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Silica-supported policresulen as a solid acid catalyst for organic reactions

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ABSTRACT

A new type of solid catalyst was prepared by coating a thin layer of policresulen, an inexpensive polymer prepared via condensation of 2-hydroxy-4-methylbenzenesulfonic acid and formaldehyde that has been used as commercially available drug, onto the surface of silica. The policresulen component is insoluble in many organic solvents and can be adsorbed on silica with the aid of hydrogen bonding. The obtained silica/policresulen composite showed remarkable catalytic activity for various organic reactions. In model reactions, the catalyst can be recycled several times without significant loss of activity. The salient features of using this acid catalyst in organic reactions include cost-effectiveness, simple and time-efficient preparation, and the convenience of controlling the acid loading on the solid.

1. Introduction

Acid catalysts have been widely used in both academia and industry, and can be categorized into two major types: homogeneous liquid acids and heterogeneous solid acids [1–3]. Although homogeneous mineral acids, such as H_2SO_4 and HF, which are corrosive and toxic, have been widely adopted by chemical industry, with increasing pressure coming from environmental protection there is a need to develop green synthetic systems based on environmentally benign acid catalysts [4–8]. The use of heterogeneous solid acid catalysts has the general advantages of easier operation, milder conditions, reduced equipment corrosion, and minimized contamination of the waste streams as well as reusability of the catalyst [9–11]. For this reason, heterogeneous solid acids have been extensively investigated [12–15], and in some chemical processes, their use has already contributed to significant improvement of both the synthetic efficiency and the greenness of the system [16–23]. Despite promising and sometime spectacular results, the practical application of solid acids in industrial processes is still hindered by many factors. Among all the methods used to prepare solid acids, the binding of catalysts to organic polymers or inorganic solids is widely used to produce a stable covalent bond between the acid center and the solid support, and is preferable to reduce the chance of leaching [24–26]. The synthesis of some solid acids with this method, however, involves

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several steps which are rather time-consuming. Furthermore, functionalization of a solid support using covalent bonds often requires harsh reaction conditions and as a consequence, calls for both a support and an acid precursor with sufficient chemical and thermal stability [27]. In many cases, a sophisticated operational procedure is also needed [28]. Therefore, some current solid acid catalysts are rather expensive and are therefore not widely used in synthesis. There thus exists a need to develop new, innovative approaches toward the design of recoverable and reusable solid acid catalysts.

Recently, the concept of solid-supported liquid phase catalysis has experienced a rekindled interest in the catalytic and synthetic community for the preparation of efficient heterogeneous catalytic materials [29–34]. With the aid of a thin layer of less volatile fluid coated onto the surface of solid support, some homogeneous catalysts have been easily immobilized without employing sophisticated operational procedures. In a selected reaction, solid form of the catalyst enables an easy recycling, but the reaction proceeded in microcosmically homogeneous conditions [35,36]. Inspired by this elegant strategy, we envision that it may be possible to transfer this concept to the development of a solid acid catalyst. To realize this idea, an acidic species that is amenable to the immobilization step and can stay stable on the surface of solid support is needed.

Policresulen is prepared by the condensation of metacresolsulfonic acid and formaldehyde and is commercially available as a clear red-brown solution. It is available at a low price in a number of countries worldwide [37]. Its systematic name is 2-hydroxy-3,5-bis(4-hydroxy-2-methyl-5-sulfobenzyl)-4-methylbenzenesulfonic acid. Policresulen is a topical hemostatic and antisepticwidely used as medicine for treating common anal disorders, such as hemorrhoids, and for gynecological infections [38]. Because the backbone of this reagent contains many hydroxyl and sulfonic acid groups, it is barely soluble in many organic solvents, such as toluene, ethyl acetate, and dichloroethane. The thermal stability and chemical stability of policresulen are quite good, making the extension of its applications to other fields possible. Considering that policresulen is a strong organic acid, and also taking into account its hydrophilic properties, we propose that it may be possible to construct a new heterogeneous acid catalyst using this reagent as a homogeneous counterpart in conjunction with silica as a supporting material. Thus, we herein report a new solid acid composed of silica and policresulen that displays remarkable catalytic activity in many organic reactions. Compared with conventional solid acids, such as silica-supported sulfonic acid catalysts and Amberlyst-15, the materials obtained by our method have several advantages including simple and time-efficient preparation, low cost, and controllable sulfonic acid loading as well as tunable catalytic activity.

2. Experimental

2.1. Preparation of SiO_2/policresulen composite catalysts ***1a–1d***

In a typical procedure used to prepare silica/policresulen composite catalyst **1b**, silica gel (10 g) was added to a 250-mL round-bottomed flask containing a mixture of aqueous policresulen solution (52 wt%, 2.09 g) and ethanol (150 mL). The suspension was stirred at room temperature for 30 min prior to the removal of the ethanol and water under reduced pressure, affording free-flowing solid **1b**. Catalysts with different amounts of loaded policresulen (**1a**, **1c**, **1d**) were prepared in an analogous way.

2.2. Preparation of TiO_2-supported benzenesulfonic acid catalyst ***1f***

Titanium oxide (5 g) and toluene (100 mL) were added to a 250-mL round-bottomed flask equipped with magnetic stirring and a Dean-Stark apparatus. After 10 h of reflux, 4-hydroxybenzenesulfonic acid (3.87 g) dissolved in acetonitrile (7 mL) was added to the system and refluxed for another 16 h. At the end of the reaction, the solid was filtered, washed with ethanol (50 mL × 5) and dried under vacuum conditions, yielding catalyst **1f**. The ion exchange capacity of this catalyst was measured by titration. The obtained result was in good agreement with elemental analysis of the sulfur and carbon content.

Yanlong Gu *(Huazhong University of Science and Technology)* ***received the Catalysis Rising Star Award in 2012****, which was presented by The Catalysis Society of China. Professor Yanlong Gu received his Ph.D. degree in Physical Chemistry from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, in 2005. He then started a journey as post-doc researcher in the group of Prof. Shu Kobayashi, The University of Tokyo, Japan, and the group of Prof. Francois Jerome, The University of Poitiers, France. Since October 2008, Yanlong Gu become a professor in School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology. In 2009, he received an award of New Century Excellent Talents in Chinese Universities. He has a broad interest in homogeneous and heterogeneous catalysis, organic synthesis, biomass valorization and utilization. His research efforts are focusing on (1) catalysis with acids and ionic liquids; (2) green organic reactions for organic synthesis; and (3) eco-efficient processes based on utilization of biomass. He has published more than 80 research papers, 4 reviews in international peer review journals, and contributed two book chapters in the fields. H index of his publications reached 31 in 2015. Currently, he is a board member of Current Organic Chemistry and a committee member of ionic liquid division, Chemical Industry and Engineering Society of China.*