



Perlite: A cheap natural support for immobilization of sulfonic acid as a heterogeneous solid acid catalyst for the heterocyclic multicomponent reaction



Eskandar Kolvari*, Nadia Koukabi, Maliheh M. Hosseini

Department of Chemistry, Semnan University, Semnan, Iran

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ABSTRACT

Perlite sulfonic acid (Perlite-SO₃H (PeSA)) has been synthesized by grafting the sulfonic groups on the perlite surface as naturally and cheap support to produce novel heterogeneous reusable solid acid catalysts. FT-IR, XRD, SEM, TGA, pH analysis and Hammett acidity function were employed to characterize the properties of the synthesized PeSA. Significantly, the as-prepared PeSA exhibits a high catalytic activity in multicomponent reaction for the one-pot synthesis of heterocyclic compound such as 3,4-dihydropyrimidin-2(1H)-ones, 2,4,5-trisubstituted imidazoles, coumarins and bis(indolyl)methanes. Additionally, the newly synthesized heterogeneous solid acid catalyst can be reused for several times without apparent loss of its catalytic activity, confirming the stability of the covalent bonding of acidic centers. PeSA has advantages such as low cost, ease of preparation, more stability and reusability, low toxicity and ease of handling.

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1. Introduction

Acid catalyzed chemical processes are widely used in the organic chemistry to produce various chemicals. Homogeneous acid catalysts such as sulfuric acid, fluorhydric acid, hydrochloric acid and phosphoric acid are commonly used in organic syntheses and industrial processes [1–4]. However, these acids are not environmentally benign because of their corrosive properties and difficult separation of the catalyst from the products, which necessitates specialized reaction equipment and increases operating difficulty. These drawbacks lead to loss of energy and the formation of large amounts of waste products. In recent years, owing to these disadvantages which are far from the concept of “Sustainable Chemistry”, development of novel, nontoxic, low cost, eco-friendly, recyclable heterogeneous catalysts with improved efficiency has been the subject of immense interest and can also meet green chemistry demands [5–15]. Heterogenization of homogeneous catalysts by their immobilization on various solid supports has been the subject of extensive research during the past decade [16–21]. This process leads to improved processing steps,

better process economics, and environmentally friendly industrial manufacturing.

Sulfonation with chlorosulfonic acid is convenient, fast and efficient method for heterogenization of homogeneous catalysts that has been much attention [22–27] after Zolfigol's report on the preparation of silica sulfuric acid [28].

Perlite is a kind of mineral oxide mixture which contains approximately 70–75% of SiO₂ and 12–18% of Al₂O₃ [29]. Perlite has several advantages such as high porosity with strong adsorbability, excellent thermal and chemical resistance, light weight, low cost, low toxicity and ease of handling [30–34]. Due to the extremely porous structure and silica content of perlite, there is a possibility to use it for insulation, moisture control, absorbent, filter and filling material for variety of processes in construction and manufacturing industry [35,36].

Hence, in this context, taking advantage of the above mentioned properties of perlite and as a continuation of our efforts to investigate the applications of solid acid in chemical transformations [22], we have designed and synthesized novel, sustainable perlite sulfonic acid and we hope to report herein, PeSA catalyzed multicomponent one-pot synthesis of heterocyclic compound such as 3,4-dihydropyrimidin-2(1H)-ones, 2,4,5-trisubstituted imidazoles, coumarins and bis(indolyl)methanes. In this reaction, the catalyst could be recycled several times without significant loss of its catalytic activity.

* Corresponding author. Tel.: +98 23 336 54058; fax: +98 23 336 54110.
E-mail address: Kolvari@semnan.ac.ir (E. Kolvari).

2. Experimental

2.1. General remarks

All chemicals reagents were used without any further purification and purchased from the Merck and Aldrich chemical companies. Solvents were purified by conventional methods. Perlite obtained from Iran, Semnan sources.

Fourier transform infrared spectroscopy (FTIR) was recorded on a Shimadzu 8400s spectrometer using KBr pressed powder discs. Field emission scanning electron microscope (FESEM) images were acquired with a Philips XL30 field emission scanning electron microscope (Royal Philips Electronics, Amsterdam, The Netherlands) instrument operating at 10 kV. Powder XRD patterns were obtained with a Siemens D5000 (Siemens AG, Munich, Germany) X-ray diffractometer using Cu-K α radiation of wavelength 1.54 Å. Thermo gravimetric analyses (TGA) were carried out on a Du Pont 2000 thermal analysis apparatus at a heating rate of 5 °C min⁻¹ under air atmosphere. The NMR spectra were measured in pure deuteriated chloroform and dimethyl sulfoxide with a Bruker Avance 300 MHz instruments (¹H NMR 300 MHz) with tetramethylsilane (TMS) as the internal reference.

The purity of products was checked by thin layer chromatography (TLC) on glass plates coated with silica gel 60 F254 using *n*-hexane/ethyl acetate mixture as mobile phase.

2.2. Providing of neat perlite powder

10 g of perlite powder was washed by stirring overnight in 200 ml methanol and ethanol to remove organic components, then were washed by distilled water, methanol and ethanol three times and following that were heated in aqueous solution of NaOH 5 N for 20 min. Precipitated perlite was filtered and rinsed with excess water until NaOH removed and then dried at 100 °C.

2.3. Preparation of PeSA

In a typical experimental run, a suction flask equipped charged with 1.0 g of perlite, was equipped with a constant-pressure dropping funnel containing chlorosulfonic acid (0.3856 g, 0.0033 mol) and a gas inlet tube for conducting HCl gas into water as an adsorbing solution. Chlorosulfonic acid was added dropwise over a period of 15 min in an ice bath (0 °C) during which HCl was evolved immediately. After completion of the addition, the reaction mixture is allowed to stand for 1 h at room temperature, while the residual HCl was eliminated by suction [28]. In this step, the modified PeSA (1.44 g) was obtained as a solid acid catalyst in the organic synthesis.

2.4. PeSA, solid acid catalyst for multicomponent one-pot synthesis of heterocyclic compounds

2.4.1. General procedure for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones

A mixture of aromatic aldehyde (1.0 mmol), methyl acetoacetate (1.0 mmol), and urea (1.5 mmol) was stirred at 90 °C utilizing PeSA (0.03 g, 15 wt.% with respect to benzaldehyde) for the appropriate time until the reaction was complete. The reaction was monitored by thin layer chromatography (TLC) [7:3 hexane:ethyl acetate]. After the completion of the reaction, the reaction mixture was filtered at hot condition using Whatmann 41 filter paper, organic solvent was evaporated under reduced pressure and the resulting solid product was then crystallized from hot ethanol.

2.4.2. General procedure for the synthesis of coumarins

In a round bottom flask, PeSA (0.03 g, 15 mol%) was added to the mixture of phenolic compound (1.0 mmol) and methyl acetoacetate (1.0 mmol) at 100 °C and the reaction mixture stirred for the appropriate time. The progress of reaction was monitored by TLC (eluent, *n*-hexane:ethyl acetate, 4:1). After the completion of the reaction, the reaction mixture was separated out in the flask as a solid mass. The product was isolated by dissolving in acetone and filtered. The catalyst was removed by filtration and the filtrate was concentrated under vacuum. The resultant compound was washed with water, filtered and dried at 100 °C. The product was purified by recrystallization using ethanol.

2.4.3. General procedure for the synthesis of 2,4,5-trisubstituted imidazoles

To a well-stirred mixture of aromatic aldehyde (1.0 mmol), benzil (1.0 mmol), ammonium acetate (2.5 mmol) and PeSA (0.03 g, 15 mol%) as catalyst was reacted in an oil bath at 90 °C without solvent for the appropriate time. After completion of the reaction, the solid materials residue was then washed with acetone, desired insoluble catalyst was collected by filtration and the solvent was evaporated to give the crude product. For further purification it was crystallized from ethanol to afford pure imidazole derivatives.

2.4.4. General procedure for the synthesis of bis(indolyl)methanes

A mixture of indole (1.0 mmol), benzaldehyde (0.5 mmol), and PeSA (0.02 g, 10 mol%) was stirred at room temperature for the appropriate time. The progress of the reaction was monitored by TLC. After completion of the reaction, as indicated by TLC, the reaction mixture was dissolved in ethanol, then catalyst was filtered off. The ethanol solvent poured into water. The resulting precipitate was filtered and purified by recrystallization from ethanol to afford the desired compound in pure form.

2.4.5. General procedure for recycling of PeSA

Recyclability of the catalyst (15 mol%) was tested for the synthesis of 2,4,5-triphenyl-1H-imidazole between benzaldehyde (1 mmol), benzil (1 mmol) and ammonium acetate (2.5 mmol) under solvent-free condition for 20 min at 90 °C. After completion of the reaction, the heterogeneous catalyst was easily separated from the production mixture by vacuum filtration, washed with ethanol (2 × 15 ml), acetone (2 × 10 ml) to remove the organic compounds and dried in oven to be used in the next cycles. In every run, the yield of product was performed in constant time. This process was repeated four more times, affording the desired product in good yields, with undiminishing efficiency.

3. Results and discussion

In the present work, we demonstrate the synthesis of perlite sulfonic acid and discuss its performance as solid acid catalyst according to our earlier report with magnetic particle-supported sulfonic acid catalysts [22]. Perlite is a type of widespread natural mineral material which provides a cheap and suitable support. A new heterogeneous PeSA catalyst was prepared by the concise route outlined in Scheme 1. Perlite reacted with chlorosulfonic acid at room temperature gave perlite sulfonic acid (PeSA). It is important to note that, this reaction is easy and clean without any work-up procedure due to HCl gas is evolved from the reaction vessel immediately. The current work shows unique advantages such as simplification of the catalyst system and its synthesis, and the application of inexpensive and available precursors. This white homogeneous, nonhygroscopic solid acid is very stable under reaction conditions. The “inorganic solid acid catalysts” were

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