

Sustainable carbon-based materials as heterogeneous catalysts in solvent-free acetylation reactions †

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† Presented at the 22nd International Electronic Conference on Synthetic Organic Chemistry, Lugo (Spain), Nov. 15, 2018.

Received: date; Accepted: date; Published: date

Abstract: The catalytic activity of six different carbons have been tested in the solvent-free acetylation reaction of alcohols, phenols and monosaccharides with acetic anhydride. Three commercial carbons, a basic activated carbon M (Merck KGaA), a moderately basic carbon gel X (Xerolutions S.L.), and an activated carbon N (Norit Netherland B.V.), have been studied. From these commercial carbons, three acidic activated carbons have been obtained, M-S, X-S, and N-S, respectively, by treatment with sulphuric acid. All six carbons have been characterised by means of nitrogen adsorption capacity, porosimetry, elemental organic analysis, X-ray photoelectron spectroscopy (XPS), and point of zero charge (PZC) determination. The experiments carried out show good catalytic activity, the magnitude of which depends on the type of carbon used. The best catalyst is X-S, which combines high acidity with the largest mesoporous volume. Second in line is the commercial carbon M, which is the most basic. The protocol reported herein encompasses several of the characteristics related to the sustainability of chemical processes, such as, the innocuous nature and the affordable cost of the catalytic material, the absence of reaction solvent, and the ease of reaction work-up.

Keywords: Activated carbons, Heterogeneous Catalysis, Acetylation, Acylation.

1. Introduction

Catalysis is one of the fundamental pillars of Green Chemistry. The design and application of new catalysts and catalytic systems are simultaneously achieving the dual goals of environmental protection and economic benefit [1]. Thus, the development of new materials that present catalytic activity that allows target molecules to be obtained in less time and with greater energy efficiency, hence optimising the sustainability of chemical synthesis processes, is paramount. In addition, the environmentally benign nature of the catalysts is another desirable property therein [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 possess a high 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]. These materials are interesting because, as heterogeneous catalysts, reaction work-up is not complicated, since they can be separated from the reaction products by simple filtration. Their use may save energy and may diminish solvent use in many reactions. They can also be recovered in their active form and recycled in many cases.

Activated carbons can be used not only as catalyst support but also as catalysts themselves in fine-chemical synthesis [4, 5]. The use of activated carbons as catalysts, replacing the liquid-phase systems, is very promising; the examples of their use as catalysts in fine-chemical synthesis relate mainly to basic carbons [6-8]. In this context, activated carbons have attracted much attention and have catalysed successfully 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], and *N*-alkylation of imidazole [11-17], and acetylation of glycerol [18].

On the other hand, 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 synthesis, to mask this moiety, because of its feasibility and reversibility [19]. According to the principles of green chemistry, protection/deprotection steps should be avoided [2], yet, sometimes this is not possible. If protection steps are required, they would better proceed readily, quantitatively, and keeping waste formation and costs to a minimum. *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 [20]. 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 [21]. Pyridine derivatives, 4-dialkylaminopyridines greatly accelerate the reaction when used as cocatalyst with pyridine [22-24]. Other amine bases show good catalytic activity, as well [25]. Metal triflates show good catalytic activity [26-37]. Some metal salts, mainly perchlorates, have been used successfully, as well [38-40]. Different heterogeneous catalysts have been reported [41-45]. Salen cobalt complex is a reusable catalyst for this reaction [46]. Iodine proved to be a powerful catalytic acetylating agent [47]. A series of bicarbonates and carbonates were tested; good catalytic activity for the acetylation of primary alcohols and phenols was reported [48]. Modified zirconia catalyses the process too [49]. Tributylphosphine has shown to be an efficient catalyst for acylation reactions too [50]. Task-specific ionic liquids showed very good catalytic performance in the acetylation of alcohols and phenols [51].

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 that reason, there is still the need to explore novel methodologies that allow using environmentally friendly catalysts, while reducing energy costs and solvent use, and simplifying work-up.

In our search of catalytic systems that may prove most adequate in terms of sustainable chemical processes, we have obtained and characterise three activated carbons. These AC are obtained from three commercial carbons, which have been tested as well. We have assessed the catalytic activity of these AC in the acetylation reaction of alcohols, phenols and monosaccharides. We report, herein, a novel and efficient solvent-free, activated-carbon catalysed protocol for the acetylation of 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 from Cabot Corporation, formerly Norit Nederland B.V., labelled carbon N; mesoporous carbon Xerogel from Xerolutions S.L., labelled carbon X; and activated carbon Merck charcoal activated extra pure food grade from 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.

2.2. Synthesis and characterisation of the catalysts

The commercial carbon materials M, N and X were treated with a concentrated H₂SO₄ solution, at room temperature for 1.5 h (1 g / 20 cm³) [52]. The materials were then washed with deionised water in soxhlet until constant pH and dried in oven at 110 °C. The activated carbons obtained from M, N, and X are termed M-S, N-S, and X-S, respectively. All six carbon were tested for catalytic activity.

2.2.1. Adsorption isotherms and Porosimetry

The commercial carbons are mainly microporous, and the nitrogen adsorption capacity is higher for N, then M and finally X (Figure 1). Treatment with sulphuric acid to produce M-S, N-S, and X-S slightly diminishes their N₂ adsorption capacity; however, their porosity remains nearly the same, except for the N-S carbon, which is significantly smaller than that of N (Table 1) [53].

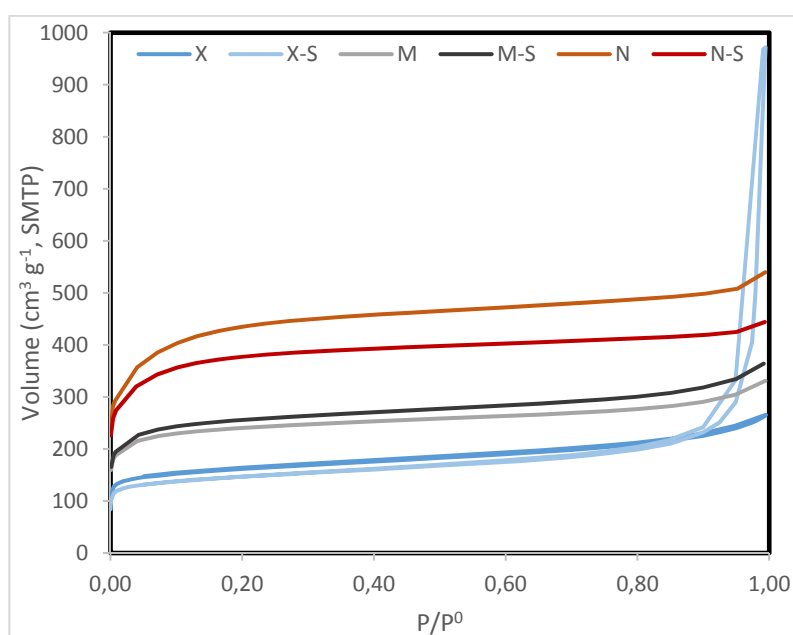


Figure 1. Isotherms of nitrogen adsorption at 77 K.

Table 1. Porosity of carbons.

Carbon	$V_{\text{micro}} \text{ (cm}^3 \cdot \text{g}^{-1})^{\text{a}}$	$V_{\text{meso}} \text{ (cm}^3 \cdot \text{g}^{-1})^{\text{b}}$	$V_{\text{macro}} \text{ (cm}^3 \cdot \text{g}^{-1})^{\text{c}}$
N	0.782	0.460	0.108
N-S	0.701	0.095	0.828
X	0.268	0.790	0.700
X-S	0.249	0.750	0.390
M	0.392	0.155	0.283
M-S	0.307	0.188	0.351

^a Dubinin-Ashtakov method.

^b Mercury porosimetry.

^c Mercury porosimetry.

The adsorption data agree with those of specific surface obtained by applying the model of Brunauer, Emmett and Teller (BET) to the data of the previous isotherms (Table 2).

Table 2. Specific surface of carbons.

Carbon	m ² ·g ⁻¹
N	1383
N-S	1114
X	484
X-S	448
M	731
M-S	684

2.2.2. Elemental analysis

The organic elemental analysis (C, H, N and S) was performed in a LECO CHNS 932 equipment. Values are shown in Table 3.

Table 3. Elemental analysis of carbons.

Carbon	C	H	N	O ^a	S
N	89.05	1.36	0.50	8.62	0.47
N-S	89.19	0.98	0.51	8.23	1.09
X	85.67	2.34	0	11.95	0.04
X-S	81.20	2.59	0	15.54	0.67
M	94.60	0.70	1.00	3.20	0.70
M-S	92.92	0.67	0.70	4.43	1.08

^a Oxygen content determined by difference.

The treatment of X and M with sulfuric acid lowers the carbon content, oxidises 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 increases the sulphur content.

2.2.3. X-ray photoelectron spectroscopy (XPS)

The experiments were performed on a K-Alpha equipment from Thermo Scientific, with monochromatic K α Al radiation, 12 KV voltage, and 6 mA current.

The composition, in general, is similar to that of the elemental analysis shown previously (Table 4). The relative increase in the amount of S in X-S indicates that this atom is mostly on the surface.

Table 4. XPS analysis of carbons.

Carbon	C 1s	O 1s	N 1s	S 2p
X	92.8	7.2	0	0
X-S	90.6	8.5	0	0.9
M	92.5	6.1	0.7	0.7
M-S	90.5	7.9	0.4	1.2
N	90.3	9.2	0.5	0.0
N-S	87.6	11.5	0.0	1.0

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

2.2.4. Point of zero charge (PZC)

To carry out this measurement, a 0.1 M solution of sodium nitrate is prepared and 7% in weight of the catalyst is added, keeping it stirred for 48 hours at 25 °C in a thermostatic bath. Subsequently, it is filtered and the pH of the filtered solution is measured with a pH-meter, this pH value is the point of zero charge.

Table 5. Point of zero charge (PZC) of the carbons.

Carbon	PZC
N	7.4
N-S	2.7
X	7.2
X-S	2.5
M	10.0
M-S	3.8

Catalysts X and N are less alkaline than M. This can be explained X and N have a higher oxygen content that leads to the formation of acidic oxygenated groups (alcohols and carboxylic acids). The treatment with sulphuric acid increases the acidity of these materials. This is not only due to oxidation but also to the formation of sulphonic groups. The effect is similar in the three carbons, but since M is a more alkaline carbon, the final acidity of M-S is lower. In the case of X-S carbon, the acidity is most likely originated mainly by the formation of sulphonic groups.

2.3. Acetylation procedure

According to the best results obtained, the procedure implies that 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 completion of the reaction, as determined by tlc. Once the reaction is completed, the carbon is filtered off and the filtrate is treated with distilled water, washed twice with NaHCO₃ (10%), then it is extracted twice with diethyl ether; the organic phase is dried with anhydrous MgSO₄, and evaporated at reduced pressure to yield the pure product. All products obtained are known and have been identified by their NMR spectra. In some cases, the acetylated product could be isolated by distillation.

In the case of the monosaccharides, the carbon is filtered off and the filtrate is treated with distilled water, washed twice with NaHCO₃ (10%), then it is extracted twice with dichloromethane; the organic phase is dried with anhydrous MgSO₄, and evaporated at reduced pressure to obtain the desired product.

3. Results and Discussion

To test the catalytic performance of the different activated carbons, we chose the acetylation reaction of benzyl alcohol (BA) with acetic anhydride (AA) in absence of solvent. Based on previous studies performed in our laboratory, the first activated carbon to be tested was N-S. We started by trying to adjust the reactant proportions and load of catalyst at room temperature (Table 6, entries 1-5). The results show no complete reaction at 24 h, even with a 10:1 AA:BA ratio and a 10 mol% load of catalyst. In order to improve the protocol we decided to heat the reaction while reducing the amount of AA (Table 6, entry 6).

Table 6. Acetylation of benzyl alcohol with acetic anhydride and catalyst.

Entry	Catalyst	Equiv. BA	Equiv. AA	Cat. mol% ^a	T (°C)	Time to completion ^b
1	N-S	1	1.1	5	r.t.	No (at 24h)
2	N-S	1	1.1	10	r.t.	No (at 24h)
3	N-S	1	2.2	10	r.t.	No (at 24h)
4	N-S	1	5	10	r.t.	No (at 24h)
5	N-S	1	10	10	r.t.	No (at 24h)
6	N-S	1	5	10	60	4 h
7	X-S	1	5	10	60	1 h
8	M-S	1	5	10	60	4 h
9	N	1	5	10	60	4 h
10	X	1	5	10	60	4 h
11	M	1	5	10	60	2 h

^a Catalyst load referred to AA equiv.

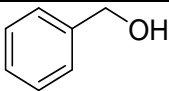
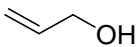
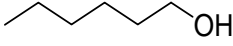
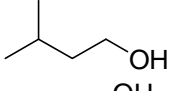
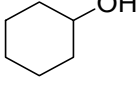
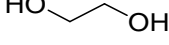
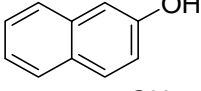
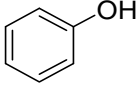
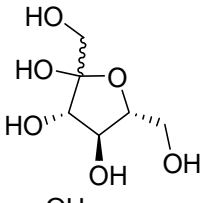
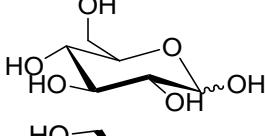
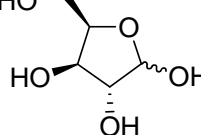
^b Time for 100% conversion by tlc monitoring.

Having established the reaction conditions as those of entry 6 in Table 6, our next step was to check the activity of the other two catalysts prepared and the three commercial carbons. All the modified AC are acidic, whereas the N is neutral activated carbon, the X is a mildly basic carbon gel, and the M is a basic activated carbon (Table 6, entries 6-11).

The acetylation reaction is suitable of either acidic or basic catalysis. The modified X-S is the best catalyst, and that has probably to do with its acidity. However, N-S is nearly as acidic as X-S, and yet, its catalytic performance is poorer. This may be explained by the fact that N-S has a larger microporous volume and a smaller mesoporous volume than X-S (see Table 1); hence, the larger mesoporous network of X-S would facilitate access of the reactants to the active sites. M-S is less acidic and this explains its less satisfactory performance. Within the commercial carbons, M is the most basic, and that 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 the results, the activated carbon X-S is selected for further testing. Our next goal was to try 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 X-S, at 60 °C, the reaction was completed in 75 min. This is only a bit longer than the reaction in which a 1:5 BA:AA ratio in the presence of 10 mol% of catalyst was used. Since the saving in both acetic anhydride and catalyst is substantial whereas the length of the reaction is only slightly longer, we decided that these would be the standard conditions for this protocol for further testing. Therefore, the protocol entails the use of the best catalyst, X-S, in 4 mol% load, at 60 °C, 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, we extended the study to other substrates to establish the scope of this procedure. The primary, secondary, allylic, benzylic and glycol alcohols tested were acetylated in 3h or less (Table 7, entries 1-6). It is worth mentioning that the reaction of benzyl alcohol in the same conditions but without catalyst had not completed after 24h, thereby confirming the good catalytic performance of the system. β -Naphthol was acetylated in 8 hours, 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) were reacted (Table 3, entries 9-11, respectively). It was found that D-fructose was peracetylated in 1 h; besides, D-fructose and D-glucose took 7 h and 8 h to yield the pentaacetates, respectively.

Table 7. Acetylation with AA and X-S of different substrates*

Entry	Substrate	Time (h) ^a	Yield (%) ^{b, c}
1		1.25 ^d	67
2		3	81
3		2	59
4		3	74
5		2.5	93
6		3	99
7		8	99
8		24	97
9		1	85
10		8	87
11		7	96

* 1 equiv. substrate, 2.5 equiv. acetic anhydride per hydroxyl group, 4 mol% X-S, 60 °C.

^a Time for 100% conversion by tlc monitoring

^b Isolated yield (not optimised)

^c The reaction with no-catalyst is not completed in 24h.

4. Conclusions

In conclusion, we have demonstrated that the three commercial carbons and the three acidic activated carbons obtained from them can catalyse 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 X-S, has been obtained from the commercial xerogel carbon (X). This catalyst (X-S) 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. This protocol constitutes a clean, efficient method for the acetylation of hydroxyl groups with an environmentally friendly catalyst.

Author Contributions: conceptualization, I.M.L.-C. and C.J.D.-V.; methodology, I.M.L.-C., S.I. and C.J.D.-V.; investigation, I.M.L.-C., S.I., G.S., C.J.D.-V.; writing—original draft preparation, I.M.L.-C., S.I. and C.J.D.-V.; writing—review and editing, I.M.L.C, S.I., G.S. and C.J.D.-V.; supervision, I.M.L.-C.; project administration, I.M.L.-C.; funding acquisition, I.M.L.-C., G.S., C.J.D.-V.

Funding: Financial support for this research and funding for a research fellowship (S.I.) from the Regional Government “Junta de Extremadura” (Spain) and European Regional Development Fund (ERDF) are gratefully acknowledged (Project IB16167).

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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