

ORIGINAL RESEARCH PAPER

Synthesis of Unsymmetrical Ethers Catalysed by Polyvinyl Sulfuric Acid & PVSA / Nano RH SiO₂ as a Novel Solid Acid Nanocomposite

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ABSTRACT

The methodology involves preparing polyvinyl sulfuric acid as a solid acid by simple mixing of polyvinyl alcohol with chlorosulfonic acid in CH₂Cl₂ at room temperature. The catalytic ability of the solid acid was investigated for the facile conversion of benzylic alcohols to the unsymmetrical ethers with aliphatic alcohols in the presence of the solid acid. Results show that the solid acid is an appropriate catalytic agent for these condensation reactions. The silica was also extracted from low-cost rice husk and the amorphous silica gel nanoparticles were prepared with sol-gel method. The polyvinyl sulfuric acid was supported on nano rice husk silica. Then the catalytic effect of this system was investigated for synthesis of unsymmetrical ethers which consisted of a combination of high acidic power for this solid acid and high-surface area of nanoparticles. Results show that totally catalytic effect of polyvinyl sulfuric acid supported on nano silica is more suitable than polyvinyl sulfuric acid. The reason for this is in its ability to produce the end products in shorter reaction times while having high isolated yields.

Keywords: Silica nanoparticles; Polyvinyl sulfuric acid; Unsymmetrical ethers; Sol-gel method; Rice husk
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INTRODUCTION

Green chemistry is an emerging scientific perspective to the synthesis, processing and application of chemical substances in the real-world situations with the objective of mitigating the potential and real risks to humans, eco-system and the physical environment [1]. It is clear that green chemistry, as is known in the literature, requires the application of environmentally-benign reagents and solvents as a means of being able to recover and reuse the catalyst [2]. Recent trend in

environmental consciousness, particularly in the post-industrial and post-modern digital societies, has been the underlying urgency in undertaking applied research into optimum utilization of agricultural and horticultural byproducts. Rice husk can be said to constitute as one of those cases of crop wastes that is plentifully produced nationally and globally. For its significantly high silicon content, rice husk has emerged as a major ingredient for producing elementary silicon and numerous silicon compounds like silicon nitride [3], sodium silicate [4] and silicon carbide [5]. The major inorganic constituent of the rice husk is silica

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that is produced in various ways. Davarpanah et al. for example, used a method that involves extraction of amorphous nano silica from rice husk (RH-SiO₂). They have also investigated the catalytic application of silver nanoparticles immobilized to rice husk-SiO₂-aminopropylsilane composite as recyclable catalyst in the aqueous reduction of nitroarenes [6]. In another research study, green synthesis of nano silica was obtained by thermal decomposition of pine cones and pine needles have been reported. [7]. Application of solid acids as heterogeneous catalysts, has extensively received attention in various specialized domains of organic synthesis [1]. They have numerous advantages, among which are easy physical handling, decreased reactor and plant corrosive problems, environmentally-safe disposal in different chemical processes compared with the conventional liquid acid catalysts. The potential wastes and by-products can be minimized by the application of solid acids in developing cleaner synthesis routes [2,8]. A variety of organic reactions are catalyzed in the presence of solid acids such as nano silica gel supported by thionyl chloride [9], phospho sulfonic acid [10], silica chloride [11], alumina sulfuric acid [12], silica sulfuric acid [13], cellulose sulfuric acid [14], etc.

Organic ethers are among the prominent classes of chemicals that have widespread applications in various sectors of chemical and agro-chemical industries. They constitute as the major ingredients of herbicides, pharmaceuticals, disinfectors, plasticizers, solvents and Intermediates [15]. They also found in production of perfumes, agrochemicals and pharmaceutical leads, as well as serving as a multi-purpose building block in organic synthesis [16]. One of the most common methods of ether production is the Williamson ether synthesis [17]. Various ether synthesis methods have been reported, the principal among them are reductive etherification of alkoxydialkylsilanes with carbonyl compounds using the BiBr₃/ClR₂Si-H catalytic system [18]. It also involved etherification of benzyl alcohols with 1-hexanol by propyl and arene-SO₃H-modified mesostructured SBA-15 materials as catalysts [19], alcoholises of benzylic and allylic alcohols catalyzed by Iron (III) as FeCl₃ and Fe(ClO₄)₃ [20]. The work also involved etherification of benzylic alcohols with different alcohols in the presence of AlPW₁₂O₄₀ [21]. The transformation of benzyl alcohols into their methyl or ethyl using 2,4,6-trichloro-1,3,5-triazine catalyzed by dimethyl sulfoxide [22] was

also carried out. The final stage involved the conversion of aryl aldehydes to dibenzyl ethers through reductive etherification in the presence of Et₃SiH with catalytic amount of InCl₃ [16].

The present paper aims to investigate the processes involved in converting benzylic alcohols to the unsymmetrical ethers with aliphatic alcohols catalyzed by polyvinyl sulfuric acid as a solid acid. Further, amorphous silica nanoparticles were obtained from low-cost rice husk (RH-SiO₂) by carrying out acid chemical treatment followed by the burning process. Silica nanoparticles was then prepared with sol-gel method. The polyvinyl sulfuric acid was supported on nano rice husk silica, the catalytic effect of this system was subsequently investigated for synthesis of unsymmetrical ethers.

EXPERIMENTAL

All chemical reagents were purchased from Merck Chemical Company and were used without purification. Rice husk (RH) was collected from a rice mill in Khozestan-Baghmalek (Iran). The progress of the reactions was accomplished by TLC on silica-gel polygram SILG/UV₂₅₄ plates. Plates were visualized by UV light. FT-IR spectra were recorded using Perkin-Elmer model BX-II instrument. The ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer in CDCl₃ using TMS as an internal reference. EDX analysis of the catalyst was recorded using scientific instrument UK model SIRIUS SD. The Morphology and particle dispersion were investigated using FESEM (Hitachi S-4160).

Extraction of silica from rice husk

The dried rice husk (30.0 g) was stirred in 750 mL of 1.0 M nitric acid for 24 h at room temperature. It was subsequently washed thoroughly with distilled water until the pH of the rinsed product became constant (PH=6). It was then dried in an oven for 24 h at 100°C and was burned for 6 h in a muffle furnace at 800°C. Silica extraction from RH was carried out by stirring the rice husk in 500 mL of 1.0 M sodium hydroxide for 24 h at room temperature. The mixture was subsequently filtered and titrated with 3.0 M HNO₃, during which the pH of the solution reached 5, the titration was stopped. It then underwent the process of aging for 24 h. The silica gel/precipitate was filtered, comprehensively washed with distilled water and dried for 18 h at 100°C [23].

Preparation of polyvinyl sulfuric acid (PVSA)

A 50 ml suction flask was equipped with a constant- pressure dropping funnel containing mixture of chlorosulfonic acid (2.6 g, 22.7 mmol) and 3 ml of dried dichloromethane. The gas outlet was connected to a vacuum system through an adsorbing solution (5% NaOH). Polyvinyl alcohol (MW=145000), (1.0 g, 22.7 mmol) and 10 ml of dried dichloromethane were charged into the flask and chlorosulfonic acid in CH_2Cl_2 was added dropwise over a period of 50 min at room temperature. After the addition was completed, the mixture was stirred for 5 min, while the residual HCl was removed by suction. The mixture was then washed with excess of dried CH_2Cl_2 (5 ml). Finally,

the obtained black solid (PVSA, 2.4 g) was placed in oven at 50°C for 1 h.

General procedure for etherification of benzylic alcohols with various aliphatic alcohols catalyzed by PVSA

A mixture of benzylic alcohol (1mmol), aliphatic alcohol (2 ml) and polyvinyl sulfuric acid (0.1 g) was stirred magnetically at 70°C for the suitable time (Table 1). The dried CH_2Cl_2 (10 ml) was added to the reaction mixture after completion of the reaction (monitored by TLC). The reaction mixture was filtrated in order to separate the solid catalyst from the residue washed with dried CH_2Cl_2 (5 ml). The pure product in high isolated yield (70-94 %) was obtained after the evaporation of the solvent.

Table 1. Preparation of unsymmetrical benzyl ethers catalyzed by PVSA at 70°C^a

Entry	Benzylic alcohols	Aliphatic alcohols	Time(min.)	Yield (%)
1	<i>p</i> -MeOC ₆ H ₄ CH ₂ OH	Ethanol	360	0 ^b
2		Ethanol	12	90
3		1-Propanol	14	89
4		2-Propanol	14	87
5		<i>sec</i> -Butyl alcohol	10	92
6		<i>tert</i> -Butyl alcohol	12	86
7	<i>p</i> -MeC ₆ H ₄ CH ₂ OH	Ethanol	10	94
8		1-Propanol	8	92
9		2-Propanol	8	91
10		<i>sec</i> -Butyl alcohol	14	88
11		<i>tert</i> -Butyl alcohol	15	82
12	Ph ₂ CHOH	Ethanol	35	80
13		1-Propanol	40	82
14		2-Propanol	45	81
15		<i>sec</i> -Butyl alcohol	30	84
16		<i>tert</i> -Butyl alcohol	40	84
17	(<i>p</i> -ClC ₆ H ₄)PhCHOH	Ethanol	60	70
18		1-Propanol	60	75
19		2-Propanol	70	74
20		<i>sec</i> -Butyl alcohol	40	80
21		<i>tert</i> -Butyl alcohol	35	82
22	PhCH(OH)CH ₃	Ethanol	25	88
23		1-Propanol	20	89
24		2-Propanol	25	86
25		<i>sec</i> -Butyl alcohol	15	84
26		<i>tert</i> -Butyl alcohol	20	90

^a Conditions: benzylic alcohols (1mmol), aliphatic alcohols (2 ml) and polyvinyl sulfuric acid (0.1 g), ^b In the absence of PVSA.

General procedure for etherification of benzylic alcohols with ethyl alcohol catalyzed by PVSA/ Nano RH SiO₂

The mixing of polyvinyl sulfuric acid (0.1 g) and nano rice husk silica (0.05 g) were added to a solution of benzylic alcohol (1mmol) and ethyl alcohol (2 ml). The mixture was subsequently stirred magnetically at 70°C for the suitable time (Table 2). The progress of reaction was systematically monitored by TLC. Dried CH₂Cl₂ (10 ml) was added to the reaction mixture that was later filtrated in order to separate the catalyst from the residue washed with dried CH₂Cl₂ (5 ml). The pure product in high isolated yield (84-95%) was obtained after the evaporation of the solvent.

RESULT AND DISCUSSION

According to the previously reported method, polyvinyl sulfuric acid was produced by mixing of polyvinyl alcohol and chlorosulfonic acid under solvent free condition at room temperature [24]. In the present research, however, this polymeric solid acid was prepared using a similar method. The only difference being that the CH₂Cl₂ was added to the reactants in the synthesis procedure for convenience.

This reaction was comfortable and clean, because the HCl was the only by-product that immediately evolves from the reaction vessel (Scheme 1).

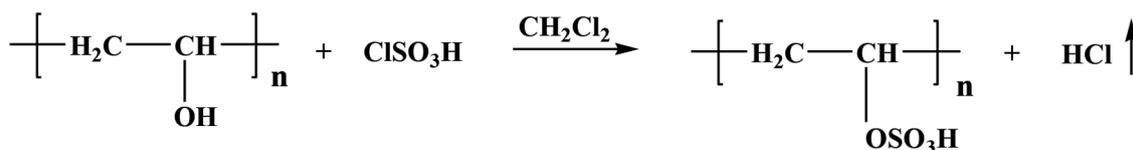
The acidic power of polyvinyl sulfuric acid was obtained by titration using NaOH (0.1 N). The result showed that the acidic capacity of catalyst is 9.84 mmol/g and it can be reduced the pH to about 0.57.

The conversion of alcohols into unsymmetrical ethers is one of the most important synthetic reactions. We first examined etherification of ethanol and *p*-methoxybenzyl alcohol as a model in the presence of polyvinyl sulfuric acid. It was found that for the facile etherification reaction, 0.1 g of the catalyst was required. The condensation reaction evenly performed and obtained *p*-methoxybenzyl ethyl ether in 90% yield after 12 min at 70°C. (Table 1, entry 2). In the absence of the PVSA as a catalyst, a similar reaction was not proceed at 70°C after six hours. (Table 1, entry 1). In order to show the general application of the protocol, we have studied the etherification of benzylic alcohols with ethanol, 1-propanol, 2-propanol, *sec*-butyl alcohol and *t*-butyl alcohol (Scheme 2). All the reactions proceeded well in short reaction times with the production of benzyl alkyl ethers in excellent isolated yields (Table 1).

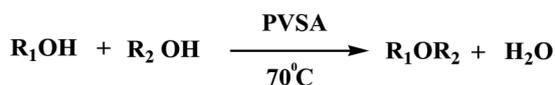
Table 2. preparation of unsymmetrical benzyl ethers catalyzed by PVSA / Nano RH SiO₂ at 70°C.^a

Entry	Benzylic alcohols	Aliphatic alcohol	Time (min.)	Yield (%)
1	<i>p</i> -MeOC ₆ H ₄ CH ₂ OH	Ethanol	7	94
2	<i>p</i> -MeC ₆ H ₄ CH ₂ OH	Ethanol	5	95
3	Ph ₂ CHOH	Ethanol	5	86
4	(<i>p</i> -ClC ₆ H ₄)PhCHOH	Ethanol	22	84
5	PhCH(OH)CH ₃	Ethanol	8	92

^a Conditions: benzylic alcohols (1mmol) , ethanol (2 ml) and the catalyst (0.15 g).



Scheme 1. Preparation of polyvinyl sulfuric acid



R₁: benzylic

R₂: Et, 1-Pr, 2-Pr, sec-Bu, t-Bu

Scheme 2. Preparation of unsymmetrical benzyl ethers in the presence of PVSA as the catalyst at 70°C.

Results show that the solid acid is an appropriate catalytic agent for these condensation reactions. The results were shown in Table 1.

Amorphous nano silica comfortably was extracted from low-cost rice husk (RH) and then was prepared with sol- gel method. The morphology and quantitative analysis of extracted nano silica was examined by FESEM (Hitachi S-4160). According to Fig. 1(a), the RH-SiO₂ nanoparticles size distribution has an average of 30 nm. The polyvinyl sulfuric acid was supported on nano rice husk silica by simple mixing of polyvinyl sulfuric acid and nano silica in 2:1 ratio. According to Fig. 1(b), the PVSA/ Nano RH SiO₂ nanoparticles size distribution

has an average of 200 nm.

In addition, to confirm the structure of the nanocomposite, EDX spectra has been recorded. EDX spectra confirmed the presence of the Si, C, O, and S elements in the catalyst structure (Fig. 2).

The FTIR spectroscopy was used to characterize the structure of catalyst. Fig. 3 shows the FTIR spectra of PVSA (3a) and PVSA / Nano RH SiO₂ (3 b). The IR spectrum of PVSA (3a) showed the broad O-H absorption around 3404 cm⁻¹, strong S=O absorptions between 1172 and 1289 cm⁻¹ and strong S-O absorption at 578 cm⁻¹. PVSA/Nano RH SiO₂ (3 b) showed the broad band around 3401 cm⁻¹ is due to the stretching vibration of Si-O-H bond, the HO-H vibration of water molecules adsorbed on the silica surface and O-H absorption of Hydrogen sulfate groups. The strong S=O absorptions between 1170 and 1289 cm⁻¹ and strong S-O absorption at 584 cm⁻¹ were also shown. The band around 1631 cm⁻¹ is also due to the bending vibration of water molecules bound to the silica matrix and the strong peak at 1077 cm⁻¹ is due to asymmetric stretching vibration of the structural siloxane bond, Si-O-Si.

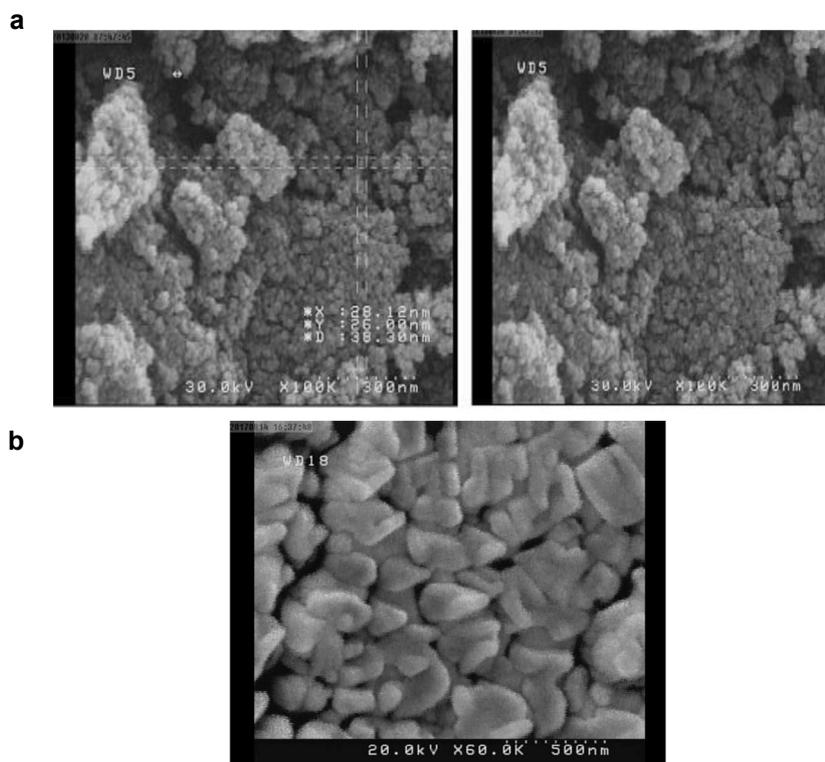
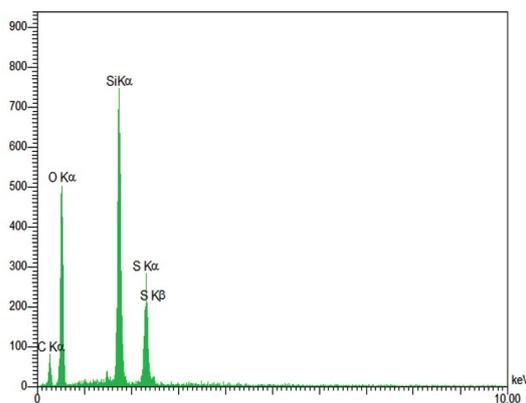
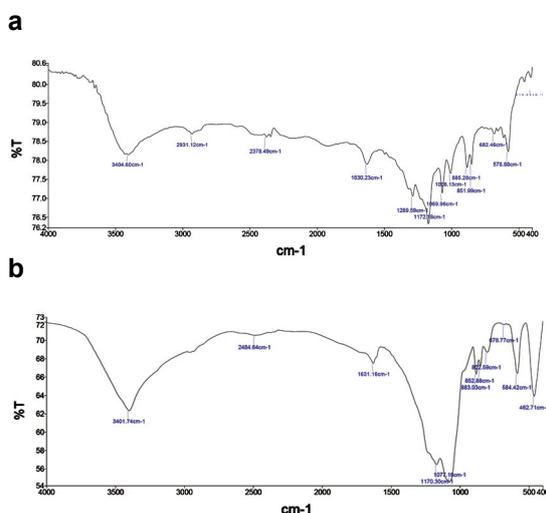
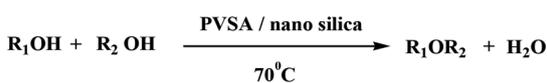


Fig. 1. (a) FESEM images of the extracted nano silica, (b) FESEM image of PVSA / Nano RH SiO₂.

Fig. 2. EDX analysis of PVSA / Nano RH SiO₂.Fig. 3. The FT-IR spectra of a) PVSA, b) PVSA / Nano RH SiO₂.

Then the catalytic effect of PVSA / Nano RH SiO₂ was investigated for the synthesis of *p*-methoxybenzyl ethyl ether as a model reaction. It was found that 0.15 g of nanocomposite proceeded well in the minimum time with maximum yield (7min., 94%). In order to show the general application of the protocol, we have studied the etherification of benzylic alcohols with ethanol in the presence of this acidic nanocomposite (Scheme 3, table 2).



R₁: benzylic
R₂: Et

Scheme 3. Preparation of unsymmetrical benzyl ethers in the presence of PVSA/Nano RH SiO₂ as the catalyst at 70°C.

As shown in Table 2, the unsymmetrical ethers were produced in excellent isolated yields. The comparison of the results for etherification in the presence of polyvinyl sulfuric acid (Table 1) with polyvinyl sulfuric acid supported on nano rice husk silica (Table 2), were clearly shown that the later is better and the produced the products in shorter times. The morphology of the nanocomposite was also determined by FESEM images as shown in Fig. 1(b). The PVSA / Nano RH SiO₂ nanoparticles distribute in average size of 200 nm.

It is should be point out that, in 2005, Firouzabadi et al. [21] introduced ALPW₁₂O₄₀ as an efficient catalyst for the synthesis of unsymmetrical ethers. The condensation of 1-phenyl ethanol as secondary benzylic alcohol by ethanol was proceeded in the presence of this heterogeneous catalyst and afford the corresponding ether after 7 hours in 86% yield. The similar condensation reaction catalyzed by PVSA / Nano RH SiO₂, it required shorter time and produced the product in higher isolated yield (8 min and in 92% yield). This is shown that, the ability of this nanocomposite to produce the end-product in a shorter reaction time while having a high isolate yield. Because of possessing an inorganic-base (SiO₂) derived from plant residues of rice husk (green chemistry and eco-friendly features), also the nanocomposite as a catalyst, proves to be environmentally safe as well as being relatively accessible and economically feasible to use.

CONCLUSION

In conclusion, polyvinyl sulfuric acid as a heterogeneous solid acid catalyst that is environmentally- safe. This is a suitable proton source and insoluble in the organic solvents. A simple and convenient protocol has described in the presence of this solid acid for the synthesis of unsymmetrical ethers. The unsymmetrical ethers were obtained in short reaction times while having high isolated yields. Also in the present study, nanosilica was easily extracted from rice husk. The polyvinyl sulfuric acid was supported on nano rice husk silica, then the catalytic effect of this system was investigated for synthesis of unsymmetrical ethers which is consisted of a combination of high acidic power for this solid acid and high- surface area of nanoparticles. The attractive features of this method are simple procedure, cleaner reaction, easy work-up, short reaction times with the production of benzyl alkyl ethers in excellent yields.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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