Chemical Engineering Journal 230 (2013) 567–572

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Esterification of free fatty acids over chitosan with sulfonic acid groups

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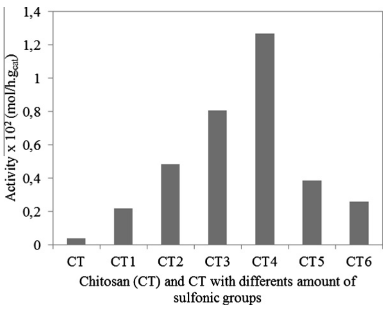
HIGHLIGHTS

- Sulfonic acid catalysts supported on chitosan were prepared.
- Esterification of fatty acids was carried out over chitosan with sulfonic groups.
- High catalytic activity was observed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 April 2013
Received in revised form 15 June 2013
Accepted 19 June 2013
Available online 27 June 2013

Keywords:
Biodiesel
Free fatty acids
Esterification
Chitosan
Sulfonic acid groups

ABSTRACT

Chitosan, which is an abundant biopolymer, with sulfonic acid groups was used as an efficient, environmentally friendly heterogeneous catalyst for the esterification of free fatty acids with methanol into their more fatty acid methyl ester. Sulfonic acid catalysts supported on chitosan have been studied in the esterification of palmitic acid with methanol at 60 °C. The sulfonic acid groups were introduced onto chitosan (CT) through cross-linking with sulfosuccinic acid (SSA). The catalytic activity increased as the amount of sulfonic acid groups present in chitosan was increased. However, with large amounts of sulfonic acid groups, the catalytic activity decreased. This behaviour can be explained by the factors that limit the diffusion. The catalytic stability of the CT4 (2.08 mmol sulfonic acid groups/g) sample was evaluated through consecutive batch runs performed with the same catalyst sample. After the second batch, the catalytic activity stabilised. The CT4 catalyst was also used as a catalyst in the esterification of oleic and stearic acids with methanol. A good catalytic activity of CT4 for the different substrates used in the esterifications was observed.

1. Introduction

Biodiesel is a renewable and biodegradable fuel that can be an attractive substitute for petrodiesel fuel. It features a lower combustion emission profile (particularly with respect to SOx) and decreased greenhouse gas emissions because of the closed CO_2 cycle. Biodiesel contains fatty acid alkyl esters (usually methyl esters, FAME) derived from either the transesterification of triglycerides (TGs) or the esterification of free fatty acids (FFAs) with low-molecular-weight alcohols in the presence of acid or base catalysts [1–5]. Biodiesel can also be prepared through the esterification of the free fatty acids present in animal fats (e.g. lard or tallow) with methanol over acid catalysts [1,2].

Traditionally, the esterification reactions have been conducted in the presence of homogeneous acid catalysts (mineral acids). However, these catalysts are corrosive and must usually be neutralised after the reaction (with consequent salt formation). Therefore, to qualify such esterification reactions as "green" processes, researchers have replaced homogeneous catalysts with heterogeneous ones. The solid acid catalysts are preferred because they are easily separated from the reactants and products via filtration [6].

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http://dx.doi.org/10.1016/j.cej.2013.06.050

The esterification of fatty acids has been performed in the presence of different acid catalysts [7–12]. The esterification of palmitic acid with methanol has been performed over various solid acids, including heteropolyacids [13] and heteropolyacids supported on solids such as zirconium oxide [14], activated carbon [15] and silica [16,17]. Sulphonic acid catalysts on a range of supports, including silica [18,19], activated carbon [20], polyvinyl alcohol [21] and polystyrene [22–25], have also been studied in esterification reactions.

Chitosan is a natural and low-cost biopolymer that is present in the exoskeletons of crustaceans, the cuticles of insects and the cell walls of most fungi. It is a highly abundant polymer obtained via the alkaline deacetylation of chitin (a polymer that consists of acetylglucosamine units). Chitosan and its derivatives exhibit interesting properties, such as nontoxicity, biocompatibility and controllable biodegradability [26,27]. These properties make chitosan an attractive biopolymer for applications in a wide variety of fields, including biotechnology, pharmaceuticals, wastewater treatment, cosmetics, agriculture, food science and textiles [28]. Because of the easy modification of its properties, chitosan-based materials have been used in heterogeneous catalysts for applications in hydrogenation, oxidation and fine-chemical synthesis reactions [26,29]. Chitosan has been used as a support for the immobilisation of calcium oxide [30]. Chitosan crosslinked with sulfosuccinic acid has also been prepared and used for the pervaporation separation of water/alcohol mixtures [31].

In this work, we attempt to develop an efficient heterogeneous catalytic process for esterification of free fatty acids (palmitic, stearic and oleic acid) in the presence of chitosan with sulfonic acid groups. Chitosan being natural product has the advantage of green catalysis. Catalysts with different amount of sulfonic acid groups are prepared. The catalytic stability of CT4 is also studied.

2. Experimental

2.1. Catalysts preparation

Chitosan was obtained from Sigma–Aldrich, USA. Chitosan (0.4 g) was dissolved in 50 mL of distilled water that contained 2% acetic acid with constant stirring for approximately 24 h at room temperature. An appropriate amount of sulfosuccinic acid solution (70%) (0.25, 0.50, 0.75, 1.0, 1.5 and 2.0 mmol for the catalysts CT1, CT2, CT3, CT4, CT5 and CT6, respectively) was subsequently added to the chitosan solution, which was vigorously stirred at room temperature for 24 h. The homogeneous solutions were poured and cast onto a Teflon plate. The cast polymers were allowed to dry at 60 °C for 24 h. The dried chitosan matrix was heated at 100 °C under moderate vacuum for 2 h.

2.2. Catalyst characterisation

The swelling degrees of the polymers were measured by immersion of the matrix samples in methanol and water at 60 °C for 24 h. The polymeric samples were subsequently removed, wiped with tissue paper and weighed. The swelling degree, Q, was calculated by:

$$Q = \frac{m - m_0}{m_0} \qquad (1)$$

where m is the mass of swollen sample, and m_0 is the initial mass.

Acid capacity was measured via the determination of cation-exchange capacities. The ion capacities of the sulfonic acid groups in the functionalised chitosan were quantified using 0.1 M NaCl (aq) as the ion-exchange agent. One hundred milligrams of the sample was added to 15 ml of the salt solution, and the mixture was shaken for 24 h at room temperature. Thereafter, the solution was titrated via the dropwise addition of 0.025 M NaOH (aq).

The FTIR spectra were recorded in a Bio-Rad FTS 155 instrument.

The sulphur content was determined on a CHNS Elemental Analyser 1112 series instrument from Thermo Finnigan.

Thermal stability of the chitosan and chitosan with sulfonic groups was investigated using a Netzsch STA 449F3 thermogravimetric analyser. The sample weights ranged from 7 to 10 mg and were heated from ambient to 700 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

Scanning electron microscopy (SEM-FIB) was performed on a Zeiss Auriga scanning electron microscope operated at 2 kV.

2.3. Catalytic experiments

The catalytic experiments were performed in a stirred batch reactor at 60 °C. In a typical experiment, the reactor was loaded with 30 mL of methanol and 0.2 g of polymer that contained sulfonic acid groups. The reactions were started by the addition of 8 mmol of free fatty acid. The stirrer speed used to avoid the diffusion limitations was 600 rpm.

Stability tests of the CT4 catalyst were performed by running five consecutive experiments with the same reaction conditions. After the esterification reaction, the CT4 catalyst was separated from the reaction mixture by filtration, washed with methanol and dried overnight at 80 °C.

A hot-filtration test was conducted for the catalyst sample CT4. The reaction was performed as previously described; after 3 h (palmitic acid conversion: 65%) the catalyst was removed via hot-filtration. Sampling of the liquid was continued for 30 h after the beginning of the experiment.

Undecane was used as the internal standard. Samples were periodically collected and analysed via GC on a Hewlett Packard instrument equipped with a 15 m × 0.53 mm HP-5 column. Helium was used as carrier gas. The injector and detector temperatures were, respectively, 250 and 280 °C. The split ratio was fixed at 100. The oven temperature program was as follows: start at 80 °C (4 min), ramp at 5 °C/min to 300 °C.

2.4. Calculations

The catalytic activity was calculated from the maximum slope of the experimental kinetic curve of methyl ester divided by the amount of catalyst.

The diffusivities of fatty acids were calculated assuming a first-order irreversible reaction. Specifically, the values of the maximum reaction rate were calculated from the slopes of the kinetic curves obtained for two different pellet sizes. Plate geometry was assumed for the pellet, and the following relationships for the Thiele modulus and the effectiveness factor were used:

$$\phi = L \times \sqrt{\frac{k' \times \rho_p}{De}} \qquad (2)$$

$$\eta = \frac{\tanh(\phi)}{\phi} \qquad (3)$$

where k' is the intrinsic kinetic constant, De is the effective diffusivity, L is the polymeric matrix half thickness and ρ the pellet volumic mass.

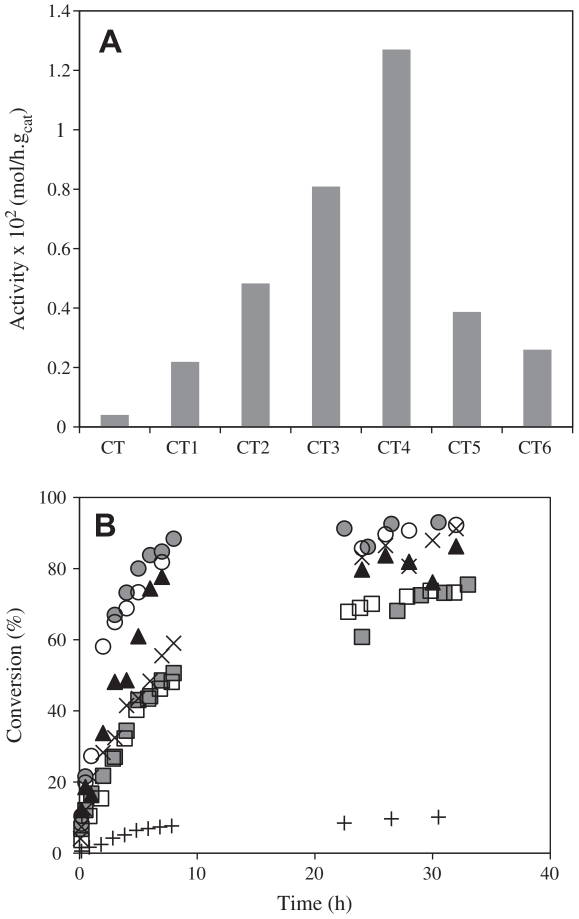

Fig. 1. Esterification of palmitic acid with methanol in the presence of chitosan with sulfonic acid groups, at 60 °C. (A) Initial activities taken as the maximum observed reaction rate, calculated from the maximum slope of the methyl palmitate kinetic curve. (B) Conversion (%) versus time (h). (+) CT; (■) CT1; (×) CT2; (o) CT3; (●) CT4; (▲) CT5; (□) CT6.

3. Results and discussion

3.1. Catalytic experiments

Chitosan with sulfonic acid groups was used as an acid catalyst in the esterification of palmitic acid with methanol at 60 °C. Fig. 1A shows the initial catalytic activities of sulfonic-acid-functionalised chitosan in the esterification of palmitic acid with methanol, as calculated from the maximum slopes of the ester kinetic curves. The initial catalytic activity increased with the sulfonic acid content until a maximum was reached, which was obtained with the CT4 catalyst. A greater amount of sulfonic acid on chitosan resulted in a decrease in the catalytic activity. With low sulfonic acid loadings, the increase in the sulfonic acid content led to increased activity, most likely via a kinetic effect. However, higher sulfonic acid loadings on chitosan led to diminished catalytic activity. These results can most likely be explained by an increase in the restriction of molecular mobility in the chitosan matrix. In fact, the diffusivity of palmitic acid decreased with crosslinking degree of the chitosan catalysts (Table 1).

After 6 h of reaction, the palmitic acid conversion (%) was 51%, 59%, 82%, 89%, 78% and 49% for the CT1, CT2, CT3, CT4, CT5 and CT6 catalysts, respectively (Fig. 1B).

We evaluated the catalytic stability of the CT4 catalyst by performing consecutive batch runs with the same catalyst sample. After the second batch, the activity was observed to stabilise (Fig. 2). After the fourth run, the amount of S present on chitosan was measured by elemental analysis, and the S amount on chitosan was similar before and after the reaction.

To confirm the catalytic stability of CT4, a hot-filtration experiment was performed with the catalyst sample. After 3 h of reaction, the catalyst was separated from the reaction mixture, and its composition was then monitored for 30 h. Fig. 3 compares the conversion obtained for the hot-filtration experiment and that obtained for a *normal* catalytic experiment. When the catalyst was removed from the reaction mixture, the reaction stopped, whereas it continued to proceed in the normal experiment.

The chitosan with sulfonic acid groups (sample CT4) was also used as a catalyst in the esterification of stearic and oleic acids with methanol at 60 °C. Fig. 4 compares the initial catalytic activities of CT4 in the esterification of palmitic, stearic and oleic acids, as calculated from the maximum slopes of the ester kinetic curves. A slight decrease in the catalytic activity was observed with increased chain length of the fatty acids. The CT4 catalytic activity obtained with stearic acid was also greater than that obtained with oleic acid. This behaviour can be explained by the stearic acid being a saturated fatty acid with linear structure, whereas the linearity of the oleic acid molecules is distorted. Linear fatty acids can easily pass through the pores and adsorb onto the catalyst surface to be available for the reaction. In the case of unsaturated fatty acids, their nonlinearity may decrease the rate of diffusion and leading

Table 1
Characterisation of chitosan with sulfonic acid groups.

Sample	Thickness (mm)	Acid capacities		Methanol swelling[c] (%)	Water swelling[d] (%)	De *x* 10^{11} (m^2/h)
		Titration[a]	Scontent[b]			
CT	0.0020	0.41	–	0.094	1.62	
CT1	0.0022	0.80	0.83	0.063	1.42	6.6
CT2	0.0026	1.00	1.01	0.051	1.23	5.0
CT3	0.0024	1.51	1.53	0.042	1.11	3.6
CT4	0.0032	2.04	2.08	0.030	1.03	2.2
		2.03[e]	2.04[e]			1.1[g]
		2.02[f]	2.01[f]			0.54[h]
CT5	0.0028	2.31	2.38	0.025	0.84	1.2
CT6	0.0024	2.40	2.43	0.021	0.75	0.44

[a] Amount of brönsted acid sites was determined by acid–base titration (mmol/g).
[b] Sulphur molar content determined by elemental analysis (mmol/g).
[c] Methanol swelling was measured by immersing dried pieces catalysts in methanol, at 60 °C.
[d] Water swelling was measured by immersing dried pieces of catalysts in water, at 60 °C.
[e] After second use of CT4 as catalysts.
[f] After four use of CT4 as catalysts.
[g] Diffusivity of stearic acid.
[h] Diffusivity of oleic acid.

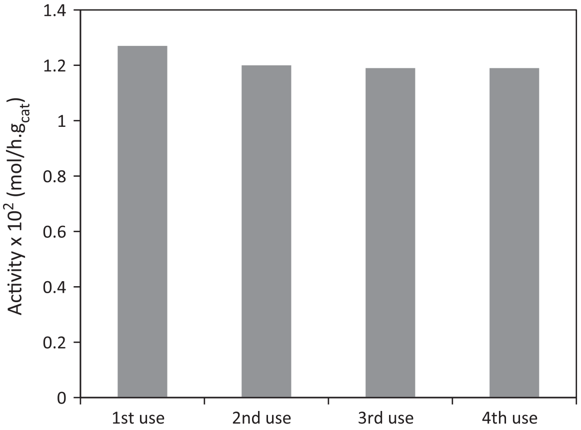

Fig. 2. Stability studies of the CT4 catalyst on esterification of palmitic acid with methanol. Catalytic activity calculated as the initial reaction rate of the esterification reaction of palmitic acid with methanol, in four consecutive experiments.

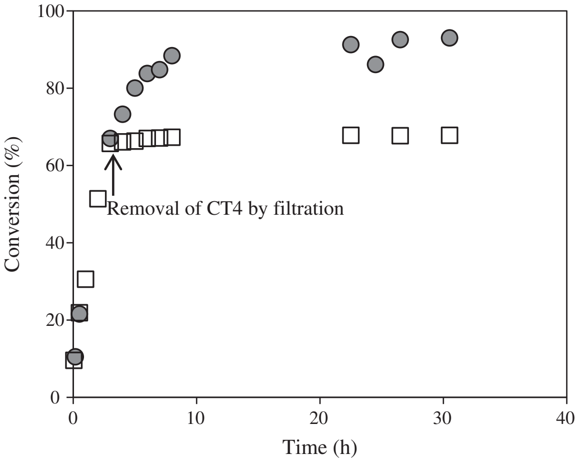

Fig. 3. Esterification of palmitic acid with methanol in the presence of chitosan with sulfonic acid groups, at 60 °C. Conversion (%) versus time (h) obtained with the catalyst sample CT4. (□) hot-filtration test; (●) *normal* experiment.

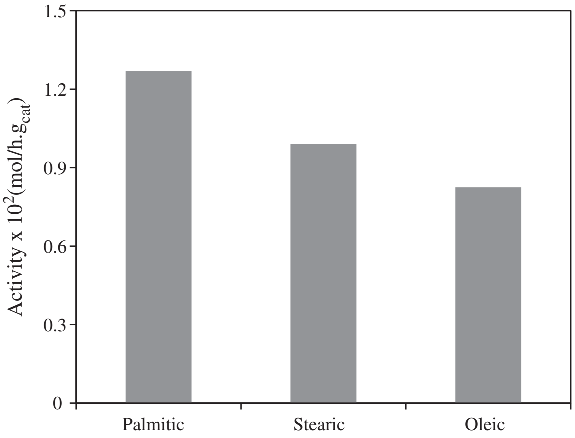

Fig. 4. Esterification of free fatty acid with methanol in the presence of CT4 at 60 °C. Initial activities taken as the maximum observed reaction rate, calculated from the maximum slope of the methyl ester kinetic curve.

to a decrease in reactivity [32–34]. In fact, the diffusivity of stearic acid through the chitosan matrix (CT4) was higher than that of the oleic acid (Table 1).

3.2. Catalyst characterisation

Chitosan with sulfonic acid groups was prepared via the esterification of the sulfosuccinic acid (SSA) on the chitosan –OH groups according to Fig. 5.

Fig. 6A and B shows the FTIR spectra of chitosan (CT) and chitosan crosslinked with sulfosuccinic acid (CT4). The appearance of the absorption band at 1730–1735 cm^{-1} in the spectrum of CT4, which is usually assigned to the ester group (–CO–O–), suggests that the crosslinking with SSA was successful. The absorption band at 1255 cm^{-1} in the spectrum of CT4, which does not appear in the spectrum of CT, indicates the presence of a sulfonic acid group introduced by SSA [35]. Additionally, the band at 808 cm^{-1}, which can be attributed to the C–O–S group, indicates that the sulfonic acid groups were grafted onto chitosan [29]. The peak at 1543 cm^{-1} is assigned to the specific absorbance of N–H bonds in NH_3^+ groups [29]. In addition, a broad NH_3^+ peak at 2200–2000 cm^{-1} may indicate the formation of ionic bonds. The sulfonic groups functioned as proton providers to form intermolecular protonation [29].

The thermal stability of chitosan and chitosan with sulfonic groups (CT4 sample) was studied by thermal gravimetric analysis (TGA), as shown in Fig. 7. Two major weight-loss stages at approximately 40–200 °C and 200–670 °C were observed in the tested temperature range. The first weight loss at approximately 40–200 °C is due to the volatilisation of small molecules, such as physically absorbed water, acetic acid and sulfosuccinic acid. The second weight loss is due to the degradation of chitosan and the CT4 catalyst, which can be assigned to the structural collapse of the chitosan and the thermal decomposition of the polymeric network [29]. The chitosan with sulfonic groups (CT4 sample)

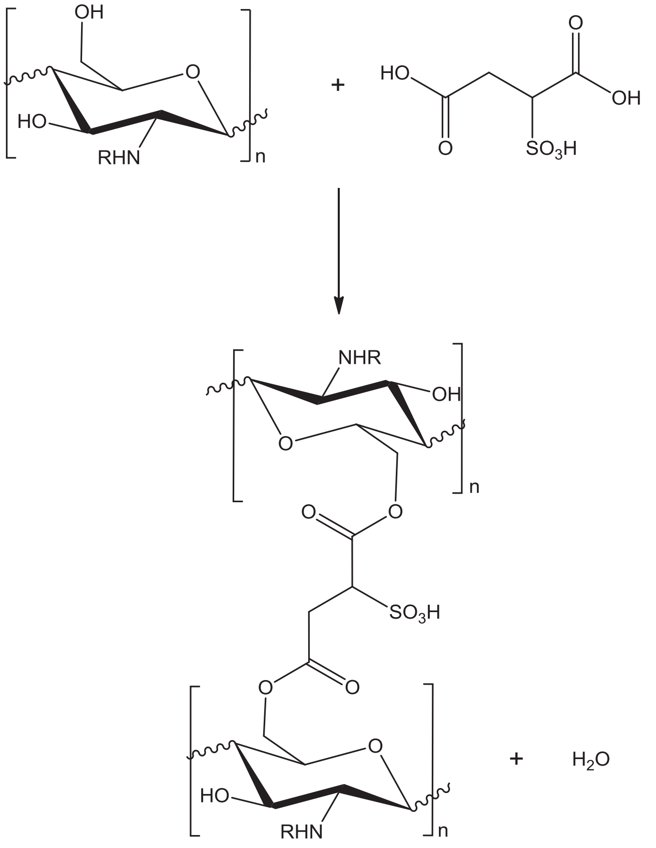

Fig. 5. The preparation pathway of chitosan with sulfonic acid groups (R = –H or –$COCH_3$).

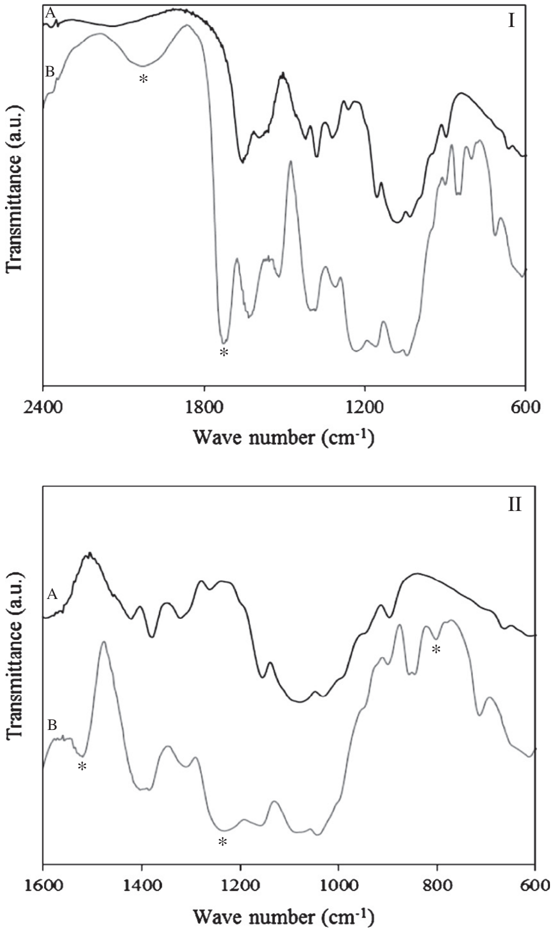

Fig. 6. FT-IR spectra of catalysts: (A) chitosan; (B) CT4.

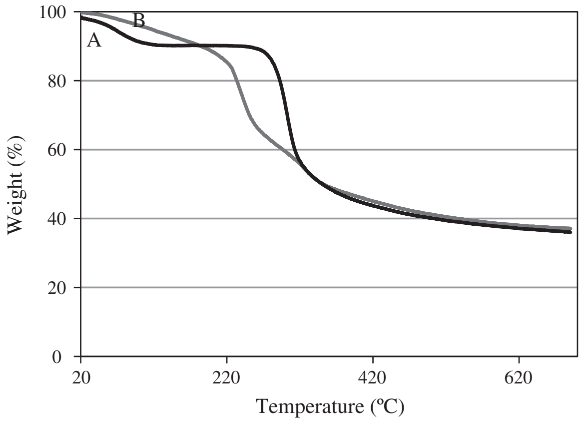

Fig. 7. TG curves of the pure chitosan (A) and the CT4 catalyst (B).

maintained good thermal stability, similar to the behaviour of pure chitosan. The CT4 catalyst is therefore stable at the desired operating temperatures (<60 °C) for the esterification of fatty acids.

Fig. 8A and B show the surface SEM micrographs for chitosan (CT) and chitosan with sulfonic acid (CT4 sample). The pure chitosan exhibits a void-free dense structure (Fig. 8A). The CT4 catalyst exhibits voids and cracks in its structure, which can improve the reactantś access to the active sites [29].

The characteristics of polymeric catalysts are shown in Table 1. The acidity of the catalysts increased as the degree of chitosan cross-linking increased because the number of sulfonic acid groups introduced was also increased. The sulphur content in the chitosan, as determined via elemental analysis, is shown in Table 1. The acid capacities, obtained by acid–base titration and those obtained by elemental analysis were similar.

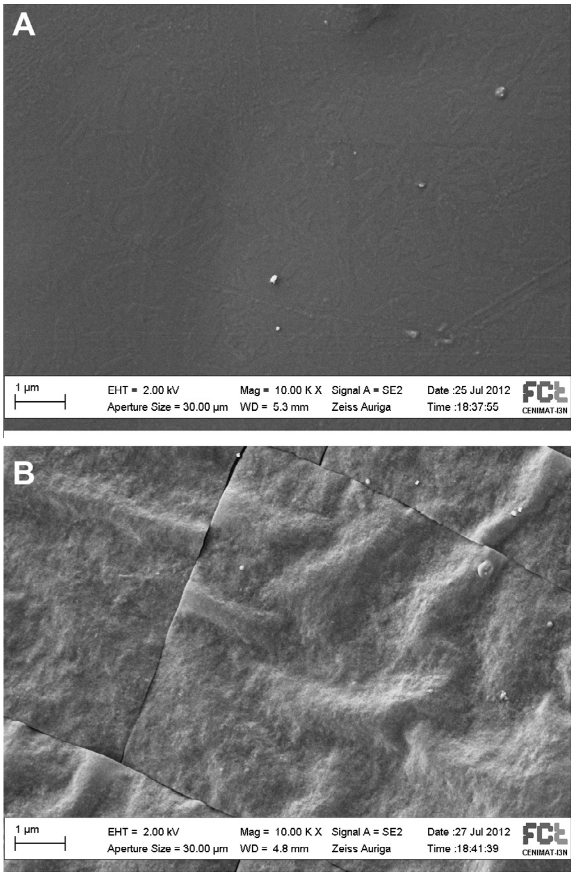

Fig. 8. SEM morphology images of the surface of the chitosan (A) and CT4 catalyst (B).

The acid capacity of the CT4 catalyst was measured after the second use (Table 1). It was observed that the acid capacity decreased slightly after the first use. This behavior could be explained due to some leaching of sulfonic acid groups. In fact, the amount of S decreased slightly after the first use (Table 1).

The swelling degree of chitosan and chitosan with sulfonic acid groups, for methanol and water, decreased when the sulfosuccinic acid content was increased (Table 1). This swelling behaviour is most likely due to the decrease in the free volume, even though the polymeric matrix contains more hydrophilic functional groups. Similar behaviour has been observed by Rhim et al. [35], who reported that the swelling degree of PVA cross-linking with SSA, for methanol, decreased as the SSA content increased.

Table 1 shows also the palmitic acid diffusivity through chitosan matrix. A decrease of palmitic acid diffusivity from the CT1 to CT6 catalyst was observed. This behaviour can probably be explained due to the increase in the restrictions to molecules motion, which are expected to occur with the increase of crosslinking. In a previous work [36], we observed that the α-pinene diffusivity decreases with the increases of crosslinking degree.

4. Conclusions

Chitosan functionalised with sulfonic acid was used as a catalyst in the esterification of palmitic acid with methanol at 60 °C.

The catalytic activity of chitosan increased as the amount of sulfonic acid catalyst increased until a maximum was reached, which was obtained with the CT4 sample. When the sulfonic acid loading was high, decreased catalytic activity was observed.

The catalytic stability of the CT4 sample was evaluated through different consecutive batch runs with the same catalyst. The activity stabilised after the second batch.

The CT4 catalyst was also used in the esterification of stearic and oleic acids with methanol at 60 °C. The catalytic activity decreased slightly as the length of the carbon chain of the fatty acid increased.

Acknowledgement

This work was carried out with support from the Project PTDC/CTM-POL/114579/2009.

References

[1] F. Ma, M. Hanna, Biodiesel production: a review, Bioresour. Technol. 70 (1999) 1–15.

[2] S. Furuta, H. Matsuhashi, K. Arata, Biodiesel fuel production with solid superacid catalysis in fixed bed reactor under atmospheric pressure, Catal. Commun. 5 (2004) 721–723.

[3] D.A.G. Aranda, R.T.P. Santos, N.C.O. Tapanes, A.L.D. Ramos, O.A.C. Antunes, Acid-catalyzed homogeneous esterification reaction for biodiesel production from palm fatty acids, Catal. Lett. 122 (2008) 20–25.

[4] Y.C. Sharma, B. Singh, J. Korstad, Advancements in solid acid catalysts for ecofriendly and economically viable synthesis of biodiesel, Biofuels Bioprod. Bioref. 5 (2011) 69–92.

[5] A. Sivasamy, K.Y. Cheah, P. Fornasiero, F. Kemausuor, S. Zinoviev, S. Miertus, Catalytic applications in the production of biodiesel from vegetable oils, ChemSusChem 2 (2009) 278–300.

[6] A. Corma, H. Garcia, S. Iborra, J. Primo, Modified faujasite zeolites as catalysts in organic reactions: esterification of carboxylic acids in the presence of HY zeolites, J. Catal. 120 (1989) 78–87.

[7] R. Tesser, L. Casale, D. Verde, M. Di Serio, E. Santacesaria, Kinetics of free fatty acids esterification: batch and loop reactor modeling, Chem. Eng. J. 154 (2009) 25–33.

[8] R. Tesser, L. Casale, D. Verde, M. Di Serio, E. Santacesaria, Kinetics and modeling of fatty acids esterification on acid exchange resins, Chem. Eng. J. 157 (2010) 539–550.

[9] M. Berrios, M.A. Martín, A.F. Chica, A. Martín, Study of esterification and transesterification in biodiesel production from used frying oils in a closed system, Chem. Eng. J. 160 (2010) 473–479.

[10] L. Hermida, A.Z. Abdullah, A.R. Mohamed, Synthesis of monoglyceride through glycerol esterification with lauric acid over propyl sulfonic acid post-synthesis functionalized SBA-15 mesoporous catalyst, Chem. Eng. J. 174 (2011) 668–676.

[11] L.H. Chin, A.Z. Abdullah, B.H. Hameed, Sugar cane bagasse as solid catalyst for synthesis of methyl esters from palm fatty acid distillate, Chem. Eng. J. 183 (2012) 104–107.

[12] G.N. Shao, R. Sheikh, A. Hilonga, J.E. Lee, Y.-H. Park, H.T. Kim, Biodiesel production by sulfated mesoporous titania–silica catalysts synthesized by the sol–gel process from less expensive precursors, Chem. Eng. J. 215–216 (2013) 600–607.

[13] K. Narasimharao, D.R. Brown, A.F. Lee, P.F. Siril, K. Wilson, Structure–activity relations in Cs-doped heteropolyacid catalysts for biodiesel production, J. Catal. 248 (2007) 226–234.

[14] K.N. Rao, A. Sridhar, A.F. Lee, S.J. Tavener, N.A. Young, K. Wilson, Zirconium phosphate supported tungsten oxide solid acid catalysts for the esterification of palmitic acid, Green Chem. 8 (2006) 790–797.

[15] M.G. Kulkarni, R. Gopinath, L.C. Meher, A.K. Dalai, Solid acid catalyzed biodiesel production by simultaneous esterification and transesterification, Green Chem. 8 (2006) 1056–1062.

[16] C.S. Caetano, I.M. Fonseca, A.M. Ramos, J. Vital, J.E. Castanheiro, Esterification of free fatty acids with methanol using heteropolyacids immobilized on silica, Catal. Commun. 9 (2008) 1996–1999.

[17] A.I. Tropecêlo, M.H. Casimiro, I.M. Fonseca, A.M. Ramos, J. Vital, J.E. Castanheiro, Esterification of free fatty acids to biodiesel over heteropolyacids immobilized on mesoporous sílica, Appl. Catal. A: Gen. 390 (2010) 183–189.

[18] I.K. Mbaraka, K.J. McGuire, B.H. Shanks, Acidic mesoporous silica for the catalytic conversion of fatty acids in beef tallow, Ind. Eng. Chem. Res. 45 (2006) 3022–3028.

[19] J.A. Melero, L.F. Bautista, G. Morales, J. Iglesias, R. Sanchez-Vazquez, Sulfonated polystyrene-modified mesoporous organosilicas for acid-catalyzed processes, Chem. Eng. J. 161 (2010) 323–331.

[20] X. Mo, E. Lotero, C. Lu, Y. Liu, J.G. Goodwin, A Novel sulfonated carbon composite solid acid catalyst for biodiesel synthesis, Catal. Lett. 123 (2008) 1–6.

[21] C.S. Caetano, L. Guerreiro, I.M. Fonseca, A.M. Ramos, J. Vital, J.E. Castanheiro, Esterification of fatty acids to biodiesel over polymers with sulfonic acid groups, Appl. Catal. A: Gen. 359 (2009) 41–46.

[22] B.M.E. Russbuelt, W.F. Hoelderich, New sulfonic acid ion-exchange resins for the preesterification of different oils and fats with high content of free fatty acids, Appl. Catal. A: Gen. 362 (2009) 47–57.

[23] E. Andrijanto, E.A. Dawson, D.R. Brown, Hypercrosslinked polystyrene sulphonic acid catalysts for the esterification of free fatty acids in biodiesel synthesis, Appl. Catal. B: Environ. 115–116 (2012) 261–268.

[24] N. Özbay, N. Oktar, N.A. Tapan, Esterification of free fatty acids in waste cooking oils (WCO): Role of ion-exchange resins, Fuel 87 (2008) 1789–1798.

[25] J.M. Marchetti, V.U. Miguel, A.F. Errazu, Heterogeneous esterification of oil with high amount of free fatty acid, Fuel 86 (2007) 906–910.

[26] J. Ge, Y. Cuia, Y. Yana, W. Jiang, The effect of structure on pervaporation of chitosan membrane, J. Membr. Sci. 165 (2000) 75–81.

[27] Y. Wan, K.A.M. Creber, B. Preppley, V.T. Bui, Chitosan-based solid electrolyte composite membranes I. Preparation and characterization, J. Membr. Sci. 280 (2006) 666–674.

[28] E. Guibal, Heterogeneous catalysis on chitosan-based materials: a review, Prog. Polym. Sci. 30 (2005) 71–109.

[29] Y. Xiang, M. Yang, Z. Guo, Z. Cui, Alternatively chitosan sulfate blending membrane as methanol-blocking polymer electrolyte membrane for direct methanol fuel cell, J. Membr. Sci. 337 (2009) 318–323.

[30] Chun-Chong Fu, Tien-Chieh Hung, Chia-Hung Su, Devi Suryani, Wen-Teng Wu, Wei-Chen Daic, Yea-Tyam Yeh, Immobilization of calcium oxide onto chitosan beads as a heterogeneous catalyst for biodiesel production, Polym. Int. 60 (2011) 957–962.

[31] J. Jegal, Kew-Ho Lee, Chitosan membranes crosslinked with sulfosuccinic acid for the pervaporation separation of water/alcohol mixtures, J. Appl. Polym. Sci. 71 (1999) 671–675.

[32] Y. Liu, E. Lotero, J.G. Goodwin Jr, Effect of carbon chain length on esterification of carboxylic acids with methanol using acid catalysis, J. Catal. 243 (2006) 221–228.

[33] D. Martín Alonso, M. López Granados, R. Mariscal, A. Douhal, Polarity of the acid chain of esters and transesterification activity of acid catalysts, J. Catal. 262 (2009) 18–26.

[34] K. Srilatha, N. Lingaiah, P.S.S. Prasad, B.L.A.P. Devi, R.B.N. Prasad, S. Venkateswar, Influence of carbon chain length and unsaturation on the esterification activity of fatty acids on Nb_2O_5 catalyst, Ind. Eng. Chem. Res. 48 (2009) 10816–10819.

[35] J.W. Rhim, H.B. Park, C.S. Lee, J.H. Jun, D.S. Kim, Y.M. Lee, Crosslinked poly(vinyl alcohol) membranes containing sulfonic acid group: proton and methanol transport through membranes, J. Membr. Sci. 238 (2004) 143–151.

[36] D.S. Pito, I.M. Fonseca, A.M. Ramos, J. Vital, J.E. Castanheiro, Methoxylation of α-pinene over poly(vinyl alcohol) containing sulfonic acid groups, Chem. Eng. J. 147 (2009) 302–306.