Microporous and Mesoporous Materials 196 (2014) 277–283

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Preparation and catalytic properties of RuSalen-functionalized periodic mesoporous silicas

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ARTICLE INFO

Article history:
Received 19 January 2014
Received in revised form 16 May 2014
Accepted 20 May 2014
Available online 29 May 2014

Keywords:
PMOs
RuSalen
Cyclohexene
Oxidation
Functionalization

ABSTRACT

A new approach was employed to prepare metal complex-functionalized periodic mesoporous silica. This approach mainly involves the following three steps, that is, chloromethylation of –C_6H_4– sites in the framework of PMOs into active –$C_6H_3CH_2Cl$–, amination of PMOs via reacting –$C_6H_3CH_2Cl$– with piperazine and covalent attachment of RuSalen by refluxing the aminated PMOs in RuSalen ethanol solution. The obtained hybrid material was characterized with XRD, N_2 sorption, FTIR, diffuse reflectance UV–vis spectroscopy, TEM and ^{13}C MAS NMR techniques. It shows higher activity and stability in the oxidation of cyclohexene with H_2O_2 than the corresponding RuSalen functionalized SBA-15 prepared by the similar method except that the introduction of active –C_3H_6Cl was achieved by grafting 3-chloropropyltriethoxysilane on SBA-15.

1. Introduction

Periodic mesoporous organosilicas (PMOs) synthesized with bridged silsesquioxanes as silica sources is an emerging family of novel porous materials that combine organic and inorganic chemical properties in a composite material [1,2]. Up to date, various organic molecules, including methylene [3], ethylene [4], phenylene [5], biphenylene [6], thiophene [7] and cyclic CH_2 [8], have been bridged in the framework of PMOs. However, most of the bridging organic groups are chemically inert, and hence, lack feasible functionalities for applications. To overcome this shortage, introduction of active sites into PMOs has attracted a lot of attention. Thus, many heteroatoms such as Al [9], Ti [10,11], Cr [12], and V [13,14], and functional groups, e.g. sulfonic acid [15,16], amines [17] and metal complexes [18,19], have been incorporated in the pore wall or in the nanopores of PMOs through combination with organic bridging groups, and the functionalized PMOs generally shows higher catalytic activity than its mesoporous silica counterparts because of its improved surface hydrophobicity [10,12,14–16,19]. In addition, the framework organic moieties in PMOs make it possible to construct highly functionalized and controlled chemical environments with uniform and stable mesopore spacing by chemical modification [20]. In this context, the bridging phenylene groups in Ph-PMOs have been sulfonated or aminated with fumed sulfuric acid or HNO_3–H_2SO_4 and $SnCl_2$–HCl [20,21]. In addition, arenetricarbonyl complex was incorporated in the Ph-PMOs framework by simply treating it with $Cr(CO)_6$ or $Mo(CO)_6$ vapor (CVD method) [22]. A complicated modification of framework ethenylene groups was reported by Nakajima and coworkers, in which phenylene sulfonic acid species were generated via Diels–Alder reaction. The obtained materials exhibited high and stable catalytic activities in esterification reaction [23]. Regardless of the significant progress made, the functionalization of PMOs with transition metal complexes by means of bridging organic moieties has not been paid much attention.

Actually, this is an effective way for the heterogenization of homogeneous catalysts. The generally used methods for immobilization of metal complexes on porous hosts mainly include: (i) ship-in-a-bottle encapsulation of metal complexes in zeolite cavities [24]; (ii) functionalization of mesoporous hosts with silylation agents, and subsequently immobilization of metal complexes on their surfaces [25,26]; and (iii) anchor of metal complexes on the mesoporous hosts by the ion-exchange, the adsorption or the electrostatic attraction method [27]. However, the transition metal complex immobilized by the above methods often shows lower activity due to its configuration distortion and/or its limited accessibility to substrate molecules, or its poor stability resulting in the leaching of metal species into the reaction medium. Therefore, it is necessary and imperative to develop a new strategy for immobilization of metal complexes on porous materials. Here, a new approach involving the chemical modification of bridging phenylene groups in PMOs and subsequent covalent combination with

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http://dx.doi.org/10.1016/j.micromeso.2014.05.022
1387-1811/

RuSalen is reported. The prepared material shows high catalytic activity and stability for the oxidation of cyclohexene with aqueous H_2O_2 solution.

2. Experimental

2.1. Chemicals

All the analytical-grade chemicals were used as purchased without further purification. 1,4-Bis(triethoxysilyl)benzene (BTEB), Pluronic P123, (3-chloropropyl)trimethoxysilane, piperazine and cyclohexene were purchased from Aldrich. Tetraethyl orthosilicate (TEOS) and the other routine reagents were bought from Tianjin Chemical Reagent Corporation.

2.2. Preparation

2.2.1. Synthesis of –C_6H_4– bridged mesoporous silicas

In a typical batch, 1 g of P123 was dissolved in 100 mL of 1 M aqueous HCl solution. After complete dissolution, a mixture of 3.15 g of TEOS and 2.89 g of 1,4-BTEB was dropwise added to the P123 solution under vigorous stirring condition. The reaction mixture was stirred at room temperature (RT) for 2 h and 40 °C for 20 h. Then, it was heated to 80 °C and kept at this temperature for 6 h under static condition. The powder product was filtered, thoroughly washed with deionized water and dried at RT. The surfactant was extracted by refluxing the sample in an ethanol/HCl solution (0.12 M). The obtained sample was denoted as Ph-PMOs.

2.2.2. Synthesis of SBA-15

4.8 g of P123 was first dissolved in 150 mL of 2 M aqueous HCl solution. Then, 10.2 mL of TEOS was added under vigorous stirring condition. The reaction mixture was stirred at 40 °C for 20 h, and then transferred to a Teflon-lined autoclave for static crystallization at 100 °C for 24 h. The product was filtered, thoroughly washed with deionized water and dried at RT. The surfactant was removed by the same method as that employed for Ph-PMOs.

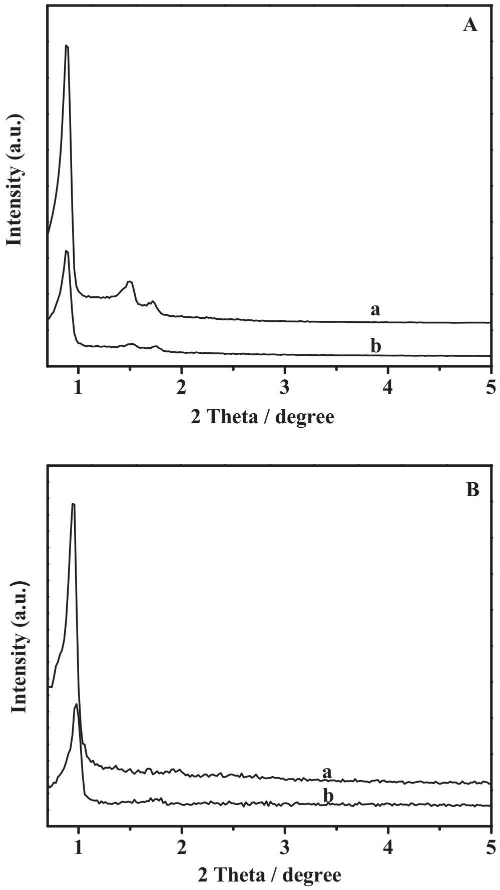
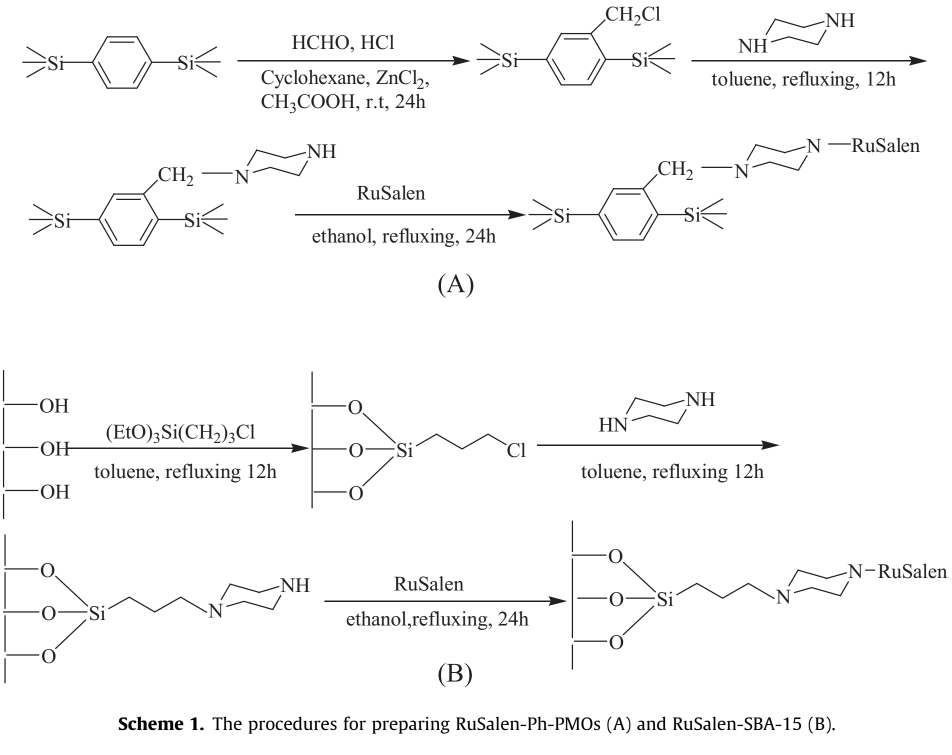


Fig. 1. (A) XRD patterns of (a) SBA-15 and (b) RuSalen-SBA-15 and (B) XRD patterns of (a) Ph-PMOs and (b) RuSalen-Ph-PMOs.

2.2.3. Chloromethylation of framework phenylene groups of Ph-PMOs

1.5 g of Ph-PMOs, 4 g of $ZnCl_2$, 3 mL of acetic acid, 20 mL of cyclohexane and 10 mL of formaldehyde aqueous solution (37%)



Scheme 1. The procedures for preparing RuSalen-Ph-PMOs (A) and RuSalen-SBA-15 (B).