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Mesoporous solid acid catalysts of sulfated zirconia/SBA-15 derived from a vapor–induced hydrolysis route

Binbin Chang, Jie Fu, Yanlong Tian, Xiaoping Dong*

Department of Chemistry, School of Sciences, Zhejiang Sci-Tech University, 5 Second Avenue, Xiasha Higher Education Zone, Hangzhou 310018, China

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ABSTRACT

Mesoporous solid acid catalyst, sulfated zirconia loaded mesoporous silica, was reported here by a facile vapor–induced hydrolysis method. The zirconia precursor of $Zr(SO_4)_2$ was introduced into the mesopore of SBA-15 by impregnation, and then hydrolyzed under a NH_3/H_2O vapor ambience to form a thin zirconia layer coated on the pore surface of SBA-15, which was followed by the sulfation of SO_4^{2-} ions with calcinations. The catalyst was characterized by powder X-ray diffraction, N_2 adsorption–desorption, transmission electron microscopy and infrared spectroscopy, and the results indicated that the catalyst retained the ordered mesoporous structure, high BET surface area, connected pore channel without pore blocking and a 0.7 nm thin layer of sulfated zirconia coated on the pore surface. This super acid catalyst showed much higher activity compared with those of unloaded sulfated zirconia and sulfated zirconia loaded SBA-15 hydrolyzed by ammonia aqueous solution, for catalyzing the esterification reaction of oleic acid and methanol. The experimental parameters including the molar ratio of reactants and reaction time were optimized, and approximately 70% of acid sites were remained after three cycles.

1. Introduction

Acid catalysts are essential for various chemical reactions in the industrial production. Although traditional liquid acid catalysts exhibit high catalytic activities, their shortcomings, including the difficulty in recycling and corrosiveness, are manifest. Solid acid catalysts having interconnected system of large pores, a moderate to strong acid sites and a hydrophobic surface would be ideal for eliminating corrosion, separation and environmental problems [1]. Among numerous solid acid catalysts, sulfated zirconia offers a number of advantages such as strong acidity and stability, which has been extensively exploited in solid acid catalysis [2–6].

Conventional synthetic methods to prepare sulfated zirconia include the impregnation of zirconium hydroxide with sulfate ions followed by further heat treatment, or directly calcining zirconium sulfates. However, the catalytic activities of these materials were drastically limited on account of their low surface area and non-porosity. One approach to improve the catalytic activity is to introduce mesopores into solid acid catalysts, which possess high surface area and porous structure for accommodating relative large molecules. Many researchers have devoted themselves to the development of mesoporous zirconia with high surface area and uniform pore structure [7–15]. Nevertheless, the amorphous pore wall of surfactant-templated mesoporous zirconia will crystallize under high temperatures (>773 K), which leads to the collapse of porous structure [16]. An alternative strategy is to load sulfated zirconia on heat stable mesoporous materials, such as mesoporous silica.

The unique characteristics and the advanced properties exhibited by mesoporous silica make it to be ideal supports in developing of a new class of sulfated zirconia catalysts. Continuing breakthroughs have been made to obtain well dispersed sulfated zirconia loaded mesoporous silica materials, including SO_4^{2-}/ZrO_2 prepared in a post-synthesis grafting method followed by calcinations or a single step by using triblock copolymer surfactant as the structure directing agent [17,18]. However, the blocking of pores would be observed as enhancing the loading amount of metal oxides [19], which would result in a serious degeneration of their catalytic activities due to the difficulty in mass transfer. Therefore, increasing the loading amount meanwhile keeping pore channel connecting is vital to prepare sulfated zirconia loaded mesoporous silica with a high catalytic activity.

Obviously, coating sulfated zirconia on the pore surface as a thin layer, instead of nanoparticles, can effectively eliminate the pore blocking. By controlling the hydrolysis rate of zirconia precursors in the pore channel, high loading amount of zirconia have been successfully coated on the pore surface of mesoporous silica without pore blocking [19]. Herein, we reported the synthesis of sulfated zirconia coated mesoporous silica catalyst by a NH_3/H_2O vapor-induced hydrolysis (VIH) method. Such mesoporous solid

* Corresponding author. Tel.: +86 571 86843228; fax: +86 571 86843653.
E-mail address: xpdong@zstu.edu.cn (X. Dong).

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