

Solvent-free conversion of glycerol to solketal catalysed by activated carbons functionalised with acid groups†

Cite this: *Catal. Sci. Technol.*, 2014, 4, 2293

Raphael Rodrigues,^{ab} Maraisa Gonçalves,^a Dalmo Mandelli,^a Paolo P. Pescarmona^{*b} and Wagner A. Carvalho^{*a}

Activated carbons prepared from agricultural waste were modified to introduce surface acid sites by treatment with HNO₃ or H₂SO₄. These acid-functionalised materials were studied as heterogeneous catalysts for the solvent-free acetalisation of acetone with glycerol to produce 2,2-dimethyl-1,3-dioxolane-4-methanol (solketal). The best catalyst was prepared by treatment with concentrated sulphuric acid and achieved 97% conversion of glycerol with high selectivity towards solketal by reaction with acetone at room temperature. The catalytic behaviour of the activated carbons was correlated with their physico-chemical properties through characterization by N₂-physisorption, XPS, elemental analysis, TGA and Boehm titration of the acid sites.

Received 11th February 2014,
Accepted 30th March 2014

DOI: 10.1039/c4cy00181h

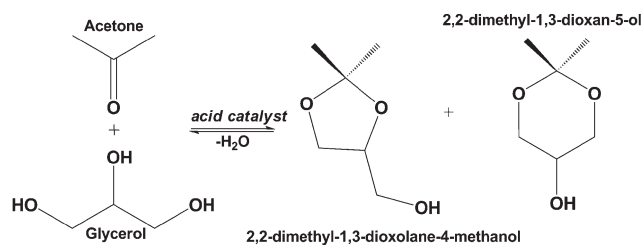
www.rsc.org/catalysis

Introduction

The current worldwide dependence on a finite resource such as fossil fuels has prompted the development of alternative and renewable fuels, among which biodiesel has gained prominence in recent years. Biodiesel is considered a promising substitute for petroleum-based diesel due to intrinsic advantages including renewability, lower toxicity, biodegradability, biocompatibility and lower emission profile.^{1,2} Biodiesel consists of fatty acid esters that are typically obtained by transesterification of vegetable oil with a short chain alcohol (ethanol or methanol), catalysed by an alkaline catalyst (*e.g.* NaOH or KOH). It is estimated that the production of 100 m³ of biodiesel generates 10 m³ of crude glycerol, and the growing trend of the production of this fuel is leading to an oversupply of glycerol and a drop in its market value.³ As a consequence, an increasing number of scientific studies have investigated routes for the transformation of glycerol into added-value products with different applications.⁴ Viable chemical processes for upgrading glycerol to useful products include oxidation,⁴ hydrogenolysis,⁵ halogenation,⁶ etherification,⁷ esterification,⁸ dehydration,⁹ and acetalisation of ketones or aldehydes.^{10,11} In this work, we focus on a reaction of the last

group, *i.e.* the acetalisation of acetone with glycerol (Scheme 1), for which we present a new class of highly active and selective heterogeneous catalysts consisting of acid-functionalised activated carbons. 2,2-Dimethyl-1,3-dioxolane-4-methanol, better known as solketal, is a five-membered ring ketal with an interesting range of potential applications as a solvent, low-temperature heat-transfer fluid, surfactant and fuel additive.^{12–14}

The acetalisation of ketones and aldehydes with glycerol is typically catalysed by Brønsted acids.^{1,15} The mineral acids that were initially employed as catalysts, such as HCl, H₂SO₄ and HF,¹⁶ are unsuitable due to the inherent economic disadvantages and environmental issues of these homogeneous catalytic systems. These limitations stimulated the development of suitable solid acid heterogeneous catalysts, which include zeolites, metal-substituted mesoporous silicates, mixed metal oxides, polymers with acid functional groups and supported heteropolyacids.^{1,12,14,17–20} In this work, we report for the first time the successful application of activated carbons functionalised with acid groups as catalysts for the acetalisation of acetone with glycerol.



Scheme 1 Acetalisation of acetone with glycerol.

^a Centre of Natural and Human Sciences, Federal University of ABC (UFABC), Santa Adélia Street, 166, Bangu, Santo André, SP, 09210-170, Brazil.

E-mail: wagner.carvalho@ufabc.edu.br

^b Centre for Surface Chemistry and Catalysis, KU Leuven, Kasteelpark Arenberg 23, 3001 Heverlee, Belgium. E-mail: paolo.pescarmona@biw.kuleuven.be

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4cy00181h

Activated carbons are widely used in different application fields, mainly in adsorption and catalysis, due to their extensive surface area and pore distribution in the micro- and mesopore ranges and the possibility of functionalising their surfaces with different chemical groups.^{21–24} Activated carbon can be prepared from a wide range of organic wastes such as sugar cane bagasse, pecan shells, and date or olive stones.^{25–28} The latter was used as the starting material for preparing the activated carbons employed as catalysts in this work. The yearly world olive oil production exceeds 3 000 000 metric tons. The composition of olives, which are the raw material for olive oil extraction, is very variable and depends on several factors such as plant variety, soil type and climatic conditions, but in general olives consist of 18–28% oil, 30–35% olive pulp, and 40–50% vegetation water and stone.²⁹ The stone, which contains the seed, corresponds to 18–22% of the olive's weight.³⁰ Considering the large and increasing worldwide production of olive oil,²⁹ the fabrication of activated carbon from olive stones appears to be an appropriate destination for this agricultural waste.

The surface of activated carbons can be modified by generating oxygenated functional groups with Brønsted acid properties (*i.e.* carboxyl groups, carboxylic anhydrides, lactones, and phenolic hydroxyl groups³¹) through treatment with strong oxidising agents such as HNO₃ and H₂SO₄. In addition, the treatment with H₂SO₄ can introduce sulphonic acid groups (–SO₃H) on the carbon surface. These activated carbons functionalised with acid groups have displayed promising performance as heterogeneous catalysts for several acid-catalysed processes.^{32,33} Therefore, these materials are excellent candidates for catalysing the conversion of glycerol to solketal, with the aim of achieving high activity and selectivity under green conditions (solvent-free reaction at mild temperature).

Experimental

Preparation of the activated carbon

Activated carbon (AC) was prepared by chemical activation of olive stone wastes (particle size, 0.5–2 mm) from Rio Grande do Sul, Brazil. The inorganic content of the olive stones was removed by washing with 6 M aqueous H₂SO₄. Next, the olive stones were impregnated with a 73% aqueous solution of H₃PO₄ (v/v) at 357 K for 4 h, using a solution to olive stone mass ratio of 1 : 1.³⁴ The activation was carried out in a vertical glass reactor under a nitrogen gas flow of 100 mL min^{–1} at 723 K for 2 h. Then, the activating agent (H₃PO₄) was removed by washing with hot distilled water and the solid was dried at 373 K for 12 h. The obtained activated carbon was denoted as AC-untreated.

Acid treatment of the activated carbon

The acid treatment of the activated carbon was carried out by stirring 10 g of AC-untreated in 100 mL of an acid solution at room temperature for 3 h. Afterwards, the material was washed with distilled water in a Soxhlet extractor in order to remove the remaining physisorbed oxidant, and then dried at

373 K for 15 h. The aqueous acid solutions employed as oxidising agents were aqueous HNO₃, either 6 M or 15 M, and aqueous H₂SO₄, either 6 M or 18 M, which produced the catalysts denoted as AC-N-6M, AC-N-15M, AC-S-6M and AC-S-18M, respectively.

Characterisation

The textural properties of the prepared materials were obtained by nitrogen adsorption/desorption measurements at 77 K using an Autosorb-1MP device (Quantachrome Instruments). The surface area, micropore volume and pore distribution were calculated by the Brunauer–Emmett–Teller (BET) method,³⁵ the Dubinin–Radushkevich (DR) equation³⁶ and density functional theory (DFT),³⁷ respectively, by using the Quantachrome™ AS1Win™ software. The number of acid sites per gram of the material was evaluated using Boehm titration.³¹ For this test, 0.2 g of each carbon sample was added to 25 mL of an aqueous basic solution (0.05 M NaHCO₃ to titrate the stronger acid sites, such as sulphonic acid groups and carboxyl groups, and 0.1 M NaOH to determine the total amount of acid sites). The suspensions were stirred for 24 h at room temperature and filtered prior to titration. Aliquots containing 10 mL of the filtered solutions were titrated with 0.1 M HCl using an automatic titrator (Metrohm 905 Titrando). The nature and amount of the surface groups in the acid-treated activated carbons were studied by X-ray photoelectron spectroscopy (XPS) using a VG-Microtech Multilab 3000 spectrometer equipped with a hemispherical electron analyser using a Mg Kα (1253.6 eV) 300 W X-ray source. The deconvolution and integration of the XPS signals were performed by subtracting the S-shaped background, followed by fitting of the resulting signal with a combination of Lorentzian (30%) and Gaussian (70%) curves. The carbon, nitrogen and sulphur content of all materials was quantified by means of an elemental analyser (EA1112 Thermo Finnigan FLASH). The thermal stability of the activated carbons used as catalysts was verified by thermogravimetric analysis (TGA) using a Q500 TGA device (TA Instruments) under N₂ atmosphere (gas flow of 50 mL min^{–1}) at a heating rate of 10 K min^{–1} in the range of 300–1000 K.

Catalytic tests

Acetalisation reactions of glycerol with acetone were performed in a high-throughput reaction platform, equipped with a heating and stirring unit containing multiple parallel wells that can host 10 mL glass vials.³⁸ In a typical catalytic test, 0.921 g (0.01 mol) of highly purified glycerol (99%), a selected amount of acetone [*i.e.* 0.581 g (0.01 mol), 1.162 g (0.02 mol) or 2.324 g (0.04 mol)] and 0.132 g (0.0015 mol) of 1,4-dioxane, as the GC internal standard, were weighed in a 10 mL glass vial containing 25 mg of the catalyst. The mixture was stirred at 800 rpm for 6 h in a capped vial at the selected temperature (room temperature, 323 K or 353 K). In all cases, the reaction solution was originally biphasic and became monophasic during the reaction. The reaction products were analysed by gas chromatography (GC) using a Trace GC Ultra from Interscience

(PH POR-Q column, FT-3, 10 m, 0.25 mm). The temperature profile of the GC analysis was: 0.6 min at 373 K, from 373 to 543 K at 170 K min⁻¹, 2.0 min at 543 K.

Results and discussion

In the present study, activated carbons prepared from olive stones and modified by treatment with HNO₃ or H₂SO₄ were tested for the first time as heterogeneous catalysts for the production of solketal by acetalisation of acetone with glycerol. Aiming at a sustainable process, the catalytic reactions were performed under solvent-free conditions and at mild temperature. The activated carbons were prepared by chemical activation of olive stones with phosphoric acid (typical yield of about 30 wt%) and then modified by treatment with either HNO₃ or H₂SO₄. The physicochemical features of the obtained materials were studied by a combination of characterisation techniques. N₂ adsorption/desorption was employed to elucidate the textural properties of the materials. The N₂-physisorption isotherms of the parent and acid-treated activated carbons are classified as type I with an H4 hysteresis loop according to the IUPAC classification, which are typical features of microporous adsorbents (Fig. 1.a).^{39,40} The pore size distribution spans the micropore and early mesopore ranges, and confirms the dominant micropore contribution in all materials (Fig. 1.b).

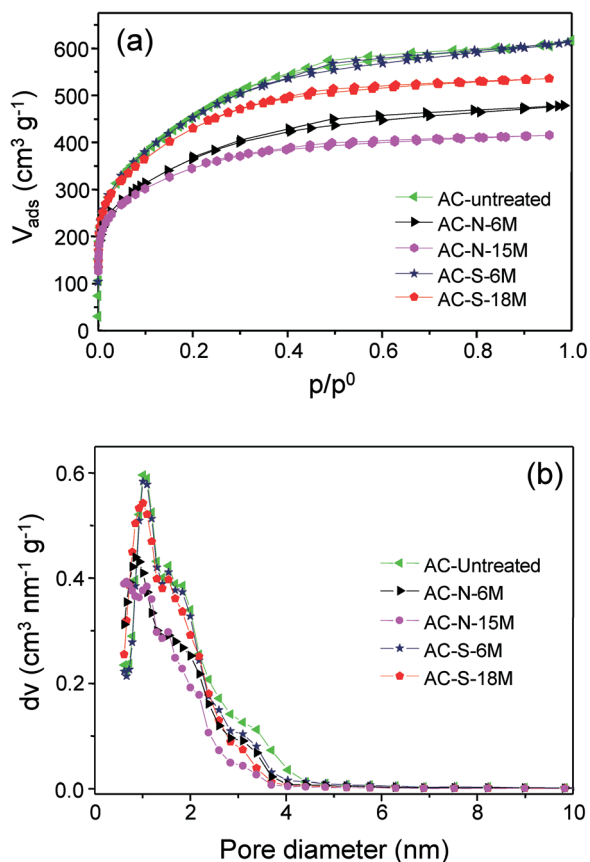


Fig. 1 N₂ adsorption/desorption isotherms (a) and pore size distribution (b) of the parent and acid-treated activated carbons.

The untreated activated carbon displays a very large specific surface area of 1550 m² g⁻¹, which is above the average value for activated carbons, and a total pore volume of 0.94 cm³ g⁻¹, of which 0.55 cm³ g⁻¹ originates from the micropores (Table 1). This material displays a population of acid sites (0.60 mmol g⁻¹, see Table 1), as determined by Boehm titration with aqueous solutions of NaOH and NaHCO₃.³¹ These acid sites can be related to the carboxyl and phenolic groups present in the precursor or to species formed during the treatment with phosphoric acid⁴¹ and are mainly mild as indicated by the low fraction of stronger acid sites (0.17 mmol g⁻¹). An oxidising treatment with HNO₃ and H₂SO₄ is necessary in order to generate a higher amount of surface acid sites, in the form of carboxyl groups, carboxylic anhydrides, lactones and phenolic hydroxyls (in order of decreasing acid strength).^{23,40} The treatment with H₂SO₄ also leads to the formation of strongly acidic sulphonic groups (-SO₃H) on the surface of the activated carbon. The activated carbons treated with nitric acid display a significant increase in the population of acid sites compared to the parent material (Table 1), with this effect being much more relevant for the treatment with higher acid concentration (6.52 mmol g⁻¹ of acid sites for AC-N-15M).^{22,42} The treatment with HNO₃ is also accompanied by a decrease in the surface area and pore volume of the material (Table 1), in line with previous reports.⁴³⁻⁴⁵ However, a very large surface area (1240 m² g⁻¹) is preserved even after treatment with 15 M HNO₃. The observed drop in the surface area and pore volume is most likely related to the generation of a large amount of oxygen-containing functional groups on the surface of the activated carbon, though the collapse of a fraction of the pores cannot be excluded. On the other hand, the treatment with sulphuric acid causes only a slight decrease in the surface area and pore volume compared to the parent activated carbon but generates a lower total amount of acid sites compared to the treatment with nitric acid with comparable concentration (Table 1 and Fig. 1). It can be concluded that the oxidising treatment with H₂SO₄ is milder and leads to a less pronounced modification of the material. Notably, the relative amount of stronger acid sites in the activated carbons treated with H₂SO₄ (AC-S-6M and AC-S-18M) is much higher compared to those in the parent material and those treated with HNO₃ (Table 1). This can be attributed to the surface sulphonic acid groups that formed upon treatment with H₂SO₄.^{46,47} Indeed, the presence of these -SO₃H species is demonstrated by the doublet of S 2p_{1/2} (168.1 eV) and S 2p_{3/2} (169.4 eV) in the S(2p) XPS spectra of AC-S-18M and AC-S-6M (Fig. 2 and Table 2), which has been assigned to sulphonic acid groups.^{48,49} Similarly, the treatment with HNO₃ can lead to the insertion of nitrogen into the material as shown by the N(1s) XPS spectra of AC-N-15M and AC-N-6M (Fig. 2 and Table 2), which present a main peak at around 406 eV ascribed to the nitro groups (-NO₂) introduced through a reaction similar to benzene nitration,^{50,51} and a much less intense signal at around 400-401 eV, which is characteristic of the pyrrolic and/or pyridone nitrogen.^{48,51} However, the -NO₂ species present in the carbon matrix do not have acidic features and, therefore,

Table 1 Textural properties and acidity of the parent and acid-treated activated carbons

	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{total} ($\text{cm}^3 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	Total acid sites ^a (mmol g^{-1})	Stronger acid sites ^a (mmol g^{-1})
AC-untreated	1550	0.94	0.55	0.60	0.17
AC-N-6M	1290	0.73	0.47	1.30	0.62
AC-N-15M	1240	0.64	0.44	6.52	1.0
AC-S-6M	1550	0.94	0.55	0.72	0.48
AC-S-18M	1495	0.83	0.53	1.88	0.90

S_{BET} = specific surface area, V_{total} = total pore volume, V_{micro} = microporous volume. ^a The total acid sites were determined by titration with NaOH, whereas the stronger acid sites (*i.e.* carboxyl groups and, for AC-S-6M and AC-S-18M, sulphonic acid groups) were determined by titration with NaHCO_3 .

are not expected to function as catalytic sites in the title reaction. XPS provides further information on the chemical state and amount of O and C atoms present at the surface of the activated carbon materials. The O(1s) XPS spectra of the activated carbons all present a complex signal that can be deconvoluted into three peaks (Fig. 2), which are characteristic of C=O bonds of isolated carbonyls or quinone groups (around 531–532 eV), of C–OH bonds in phenols (around 533 eV) and of $-\text{CO}_2\text{H}$ groups (around 534 eV).⁴⁸ As expected, the relative amount of these oxygen-containing groups is higher in the acid-treated activated carbons compared to the parent material (Table 2). The sample treated with 15 M HNO_3 (AC-N-15M) shows the largest amount of species with acidic character (signals at 533 and 534 eV in Table 2), thus correlating well

with the total amount of acid sites measured by titration (Table 1). When considering the spectra of AC-S-6M and AC-S-18M, it should be noted that the binding energies of O(1s) in S=O and S–O in sulphonic acid groups appear in the same range as those of O(1s) in C=O and C–O bonds, respectively.⁴⁹ The C(1s) XPS signal of the activated carbons can be deconvoluted into three components (Fig. 2), which represent graphitic carbon (284.7–285.2 eV), C–O bonds in phenol or ether (286.6–287.1 eV, possibly overlapping with the peak of C=O at around 287.2 eV) and O=C–O bonds of carboxyl groups (288.8–289.3 eV).^{48,52} These data confirm the formation of the oxidised species already evidenced by the O(1s) XPS signals and show that the content of graphitic carbon decreases significantly upon treatment with HNO_3 , particularly

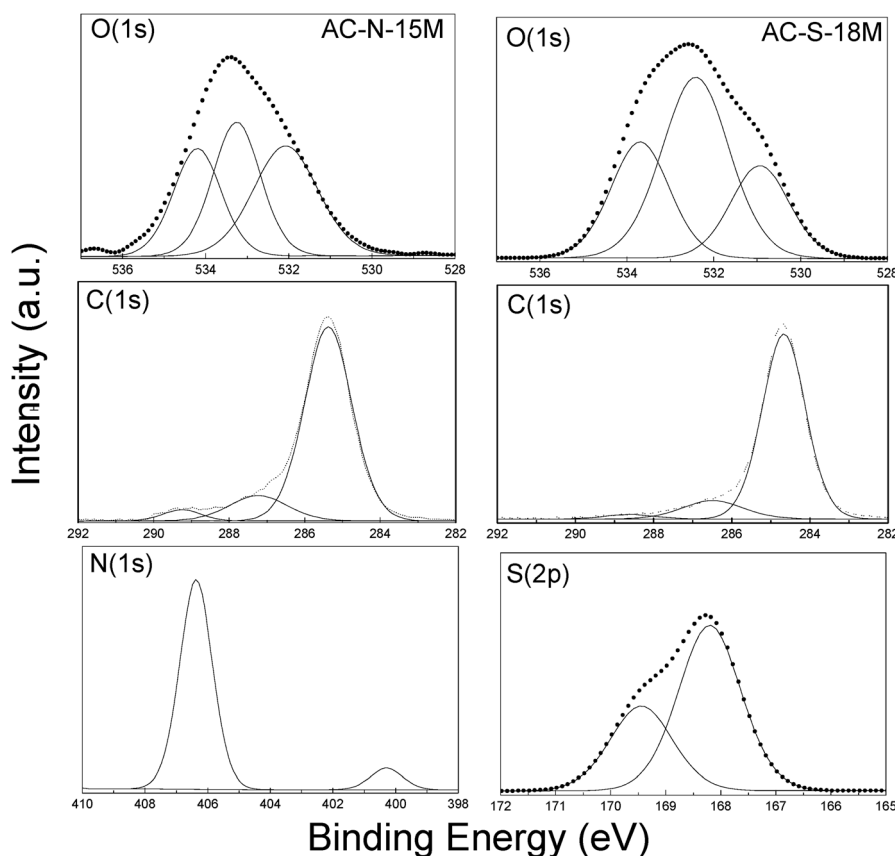


Fig. 2 XPS spectra of AC-N-15M and AC-S-18M in the range of O(1s), C(1s), S(2p) and N(1s) binding energy.

Table 2 Relative atomic content (%) of C, O, S and N and their binding energy (in brackets, in eV) for the parent and acid-treated activated carbons (n.d. = not determined)

	Carbon (%)			Oxygen (%)			Nitrogen (%)		Sulphur (%)	
	Graphitic	C-O/C=O	O=C-O	C=O	C-OH	-CO ₂ H	Pyrrolic/ pyridone	-NO ₂	-SO ₃ H (2p1/2)	-SO ₃ H (2p3/2)
AC-untreated	79.8 (284.7)	11.3 (286.6)	1.97 (288.7)	2.01 (531.3)	3.94 (533.0)	0.99 (534.2)	n.d.	n.d.	n.d.	n.d.
AC-N-6M	71.1 (285)	11.6 (286.9)	2.21 (289)	3.86 (531.5)	6.47 (533.2)	2.85 (534.4)	0.34 (400.4)	1.65 (406)	n.d.	n.d.
AC-N-15M	67.3 (285.2)	10.4 (287.1)	3.03 (289.3)	5.79 (531.2)	6.47 (533.2)	4.90 (534.2)	0.19 (400.8)	1.92 (406.4)	n.d.	n.d.
AC-S-6M	78.6 (284.8)	10.2 (284.8)	1.94 (288.9)	2.7 (531)	4.81 (533.1)	1.50 (534.1)	n.d.	n.d.	0.22 (168.3)	0.15 (169.5)
AC-S-18M	76.5 (284.7)	9.81 (286.6)	2.27 (288.7)	2.46 (530.9)	5.73 (532.9)	2.78 (533.9)	n.d.	n.d.	0.28 (168.1)	0.19 (169.4)

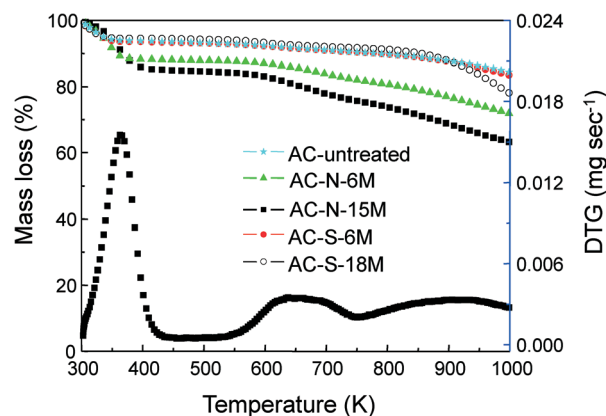
if at higher concentration, while it is only slightly affected by treatment with H₂SO₄ (Table 2), in line with the observations based on the N₂-physisorption data (*vide supra*). Elemental analysis confirms the trends observed by XPS concerning C, N and S content (Table 3), although the intrinsic differences between the two techniques (XPS is a surface technique limited to a depth of few nanometers) and the differences in the analysis conditions limit the comparison to a qualitative level.

The hydrophilicity and the thermal stability of the functional groups of the activated carbons were studied by thermogravimetric analysis (TGA). All materials showed a mass loss at about 428 K corresponding to vaporisation of physisorbed water (Fig. 3). This mass loss is more pronounced for AC-N-6M and AC-N-15M, indicating that these materials are more hydrophilic, as a consequence of their higher amount of oxidised species (*vide supra*). Furthermore, other small mass losses are observed at higher temperature. These losses are visualised more clearly in the derivative thermogravimetric curve (DTG) of AC-N-15M, which shows two thermal events with a maximum mass loss at approximately 650 K and 900 K (Fig. 3), ascribed to CO and CO₂ evolution, respectively. The elimination of CO₂ is ascribed to the decomposition of carboxyl, anhydride and lactone groups, while that of CO is associated with the decomposition of quinone and mono-oxygen species (carbonyls and phenols).^{53–55} The presence of these oxidised species in the acid-treated material is in full agreement with the analysis of the acid sites and of the XPS signals discussed above.

All of the activated carbons presented above display surface acid sites and a very large surface area. Therefore, they are promising candidates as heterogeneous catalysts for the acetalisation of acetone with glycerol (Scheme 1). Indeed,

Table 3 C, H, N and S mass content (%) of the parent and acid-treated activated carbons, as determined by elemental analysis

	Nitrogen %	Carbon %	Hydrogen %	Sulphur %
AC-untreated	0.3 ± 0.1	72 ± 2	1.6 ± 0.1	—
AC-N-6M	1.4 ± 0.4	61 ± 3	1.91 ± 0.04	—
AC-N-15M	2.0 ± 0.3	58 ± 1	1.29 ± 0.04	—
AC-S-6M	0.30 ± 0.04	72 ± 1	1.7 ± 0.1	0.33 ± 0.05
AC-S-18M	0.20 ± 0.06	65 ± 3	1.8 ± 0.3	1.3 ± 0.4

**Fig. 3** Thermogravimetric analysis of the parent and acid-treated activated carbons and derivative thermogravimetric analysis of AC-N-15M (bottom curve).

all of the materials are active for catalysing the reaction at room temperature, with a glycerol to acetone molar ratio of 1:1 and with lower catalyst loading compared to that typically employed for other heterogeneous catalysts active in this reaction (Table 4).^{1,12,14,18} As a reference, a blank reaction was carried out under the same conditions but without the addition of a solid catalyst, giving negligible conversion of glycerol. All of the acid-treated activated carbons gave a similar glycerol conversion of around 60%, whereas the parent material, AC-untreated, only achieved 44% conversion under the same reaction conditions (Table 4). The lower conversion observed for AC-untreated is ascribed to its lower amount of stronger acid sites (*i.e.* carboxyl groups or sulphonic acid groups, see Table 1), which are logically expected to display higher catalytic activity in the acid-catalysed condensation of glycerol with acetone compared to milder acid sites.^{54,56} The parent and acid-treated activated carbons were also tested at higher reaction temperatures, namely 323 and 353 K (Table 4). The trend in the catalytic activity is similar to that observed in the reaction at room temperature, with the acid-treated catalysts reaching significantly higher glycerol conversion compared to the untreated activated carbon, and with AC-S-18M consistently performing slightly better than the other three

Table 4 Acetalisation of acetone with glycerol over the parent and acid-treated activated carbon catalysts at room temperature, 323 and 353 K (glycerol : acetone molar ratio of 1 : 1, 2.7 wt% of catalyst, 6 h)

	Glycerol conversion (%)	Solketal selectivity (%)	6MR selectivity (%)	Temperature (K)
AC-untreated	44	97	3	298
AC-N-6M	60	96	4	298
AC-N-15M	61	98	2	298
AC-S-6M	60	98	2	298
AC-S-18M	63	98	2	298
AC-untreated	40	97	3	323
AC-N-6M	59	96	4	323
AC-N-15M	61	98	2	323
AC-S-6M	57	97	3	323
AC-S-18M	65	98	2	323
AC-untreated	35	93	7	353
AC-N-6M	54	97	3	353
AC-N-15M	56	97	3	353
AC-S-6M	54	97	3	353
AC-S-18M	64	94	6	353

acid-treated carbons at each of the three temperatures. The increase in temperature did not lead to higher glycerol conversion, and the average conversion was actually slightly lower at 353 K. This behaviour can be explained by considering that the acetalisation of acetone with glycerol does not reach full conversion unless H_2O is removed from the system or acetone is used in excess.^{12,14,18} After 6 h of reaction, the equilibrium conditions are typically reached (*vide infra*) and, since the acetalisation reaction is exothermic,^{16,56} the equilibrium concentration will shift towards the reactants upon increasing the reaction temperature. This justifies the slightly lower glycerol conversion to solketal observed in the reaction carried out at intermediate (323 K) and higher (353 K) temperatures.

The selectivity towards solketal was higher than 93% for all studied catalysts and was not affected by the reaction temperature (Table 4). The only observed side-product is the six-membered ring 2,2-dimethyl-1,3-dioxan-5-ol (6MR),¹ which is the other possible product of the condensation of glycerol with acetone (Scheme 1). The acetalisation of acetone with glycerol over Brønsted-acid catalysts occurs through the established mechanism of ketal formation.¹⁴ The high selectivity towards the five-membered ring solketal is generally observed, regardless of the nature of the catalyst, and has been associated with lower thermodynamic stability of the six-membered ring product due to the steric hindrance between the methyl group in the axial position and the two hydrogen atoms in the other axial positions of the ring.⁵⁷

The differences in activity between the catalysts are more clearly observed by carrying out the acetalisation reaction at room temperature with five-fold lower loading of the catalysts (Table 5). Under these conditions, the best catalyst (AC-S-18M) achieved a lower but still appreciable glycerol conversion of 24%.

The role of the acid sites of the activated carbons in catalysing the acetalisation of acetone with glycerol was confirmed in a control experiment carried out by pyrolysing AC-N-15M and AC-S-18M at 923 K and testing them again in the title reaction. In agreement with the TGA data (Fig. 3), the pyrolysis treatment at 923 K caused a dramatic decrease in the population of acid sites, which was accompanied by the almost complete deactivation of the catalysts (Table S1 in the ESI†).

An approach that can be employed to reach a higher degree of glycerol conversion in the condensation reaction with acetone consists of using an excess of acetone relative to glycerol.¹⁸ Accordingly, the conversion of glycerol increased by varying the glycerol to acetone molar ratio from 1 : 1 to 1 : 4 for all the tested activated carbon catalysts (Fig. 4.a). The previously observed trend of high solketal selectivity was not affected by changing the initial concentration of acetone (Fig. 4.b). The catalytic tests performed with an excess of acetone with respect to glycerol also allow confirmation of the differences in catalytic activity among the four acid-treated activated carbons: AC-S-18M was the most active catalyst, reaching a glycerol conversion of 97% and a solketal selectivity

Table 5 Acetalisation of acetone with glycerol over the parent and acid-treated activated carbon catalysts at room temperature and with low catalyst loading (glycerol : acetone molar ratio of 1 : 1, 0.54 wt% of catalyst, 6 h)

	Glycerol conversion (%)	Solketal selectivity (%)	6MR selectivity (%)	Temperature (K)
AC-untreated	8	80	20	298
AC-N-6M	17	89	11	298
AC-N-15M	22	92	8	298
AC-S-6M	15	88	12	298
AC-S-18M	24	92	8	298

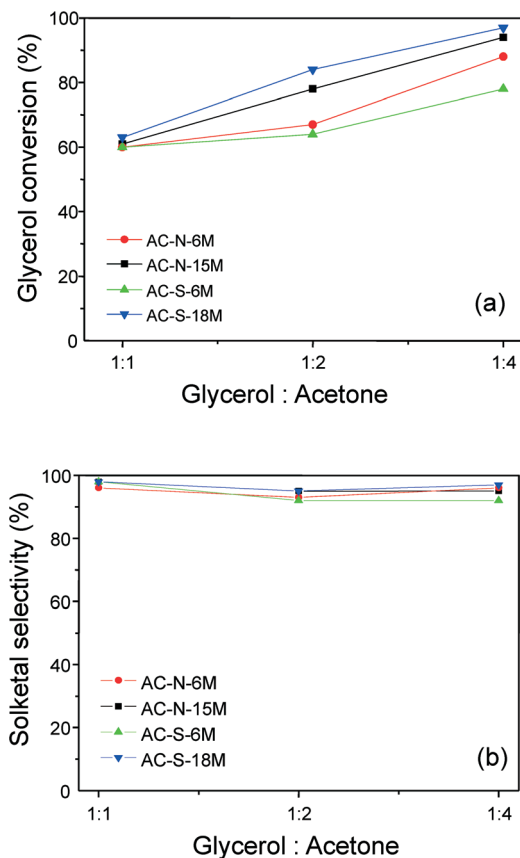


Fig. 4 Effect of the variation of the glycerol to acetone ratio on the acetalisation reaction (2.7 wt% of catalyst, 6 h at room temperature): (a) glycerol conversion and (b) solketal selectivity.

of 96% when using a glycerol to acetone ratio of 1 : 4, followed by AC-N-15M, AC-N-6M and finally AC-S-6M. This ranking can be partially explained in terms of the number of acid sites per gram of the catalyst, and particularly of stronger acid sites, as already evidenced in the comparison with AC-untreated (*vide supra*). However, based on the population of acid sites determined by Boehm titration (Table 1), AC-N-15M is expected to perform better than AC-S-18M, indicating that a more detailed analysis is necessary and that other factors contribute to the activity of the catalysts in this reaction. The first item to be considered to explain the higher activity of AC-S-18M is the presence of sulphonic acid groups on the surface of this material, as proven by XPS. Although the XPS data indicate that these species are present in lower amounts compared to carboxyl groups on the surface of AC-S-18M (Table 2), the sulphonic acid groups are much stronger Brønsted acids compared to carboxyl groups and their contribution to the catalytic activity is expected to be more relevant (per acid site). Therefore, the presence of the sulphonic acid groups, which are absent in the HNO₃-treated activated carbons, can account for the better catalytic performance of AC-S-18M compared to AC-N-15M, despite the slightly higher total amount of relatively strong acid sites of the latter (see amounts of 'stronger acid sites' in Table 1). This analysis also suggests that the mildly acidic groups that are present in a much larger

amount in AC-N-15M than in any other catalyst (see Table 1) do not play a major role in the activity of the activated carbons in this reaction. A second factor that contributes to the slightly higher activity of AC-S-18M compared to AC-N-15M is the lower hydrophilicity of the former, as evidenced by TGA. The influence of the hydrophilicity of the catalyst surface on the activity in the acetalisation of acetone with glycerol has been already reported for other heterogeneous catalysts.¹⁸ A relatively hydrophobic surface can help remove the water formed in the condensation of glycerol with acetone from the active site region, thus reducing the probability of the reverse reaction to occur, *i.e.* the hydrolysis of the formed solketal (Scheme 1).

The catalytic behaviour of the activated carbons was investigated further by performing a kinetic study of the acetalisation of acetone with glycerol at room temperature with a glycerol to acetone molar ratio of 1 : 4 and catalyst loading of 2.7 wt% (Fig. 5). In all of the tested catalysts, the conversion of glycerol tends to reach a plateau after 5 h of reaction. In line with the catalytic trends discussed above, AC-S-18M was remarkably more active than the other catalysts in the first 30 min of reaction, reaching a glycerol conversion of 36% that corresponds to a high turnover frequency (TOF = 153 h⁻¹, if calculated as moles of glycerol converted per mole of acid sites of the catalyst per hour; and TOF = 320 h⁻¹, if calculated as moles of glycerol converted per mole of stronger acid sites of the catalyst per hour). This experiment also underlined the superior catalytic activity of the four acid-treated carbons compared to the untreated activated carbon, confirming the importance of the higher number and strength of acid sites generated by the acid treatments.

The heterogeneous nature of the acid-treated activated carbon catalysts was investigated by means of leaching tests performed by removing the catalyst from the reaction mixture after 30 min by filtration at the reaction temperature and by allowing the liquid phase to react for further 5 h 30 min

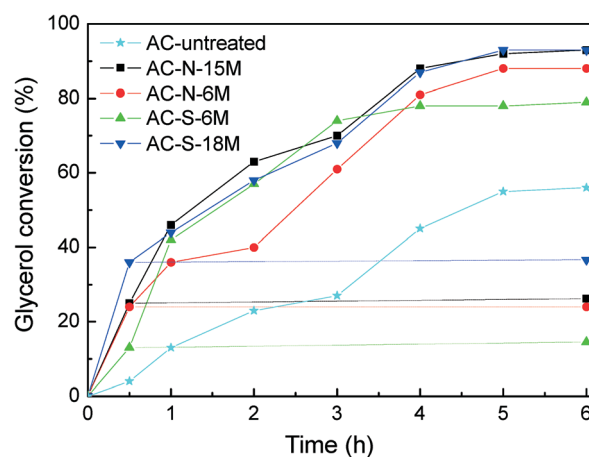


Fig. 5 Kinetic study (solid lines) and leaching test (dashed lines) of the acetalisation of acetone with glycerol catalysed by the parent and acid-treated activated carbons (glycerol:acetone molar ratio of 1:4, 2.7 wt% of catalyst, room temperature).

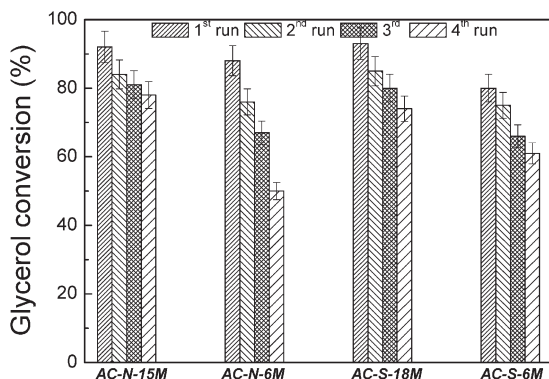


Fig. 6 Recycling tests of the activated carbon catalysts in the acetalisation of acetone with glycerol (glycerol:acetone molar ratio of 1:4, 2.7 wt% of catalyst, 6 h at room temperature).

under the same experimental conditions.⁵⁸ In all cases, no or negligible increase in the glycerol conversion was observed after removal of the catalyst (Fig. 5), indicating that the active species present on the activated carbon surface did not leach during the acetalisation reaction and thus proving the truly heterogeneous nature of these catalysts.

Finally, the reusability of the catalysts in consecutive runs was investigated. After each catalytic run, the activated carbon was separated from the reaction medium by filtration, washed three times with ethanol to remove physisorbed compounds and dried at 373 K for 24 h. A gradual, moderate decrease in glycerol conversion was observed upon recycling of all the catalysts (Fig. 6). This slow, steady deactivation of the catalysts can be attributed to the adsorption of glycerol on the active sites and/or to the formation of carboxylate and sulphonate esters through reaction of the $-\text{CO}_2\text{H}$ and $-\text{SO}_3\text{H}$ acid sites with glycerol.^{59,60} Anyhow, it should be noted that the most active catalysts, AC-S-18M and AC-N-15M, still retained most of their original activity in the 4th recycle (80% and 85% of the original conversion degree, respectively).

Conclusions

Acid-functionalised activated carbons were prepared by chemical activation of olive stones, an abundant agricultural solid waste, followed by treatment with nitric or sulphuric acid. The obtained materials displayed extremely large specific surface areas (1240 to 1550 $\text{m}^2 \text{g}^{-1}$) and a relevant population of surface acid sites of different strength. These features make them suitable as heterogeneous catalysts for the conversion of a renewable and available substrate such as glycerol into solketal, through a condensation reaction with acetone. The material prepared by treatment with 18 M H_2SO_4 displayed the best catalytic performance, achieving 97% conversion of glycerol with high selectivity towards solketal under mild and environmentally friendly conditions (solvent-free reaction at room temperature) and with lower catalyst loading compared to that used for state-of-the-art heterogeneous catalysts for this reaction. The excellent catalytic performance of this catalyst is attributed to its population of carboxylic and sulphonic

acid sites, as evidenced by XPS and Boehm titration, and to its lower hydrophilicity compared to the HNO_3 -treated activated carbons.

Acknowledgements

This work was supported by FAPESP (project no. 2011/14626-3 and no. 2011/22264-4), CNPq-SWB (project no. 245705/2012-0), CNPq-FWO (CNPq-project no. 490298/2009-5, FWO-project code: VS.025.10N, V4.520.11N) and START1 (KU Leuven, project code: STRT1/10/035).

Notes and references

- B. Mallesham, P. Sudarsanam, G. Raju and B. M. Reddy, *Green Chem.*, 2013, **15**, 478–489.
- M. S. D. P. Gomes and M. S. Muylaert de Araújo, *Renewable Sustainable Energy Rev.*, 2009, **13**, 2201–2204.
- R. Rodrigues, N. Isoda, M. Gonçalves, F. C. A. Figueiredo, D. Mandelli and W. A. Carvalho, *Chem. Eng. J.*, 2012, **198**, 457–467.
- D. Mandelli, W. A. Carvalho, L. S. Shul'pina, A. M. Kirillov, M. V. Kirillova, A. J. Pombeiro and G. B. Shul'pin, *Advances in Organometallic Chemistry and Catalysis: The Silver/Gold Jubilee International Conference on Organometallic Chemistry Celebratory Book*, 2013.
- M. Balaraju, V. Rekha, P. S. S. Prasad, B. L. A. P. Devi, R. B. N. Prasad and N. Lingaiah, *Appl. Catal., A*, 2009, **354**, 82–87.
- C. A. de Araujo Filho, T. Salmi, A. Bernas and J. P. Mikkola, *Ind. Eng. Chem. Res.*, 2013, **52**, 1523–1530.
- T. S. Galhardo, N. Simone, M. Gonçalves, F. C. A. Figueiredo, D. Mandelli and W. A. Carvalho, *ACS Sustainable Chem. Eng.*, 2013, **1**, 1381–1389.
- S. Zhu, X. Gao, F. Dong, Y. Zhu, H. Zheng and Y. Li, *J. Catal.*, 2013, **306**, 155–163.
- L.-Z. Tao, B. Yan, Y. Liang and B.-Q. Xu, *Green Chem.*, 2013, **15**, 696–705.
- M. S. Khayoon and B. H. Hameed, *Appl. Catal., A*, 2013, **464–465**, 191–199.
- R. P. V. Faria, C. S. M. Pereira, V. M. T. M. Silva, J. M. Loureiro and A. E. Rodrigues, *Chem. Eng. J.*, 2013, **233**, 159–167.
- J. M. Fraile, R. Mallada, J. A. Mayoral, M. Menéndez and L. Roldán, *Chem. – Eur. J.*, 2010, **16**, 3296–3299.
- A. Mendoza, US 5484547 A 19960116, 1996.
- C. X. A. da Silva, V. L. C. Gonçalves and C. J. A. Mota, *Green Chem.*, 2009, **11**, 38–41.
- J. Deutsch, A. Martin and H. Lieske, *J. Catal.*, 2007, **245**, 428–435.
- M. R. Nanda, Z. Yuan, W. Qin, H. S. Ghaziaskar, M.-A. Poirier and C. C. Xu, *Fuel*, 2014, **117**, Part A, 470–477.
- G. S. Nair, E. Adrijanto, A. Alsahme, I. V. Kozhevnikov, D. J. Cooke, D. R. Brown and N. R. Shiju, *Catal. Sci. Technol.*, 2012, **2**, 1173–1179.

- 18 L. Li, T. I. Koranyi, B. F. Sels and P. P. Pescarmona, *Green Chem.*, 2012, **14**, 1611–1619.
- 19 C.-N. Fan, C.-H. Xu, C.-Q. Liu, Z.-Y. Huang, J.-Y. Liu and Z.-X. Ye, *React. Kinet., Mech. Catal.*, 2012, **107**, 189–202.
- 20 P. Ferreira, I. M. Fonseca, A. M. Ramos, J. Vital and J. E. Castanheiro, *Appl. Catal., B*, 2010, **98**, 94–99.
- 21 R. Yavuz, H. Akyildiz, N. Karatepe and E. Cetinkaya, *Fuel Process. Technol.*, 2010, **91**, 80–87.
- 22 C.-C. Huang, H.-S. Li and C.-H. Chen, *J. Hazard. Mater.*, 2008, **159**, 523–527.
- 23 C. Moreno-Castilla, M. A. Ferro-García, J. P. Joly, I. Bautista-Toledo, F. Carrasco-Marin and J. Rivera-Utrilla, *Langmuir*, 1995, **11**, 4386–4392.
- 24 H. Teng, Y.-T. Tu, Y.-C. Lai and C.-C. Lin, *Carbon*, 2001, **39**, 575–582.
- 25 C. Erlich, E. Björnbohm, D. Bolado, M. Giner and T. H. Fransson, *Fuel*, 2006, **85**, 1535–1540.
- 26 R. A. Shawabkeh, D. A. Rockstraw and R. K. Bhada, *Carbon*, 2002, **40**, 781–786.
- 27 N. M. Haimour and S. Emeish, *Waste Manage.*, 2006, **26**, 651–660.
- 28 R. V. R. A. Rios, M. Martínez-Escandell, M. Molina-Sabio and F. Rodríguez-Reinoso, *Carbon*, 2006, **44**, 1448–1454.
- 29 A. Bhatnagar, F. Kaczala, W. Hogland, M. Marques, C. Paraskeva, V. Papadakis and M. Sillanpää, *Environ. Sci. Pollut. Res.*, 2014, **21**, 268–298.
- 30 G. Rodríguez, A. Lama, R. Rodríguez, A. Jiménez, R. Guillén and J. Fernández-Bolaños, *Bioresour. Technol.*, 2008, **99**, 5261–5269.
- 31 H. P. Boehm, *Carbon*, 1994, **32**, 759–769.
- 32 J. Bedia, R. Ruiz-Rosas, J. Rodríguez-Mirasol and T. Cordero, *AIChE J.*, 2010, **56**, 1557–1568.
- 33 X. Qi, H. Guo, L. Li and R. L. Smith, *ChemSusChem*, 2012, **5**, 2215–2220.
- 34 Y. Nakagawa, M. Molina-Sabio and F. Rodríguez-Reinoso, *Microporous Mesoporous Mater.*, 2007, **103**, 29–34.
- 35 B. C. Lippens and J. H. de Boer, *J. Catal.*, 1965, **4**, 319–323.
- 36 N. Hutson and R. Yang, *Adsorption*, 1997, **3**, 189–195.
- 37 J. P. Olivier, W. B. Conklin and M. Vonzombathely, *Determination of pore-size distribution from Density Functional Theory – A comparison of nitrogen and argon results*, Elsevier, 1994, vol. 87, pp. 81–89.
- 38 P. P. Pescarmona and P. A. Jacobs, *Catal. Today*, 2008, **137**, 52–60.
- 39 K. S. W. Sing, D. H. Everett, R. A. W. Haul, L. Moscou, R. A. Pierotti, J. Rouquerol and T. Siemieniewska, *Pure Appl. Chem.*, 1985, **57**, 603–619.
- 40 Z. Jiang, Y. Liu, X. Sun, F. Tian, F. Sun, C. Liang, W. You, C. Han and C. Li, *Langmuir*, 2003, **19**, 731–736.
- 41 M. Danish, R. Hashim, M. N. M. Ibrahim and O. Sulaiman, *J. Anal. Appl. Pyrolysis*, 2013, **104**, 418–425.
- 42 S. Wang and G. Q. Lu, *Carbon*, 1998, **36**, 283–292.
- 43 J. Rivera-Utrilla, M. Sánchez-Polo, V. Gómez-Serrano, P. M. Álvarez, M. C. M. Alvim-Ferraz and J. M. Dias, *J. Hazard. Mater.*, 2011, **187**, 1–23.
- 44 E. Vega, J. Lemus, A. Anfruns, R. Gonzalez-Olmos, J. Palomar and M. J. Martin, *J. Hazard. Mater.*, 2013, **258–259**, 77–83.
- 45 M. Gonçalves, L. Sánchez-García, E. D. Oliveira Jardim, J. Silvestre-Albero and F. Rodríguez-Reinoso, *Environ. Sci. Technol.*, 2011, **45**, 10605–10610.
- 46 M. Gonçalves, V. C. Souza, T. S. Galhardo, M. Mantovani, F. C. A. Figueiredo, D. Mandelli and W. A. Carvalho, *Ind. Eng. Chem. Res.*, 2013, **52**, 2832–2839.
- 47 M. Okamura, A. Takagaki, M. Toda, J. N. Kondo, K. Domen, T. Tatsumi, M. Hara and S. Hayashi, *Chem. Mater.*, 2006, **18**, 3039–3045.
- 48 A. P. Terzyk, *Colloids Surf., A*, 2001, **177**, 23–45.
- 49 C. Petit, K. Kante and T. J. Bandoz, *Carbon*, 2010, **48**, 654–667.
- 50 J. P. S. Sousa, M. F. R. Pereira and J. L. Figueiredo, *Fuel Process. Technol.*, 2013, **106**, 727–733.
- 51 R. Pietrzak, *Fuel*, 2009, **88**, 1871–1877.
- 52 A. M. Puziy, O. I. Poddubnaya, R. P. Socha, J. Gurgul and M. Wisniewski, *Carbon*, 2008, **46**, 2113–2123.
- 53 J. L. Figueiredo, M. F. R. Pereira, M. M. A. Freitas and J. J. M. Órfão, *Carbon*, 1999, **37**, 1379–1389.
- 54 J. Jaramillo, P. M. Álvarez and V. Gómez-Serrano, *Appl. Surf. Sci.*, 2010, **256**, 5232–5236.
- 55 F. de Clippel, M. Dusselier, R. Van Rompaey, P. Vanelderden, J. Dijkmans, E. Makshina, L. Giebler, S. Oswald, G. V. Baron, J. F. M. Denayer, P. P. Pescarmona, P. A. Jacobs and B. F. Sels, *J. Am. Chem. Soc.*, 2012, **134**, 10089–10101.
- 56 I. Agirre, I. Garcia, J. Requies, V. L. Barrio, M. B. Gueemez, J. F. Cambra and P. L. Arias, *Biomass Bioenergy*, 2011, **35**, 3636–3642.
- 57 L. P. Ozorio, R. Pianzollini, M. B. S. Mota and C. J. A. Mota, *J. Braz. Chem. Soc.*, 2012, **23**, 931–937.
- 58 R. A. Sheldon, M. Wallau, I. W. C. E. Arends and U. Schuchardt, *Acc. Chem. Res.*, 1998, **31**, 485–493.
- 59 W. Zhao, B. Yang, C. Yi, Z. Lei and J. Xu, *Ind. Eng. Chem. Res.*, 2010, **49**, 12399–12404.
- 60 J. M. Fraile, E. García-Bordejé and L. Roldán, *J. Catal.*, 2012, **289**, 73–79.