Green heterogeneous catalysts for cleaner solvent-free production of acetates

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Abstract

The development of new chemical synthetic methodologies that transform industrial chemical processes into more sustainable ones, constitutes one of the challenges and objectives of chemical research both in academia and in industry. The use of activated carbons as heterogeneous catalysts represents one of the most beneficial options for process efficiency in terms of reaction rate, yield, and ease of work-up. We have produced six new activated carbons by treatment of three affordable commercial carbons with either nitric acid, or with sulfuric acid. The complete characterization of these nine activated carbons has been carried out through the measurement of nitrogen adsorption capacity, porosimetry, elemental organic analysis, X-ray photoelectron spectroscopy, scanning electron microscopy and determination of the point of zero charge; transmission electron microscopy was also performed on two of them. The catalytic activity of these nine catalysts has been tested in the acetylation reaction of hydroxyl groups, undoubtedly one of the most versatile and widely used chemical transformations both at the laboratory and industrial scale. The results show that by means of a simple and affordable modification of commercial xerogel with sulfuric acid, a more efficient catalyst is formed. Acetylation with the best catalyst is completed in 90 min at room temperature and the product is easily isolated in quantitative yield. The system can be reutilized for five runs with only a small loss of catalytic activity.

Keywords Activated carbons · Heterogeneous catalysis · Acetylation · Acetates esters · Green chemistry

1 Introduction

Catalysis is one of the fundamental pillars of Green Chemistry. The design and application of new catalyst systems are simultaneously achieving the dual goals of environmental protection and economic viability [1]. Therefore, developing new synthetic methodologies based on affordable green catalysts saves time and energy, thus optimizing the sustainability of chemical synthesis processes [2].

Activated carbons (AC) constitute a group of materials that possess several advantageous properties. Apart from the low environmental impact and the reduced cost, activated carbons have a large surface area that makes them interesting for heterogeneous catalysis. Moreover, their large pore volume, and chemical surface nature can be modified in order to improve their catalytic performance [3]. Activated carbons are very interesting heterogeneous catalysts because they provide access to easy reaction work-up and can be separated by simple filtration. Its use would therefore save energy and reduce the consumption of solvents in a wide variety of chemical processes. Furthermore, on many occasions, they can also be recovered and recycled several times without significant loss of catalytic activity.

Activated carbons have been used to a limited extent in the synthesis of fine chemicals. But advances in recent decades in the study of these materials and the possibility of modifying the surface chemistry of carbonaceous materials

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have allowed their use as catalysts in these reactions. Among their advantages are their high specific surface area and pore volume, resistance to acids, bases, and high temperatures, and the aforementioned possibility of modifying their surface chemical and physical properties.

It is worth mentioning that AC have been successfully applied in fine-chemical synthesis [4–8]. In this context, AC have attracted much attention in several kinds of organic transformations, such as the synthesis of α,β-unsaturated nitriles [9], the epoxide ring-opening reaction [10], synthesis of chalcones [8], N-alkylation of imidazole [11–17], and acetylation of glycerol [18].

The acetylation of hydroxyl groups in a variety of substrates, such as alcohols, phenols, and carbohydrates, constitutes a major protection procedure that is extensively applied in chemical synthesis [19]. According to the principles of green chemistry, protection/deprotection steps should be avoided [2], yet, sometimes this is not possible. If moiety protection steps are required, they ought to proceed readily, quantitatively, and keep waste formation and costs to a minimum. Furthermore, acetylation is also used to enhance the bioactivity of certain substrates [20, 21].

O-acetylation is typically performed with an excess of acetic anhydride with basic or acidic catalysis; sometimes the noxious acyl halides are used instead. Pyridine is commonly used as a catalyst and as a solvent, despite its toxicity [22]. This reaction is so widely used, not only in organic and pharmaceutical syntheses, but also in cosmetic and food industry, that many reports on different catalytic procedures have been published [23]. Pyridine derivatives, 4-dialkylaminopyridines, greatly accelerate the reaction when used as cocatalyst with pyridine [24–26]. Other amine bases show good catalytic activity, as well [27]. Metal triflates show good catalytic activity [28–39]. Some metal salts, mainly perchlorates, have met with some success [40–43], and different types of heterogeneous catalysts have been reported [44–48]. Vanadium-based catalysts have been applied to transform the naturally occurring phenol, thymol, to its biologically active acetyl derivative [49]. Salen cobalt complex is a reusable catalyst for this reaction [50]. Iodine proved to be a powerful catalytic acetylating agent [51]. A series of bicarbonates and carbonates were tested; good catalytic activity for the acetylation of primary alcohols and phenols was reported [52]. Modified zirconia catalyzes the process too [53]. Tributylphosphine has shown to be an efficient catalyst for acylation reactions too [54]. Task-specific ionic liquids with excellent results in the acetylation of alcohols and phenols have been studied in our group [55], and elsewhere [56]. In another paper, acetylation of alcohols and amines under light irradiation with the use of a photosensitizer has been reported [57]. Nanocapsules of zirconium and polymer composite have been also applied to the acetylation of alcohols with good results [58].

Many of the methods reported achieve good results, however, some of them present drawbacks associated with heavy-metal waste production, energy costs, use of noxious compounds, harsh reaction conditions, long reaction times, or complicated workup procedures. For these reasons, there is still the need to explore novel methodologies that enhance the sustainability of this process. This goal can be achieved by using environmentally friendly catalysts while reducing energy costs and solvent use and simplifying work-up. Modified activated carbons have been successfully applied to the synthesis of high value-added products [59–61]. In our search of catalytic systems that may prove to be most adequate in terms of sustainable chemical processes, we have obtained and characterized six activated carbons. Since the acetylation of alcohols can be catalyzed by acids, we prepared six AC by treatment of three commercial carbons either with sulfuric acid or nitric acid. It is known that treatment of AC with acids provides oxidized sites on the surface of the material, and enhances its hydrophilicity; moreover, these treatments increase the acidic properties of the AC [62].

We report, herein, a novel and efficient solvent-free, activated-carbon catalyzed protocol for the acetylation of several alcohols, phenol, β-naphthol, and monosaccharides.

2 Materials and methods

Solvents of HPLC grade were purchased from Scharlab S.L. Reagents were purchased from Acros Organics and Sigma-Aldrich. Three different commercial carbons were acquired: activated carbon Norit RX 3.0 (Cabot Corporation, formerly Norit Nederland B.V.), labelled carbon N; mesoporous carbon Xerogel CX-5 (Xerolutions S.L.), labelled carbon X, and Merck charcoal activated extra pure food grade (Merck KGaA) labelled carbon M.

NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer using CDCl$_3$ as solvent, and tetramethylsilane as internal standard. TLC was performed on silica gel plates coated with fluorescent indicator F254 from Merck KGaA. Flash chromatography was performed on Merck 60 silica gel (230–400 mesh) [63].

2.1 Synthesis of the catalysts

2.1.1 Treatment with nitric acid

The carbon materials M, N, and X were treated with a commercial concentrated nitric acid solution (60%), at room temperature for 1.5 h (1 g/20 mL) [17, 64]. The materials were then washed with deionized water in soxhlet until constant pH and dried in an oven at 110 °C. The activated carbons

obtained from M, N, and X by this method are termed MN, NN, and XN, respectively.

2.1.2 Treatment with sulfuric acid

The commercial carbon materials M, N, and X were treated with a concentrated sulfuric acid solution (98%), at room temperature for 1.5 h (1 g/20 mL) [17, 64]. The materials were then washed with deionized water in soxhlet until constant pH and dried in an oven at 110 °C. The activated carbons obtained from M, N, and X by this method are termed MS, NS, and XS, respectively.

2.2 Characterization of the catalysts

Textural characterization was performed by N_2 adsorption isotherms at 77 K in a Quantachrome Autosorb-1, and the specific surface area was calculated applying the BET method [65]. Porosimetry was performed in a Quantachrome Poremaster 60 with a pressure range between 6.89×10^3 and 4.13×10^8 Pa. Elemental analysis (C, H, N, S, O) was carried out using a LECO CHMS-932 elemental analyzer. C, H, N and S were analyzed, and the difference was assigned to ash (measured from proximate analysis) and oxygen content. X-Ray Photoelectron Spectra (XPS) was registered in a Kalpha Thermo Scientific Spectroscope with monochromatic Kα Al radiation, 12 kV voltage, and 6 mA current. The points of zero charge (PZC) values were determined using the method proposed by Valente Nabais and Carrott [66]. To carry out this measurement, a 0.1 M solution of sodium nitrate was prepared and 7% in weight of the catalyst was added, keeping it stirred for 48 h at 25 °C in a thermostatic bath. Subsequently, it was filtered, and the pH of the filtered solution was measured with a pH-meter. This pH value corresponds to the point of zero charge. A field emission Scanning electron microscope (SEM) Quanta 3D FEG (FEI Company) was used to explore the surface morphological characteristics of all nine ACs. The sample analysis was performed at high vacuum, with a secondary electron detector at 10, 15 or 20 kV. The transmission electron microscope (TEM) Tecnai G2 20 Twin (FEI Company) at an operating voltage of 200 kV was used to acquire high-resolution images with a magnification of 1.05×10^6 times.

2.3 Acetylation procedure

In a typical acetylation experiment the hydroxylated substrate (1.0 mmol), acetic anhydride (2.5 equiv. per hydroxyl group of the hydroxylated substrate), and 4 mol% of catalyst (percentage referred to acetic anhydride) are stirred at 60 °C until the completion of the reaction, as determined by tlc. Once the reaction is finished, the carbon is filtered off and the filtrate is treated with distilled water, washed twice with NaHCO₃ (10%), and extracted with diethyl ether or dichloromethane. The organic phase is dried with anhydrous $MgSO_4$ and evaporated at reduced pressure to yield the pure product; in some cases, the acetylated product was further purified by distillation or flash chromatography. All the compounds have been identified by their NMR spectra, which match those of known samples.

3 Results and discussion

3.1 Characterization of catalysts

3.1.1 Isotherms of N₂ adsorption

The three commercial activated carbons are mainly microporous, and the nitrogen adsorption capacity is highest for N, then M and, finally X (Fig. 1). Comparing these commercial Acs with the Acs obtained by treatment with sulfuric acid we can observe that the adsorptive capacity for MS is slightly higher than that of M, while XS has a slightly lower capacity than X; finally, NS adsorbs markedly less N_2 than N. On the other hand, treatment with nitric acid causes the adsorption of NN to be the highest of all, while MN is greater than MS and XN is the lowest of all. It is worth noting that their porosity remains almost the same, with the exception of the NS carbon, which undergoes a considerable decrease in its volume of mesopores and an increase in the volume of macropores (Table 1) [67].

The adsorption data agree with those of specific surface obtained by applying the model of Brunauer, Emmett and Teller (BET) [65] to the data of the previous isotherms (Table 1), because the carbons with the largest specific surface area are those with the largest volume of micropores. The low specific surface area of X, XN, and XS can be attributed to the fact that X is a carbon gel, hence its structure is quite different than that of N or M.

3.1.2 Elemental analysis

Results of organic elemental analysis (C, H, N and S) are shown in Table 2. Only the composition of the organic part of the catalysts is represented since the inorganic (ash content) has been previously subtracted.

The treatment of X and M with sulfuric acid decreases the carbon content, oxidizes the catalyst and increases the O and S contents. On the other hand, the treatment of N hardly changes the oxygen and carbon content, but an increase in the sulfur content is observed. Nitric acid treatment causes, as expected, an increase in N in all of them, especially in XN. Furthermore, XN shows a notable increase in its oxygen content, while the other two ACs obtained with nitric acid (NN and MN) show a decrease in oxygen content with

Fig. 1 Isotherms of N$_2$ adsorption at 77 K
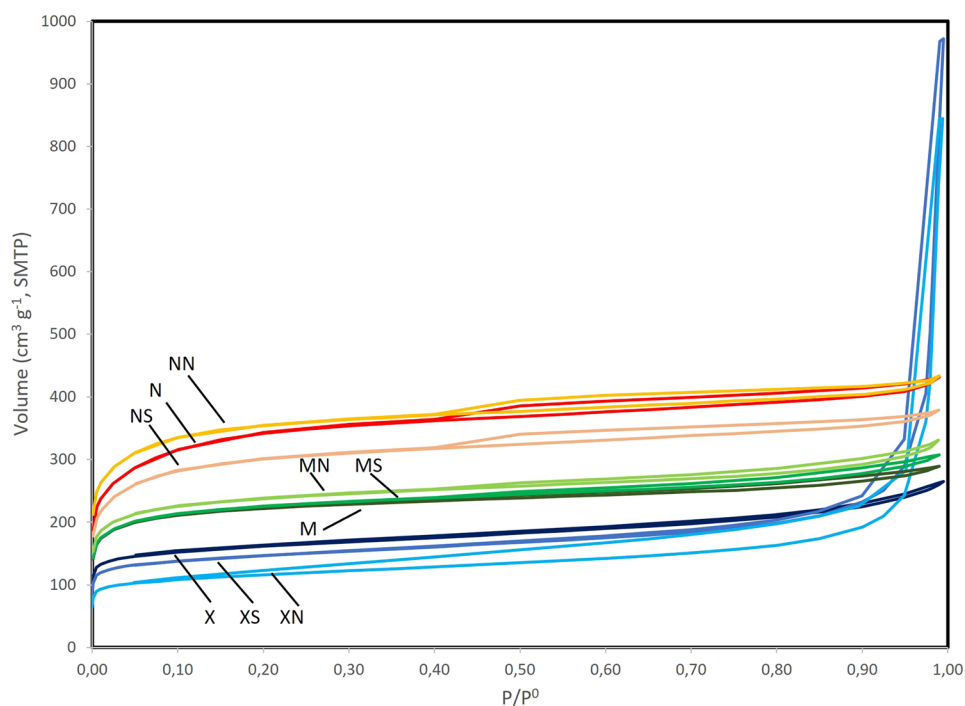
Table 1 Porosity and Specific surface of carbons

Carbon	V_{micro} (cm^3 g^{-1})^a	V_{meso} (cm^3 g^{-1})^b	V_{macro} (cm^3 g^{-1})^c	m^2 g^{-1}
N	0.628	0.104	0.464	1249
NS	0.547	0.095	0.828	1117
NN	0.648	0.135	0.479	1324
M	0.378	0.155	0.283	839
MS	0.393	0.188	0.351	847
MN	0.412	0.127	0.305	895
X	0.268	0.278	1.150	484
XS	0.249	0.153	0.990	448
XN	0.180	0.220	0.877	354

^{a}Dubinin-Ashtakov method

^{b}Mercury porosimetry

^{c}Mercury porosimetry

Table 2 Elemental analysis of activated carbons

Carbon	C	H	N	O^a	S
N	89.1	1.4	0.5	8.6	0.5
NS	89.2	1.0	0.5	8.2	1.1
NN	90.1	0.6	1.0	8.0	0.3
M	91.9	0.7	0.7	6.0	0.8
MS	83.9	1.4	0.7	13.2	1.4
MN	84.9	1.0	1.0	2.4	0.7
X	85.7	2.3	0	12.0	0.0
XS	81.2	2.6	0	15.5	0.7
XN	74.7	2.1	1.4	21.8	0.0

^{a}Oxygen content determined by difference

respect to the ACs from which they are formed (N and M, respectively).

3.1.3 X-ray photoelectron spectroscopy (XPS)

The composition, in general, is like that of the elemental analysis shown previously (Table 3). The relative difference in the amount of S between X and XS and between N and NS indicates that the sulfuric acid treatment has deposited functional sulfur groups preferably on the surface.

Table 3 XPS analysis of carbons

Carbon	C 1 s	O 1 s	N 1 s	S 2p
N	90.1	7.6	0.6	0.0
NS	89.7	10.1	0.0	0.2
NN	89.0	10.5	0.5	0.0
M	92.5	6.1	0.7	0.7
MS	90.5	7.9	0.4	1.2
MN	90.0	10.0	n.d	n.d
X	92.8	7.2	0.0	0.0
XS	90.6	8.5	0.0	0.9
XN	86.1	12.2	1.7	0.0

The signal of S in these catalysts has peaks close to 168 eV. This corresponds to oxidized forms of sulfur, such as sulfonic groups and sulfates. In untreated M and N carbons, both the 1 s orbital peak of N (near 400 eV) and the peak of the 2p orbital of S (near 164 eV) correspond to reduced forms of nitrogen and sulfur.

The N 1 s spectra observed in XN and NN show a second peak at binding energies of about 404 eV, indicating that oxidized nitrogen species have formed.

In the C1s spectrum, the main peak near 248.8 eV corresponds to the aromatic hydrocarbons which form a major part of the structure of these materials. This peak decreases in intensity when treated with nitric acid, and the peaks of higher BE value increase in intensity which is explained by the oxidation produced.

3.1.4 Point of zero charge (PZC)

The results of measurements of PZC are shown in Table 4.

Catalysts X and N are less alkaline than M; this can be explained due to the higher oxygen content of X and N, which leads to the formation of acidic oxygenated groups (alcohols and carboxylic acids). The treatment of M, N and X with nitric acid provokes an increase in the acidity of the resulting ACs (MS, NS and XS). It is worth noting, though, that NN and XN are clearly acidic whereas MN is practically neutral, due to the higher alkalinity of starting material it is formed from. The treatment with sulfuric acid increases the acidity of these materials. This is not only due to oxidation but also to the formation of sulfonic groups. The effect is similar in all three carbons, but since M is more alkaline a carbon, the final acidity of MS is lower. A more detailed discussion of the structure of the catalysts used here can be found elsewhere [17, 60, 68].

3.1.5 Scanning electron microscopy

Scanning electron microscopy images were obtained for all nine catalysts, as shown in Figs. 2, 3, 4, 5, 6, 7, 8, 9, 10.

Table 4 Point of zero charge of the carbons

Carbon	PZC
N	7.1
NS	2.8
NN	3.8
M	10.0
MS	3.8
MN	7.4
X	7.2
XS	2.5
XN	3.4
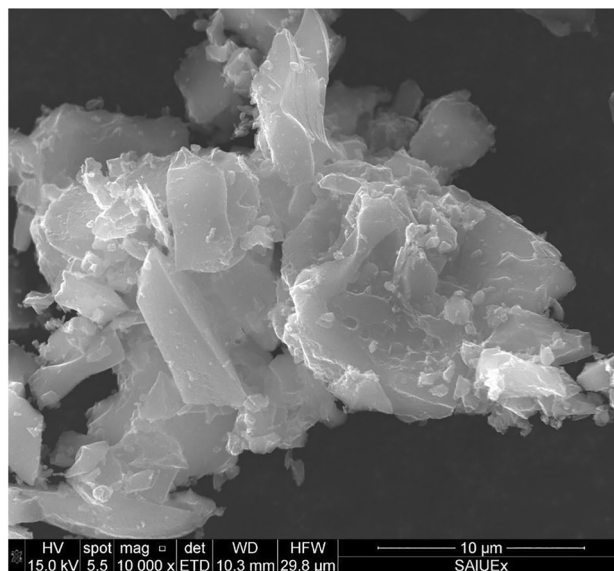
Fig. 2 SEM image of the catalyst N

The results obtained do not allow us to pinpoint remarkable changes of morphological features.

3.1.6 Transmission electron microscopy

In this case, we registered the TEM of the best catalyst (XS) and the carbon it is obtained from (X). The results for XS and X are shown in Figs. 11, 12, respectively. As with SEM, no significant difference regarding morphological features can be discovered; this is why the other activated carbons were not subjected to this characterization.
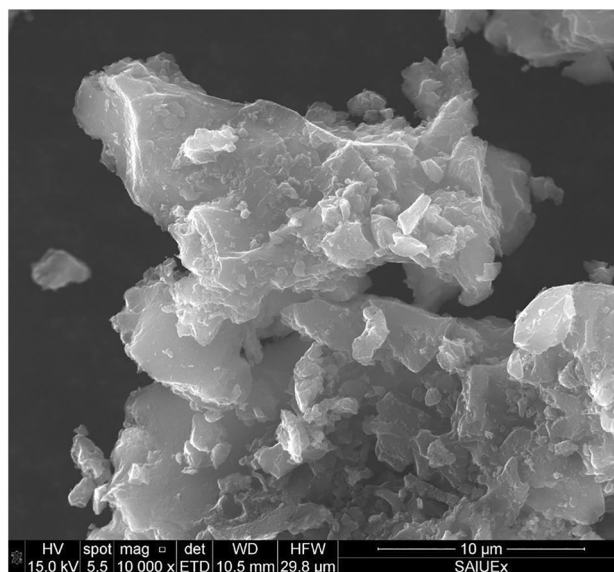
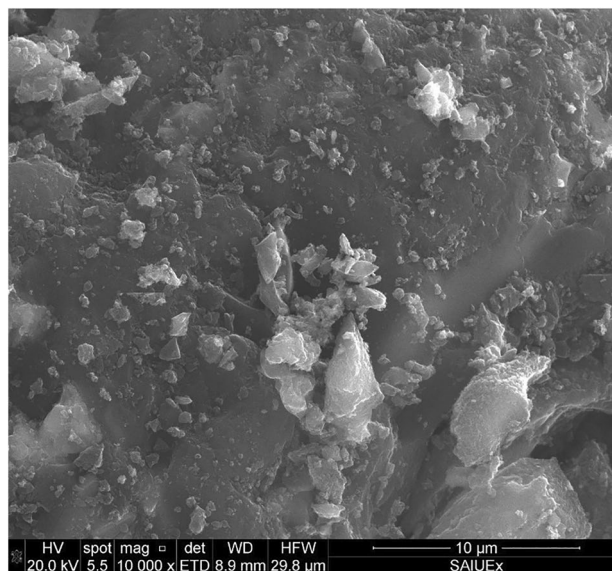**Fig. 3** SEM image of the catalyst NN
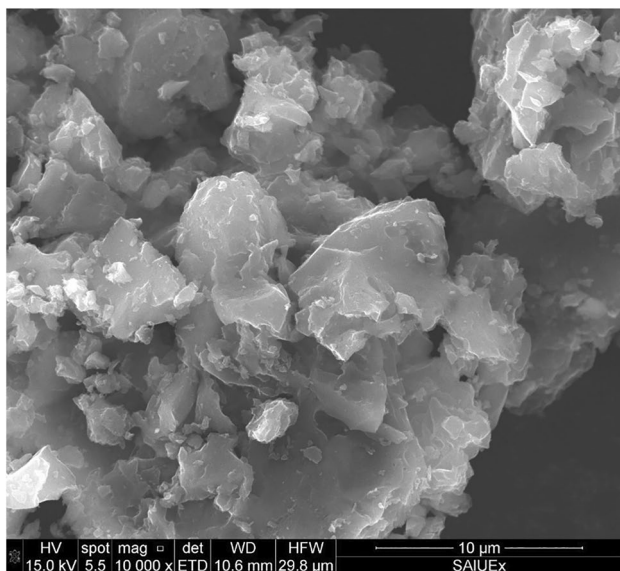
Fig. 4 SEM image of the catalyst NS

Fig. 6 SEM image of the catalyst MN
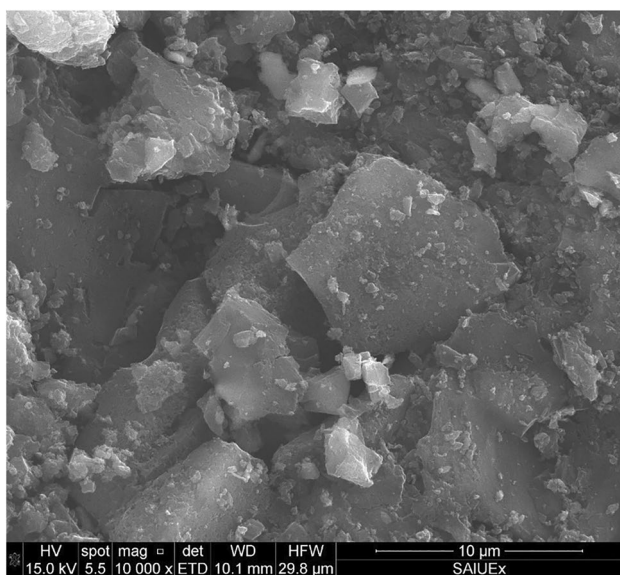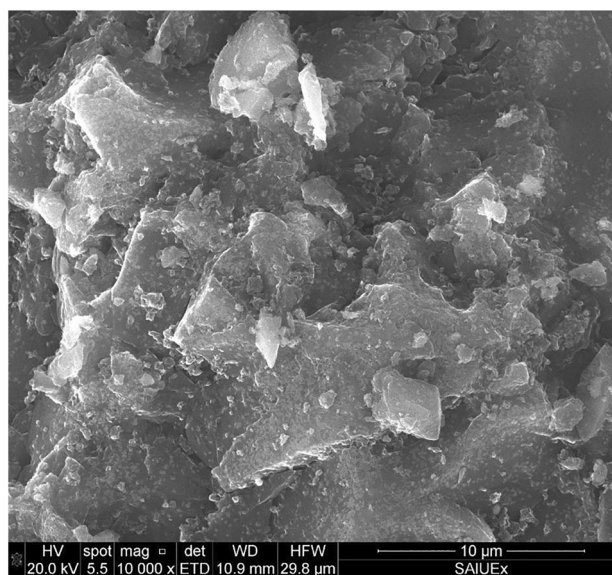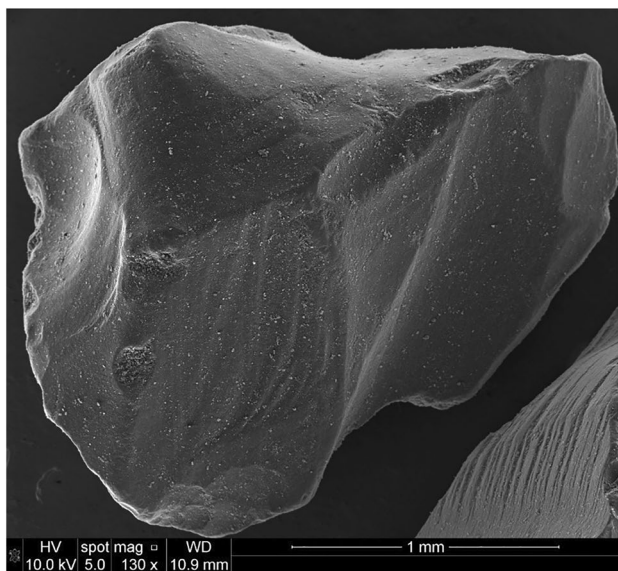

Fig. 5 SEM image of the catalyst M

Fig. 7 SEM image of the catalyst MS

3.1.7 Acetylation reaction

To test the catalytic performance of the different activated carbons, the acetylation of benzyl alcohol (BA) with acetic anhydride (AA) in the absence of solvent was selected as a model reaction.

Initial experiments with NS as a catalyst were aimed at optimizing reactant ratios and catalyst loading at room temperature (Table 5, entries 1–5). The results do not show a complete reaction at 24 h, even with an AA:BA ratio of 10:1 and a catalyst loading of 10% by mole. To improve the reaction outcome, heat was applied, and the amount of AA was reduced. Under these conditions, acetylation was completed in 4 h (Table 6 entry 6).

Using the conditions shown in entry 4 of Table 5, the catalytic activity of the other ACs was then checked, so that their relative performance could be assessed. The results are shown in Table 6.

Fig. 8 SEM image of the catalyst X
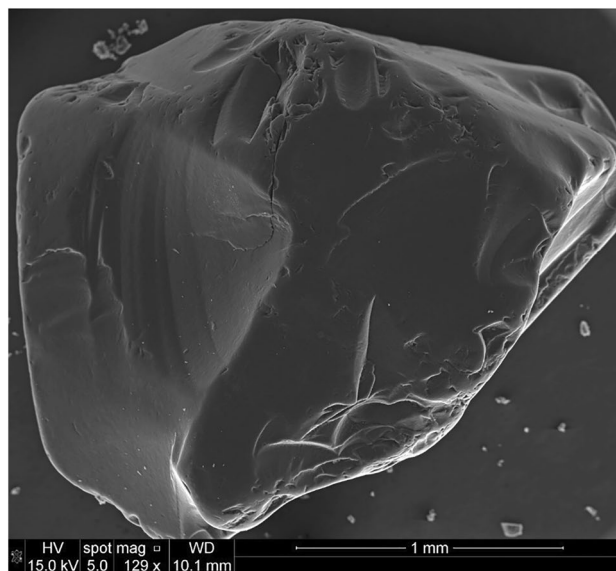
Fig. 10 SEM image of the catalyst XS
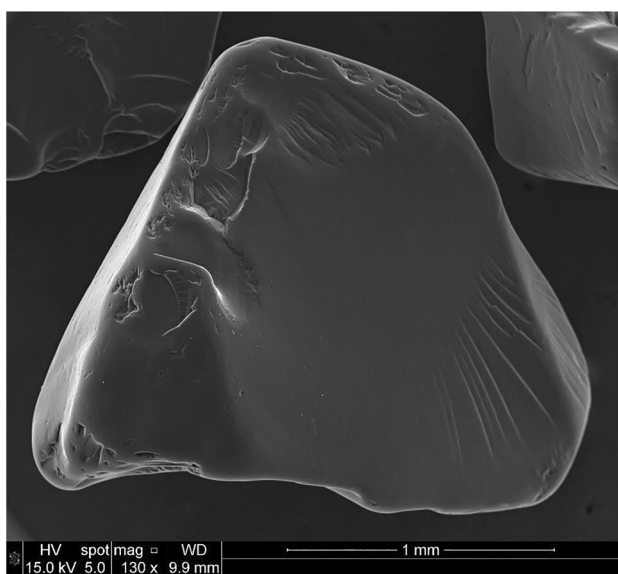
Fig. 9 SEM image of the catalyst XN
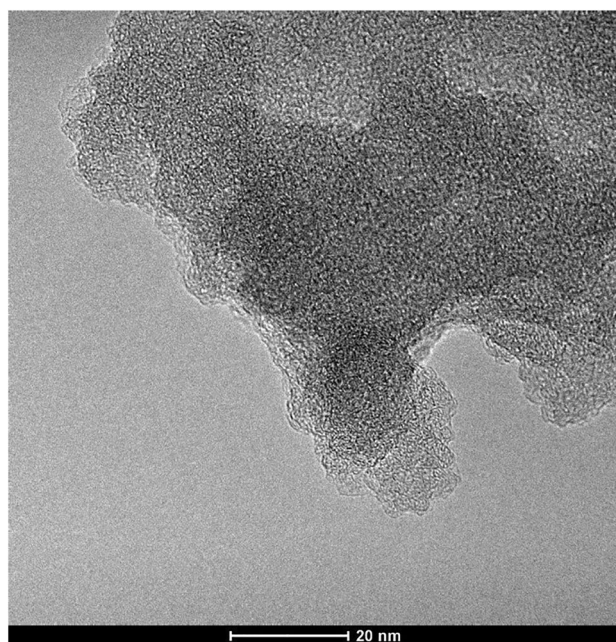
Fig. 11 TEM image of the catalyst XS

The acetylation reaction is suitable to either acidic or basic catalysis. All the modified AC are acidic, whereas N is a neutral activated carbon, X is a mildly basic carbon gel, and M is a basic activated carbon. The modified catalyst XS shows the best result, and that has to do, at least partly, with its acidity; surprisingly, NS is nearly as acidic as XS, and yet, its catalytic performance

is poorer. This fact may be explained by the fact that NS has a larger microporous volume and a smaller mesoporous volume than XS (see Table 1); hence, the larger mesoporous network of XS would facilitate access of the reactants to the active sites. MS is less acidic, and
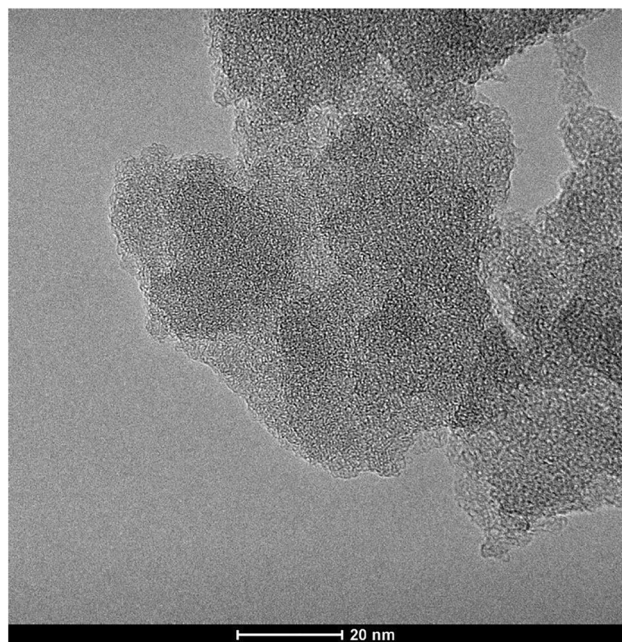
Fig. 12 TEM image of the catalyst X

Table 5 Acetylation with different catalysts[a]

Entry	Catalyst	Time (h)[b,c]
1	M	4
2	MN	3
3	MS	4
4	N	4
5	NN	4
6	NS	4
7	X	4
8	XN	4
9	XS	1.5

[a]Reaction conditions BA (1 mmol), AA (5 mmol), Cat. 10 mol%, 25 ºC

[b]Time for 100% conversion by tlc monitoring

[c]In all cases isolated yield was > 90%

Table 6 Acetylation with catalyst NS at 25 ºC

Entry	Catalyst	Equiv. BA	Equiv. AA	Cat. mol%[a]	Time (h)[b]
1	NS	1	1.1	5	–[c]
2	NS	1	1.1	10	–[c]
3	NS	1	2.2	10	–[c]
4	NS	1	5	10	4

[a]Catalyst load referred to AA equiv

[b]Time for 100% conversion by tlc monitoring

[c]Reaction did not finish in 24 h

this explains its less satisfactory performance. Within the commercial carbons, M is the most basic, and that fact most likely justifies its catalytic activity; on the other hand, the carbons X and N lack the sufficient basicity to act as well as M.
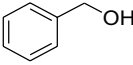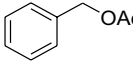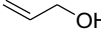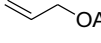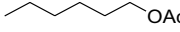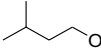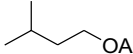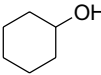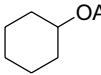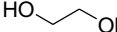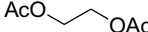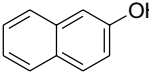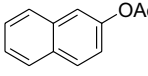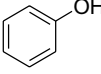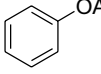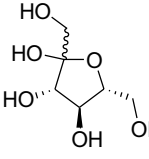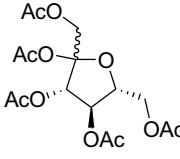
In view of these results, the activated carbon XS is selected for further testing. Our next goal was to reduce the amount of both acetic anhydride and catalyst. We found that when 1 equiv. of BA was reacted with 2.5 equiv. of AA in the presence of 4 mol% of catalyst XS, at 60 ºC, the reaction was completed in 75 min. This is slightly shorter than the reaction in which a 1:5 BA:AA ratio and 10 mol% of catalyst were used. Since the saving in both acetic anhydride and catalyst is substantial and the length of the reaction is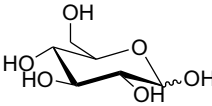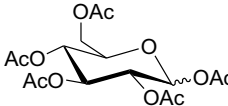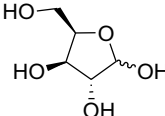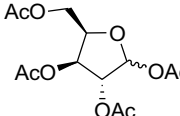 shorter, we decided that these would be the standard conditions for further testing. Therefore, the protocol entails the use of the best catalyst, XS, in 4 mol% load, at 60 ºC, for the acetylation of 1 equiv. of the hydroxylated substrate with 2.5 equiv. of acetic anhydride per hydroxyl group. Subsequently, with these reaction conditions, the study was extended to other substrates to establish the scope and limitations of this procedure. Results are shown in Table 7.

The primary, secondary, allylic, benzylic and glycol alcohols tested were acetylated in 3 h or less (Table 6, entries 1–6). It is worth mentioning that the reaction of benzyl alcohol in the same conditions but without catalyst had not completed after 24 h, thereby confirming the good catalytic performance of the system. β-Naphthol was acetylated in 8 h, whereas phenol took 24 h for complete acetylation. We finally decided to check whether this catalytic system could be applied to the per-*O*-acetylation of monosaccharides. For that purpose, a ketohexose (D-fructose), an aldohexose (D-glucose), and an aldopentose (D-xylose) where reacted (Table 6, entries 9–11, respectively). It was found that D-fructose was per-acetylated in 1 h; besides, D-xylose, and D-glucose took 7 h and 8 h to yield the pentaacetates, respectively.

To check catalyst XS reusability, the acetylation of benzyl alcohol and acetic anhydride was again chosen as a model reaction. The results are shown in Table 8.

After the complete transformation of the benzyl alcohol as determined by tlc for each reaction cycle, the catalyst was filtered, successively washed with acetone and water, and then it was dried overnight at 110 ºC. The catalyst was allowed to cool down in a desiccator and then used for the following experiment. When the catalyst load is 10 mol% high activity is kept throughout five runs with a little catalytic activity loss that results in slightly longer reaction times, growing from 1 to 3 h. Isolated yields are not optimized for these reusability experiments, hence the variability found. On the

Table 7 Acetylation with AA and XS of different substrates[a]

Entry	Substrate	Product	Time (h)[b]	Yield (%)[c]
1	benzyl alcohol (PhCH₂OH)	benzyl acetate (PhCH₂OAc)	1[d]	78
2	allyl alcohol	allyl acetate	3	81
3	hexanol	hexyl acetate	2	80
4	isoamyl alcohol	isoamyl acetate	3	74
5	cyclohexanol	cyclohexyl acetate	2.5	93
6	ethylene glycol (HO–CH₂CH₂–OH)	ethylene diacetate (AcO–CH₂CH₂–OAc)	3	99
7	2-naphthol	2-naphthyl acetate	8	99
8	phenol	phenyl acetate	24	97
9	fructose	per-O-acetyl fructose	1	85
10	glucose	per-O-acetyl glucose	8	87
11	ribose	per-O-acetyl ribose	7	96

[a]1 equiv. substrate, 2.5 equiv. acetic anhydride per hydroxyl group, 4 mol% XS, 60 ºC

[b]Time for 100% conversion by tlc monitoring

[c]Isolated yield (unoptimized)

[d]Reaction with no-catalyst is not completed in 24 h

other hand, when the catalyst load is 4 mol%, more appreciable activity loss is observed, extending the time required for the completion of the reaction from 1 to 7 h.

4 Conclusion

In conclusion, we have demonstrated that the three commercial carbons and the three acidic activated carbons obtained from them can catalyze the acetylation of benzyl alcohol with acetic anhydride. Remarkably, the most acidic carbon with the larger mesoporous volume is the most efficient catalyst; this activated carbon, labelled XS, has been obtained from the commercial xerogel carbon (X). This catalyst (XS) has been proven to be able to acetylate primary and secondary alcohols, phenol, and 2-naphthol efficiently. Two aldoses and one ketose have been successfully per-O-acetylated. The catalyst XS has been reused for five runs with only a small loss of activity. This protocol constitutes a clean, efficient method for the acetylation of hydroxyl groups with an environmentally friendly catalyst.

Table 8 Reusability of catalyst XS[a]

Entry	Run	Catalyst load (mol%)	Time (h)[b,c]
1	1	10	1
2	2	10	1.5
3	3	10	3
4	4	10	3
5	5	10	3
6	1	4	1
7	2	4	4
8	3	4	5.5
9	4	4	5.5
10	5	4	7

[a]Reaction conditions BA (10 mmol), AA (25 mmol), 60 ºC

[b]Time for 100% conversion by tlc monitoring

[c]Isolated yields range from 75 to 95%

Declarations

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