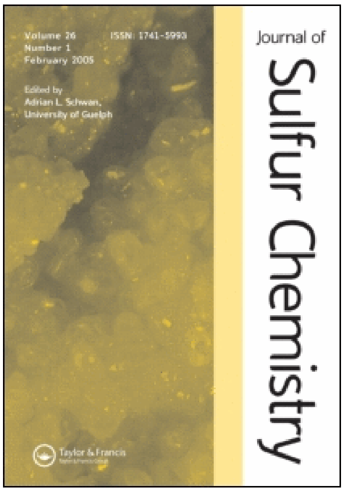

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Sulfonated charcoal as a mild and efficient catalyst for esterification and trans-esterification reactions

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RESEARCH ARTICLE

Sulfonated charcoal as a mild and efficient catalyst for esterification and trans-esterification reactions

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Sulfonated charcoal was found to be an efficient heterogeneous catalyst for the acetylation of alcohols in acetic acid. Esterification of different carboxylic acids with different alcohols was also achieved with this catalyst. Acetylation and formylation of alcohols can also be catalysed efficiently in ethyl acetate and ethyl formate in high yields.

Keywords: Esterification; Trans-esterification; Sulfonated charcoal; Acetylation; Formylation

1. Introduction

The use of supported catalysts provides a practical and attractive method with the potential application in the chemical industries for the clean and efficient preparation of chemicals. Due to the change in the dimensionality of reaction spaces by the adsorption of active reactants on the surface of inorganic solids, great increase in the reactivity and selectivity are reported [1–3].

Esterification is an important reaction in organic synthesis [4, 5]. Many useful methods for esterification have been reported in the literature [6, 7] Some of the recently developed methods involve the use of various metal salts like $Cu(NO_3)_2 \cdot 6H_2O$ [8], $ZrCl_4$ [9], $HfCl_4 \cdot (THF)_2$, [10, 11] $Al_2O_3/MeSO_3H$ (AMA) [12], metal triflates such as $Sc(OTf)_3$ [13], $Cu(OTf)_2$ [14], $Ce(OTf)_4$ [15], solid acid catalysts such as HY-zeolite [16], heteropoly acids [17, 18], silica sulfuric acid [19] and using ionic liquids as green solvents for this purpose [20–22].

Although several methods have been exploited and developed [4–30], the search for replacing current chemical processes with new environmentally benign and economically alternatives is an interesting subject. Literature survey indicates that application of sulfonated charcoal is very rare [31–34]. In continuation of our study on the esterification reactions [8, 14, 15, 17], here we extend the application of sulfonated charcoal as a cheap,

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and mild heterogeneous catalyst to acetylation, and formylation of alcohols and also trans-esterification reactions. Sulfonated charcoal is readily separated from the reaction mixture by a simple filtration, and could be reused without appreciable loss of its catalytic activity. Pure products often simply obtained by evaporation of the solvent without any further purification.

2. Results and discussion

Sulfonated charcoal was prepared according to the literature [33], by heating 50 g of charcoal with 150 g of sulfuric acid at 240 °C for 12 h. The obtained solid is very stable and can be stored without any change at room temperature for months. The acidity of the dried product has been reported to be due to both sulfonic acid and carboxylic acid groups (0.28 milliequivalent and 0.44 milliequivalent, respectively, per gram of the catalyst).

First, we optimized the reaction conditions for acetylation of alcohols in acetic acid. It was observed that structurally different alcohols can be acetylated in refluxing acetic acid in the presence of this catalyst to produce the desired esters in excellent yields. Acetylation of benzylic alcohols carrying electron-withdrawing groups is rare in the literature. However, this reaction was performed with the catalytic aid of sulfonated charcoal in acetic acid with high yield (table 1, entries 2, 3).

The reaction of secondary and tertiary alcohols took a longer time than primary ones, but the yield of the obtained products are still very high. The low isolated yields for the products of entries 7 and 10 of table 1 are due to their low boiling point which are lost during the work up.

The obtained results for esterification of different alcohols in acetic acid are summarized in table 1.

Performing the esterification of alcohols in ethyl acetate instead of using acetic acid has the advantage of having an easily removable solvent that makes the work up of the reaction much simpler. We, therefore, studied the trans-esterification reactions using ethyl acetate to convert alcohols into their corresponding acetates. It was observed that sulfonated charcoal can catalyse the acetylation reaction of primary and secondary aliphatic and benzylic alcohols in refluxing ethyl acetate to give their corresponding esters in high yields. This method is

Table 1. Acetylation of alcohols by sulfonated charcoal in acetic acid under reflux condition.[a]

$$\text{ROH} \xrightarrow[\text{AcOH, Reflux}]{\text{Sulfonated charcoal (0.3 g)}} \text{ROAc}$$

Entry	ROH	Time (h)	Yield (%)[b]	Reference[c]
1	Benzyl alcohol	1.5	92	15
2	4-Chlorobenzyl alcohol	7.5	93	37
3	4-Nitrorobenzyl alcohol	16	89	38
4	1-Adamantanol	16	95	39, 40
5	1-Octanol	4	81	8
6	2-Octanol	17	85	8
7	Cyclohexanol	3.5	60	8
8	3-Phenyl -1-propanol	5	94	8
9	2-Phenyl ethanol	6	97	8
10	3-Methyl-3-butene-1-ol	5	65	25
11	Benzhydrol	11	91	25

[a] Typical procedure is given in the experimental section.

[b] The conversion yield by GC analysis is quantitative.

[c] All the products are known compounds and were identified by their spectral data.

Table 2. Acetylation of alcohols in the presence of sulfonated charcoal in ethyl acetate under reflux condition.[a]

$$\text{ROH} \xrightarrow[\text{EtOAc, Reflux}]{\text{Sulfonated charcoal (1.0 g)}} \text{ROAc}$$

Entry	ROH	Time(h)	Conversion	Isolated yield
1	Benzyl alcohol	6	100	92
2	4-Chlorobenzyl alcohol	21	98	85
3	4-Nitrorobenzyl alcohol	35	90	78
4	1-Octanol	12	100	87
5	2-Octanol	40	95	84
6	2-Phenyl ethanol	16	100	92
7	3-Phenyl -1-propanol	14	100	93
8	adamatan-1-ol	30	0	–

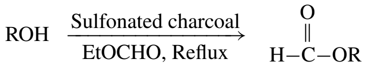
[a]Typical procedure is given in the experimental section.

even applicable for the conversion of benzylic alcohols carrying strong electron-withdrawing substituents such as $-NO_2$ group. Under these conditions, adamatan-1-ol did not react with ethyl acetate and recovered unchanged. The obtained results are shown in table 2.

Due to the possibility of the selective removal of formyl group in the presence of acetyl group, preparation of formate esters is considered as an important reaction in organic synthesis and various formylating agents have been reported over the years [23–30]. Some of these methods include formylation with formic acid in the presence of a dehydrating agent like DCC [24], trans-esterification with methyl or ethyl formate catalysed by $Cu(NO_3)_2 \cdot 3H_2O$ [8], $Ce(OTf)_4$ [15], heteropolyacids [17], and formyl transfer from enol formats [26], *N*-formyl formamide [25], and Cl_2SO-DMF/KI [27].

Most of the reported methods use rather uncommon and in some cases expensive, moisture sensitive, thermally unstable or high excess of the reagents [8, 15, 25–27]. Performing the reaction at elevated temperature, long reaction times, acidic reaction conditions or workup and moderate yields are other limitations of some of these methods. We, therefore, extended our studies with this catalyst for formylation of alcohols in ethyl formate. The trans-esterification was performed efficiently with different alcohols in refluxing ethyl formate (table 3). Isolated yields of the reactions are high except for formylation of cyclohexanol, which is presumably due to the low boiling point of the corresponding ester formate.

Table 3. Formylation of alcohols by sulfonated charcoal in ethyl formate under reflux condition.[a]

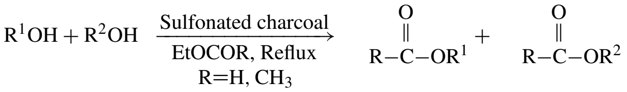


$$\text{ROH} \xrightarrow[\text{EtOCHO, Reflux}]{\text{Sulfonated charcoal}} \text{H}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{OR}$$

Entry	Alcohol	Catalyst (g)	Time (h)	Isolated yield (%)[b]	Reference to the
1	Benzyl alcohol	1.4	3	94	42
2	4-Chlorobenzyl alcohol	1.4	8	89	36
3	4-Nitrorobenzyl alcohol	1.4	30	85	35
4	3-Methyl-3-butene-1-ol	1.4	2.5	77	23
5	1-Octanol	1.4	1	92	42
6	2-Octanol	1.4	37	67	41
7	Cyclohexanol	1.4	4	65	42
8	2-Phenyl ethanol	1.4	6	83	8

[a]Typical procedure is given in the experimental section.
[b]The spectral data are given in the experimental section.

Table 4. Competitive transesterification reaction of alcohols in the presence of sulfonated charcoal.[a]



$$R^1OH + R^2OH \xrightarrow[\text{EtOCOR, Reflux} \atop \text{R=H, CH}_3]{\text{Sulfonated charcoal}} R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR^1 + R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR^2$$

Entry	Mixture of alcohols	Solvent	Time (h)/ catalyst (g)	Product and yield (%)[b]
1	1-Octanol 2-Octanol	Ethyl acetate	7/1 g	1-Octyl acetate (85 %) 2-Octyl acetate (15 %)
2	1-Octanol 2-Octanol	Ethyl formate	3/1.4 g	1-Octyl formate (100 %) 2-Octyl formate (0 %)

[a] Equimolar amounts of 1-octanol and 2-octanol were treated with ethyl acetate or ethyl formate (4 mL) under reflux condition in the presence of sulfonated charcoal as catalyst.

[b] Conversion yield by GC analysis using internal standard.

On the basis of different reaction times for esterification of primary and secondary alcohols (tables 2 and 3), we studied the selective acetylation and formylation reactions between primary and secondary alcohols. Two competitive reactions were accomplished between 1-octanol and 2-octanol with ethyl acetate and ethyl formate under the reaction conditions for acetylation and formylation reactions. The results of this study, which show high selectivity for acetylation and excellent selectivity for formylation of 1-octanol, are tabulated in table 4.

To explore the general applicability of charcoal sulfonic acid for esterification reactions, several carboxylic acids were reacted with different alcohols both in solvent or in the absence of solvent to furnish their corresponding esters. For the low boiling point alcohols or acids such as MeOH, EtOH, *n*-PrOH, and propionic acid, the reactions were performed under solvolytic conditions (table 5, entries 1–7). The reactions of the high boiling point alcohols were performed in CCl_4 (table 5, entries 8, 9) or under solvent-free conditions (table 5, entries 10–14). Reaction of benzoic acid with methanol under solvolytic condition was found to be

Table 5. Esterification of carboxylic acids in the presence of sulfonated charcoal.

Entry	Alcohol	Acid	Catalyst (g)	Time (h)/ condition	Yield (%)[a]	Reference to the products
1	1-Octanol[b]	Propionic acid	0.2	1 h/reflux	82	15
2	MeOH[c]	Stearic acid	0.56	3.5 h/reflux	94	15
3	EtOH[c]	Stearic acid	0.56	18 h/reflux	87	15
4	1-PrOH[c]	Stearic acid	0.56	50 h/reflux	90	15
5	MeOH[c]	Benzoic acid	1.12	42 h/reflux	91	15
6	1-PrOH[c]	Benzoic acid	0.56	90 h/reflux	86	15
7	MeOH[c]	Hexanoic acid	1	0.5 h/reflux	85	–[g]
8	Benzyl alcohol[d]	Stearic acid	0.28	26 h/reflux	40	15
9	1-Octanol[d]	$ClCH_2CO_2H$	0.28	8 h/reflux	93	15
10	Benzyl alcohol[e]	Stearic acid	0.14	11 h/70 °C	78	15
11	Benzyl alcohol[f]	Stearic acid	0.14	3 h/70 °C	75	15
12	1-Octanol[e]	Stearic acid	0.14	40 h/70 °C	30	15
13	Benzyl alcohol[e]	$ClCH_2CO_2H$	0.14	1.5 h/70 °C	95	15
14	1-Octanol[e]	$ClCH_2CO_2H$	0.14	2.5 h/70 °C	92	15

[a] Yield refers to the isolated product.

[b] The reaction of 1-octanol and propionic acid was carried out in refluxing propionic acid.

[c] Alcohol was used as solvent of the reaction.

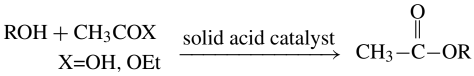
[d] The reaction was performed with equimolar amount of alcohol and carboxylic acid in CCl_4.

[e] Equimolar amount of alcohol and carboxylic acid were reacted together under solvent free condition.

[f] The reaction was performed with 2.0 mmol of alcohol and 1.0 mmol of carboxylic acid under solvent free condition.

[g] Spectral data are given in the experimental section.

Table 6. Acetylation of alcohols with different methods in the presence of solid catalysts.



$$\underset{X=OH,\ OEt}{ROH + CH_3COX} \xrightarrow{\text{solid acid catalyst}} CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OR$$

Entry	Alcohol	Acetylating reagent	Catalyst	Reaction conditions	Yield (%)[a]	Reference to the literature
1	$PhCH_2OH$ (10 mmol)	AcOH (1 mmol)	ZrO_2 (1 g)	toluene/reflux/1 h	100	[45]
2	$PhCH_2OH$ (2 mmol)	EtOAc (60 mmol)	ZrO_2 (2 g)	reflux/5 h	32[b]	[45]
3	$PhCH_2OH$ (10 mmol)	EtOAc (solvent)	ZrO_2 (2 g)	200 °C	98	[45]
5	$PhCH_2OH$	AcOH (50 mmol)	Yttria-Zirconia based Lewis acid catalyst 20 % w/w with respect to the substrate	110 °C/4 h	94	[46]
6	n-C_4H_9OH	AcOH (H_2O)	Polymer-supported sulfonimide	Solvent-free/80 °C/48 h	92.6	[48]
6	n-C_4H_9OH	AcOH (H_2O)	Nafion NR 50	Solvent-free/80 °C/24 h	86.9	[55]
6	$PhCH_2OH$ (1 mmol)	EtOAc (45 mL)	Al_2O_3 (10 g)	80 °C/12 h	80	[47]
7	$PhCH_2OH$ (1 mmol)	AcOH (2 mL)	Sulfonated charcoal (0.3 g)	reflux/1.5 h	92	–
8	$PhCH_2OH$ (1 mmol)	EtOAc (4 mL)	Sulfonated charcoal (1 g)	reflux/6 h	92	–

[a] Yield refers to isolated products.
[b] Conversion yield.

slow, whereas the reaction of aliphatic acids is faster. As an example, the reaction of n-hexanoic acid in methanol completed after 25 min; but benzoic acid reacted with methanol after 42 h to produce their corresponding esters in 91 % and 85 % yields, respectively.

Although, the reaction of aliphatic carboxylic acids with alcohols in CCl_4 was not successful, in most cases, the reaction proceeded in the absence of solvent. We carried out solvent-free esterification of alcohols with different carboxylic acids. As it is shown in table 5, the time of the reactions was greatly reduced and we also observed that the reactions were completed using smaller amounts of the catalyst.

In order to show the reusability of charcoal sulfonic acid for esterification reactions, sulfonated charcoal was regenerated simply by filtering the catalyst, washing it with acetone, and drying. The average yield of benzyl acetate from acetylation of benzyl alcohol with acetic acid with the recycled catalyst for four runs was found to be 89%.

Comparison of the present method with some of the reported methods using other solid catalysts (table 6) shows the applicability of sulfonated charcoal as a suitable catalyst for esterification and trans-esterification reactions.

3. Experimental

The products were purified by column chromatography and the purity determinations of the products were accomplished by GLC on a Shimadzu model GC-10A instrument or by TLC on silica gel PolyGram SIL G/UV 254 plates. FT-IR spectra were recorded on a Shimadzu DR-8001 spectrometer. NMR spectra were recorded on a Bruker Avance DPX 250 MHz instrument.

3.1 *Preparation of sulfonated charcoal*

A mixture of active charcoal (50 g) and sulfuric acid (150 g) was heated at 240 °C for 12 h in a furnace equipped to remove the fumes under slight vacuum [33]. Then the mixture was filtered off and washed with water until washings gave a negative barium chloride test. The filtrate was dried at 100 °C for 24 h.

3.2 *Acetylation of benzyl alcohol with acetic acid in the presence of sulfonated charcoal catalyst*

To a solution of benzyl alcohol (0.108 g, 1 mmol) in acetic acid (2 mL), sulfonated charcoal (0.3 g) was added. The reaction mixture was stirred for 3 h under reflux condition. The progress of the reaction was monitored by GC and TLC. The reaction mixture was filtered off and the sulfonated charcoal was washed with CH_2Cl_2 (20 mL). The obtained solution was washed with 10% $NaHCO_3$ (2 × 10 mL) and then with water (2 × 10 mL). The organic layer was separated and the aqueous layer was washed again with CH_2Cl_2 (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4. Evaporation of the solvent followed by chromatography on a short pad of silica gel eluted with n-hexane gave the desired benzyl acetate in 138 mg, 92% yield (b.p. 213–214°C/760 mmHg, Lit. [43] 213°C/760 mmHg).

3.3 *Acetylation of benzyl alcohol in ethyl acetate using sulfonated charcoal catalyst*

A solution of benzyl alcohol (0.108 g, 1 mmol) in ethyl acetate (2 mL) was treated with sulfonated charcoal (1 g). The reaction mixture was stirred under reflux condition for 3 h. The progress of the reaction was monitored by GC or TLC. The reaction mixture was then filtered off and the filter cake was washed with 20 mL of CH_2Cl_2. Combination of the organic solutions and evaporation of the solvent followed by chromatography on a short column of silica-gel using n-hexane as eluent gave benzyl acetate as a colorless liquid (138 mg, 92% yield).

3.4 *Formylation of benzyl alcohol catalyzed by sulfonated charcoal in ethyl formate*

To a solution of benzyl alcohol (0.108 g, 1 mmol) in ethyl formate (2 mL) sulfonated charcoal (1.4 g) was added. The reaction mixture was stirred for 3 h under reflux condition. The progress of the reaction was monitored by GC and TLC. Then, the reaction mixture was filtered off and sulfonated charcoal was washed with 20 mL of CH_2Cl_2. Combination of organic solutions and evaporation of the solvent followed by chromatography on a short column of silica-gel using n-hexane as eluent produced benzyl formate as a colorless liquid in 142 mg, 94% yield (b.p. 204 °C/760 mmHg, Lit. [42] 85–100 °C/0.01 mmHg).

3.5 *Esterification of stearic acid in methanol using sulfonated charcoal catalyst*

In a round bottom flask containing stearic acid (1 mmol, 284 mg) and sulfonated charcoal (0.56 g), methanol (2 mL) was added and the reaction mixture was stirred under reflux condition for 3.5 h. The progress of the reaction was monitored by TLC. The reaction mixture was then filtered off and the filter cake was washed with 20 mL of CH_2Cl_2. Evaporation of the organic solvent followed by chromatography on a short column of silica-gel using n-hexane as eluent gave methyl stearate as a white solid in 280 mg, 94% yield (m.p. 38 °C, lit. [44] 37.5 °C).

Selected spectral data; *3-Methy-3-butenyl acetate:* ^{1}H-NMR ($CDCl_3$/TMS), δ (ppm): 4.73 (2H, d), 4.11 (2H, t), 2.26 (2H, t), 1.99 (3H, s), 1.71 (3H, s). ^{13}C-NMR ($CDCl_3$/62.9 MHz),

δ: 171.0, 141.6, 112.1, 63.0, 36.6, 22.4, 20.9; *Benzhydryl acetate:* ^{1}H-NMR ($CDCl_3$/TMS), δ (ppm): 7.25 (10H, m), 6.84 (1H, s), 2.1 (3H, s). ^{13}C-NMR ($CDCl_3$/62.9 MHz), δ : 170.0, 140.4, 129.3, 128.3, 127.7, 76.1, 21.3; *3-Methy-3-butenyl formate:* ^{1}H-NMR ($CDCl_3$/TMS), δ (ppm): 8.1 (1H, s), 4.9 (2H, d), 4.1 (2H, t), 2.3 (2H, t), 1.9 (3H, s). ^{13}C-NMR ($CDCl_3$/62.9 MHz), δ: 160.9, 141.2, 112.5, 63.2, 37.2, 22.3; *Methyl hexanoate:* The product was characterized with its physical and spectral data with those reported in SDBS site. http://www.aist.go.jp/RIODB/SDBS/cgi-bin/direct_frame_top.cgi

Acknowledgements

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