Highly efficient solvent-free acetylation of alcohols with acetic anhydride catalyzed by recyclable sulfonic acid catalyst (SBA-15–Ph–Pr–SO_3H) — An environmentally benign method

Daryoush Zareyee, Abdollah Razaghi Ghadikolaee, and Mohammad A. Khalilzadeh

Abstract: The catalytic activity of highly thermal stable, hydrophobic, and complete heterogeneous propylsulfonic acid functionalized nanostructured SBA-15 for excellent acetylation of alcohols and phenols with acetic anhydride at ambient temperature in solvent-free conditions was examined under environmentally benign reaction conditions. The salient features of this protocol are the absence of solvent, a green experimental procedure, and simple reusability of the catalyst (at least five reaction cycles).

Key words: solid sulfonic acid, SBA-15, heterogeneous catalyst, acetylation, solvent-free.

Résumé : Le SBA-15 est un produit nanostructuré à base d'acide propylsulfonique fonctionnalisé qui est très stable vis-à-vis de la chaleur, hydrophobe et totalement hétérogène. On a étudié son activité catalytique comme excellent catalyseur pour la réaction d'acétylation d'alcools et de phénols à l'aide d'anhydride acétique, à la température ambiante, dans des conditions expérimentales sans solvant et écologiques. Ce protocole est principalement caractérisé par l'absence de solvant, par son caractère écologique et la facilité de réutilisation du catalyseur (dans au moins cinq cycles réactionnels).

Mots-clés : acide sulfonique solide, SBA-15, catalyseur hétérogène, acétylation, sans solvant.

[Traduit par la Rédaction]

Introduction

The use of protecting groups is highly significant in organic synthesis and is often the key to the success of many synthetic enterprises. Among the various protecting groups used for the hydroxyl function, acetyl is the most common group in view of its facile introduction, being stable to the acidic reaction conditions, and also being easily removable by mild alkaline hydrolysis.[1] The acetylation of alcohols and phenols provides an efficient route for protecting –OH groups during oxidation, peptide coupling, and glycosidation reactions.[2] The most common and cheap acetylating regent is activated carboxylic acid derivative acetic anhydride[3] in the presence of amine bases like pyridine,[4] 4-diaminopyridine (DMAP),[5] triethylamine,[3] and 4-pyrrolidinopyridine.[4] Protic acids are also known to catalyze the acetylation process.[6] Additionally, various Lewis acids including $Sc(OTf)_3$,[7] $In(OTf)_3$,[8] $Ce(OTf)_3$,[9] $Gd(OTf)_3$,[10] $Al(OTf)_3$,[11] $Fe(ClO_4)_3$,[12] $Mn(OAc)_2$,[13] I_2,[14] $La(NO_3)_3 6H_2O$,[15] $Sn^{IV}(TPP)(BF_4)_2$,[16] $TiCl_3(OTf)$,[17] $H_{14}[NaP_5W_{29}MoO_{110}]$,[18] and borated zirconia[19] have also been investigated to meet the demand for more efficient methods. However, some of the base catalysts are toxic and possess offensive odours,[3–5] and the other methods have some serious drawbacks such as harsh reaction conditions, long reaction times, poor yields of the desired products, and tedious workup procedures. Another disadvantage is that most of these catalysts need organic solvents as media for acylation, thereby generating large amounts of corrosive and toxic waste. On the other hand, there are some toxicity and difficulties in separating conventional homogeneous catalysts from products.

One of the most promising solutions to these problems seems to be immobilization of catalysts or using ecofriendly solvent-free reaction conditions. Heterogeneous catalysts give generally higher selectivity and typically require easier workup procedures. Along this line, alumina-supported MoO_3,[20] $NaHSO_4{\cdot}SiO_2$,[21] polymer-supported $Gd(OTf)_3$,[22] cobalt(II) salen complex,[23] and sulfuric acid ([3-(3-silicapropyl)sulfanyl]propyl)ester[24] were also reported as heterogeneous catalysts for acylation of alcohols. Despite a number of improvements, some of these procedures still suffer from long reaction times,[22,23] high temperatures,[23] the use of toxic organic solvents,[21] and nonrecoverable catalysts,[21] which result in the generation of a large amount of toxic waste. Thus, introduction of inexpensive and green catalysts for this purpose is still in much demand.

Received 12 October 2011. Accepted 26 January 2012. Published at www.nrcresearchpress.com/cjc on 26 April 2012.

D. Zareyee, A.R. Ghadikolaee, and M.A. Khalilzadeh. Department of Chemistry, Qaemshahr Branch, Islamic Azad University, Qaemshahr, Iran.

Corresponding author: Daryoush Zareyee (e-mail: zareyee@gmail.com; zareyee.d@qaemshahriau.ac.ir).

Experimental section

General acetylation procedure

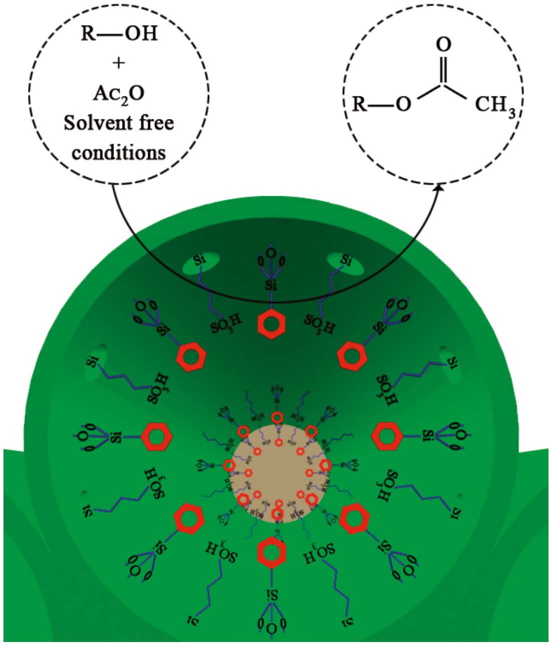
In a round-bottom flask (10 mL) equipped with a magnetic stirrer, SBA-15–Ph–Pr–SO_3H (12 mg, 2 mol %) was added to the substrate (1 mmol) and acetic anhydride (1.2 mmol), and the mixture was stirred at room temperature for the period of time indicated in Table 1. After completion of the reaction (TLC), the reaction mixture was filtered and the catalyst was rinsed with ethyl acetate and then was recovered. After the organic layer was washed with saturated $NaHCO_3$ and water, the aqueous layer was extracted with ethyl acetate and dried over anhydrous Na_2SO_4, filtered, and evaporated. The combined organic layer was subjected to column chromatography on silica gel to afford pure acetate. Characterization of some products was achieved by ^1H and ^{13}C NMR.

Results and discussion

Recently, we have prepared and used heterogeneous and hydrophobic sulfonic acid SBA-15–Ph–Pr–SO_3H as an efficient recoverable catalyst in some organic reactions.[25,26] Therefore, as a part of our continuing interest in the development and utility of this catalyst, having both acidic sites and phenyl groups inside the mesochannel of SBA-15, herein, we wish to report the applicability of SBA-15–Ph–Pr–SO_3H as an efficient, environmentally benign, and reusable catalyst in the promotion of the acetylation of alcohols and phenols with acetic anhydride. All reactions were performed in solvent-free reactions at room temperature and under complete heterogeneous reaction conditions in excellent yields (Scheme 1 and Table 1; also see the Supplementary data).

Initially, the effect of catalyst was investigated in the model reaction of benzyl alcohol with acetic anhydride, and several sets of reaction conditions were examined. Benzyl alcohol (1 mmol) was treated with acetic anhydride (1.2 mmol) in the absence of catalyst. As can be seen in Table 1, the corresponding product was obtained in 30% GC yield after 10 min (Table 1, entry 1). To evaluate the quantity of SBA-15–Ph–Pr–SO_3H, 1, 2, and 3 mol % of catalyst was used in the acetylation of benzyl alcohol for 10 min under solvent-free reaction conditions. It was observed that this reaction goes well in the presence of 2 mol % of catalyst (Table 1, entry 1). Use of a higher amount of catalyst (3 mol %) neither improves the yield nor the reaction time. Further studies have showed that all procedures work well with a 1:1.2 molar ratio of substrate to Ac_2O in the presence of 2 mol % of SBA-15–Ph–Pr–SO_3H without solvent at room temperature. On the basis of these results, we investigated the scope of the substrate alcohols and phenols with respect to the SBA-15–Ph–Pr–SO_3H catalyst-mediated acetylation, and the results obtained are summarized in Table 1.

Scheme 1. Schematic representation for solvent-free acylation of alcohols with Ac_2O using SBA-15–Ph–Pr–SO_3H.

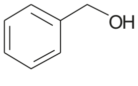
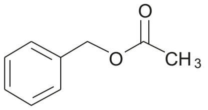
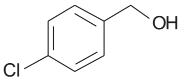
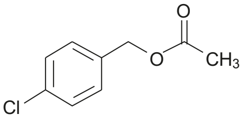
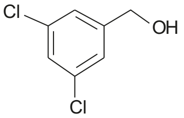
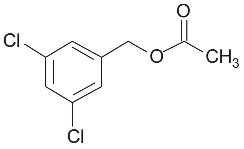
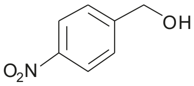
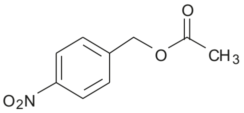
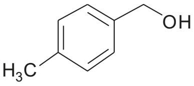
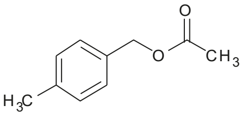
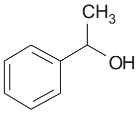
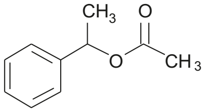
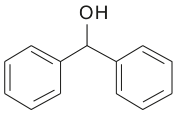
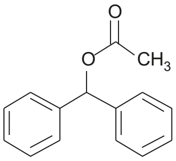
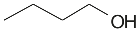
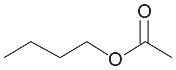
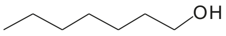
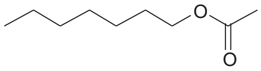
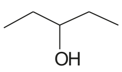
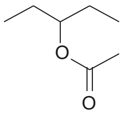
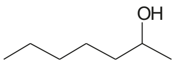
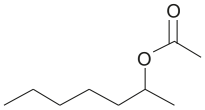
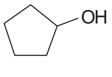
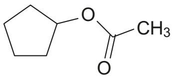
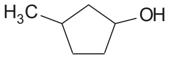
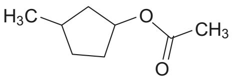
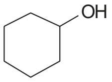
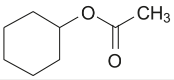


The general efficiency of this reaction is evident from the fact that a variety of hydroxy compounds, including primary (aromatic and aliphatic), secondary (acyclic, cyclic, and benzylic), tertiary alcohols, and phenols, acetylated with acetic anhydride in the presence of 0.02 mmol of catalyst at room temperature were obtained in excellent yields during a short reaction time (Table 1). Primary benzylic alcohols with electron-releasing and electron-withdrawing groups were acylated, and the corresponding acetates were obtained in excellent yields (Table 1, entries 1–5). Secondary aromatic alcohols were also transformed to the respective acetates (Table 1, entries 6 and 7). Meanwhile, acetylation of primary and secondary aliphatic alcohols was performed in excellent yields in short reaction times (Table 1, entries 8–16). Phenol (Table 1, entry 17) and its derivatives (Table 1, entries 18–23) were also subjected to acetylation satisfactorily. It was also found that SBA-15–Ph–Pr–SO_3H effectively catalyzed the acetylation of diols and triols (Table 1, entries 24–26). Interestingly, adamantanol was also converted to the corresponding acetate as a model for acetylation of the hindered tertiary alcohols (Table 1, entry 27). The assigned structures were established from their spectral properties (^1H and ^{13}C NMR) and by comparison with available authentic data.

To clarify the merit of the catalyst, we compared the results of acetylation reaction of alcohols with some heterogeneous catalysts.[21–23] It can be concluded that the higher conversion of starting materials, shorter reaction times, and solvent-free reaction conditions for catalyst SBA-15–Ph–Pr–SO_3H might likely be attributed to the larger pore size of ordered SBA-15 and the beneficial influence of phenyl groups in close proximity to the sulfonic acid groups. Based on these observations, it is clear that the pore size and hydrophobic character of the catalyst are crucial parameters in the effectiveness of sulfonic acid based catalysts for the catalysis of the acetylation reaction, especially in solvent-free reaction conditions.

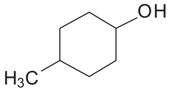
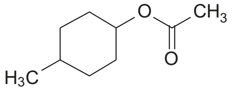
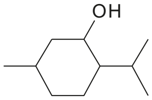
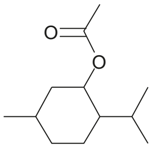
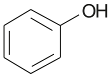
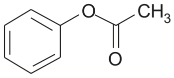
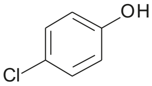
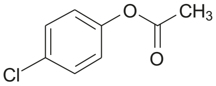
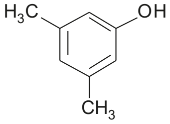
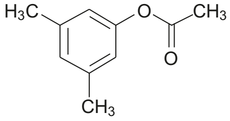
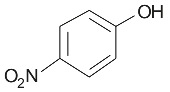
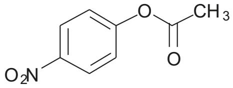
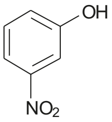
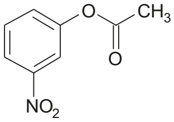
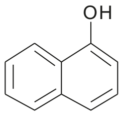
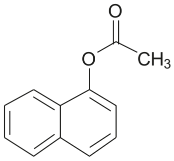
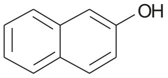
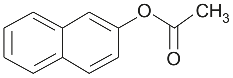
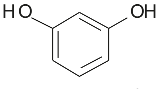
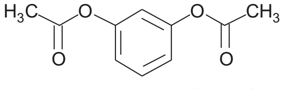
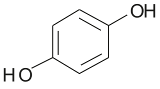
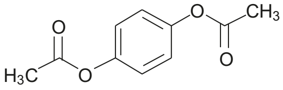
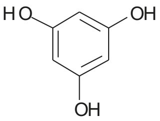
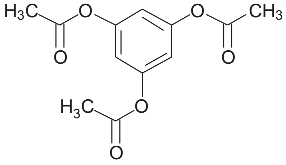
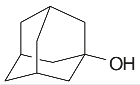
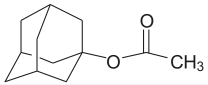
Reuse of the catalyst is an important aspect of any industrial process. Compared with traditional methods using volatile toxic solvents and nonrecoverable catalysts, which are energy consuming and environmentally malign, the ease of recycling is an attractive property of catalyst SBA-15–Ph–Pr–SO_3H for environmental protection and economic reasons. The catalyst could be stored and handled under open air conditions. To test the recyclability of the catalyst, the reaction was conducted with benzyl alcohol in the presence of catalyst

Table 1. Solvent-free acetylation of alcohols catalyzed by SBA-15–Ph–Pr–SO_3H at room temperature.

Entry	Substrate	Time (min)	Yield (%)[a,b]	Product
1		10	96 (30)[c]	
2		20	100	
3		25	95	
4		35	92	
5		10	98	
6		10	100	
7		30	91	
8		3	99	
9		3	99	
10		10	100	
11		5	100	
12		20	95	
13		20	97	
14		30	100	

for 10 min, which gave a conversion of 96%. The catalyst was quantitatively recovered by simple washing and filtration methods and proved to be reusable up to five times without any appreciable loss of catalytic activity. It is noteworthy that the catalyst-free solution was then left for 10 h, but no further reaction took place. This reusability demonstrates the high stability and turnover of catalyst under the conditions employed.

Table 1 (*concluded*).

Entry	Substrate	Time (min)	Yield (%)[a,b]	Product
15		30	100	
16		25	98	
17		15	100	
18		40	91	
19		10	100	
20		50	100	
21		45	100	
22		90	88	
23		70	100	
24		20	98	
25		17	97	
26		20	95	
27		25	98	

[a] Isolated yields.

[b] Reaction conditions: catalyst (0.02 mmol), alcohol (1 mmol), Ac_2O (1.2 mmol), room temperature, solvent-free conditions.

[c] Reaction performed in the absence of catalyst.

Conclusions

In summary, we have introduced highly efficient, hydrophobic, and reusable catalyst SBA-15–Ph–Pr–SO_3H as an active catalyst for solvent-free acetylation of alcohols at ambient temperature. In the presence of this catalyst, an almost stoichiometric amount of AC_2O is necessary. Moreover, this catalyst offers mild reaction conditions with short reaction times, performing the acylation reactions under neat conditions. Besides, the catalyst kept its activity after five catalytic cycles. Accordingly, the methodology employed is a clean alternative for the acetylation reaction, tending toward ecoefficiency due to the use of solvent-free reaction conditions and recoverable catalyst, which can easily be prepared in the laboratory and stored for an extended period of time.

Supplementary data

Supplementary data are available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/v2012-018.

Acknowledgements

The authors acknowledge the Islamic Azad University of Qaemshahr Research Councils for support of this work.

References

(1) Green, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis;* 3rd ed.; John Wiley & Sons: New York, 1999; p 150.
(2) Hanson, J. R. *Protective Groups in Organic Synthesis;* Blackwell Science: Malden, MA, 1999.
(3) Zhdanov, R. I.; Zhenodarova, S. M. *Synthesis* **1975**, *1975* (4), 222. doi:10.1055/s-1975-23714.
(4) Tomohumi, S.; Kousaburo, O.; Takeshi, O. *Synthesis* **1999**, 1141.
(5) Höfle, G.; Steglich, V.; Vorbrüggen, H. *Angew. Chem. Int. Ed. Engl.* **1978**, *17* (8), 569. doi:10.1002/anie.197805691.
(6) Cope, A. C.; Herrick, E. C. In *Organic Syntheses Collective;* Wiley: New York, 1963; Vol. IV, p 304.
(7) Ishihara, K.; Kubota, M.; Kurihara, H.; Yamamoto, H. *J. Org. Chem.* **1996**, *61* (14), 4560. doi:10.1021/jo952237x.
(8) Chauhan, K. K.; Frost, C. G.; Love, I.; Waite, D. *Synlett* **1999**, *1999* (11), 1743. doi:10.1055/s-1999-2941.
(9) Dalpozzo, R.; De Nino, A.; Maiuolo, L.; Procopio, A.; Nardi, M.; Bartoli, G.; Romeo, R. *Tetrahedron Lett.* **2003**, *44* (30), 5621. doi:10.1016/S0040-4039(03)01358-3.
(10) Alleti, R.; Perambuduru, M.; Samantha, S.; Reddy, V. P. *J. Mol. Catal. A Chem.* **2005**, *226* (1), 57. doi:10.1016/j.molcata.2004.09.024.
(11) Kamal, A.; Khan, M. N. A.; Reddy, K. S.; Srikanth, Y. V. V.; Krishnaji, T. *Tetrahedron Lett.* **2007**, *48* (22), 3813. doi:10.1016/j.tetlet.2007.03.162.
(12) Heravi, M. M.; Behbahani, F. K.; Hekmat Shoar, R.; Oskooie, H. A. *Catal. Commun.* **2006**, *7* (3), 136. doi:10.1016/j.catcom.2005.09.011.
(13) Gowda, S.; Lokanatha Rai, K. M. *J. Mol. Catal. Chem.* **2004**, *217* (1–2), 27. doi:10.1016/j.molcata.2004.03.006.
(14) Phukan, P. *Tetrahedron Lett.* **2004**, *45* (24), 4785. doi:10.1016/j.tetlet.2004.04.076.
(15) Reddy, T. S.; Narasimhulu, M.; Suryakiran, N.; Mahesh, K. C.; Ashalatha, K.; Venkateswarlu, Y. *Tetrahedron Lett.* **2006**, *47* (38), 6825. doi:10.1016/j.tetlet.2006.07.059.
(16) Moghadam, M.; Tangestaninejad, S.; Mirkhani, V.; Mohammadpoor-Baltork, I.; Taghavi, S. A. *J. Mol. Catal. A Chem.* **2007**, *274* (1–2), 217. doi:10.1016/j.molcata.2007.05.012.
(17) Firouzabadi, M.; Iranpoor, N.; Farahi, S. *J. Mol. Catal. A Chem.* **2008**, *289*, 61.
(18) Romanelli, G.; Ruiz, D.; Vázquez, P.; Thomas, H.; Autino, J. C. *Chem. Eng. J.* **2010**, *161* (3), 355. doi:10.1016/j.cej.2009.12.029.
(19) Osiglio, L.; Romanelli, G.; Blanco, M. *J. Mol. Catal. A Chem.* **2010**, *316* (1–2), 52. doi:10.1016/j.molcata.2009.09.021.
(20) Joseph, J. K.; Jain, S. L.; Sain, B. *J. Mol. Catal. A Chem.* **2007**, *267* (1–2), 108. doi:10.1016/j.molcata.2006.11.026.
(21) Das, B.; Thirupathi, P. *J. Mol. Catal. A Chem.* **2007**, *269* (1–2), 12. doi:10.1016/j.molcata.2006.12.029.
(22) Yoon, H. J.; Lee, S. M.; Kim, J. H.; Cho, H. J.; Choi, J. W.; Lee, S. H.; Lee, Y. S. *Tetrahedron Lett.* **2008**, *49* (19), 3165. doi:10.1016/j.tetlet.2008.03.005.
(23) Rajabi, F. *Tetrahedron Lett.* **2009**, *50* (4), 395. doi:10.1016/j.tetlet.2008.11.024.
(24) Niknam, K.; Saberi, D. *Appl. Catal. A Gen.* **2009**, *366* (1), 220. doi:10.1016/j.apcata.2009.07.014.
(25) Karimi, B.; Zareyee, D. *Org. Lett.* **2008**, *10* (18), 3989. doi:10.1021/ol8013107. PMID:18702496.
(26) Karimi, B.; Zareyee, D. *J. Mater. Chem.* **2009**, *19* (45), 8665. doi:10.1039/b911388f.