Stirring was maintained at 40ºC for 20 additional hours before transferring the suspension to a stainless steel autoclave to hydrothermally age the material at 110ºC for 24 h. The material was finally recovered by filtration and the surfactant was removed by ethanol washing (twice) under refluxing conditions.

2.3. Catalyst characterization

The textural properties of the arene-SO_3H-SBA-15 material were obtained by processing the N_2 adsorption-desorption isotherm data recorded at 77K in a Micromeritics TRISTAR 3000 unit. Surface area was calculated using the BET method whereas pore sizes distribution was obtained by the BJH method using the KJS correction. Total pore volume was assumed to be that recorded at p/p_0 = 0.975. Structural ordering was further assessed by means of X-ray powder diffraction (XRD), whose pattern was acquired on a Philips X´Pert diffractometer using th Cu Kα line in the 2θ angle range of 0.6-5.0° with a step size of 0.02°.

Elemental analysis, for the calculation of sulfur content, was carried out in an Elementar Vario El III unit. Acid capacity was determined by potentiometric titration of the sulfonic acid-containing material. This was accomplished by suspending the sample in a 2M NaCl solution for cation-exchange followed by direct titration of the protons released to the medium with 0.01M NaOH aqueous solution. Metals retained in the catalyst during the methanolysis tests were quantified by means of ICP-OES. The chemical environments of sulfonic group were studied by means X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS HSi instruments equipped with a charge neutraliser and using monochromatic Al Kα X-ray source. Spectra were recorded at normal emission using analyser pass energy of 40 eV and X-ray power of 225 W. Prior to the analysis, samples were outgassed at 10^{-9} bar overnight. Binding energies were referenced to the C1s line (284.8 eV) and deconvolution curves were achieved using the Casa XPS software. TG analyses were recorded using a simultaneous DSC-TGA SDT 2960 thermogravimetric scale.

Table 2 summarizes the most relevant physicochemical properties obtained for the Ar-SO_3H-SBA-15 material. Textural and structural properties, obtained by means of N_2 adsorption and XRD evidence a surface area value, narrow pore size distribution and mesoscopic ordering typical of SBA-15 mesostructured materials. The material also displays quite a good loading of sulfonic acid groups, with almost complete accessibility to each one of these acid catalytic sites.

2.4. Catalytic tests

All the experiments were carried out in a 25 mL stainless-steel batch reactor (Autoclave Engineers) fitted with temperature and mechanical stirring rate controllers and a pressure transducer. Catalytic tests were performed under the reaction conditions previously determined to be the optimal for the use of this catalyst in vegetable oil methanolysis [8]. Thus, in a typical experiment, the starting crude palm oil was placed inside the reactor vessel together with an appropriate amount of methanol (methanol to oil molar ratio 30) and catalyst (8 wt% based on oil weight). The system was then hermetically sealed and the temperature and stirring conditions fixed at 160ºC and 2000 rpm respectively. The reaction proceeded for two hours before collecting the reaction products to be analyzed. The reaction suspension was

filtered using a nylon filter to remove the catalyst, and the molar yield towards fatty acid methyl esters (FAME) was calculated by means of ^{1}H NMR analyses following the method described by Whalen et al [17]. Recycling tests were performed with intermediate catalyst washing (twice) with methanol and n-hexane to ensure the removal of the reaction media from the pores.

3. Results and discussion

This investigation consists of assessing the individual effect of several impurities on the catalytic behavior of the Ar-SO_3H-SBA-15 material in the production of biodiesel. Selected impurities and natural substances are typically present in unrefined vegetable oils and low grade oleaginous raw materials [9]. For that purpose, the influence of the presence of alkaline metal cations, phospholipids, and unsaponifiable natural compounds usually present in oleaginous feedstock has been studied. This was accomplished by means of performing catalytic tests in presence of increasing amounts of each one of these potential poisons by doping the starting crude palm oil (CPO) with sodium and potassium chlorides (to check the influence of alkaline metal cations), phosphatidylcholine (also known as lecithin, to assess the influence of phospholipids), cholesterol and retinol (unsaponifiable sterol and retinoid compounds, respectively). These substances have been added in a higher amount to that conventionally present in unrefined lipid feedstock [9] in order to boost their deactivating effect and to facilitate determining their effect on the catalytic behavior of the catalyst . Thus, the catalytic activity and stability of Ar-SO_3H-SBA-15 catalysts were evaluated in two consecutive reaction runs with intermediate double-washing of the catalyst.

3.1. Effect of alkaline metal cations

Figure 1 displays the results achieved from the catalytic experiments performed in the methanolysis of CPO with Ar-SO_3H-SBA-15 in presence of alkaline metal cations, added as sodium and potassium chloride in different amounts. Two sets of experiments are depicted, corresponding to the use of fresh catalyst and a second one in which the same catalyst sample has been reused after washing. Reactions performed over undoped crude palm oil have been included as reference. Additionally, Figure 1 also displays the remaining acid capacity, as determined by acid-base titration, in the used catalysts after the first reaction run.

Both sodium and potassium cations exert a negative influence on the catalytic activity of the heterogeneous acid catalyst when present in the reaction medium. The starting catalytic activity, corresponding to the fresh catalyst, seems to be unaffected, since this is almost the same shown by the material with undoped CPO. This is probably due

to the fact that, although sodium and potassium species can lead to cation exchange -the most probable cause of deactivation because loss of acidity [18]-, the protons released from the catalyst remain in the reaction media, leading to the promotion of methanolysis reactions. On the contrary, recycling tests evidence a reduced capability of the catalyst in the production of FAME, because some of the acid protons are removed during the filtration of the catalysts and its washing, being not regenerated in this stage. This fact becomes more evident when comparing the acid and metal loading present in catalyst samples after reaction. Table 3 displays the acid and metal loading present in samples of the Arene-SO3H-SBA-15 material used in methanolysis reactions carried out in presence of alkaline metal chlorides. Thus, in every case a loss of acidity is observed insofar as the amount of alkaline cations increases (Figure 1, right axis; Table 3). This decrease is accompanied by the metals uptake present in the reaction media, whose concentration in the used catalyst samples matches with the experienced acidity loss.

As for the observed differences between the two tested alkaline metals, although sodium is added in a higher amount than potassium because of its lower atomic mass, the capability of the former to exchange protons seems to be superior to potassium, as it can be ascertained in the efficiency of the cation exchange, especially in the reactions accomplished in presence of 500 ppm of metal chlorides. This fact can be probably due to the higher solubility of sodium chloride in methanol, compared to potassium chloride, under the assayed reaction temperature conditions [19], favoring the cation exchange process and leading to a more remarkable deactivating effect.

Sulfur content (not shown), recorded to assess the integrity of the sulfonic acid group, does not suffer any change after the reaction tests, supporting the idea about the main cause of deactivation in Ar-SO_3H-SBA-15 is the loss of acidity caused by exchange of the protons at the acid groups with the alkaline metal cations. However, there is a question mark on the notable influence of these impurities on the catalytic behaviour of the Ar-SO_3H-SBA-15 material, as the amount of sodium and potassium chloride added to the reaction media is quite low, as compared to the amount of sulfonic acid groups incorporated within the acid catalyst. This suggests the existence of a secondary reason –apart from the cation exchange- in the observed catalytic activity

decay of the sulfonic acid groups. A feasible explanation might be the action of the different impurities acompanying crude palm oil, as stated in previous works [9].

In order to assess the real influence of the presence of alkaline metal cations on the chemical environment of the sulfonic acid groups, S 2p XPS experiments were carried out for catalyst samples after being used in methanolysis reactions in presence of high amounts of sodium and potassium chloride. Results have been depicted in Figure 2, together with the results from the deconvolution of the spectra into $S2p_{3/2}$ and $S2p_{1/2}$ spin orbit components. The catalyst used in presence of undoped crude palm oil displays an S2p XPS spectrum which can be deconvoluted into two different signals, centered at 168.25 eV and 169.45 eV, which are consistent with the presence of an aromatic ring adjacent to the sulfonic acid group [19-22]. Using the Ar-SO_3H-SBA-15 material in presence of high amounts of alkaline metal cations shows new S2p core level signals located at lower binding energy values. These new species could be related to the presence of sodium or potassium sulfonate groups (-SO_3X, X=Na, K), since these appear at lower binding energy values in X-ray photoelectron spectroscopy [23]. This fact, together with the sodium and potassium contents detected in the surface of the catalyst samples (Table 3), confirms the metal alkaline cations uptake by sulfonic acid groups. In this way, cation exchange reveals as the most probable cause of catalytic activity loss in Ar-SO_3H-SBA-15 when used in presence of high amounts of alkaline metal cations. Nevertheless, this deactivating phenomenon has been proved to be reversible, and the protic form of the sulfonic acid groups can be easily regenerated by a simple washing of the catalysts with mineral acids [24].

3. 2. Effect of unsaponifiable chemicals

Another type of chemicals conventionally present in low-grade oleaginous feedstock, specially unrefined vegetable oils and animal fats, are unsaponifiable chemicals such as phospholipids, retinoids and other large organic molecules such as cholesterol [25]. Some of these substances have revealed to exert a poisoning effect in Lewis-type acid catalysts by strong adsorption [26], and thus, their influence on the catalytic behavior of Ar-SO_3H-SBA-15 deserves to be addressed. For this purpose, the influence of increasing amounts in CPO of lecithin -the common name given for phosphatidylcholine, a phosphatide of fatty acid diglycerides linked to the choline

ester of phosphoric acid-, cholesterol and retinol, as representatives of sterol and retinoid families of compounds, respectively, has been studied.

Figure 3 depicts the FAME yield (Bars, left axis), as well as the catalyst acid loading (Dots, right axis), achieved in the experiments performed in the methanolysis of CPO in presence of unsaponifiable organic compounds, both when using the fresh catalyst and in a recycling test.

First use of the Ar-SO_3H-SBA-15 catalyst leads to lower FAME yields when both lecithin and retinol are present in high amounts in the reaction media, suggesting the existence of some negative influence of these chemicals on the catalytic activity of these heterogeneous Brønsted-type acid catalysts. This effect seems to be more important in the case of lecithin as it is present at $mg \cdot kg^{-1}$ concentration levels, whereas retinol is added to the reaction media in a much higher concentration. In contrast, with regard to the influence of cholesterol (results not shown), the catalytic activity of the Ar-SO_3H-SBA-15 catalyst is well preserved, even if the concentration of this unsaponifiable chemical in the reaction mixture is as high as 10 wt% (100,000 $mg \cdot kg^{-1}$) of the total amount of oleaginous feedstock. The negative influence of lecithin and retinol on the catalytic activity of the sulfonic acid-based material is more evident when analyzing the results from the recycling tests, where a dramatic catalytic activity reduction is observed, especially if those impurities are present in high concentration. This fact is accompanied by a strong reduction in the amount of catalytic acid sites detected onto the surface of the SBA-15-based material (Figure 3, dots, right axis), which could be linked to the catalytic activity decay. The reasons lying beneath the loss of acid loading supported onto the mesostructured materials as well as the loss of catalytic activity could be two: acid sites neutralization, which seems unlikely in the case of retinol, as this compound does not show ion exchange capability, and catalytic site blockage, because of deposition of the bulky organic molecules onto them, avoiding the access of the reactant molecules to the sulfonic acid groups and preventing their transformation. In the case of cholesterol, the diffusion of this molecule inside the porous system, where the sulfonic acid groups are located, could be restricted because of its more rigid molecule conformation (Figure 4), thus preventing the deactivation of the sulfonic acid group

The causes lying beneath the deactivation of the Ar-SO_3H-SBA-15 catalysts where investigated by means of different techniques, including X-ray photoelectron spectroscopy tests and thermogravimetric analysis performed on single-used, and washed samples of the sufonic acid-based material.

In order to ascertain the influence of the tested unsaponifiable impurities in the catalytic activity of the acid sites, the interaction between these substances with sulfonic acid groups was assessed by means of S2p and O1s XPS. Differences between the different samples are quite clarifying. Figure 5 depicts the results from XPS assays performed at the S2p & O1s core levels, on used samples of Ar-SO_3H-SBA-15 material. As previously stated, S2p spectrum recorded for the starting Ar-SO_3H-SBA-15 catalyst can be deconvoluted into $S2p_{3/2}$ and $S2p_{1/2}$ signals (168.25 and 169.45 eV), corresponding to the presence of arene sulfonic-acid groups (Figure 5A). However, this is not the case when the catalyst has been previously used in methanolysis tests in presence of retinol and lecithin, where another couple of signals are detected. In both cases, the original signals are split into two, one being the very same already present in the fresh catalyst and a new one shifted towards lower binding energy values. These results suggest that a fraction of the initial catalytic acid sites loading is interacting with the tested unsaponifiables, leading to the modification of the S2p XPS spectra. The shifting of these signals towards lower binding energy values involves a lower electron withdrawal capability of the substituting groups bonded to sulfur atoms at the catalytic acid sites. However, it seems that the interaction of the lecithin and the retinol with the sulfonic acid groups has a different foundation. In the case of lecithin, phosphatidylcholine displays an ionic group (the phosphate) which could interact with the catalytic acid site by ion exchange, leading to the displacement of the acid protons and causing the catalytic activity decay. On the contrary, retinol does not show any ion exchange capability and hence, the deactivation mechanism should not be the same. Thus, the hindered access of reactant to the catalytic acid sites, due to the adsorption of retinol on the same, could be ascribed as the major cause for the catalyst deactivation by retinol, although this only occurs when this is present in very large quantities such as those tested within the present study.

Figure 5B depicts the XPS spectra recorded at the C 1s core level for the used catalyst in presence of plain CPO and CPO doped with large amounts of lecithin and retinol. All of the samples displayed two distinct signals, one located at 284.6 eV, which is attributed to the presence of saturated methylene groups (-CH_2-), such as those present in the aliphatic chains of fatty acids (either in FAME or in glyceride forms), and another one located at 286.0 eV, which is usually attributed to the presence of carbonyl groups (-COO-). In this way, these signals can be ascribed to the presence of FAME or glyceride species remaining adsorbed onto the surface of the used catalysts. However, the C1S XP spectrum recorded for the sample used in presence of lecithin displays a much higher intensity for the signal located at 286.0 eV. This suggests the detection of additional carbon environments coming from the adsorbed lecithin which provide XPS signals at the C 1S core level overlapping with that attributed to the carboxylic group. These signals are those corresponding to C-O and C-N^+ carbon species present in the phosphatidylcholine [27], and support our conclusions about the preferential adsorption of lecithin over the catalyst.

In order to provide additional support to assess the true nature of the interaction of the tested organic impurities with the surface of the heterogeneous sulfonic acid-based catalyst, thermogravimetric analyses were conducted over samples used in presence of lecithin and retinol. Figure 6 displays the TG and DTA curves obtained for those tests. These experiments were accomplished after washing the used catalyst samples with methanol and n-hexane, in order to remove the physisorbed organic molecules from the surface of the materials. All the tests led to rather similar TGA curves showing three weight losses, which are located in the following temperature regions: up to 150ºC, between 150ºC and 430ºC and above 430ºC. The first one can be ascribed to the evaporation of the washing solvents used after the catalytic assays, whereas the last is attributed to the loss of the sulfonic acid group. It is noteworthy that this weight loss is rather similar in every tested sample, suggesting that the amount of arene-sulfonic acid groups remains constant regardless the presence of organic impurities. As for the second weight loss, this can be ascribed to the presence of adsorbed organic compounds, such as lecithin and retinol, and this is the region where larger differences can be observed between samples used in presence of both

compounds. Unlike for retinol, where no evident trend is found in weight loss when increasing the amount of this unsaponifiable chemical, lecithin seems to be accumulated onto the surface of the heterogeneous acid catalysts. This is inferred from the higher weight loss detected in this region insofar as the concentration of this phosphatide is increased in the reaction media, supporting the idea of the existence of a selective interaction (ionic exchange) between the catalyst and this oleaginous impurity. In this way, it seems clear that the deactivating effect of lecithin and retinol is completely different. Thus, in the case of retinol, this seems not to strongly interact with the surface of the heterogenous acid catalysts, so that the most probable cause of deactivation is the pore blockage or the covering of the catalytic acid groups, avoiding the access of the reactants to the same. On the contrary, the deactivation caused by lecithin seems to occur with a stronger interaction with the catalyst, for instance by the formation of an ion pair at the sulfonic acid group by ion exchange, as it was predicted from XPS analyses. However, it is expected this interaction could be removed, together with the accumulated lecithin by a simple washing stage with diluted mineral acid, leading to the recovering of the protic form of the sulfonic acid group [24].

4. Conclusions

Arenesulfonic-acid functionalized SBA-15 material (Ar-SO_3H-SBA-15) has revealed to be a highly active catalyst for the transformation of low-grade oleaginous feedstock into biodiesel through the methanolysis of triglycerides and free-fatty acids present in the raw materials. However, this catalyst is quite sensitive to the presence of certain kinds of impurities, which are present in waste lipids in high amounts. Some of these poisons are cationic metal species such as alkaline metals, which can negatively influence the catalytic activity of Ar-SO_3H-SBA-15 materials because of the neutralization of the acid sites by means of cation exchange. The important uptake of these ionic species in the heterogeneous catalyst, as well as S 2p XPS spectra, supports the cationic exchange deactivating mechanism. On the other hand, certain organic compounds, such as lecithin and retinol, also present in high amounts in certain kinds of oleaginous feedstock, exert a negative influence on the catalytic activity of sulfonic acid-functionalized materials. In this case the major cause of deactivating behavior seems to be linked to the hindered access of the reactants for the catalytic acid sites because of the adsorption of these substances onto the surface of the silica matrix as well as onto the catalytic acid sites. In addition to this, in the case of lecithin the ionic interaction with the sulfonate anionic group could be also ascribed as another cause of its deactivating activity in arene-sulfonic-acid based catalysts. Nevertheless, the catalyst has also demonstrated to be highly resistant against poisoning by other bulky unsaponifiable compounds such as cholesterol.

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Table 1. Properties of crude palm oil used as feedstock for methyl ester production.

Property	Analysis Method	Value
Acid value (mg_{KOH}/g)	UNE EN ISO 660:2000	21.45
Metals (mg/kg)	ASTM D5185:2013	
	P	13.1
	Na	15.7
	K	n.d.
	Mg	4.9
	Ca	5.3
Fatty acid profile (wt%)	UNE EN ISO 5508:1996 and 5509:2000	
	Myristic acid (14:0)	0.8
	Palmitic acid (16:0)	43.3
	Palmitoleic acid (16:1)	0.0
	Stearic acid (18:0)	5.2
	Oleic acid (18:1)	39.7
	Linoleic acid (18:2)	10.5
	Linolenic acid (18:3)	0.4
Water (mg/kg)	UNE EN ISO 12937:2001	687
Unsaponifiables (wt%)	Method reported by Plank and Lorbeer, 1994 [15]	2.5

n.d.: not detected (below detection limit - <0.05 $mg \cdot kg^{-1}$).

Table 2. Physicochemical properties of the arene-SO_3H-SBA-15 catalyst.

Sample	Textural Properties					Acid Properties		
	d_{100}[a] (Å)	Dp[b] (Å)	BET_{area} (m^2/g)	Vp[c] (cm^3/g)	Wall thick[d] (Å)	Acid capacity[e] (meq/g)		Accessibility[f] (%)
						S	H^+	
Arene-SO_3H-SBA-15	106	83	706	0.89	39	1.07	1.03	96

[a] d_{100} spacing, measured from small-angle X-ray diffraction. [b] Mean pore size (D_p) from adsorption branch applying the BJH method. [c] Total pore volume (V_p) recorded at P/P_o= 0.975 single point. [d] Average pore wall thickness calculated by a_o-pore size ($a_o = 2\ d_{100} / \sqrt{3}$).[e] Acid capacity defined as meq of acid centers per g of catalyst (obtained either directly by titration or indirectly from sulfur content by elemental analysis).[f] Defined as the ratio between H^+ from acid-base titration and sulfur content from elemental analysis.

Table 3. Acid loading and sodium and potassium content in samples of arene-SO_3H-SBA-15 catalyst used in presence of sodium and potassium chloride.

Metal chloride loading	NaCl				KCl			
	$H^{+\,a}$ ($meq \cdot g^{-1}$)	$Na^{+\,b}$ ($meq \cdot g^{-1}$)	$Na^{+\,c}$ ($meq \cdot g^{-1}$)	$\eta^{\,d}$ (%)	$H^{+\,a}$ ($meq \cdot g^{-1}$)	$K^{+\,b}$ ($meq \cdot g^{-1}$)	$K^{+\,c}$ ($meq \cdot g^{-1}$)	$\eta^{\,d}$ (%)
+100 mg/kg	0.94	0.10	0.10	100	1.00	0.06	0.06	100
+500 mg/kg	0.70	0.36	0.52	69.2	0.92	0.12	0.30	40.0

[a] Acid loading remaining in the catalyst; [b] Metal content present in used samples; [c] Metal loading added to the reaction media (referred to the amount of catalyst); [d] Efficiency of the cation exchange process calculated as the amount of metal detected in used samples divided by the amount of metal added to the reacting media.

Figure captions

Figure 1. Results from methanolysis reaction tests over CPO doped with alkaline metal cations – FAME Yield mol% (Bars, Left axis) and Catalyst acid capacity after the first reaction (Dots, Right axis). Impurities contents referred to the initial amount of CPO. Reaction conditions: Temperature = 160ºC; methanol:oil molar ratio = 30; catalyst loading = 8 wt%; stirring rate = 2000 rpm; reaction time = 2 h.

Figure 2. S-2p XPS spectra recorded for Ar-SO_3H-SBA-15 catalysts used in methanolysis tests performed in presence of alkaline metals in the reaction mixture.

Figure 3. Results from methanolysis reaction tests, performed in presence arene-SO_3H-SBA-15 material, carried out over CPO doped with organic natural substances (lecithin and cholesterol). –FAME Yield mol% (Bars, Left axis) and Catalyst acid capacity after the first reaction (Dots, Right axis)-. Impurities contents referred to the initial amount of CPO. Reaction conditions: Temperature = 160ºC; methanol:oil molar ratio = 30; catalyst loading = 8 wt%; stirring rate = 2000 rpm; reaction time = 2 h.

Figure 4. Chemical structures of cholesterol, retinol and lecithin.

Figure 5. A) S-2p XPS spectra and B) C-1s XPS spectra recorded for Ar-SO_3H-SBA-15 catalysts used in methanolysis tests performed in presence of unsaponifiable compounds in the reaction mixture.

Figure 6. TG and DTA curves obtained for Ar-SO_3H-SBA-15 samples used in CPO methanolysis tests in presence of A) lecithin and B) retinol.

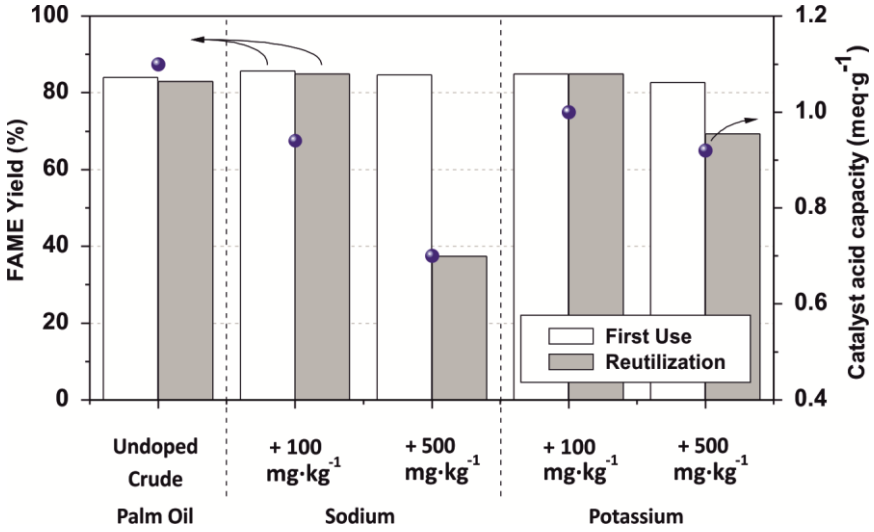

Figure 1

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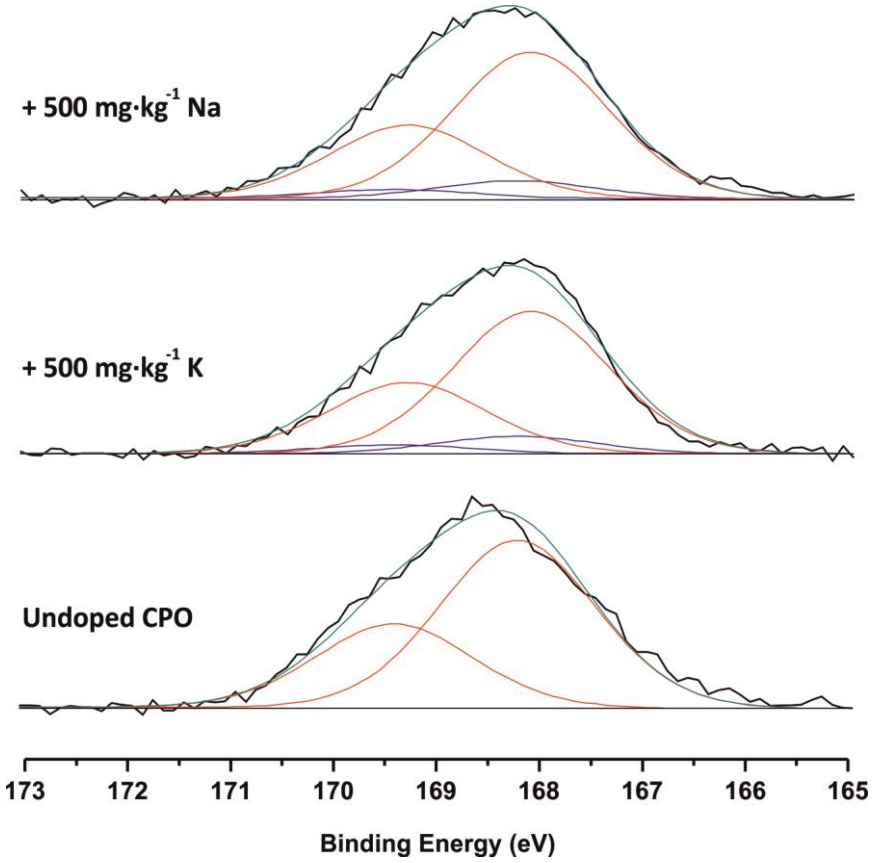

Figure 2

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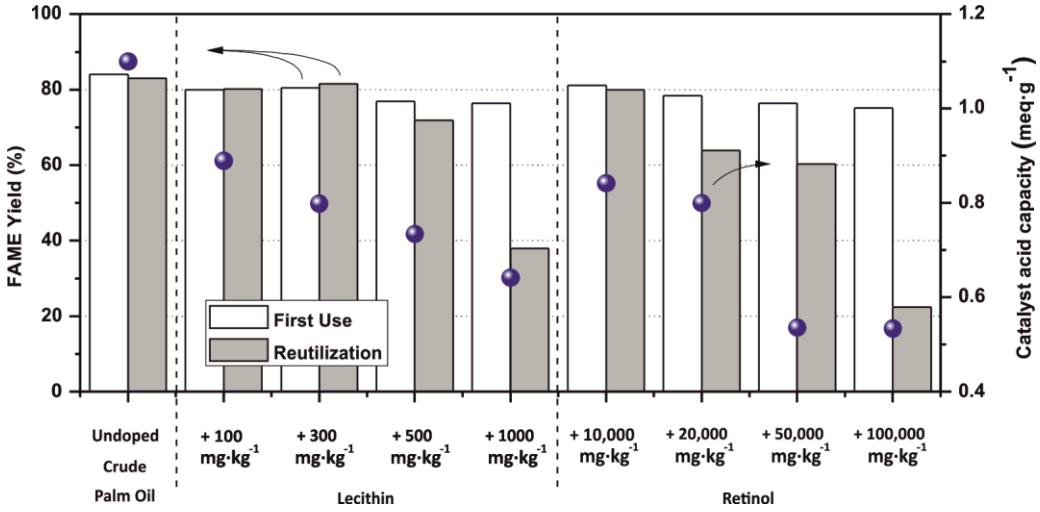

Figure 3

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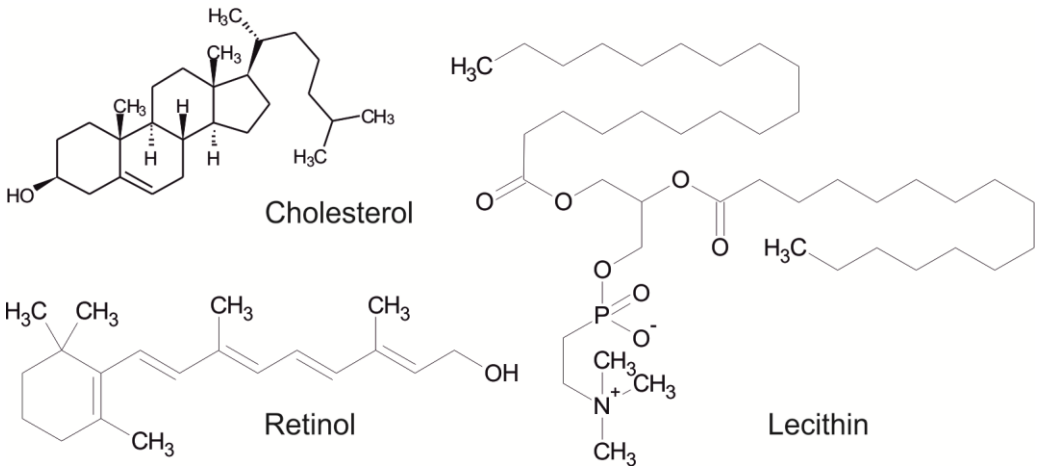

Figure 4

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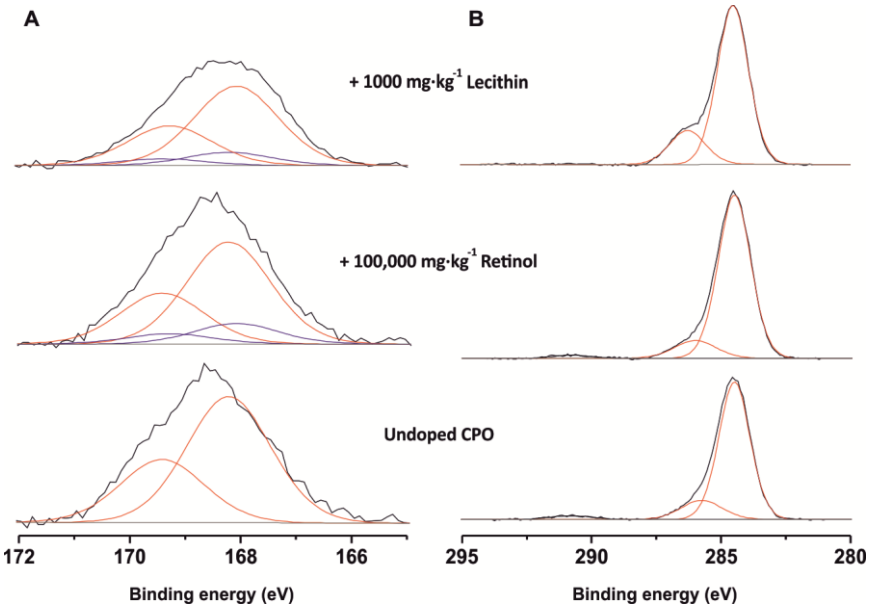

Figure 5

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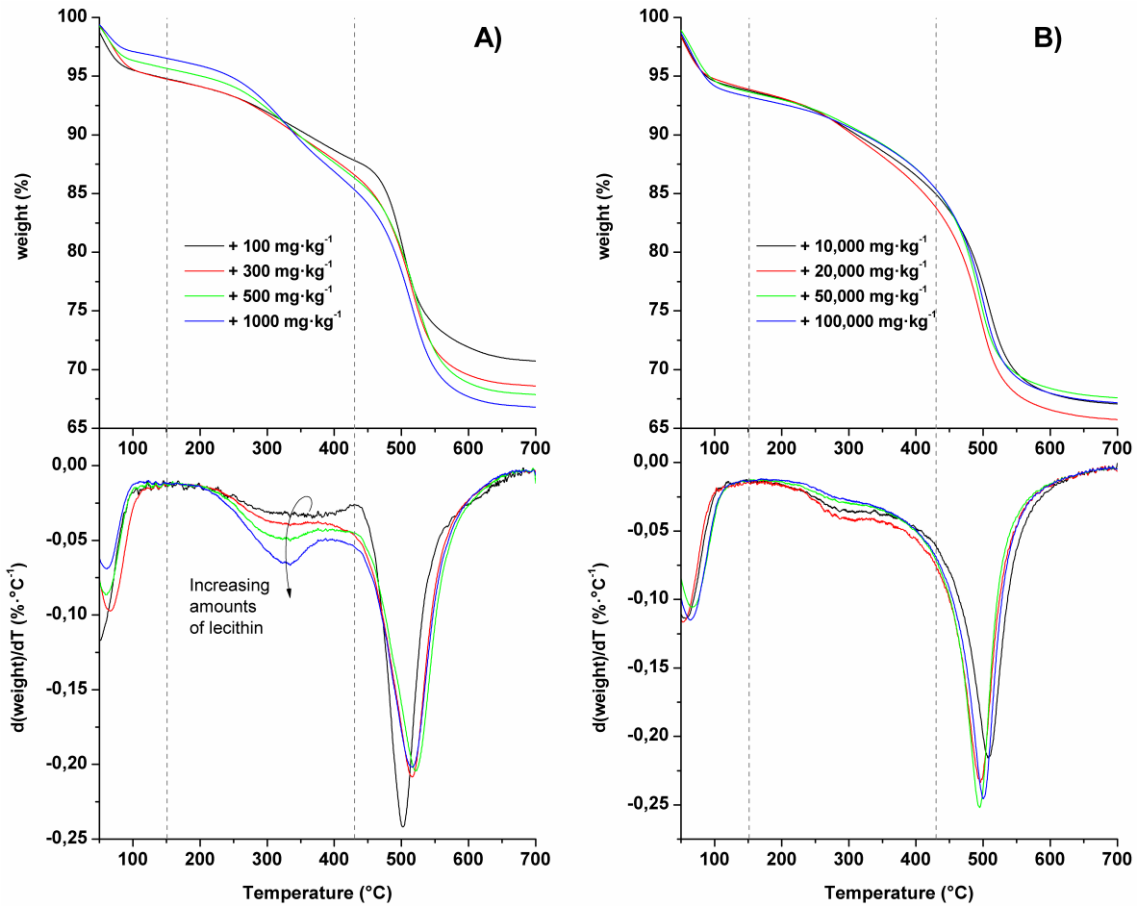

Figure 6

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