



Phospho sulfonic acid as an efficient and recyclable solid acid catalyst for the solvent-free preparation of acylals



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ABSTRACT

Phospho sulfonic acid (PSA) acts as a highly effective and reusable catalyst for the chemo-selective protection of aldehydes with acetic anhydride under solvent-free conditions. The desirable features of this new catalytic methodology include its sustainability, effectiveness in the absence of solvent, a facile work-up procedure, and economic viability. PSA is fully characterized by Fourier transform infrared spectroscopy, wide-angle X-ray scattering analysis, and scanning electron microscopy with energy dispersive X-ray spectroscopy. The catalyst can be reused several times without significant loss of activity. In addition, no chromatographic separations are needed to obtain the desired products.

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Introduction

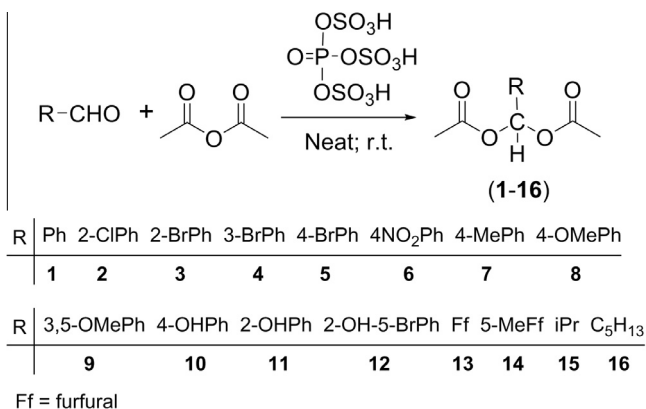
The protection of carbonyl group is an important step for a number of synthetic protocols. Reagents commonly used for protecting carbonyl groups include 2-mercaptoethanol,¹ ethane dithiol,² trialkyl orthoformate,³ acetic anhydride,⁴ and alcohols.⁵ Among these reagents, acetic anhydride is widely used for its robustness under neutral, basic, or acidic conditions. Acylals serve as important precursors for asymmetric allylic alkylation reactions,⁶ drug synthesis,⁷ and syntheses of 1-acetoxydienes and 2,2-dichlorovinylacetates (used for Diels–Alder reactions).^{8,9} Furthermore, acylals may also be used as cross-linking agents for cellulose in cotton.¹⁰ The preparation of acylals is of growing interest given their wide range of applications. Direct methods for preparing acylals include condensations of carbonyl compounds with acetic anhydride in the presence of protic acids,^{11–13} or Lewis acids.^{14–19} Moreover, reusable heterogeneous catalysts, including Keggin heteropolyacids,²⁰ solid silica sulfuric acid,²¹ and nano-ordered MCM-41-SO₃H²² have also been reported. The majority of Lewis acids are highly moisture sensitive; therefore, they are required in excess quantities. Because of this, the reaction progress is not satisfactory and byproducts are formed. Moreover, though other methods show varying degrees of success, they have limitations such as prolonged reaction times, low yields, requirement of excess reagents or catalysts, use of toxic solvents, and laborious work-up procedures. Therefore, there is a need for the develop-

ment of alternate milder and environmentally sustainable procedures for the preparation of acylals.

Solid acids are emerging materials for the development of simple and environment friendly synthetic processes. Recently, most of these reactions were carried out using protic or Lewis acids. However, the use of these materials may contribute to environmental pollution. To overcome this problem, recoverable, solid acids have been developed to catalyze a variety of reactions. Solid acid catalysis plays a key role in controlling environmental pollution by reducing the release of waste while strengthening economic development of the chemical industry.²³ Catalysts are simply removed from the reaction mixture by filtration or centrifugation without the need for neutralization, thereby enabling more eco-friendly processes. Phospho sulfonic acid (PSA) is a non-volatile, non-corrosive, recyclable, and eco-friendly solid acid catalyst. It has been used for the synthesis of indazolo [1,2-*b*]-phthalazine-triones and bis-(4-hydroxycoumarin-3-yl)methanes.^{24,25}

The recent development of neat (solvent-free) reactions based on novel, simple, and efficient synthetic approaches holds great promise for chemists. In addition, eco-friendly, less laborious methodologies for the synthesis of various organic compounds (i.e., heterocyclic and non-heterocyclic compounds) are also being developed. The most important goals of 'green chemistry' include avoidance of toxic reagents, organic solvents and the reduction of costs associated with organic synthesis. For these reasons, and because of our continued interest in the development of efficient, economical, and new methodologies,^{26–29} we here in report, the use of PSA as an environmentally benign and recyclable solid acid catalyst for the high-yielding, solvent-free synthesis of acylals (Scheme 1).

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Scheme 1. PSA-catalyzed synthesis of acylals.

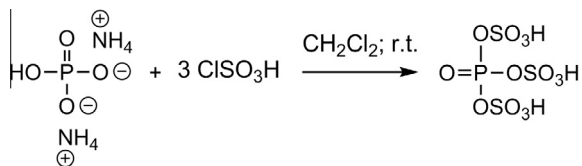
Results and discussion

Synthesis and characterization of PSA

A 25 mL reaction flask was equipped with a constant-pressure dropping funnel. The gas outlet was connected to a vacuum system through an alkali solution trap. Diammonium hydrogen phosphate (DHAMP; 7.5 mmol) was added to the flask, and chlorosulfonic acid (22.5 mmol) in CH₂Cl₂ (10 mL) was added drop-wise over a period of 15 min at room temperature. After the addition, the mixture was stirred for 2 h, and the residual HCl was eliminated by suction. The mixture was then washed with CH₂Cl₂, and was obtained as a solid, white powder (Scheme 2). The characterization of the new PSA is described below.

To evaluate the extent to which the sulfonic acid group was incorporated onto DHAMP, Fourier transform infrared (FT-IR) spectra of the individual DHAMP and PSA samples were compared (Fig. 1). The FT-IR spectrum of DHAMP shows the P=O stretching frequency at 1034 cm⁻¹ while that of PSA shows the analogous frequency at 1032 cm⁻¹. The sharp peak at 3246 cm⁻¹ corresponds to the O–H stretch of the SO₃H group. The O=S=O asymmetric and symmetric stretching peaks at 1232 and 1102 cm⁻¹, respectively, and the S–O stretching peak at 767 cm⁻¹ precisely confirmed the presence of the SO₃ group linkage. Furthermore, there are no peaks at 1232 and 1102 cm⁻¹ in the spectrum of DHAMP, indicating that sulfonation has occurred to produce PSA.

The X-ray powder diffraction (XRD) analysis shows that the diffraction pattern of the DHAMP (Fig. 2a) is completely different from that of PSA (Fig. 2b) as a result of sulfonation within the former. The diffraction pattern showed peaks characteristic of PSA, demonstrating good crystallinity. Moreover, the peaks at 2θ = 25°–28° are characteristic of the SO₃ group, confirming that PSA contains the SO₃ functionality. In addition, there are no peaks beyond 28° in Figure 2b, providing further evidence of sulfonation. The scanning electron microscopy (SEM) image of DHAMP (see Fig. S1 in Supporting information) exhibits an irregular morphology, bearing regions of both high and low surface areas, while that of PSA shows a regular, cubic shape. The sulfonation was also con-



Scheme 2. Preparation of the solid acid PSA.

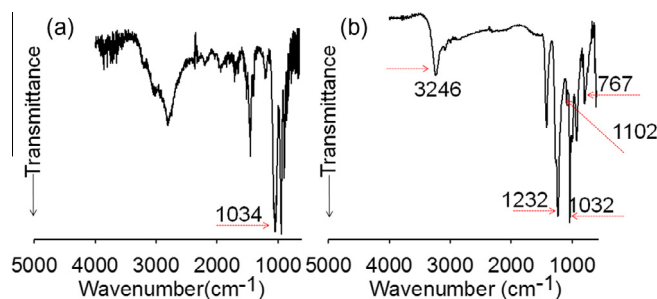


Figure 1. FT-IR spectra of (a) DHAMP and (b) PSA.

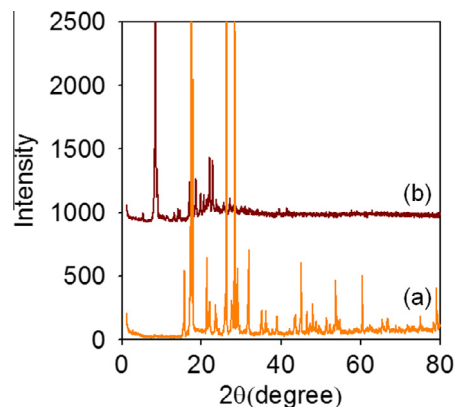


Figure 2. XRD patterns of (a) DHAMP and (b) PSA.

firmed by energy dispersive X-ray (EDX) analysis (inset in Fig. S1), which showed the presence of both sulfur and phosphorus.

PSA-catalyzed synthesis of acylals

To standardize the conditions, a model reaction using benzaldehyde and acetic anhydride was carried out using different catalysts, and the results are presented in Table 1. The preliminary experiment was performed neat in the absence of catalyst at room temperature for 24 h; no product was formed (entry 1). A number of trials using ZrOCl₂, ZrOCl₂–SiO₂, BF₃–SiO₂, ClSO₃H, KHSO₄, or oxone as catalysts gave relatively low product yields (entries 2–6). The reaction performed with DHAMP proved unproductive

Table 1

Synthesis of **1** using a variety of catalysts in the absence of solvent at room temperature^a

Entry	Catalyst	Catalyst amount (mol %)	Time (h)	Yield ^b (%)
1	Catalyst free	—	24	nr ^c
2	ZrOCl ₂	5	1	65
3	ZrOCl ₂ ·SiO ₂	5	0.3	78
4	BF ₃ ·SiO ₂	5	0.4	80
5	KHSO ₄	5	2	58
6	Oxone	5	2	62
7	ClSO ₃ H	1	0.1	75
8	(NH ₄) ₂ HPO ₄	5	12	nr ^c
9	PSA	1	0.1	85
10	PSA	1.5	0.1	90
11	PSA	2	0.1	94
12	PSA	2.5	0.1	99
13	PSA	3	0.1	99

^a Reaction conditions: ³⁰ benzaldehyde = 1 mmol, acetic anhydride = 1 mmol, and PSA = 2.5 mol %.

^b Isolated yield measured gravimetrically.

^c No reaction.

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