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Full Length Article

One-pot synthesis of ZrMo-KIT-6 solid acid catalyst for solvent-free conversion of glycerol to solketal

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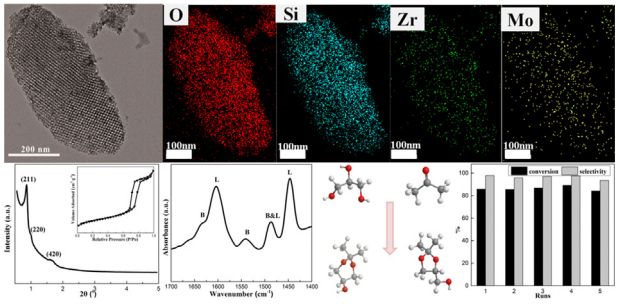
GRAPHICAL ABSTRACT



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ABSTRACT

A series of zirconium and molybdenum species incorporated into ordered mesoporous silicate KIT-6 (ZrMo-KIT-6) materials were designed and synthesized from a one-pot hydrothermal method. The influences of Zr and Mo contents and calcination temperature in ordered mesoporous structure and existing states of introduced Zr and Mo species were systematically researched by SXRD, N_2-physisorption, TEM, elemental mapping, TG-DSC, WXRD, Raman, UV and XPS techniques. The results indicated that Zr and Mo species were incorporated into the skeleton of material as designed and existed as a highly dispersed state when the content was below 7%. Also, the ZrMo-KIT-6 material had ordered mesostructure with excellent textural properties, and the ordered mesoporous pores and highly dispersed Zr and Mo species could be preserved even treated at 700 °C. The acidic properties of ZrMo-KIT-6 materials were tested by NH_3-TPD and FT-IR spectra of adsorbed pyridine techniques. Owing to the excellent acidic property, the ZrMo-KIT-6 material was employed as a solid acid catalyst for acetalization of glycerol with acetone. The ZrMo-KIT-6(5–700) material showed optimal catalytic performance (conversion of glycerol was 85.8% and selectivity of solketal was 97.8%), and there was no obvious decline in catalytic performance even after five cycles.

1. Introduction

These years, with the rapid development of global economy, the non-renewable petroleum-based fossil fuels have been largely consumed, and the problems about energy and environment have become the research focus. Biodiesel, as an attractive new and clean energy source, exhibits enormous advantages compared with the traditional diesel fuel based on petroleum. Principally, biodiesel is nontoxic and renewable, and it also can reduce the emission of CO_2 [1,2]. Besides, the emission of pollutants, such as sulfur, CO, poly aromatics, hydrocarbons, particulate matter and smoke can be largely decreased. Therefore, the substitution of biofuel has been encouraged in many

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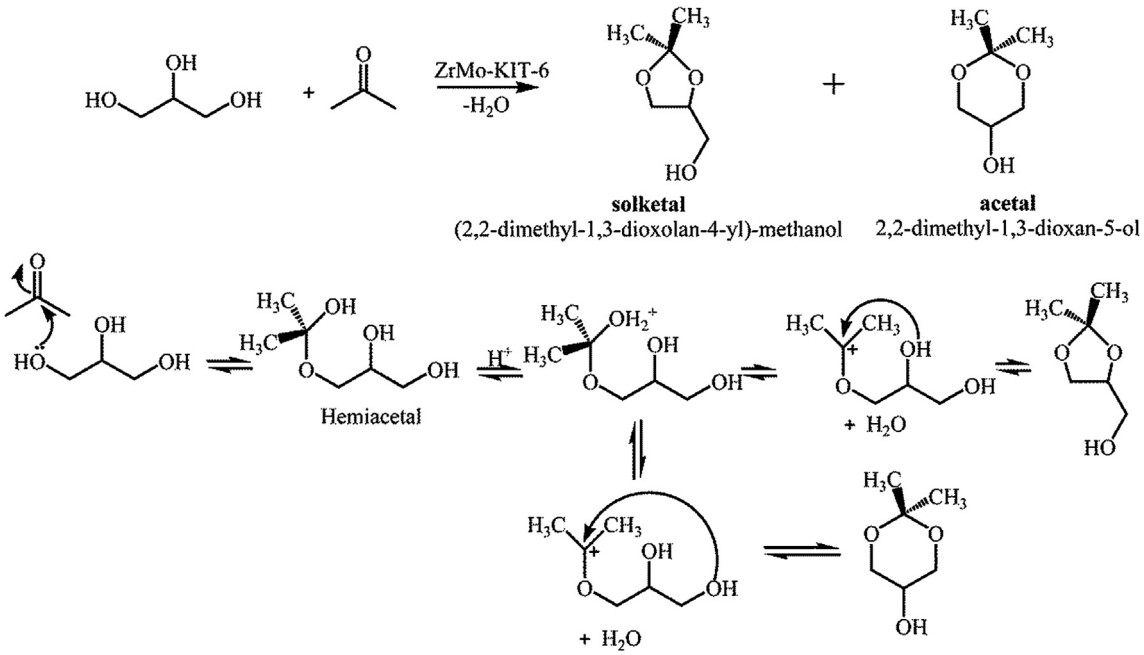

Scheme 1. Acetalization reaction of glycerol with acetone.

countries [3–6].

Typically, biodiesel is obtained from the transesterification of vegetable oils or fats with methanol. In this reaction, approximately 10% of glycerol is gained as a by-product [7]. Therefore, how to efficiently use the glycerol is valuable to be investigated [8–10]. Several reactions for glycerol conversion into value-added products have been reported, such as oxidation of glycerol to dihydroxyacetone and hydroxypyruvic acid [11,12], dehydration of glycerol to acrolein [13,14], acetylation of glycerol to triacetin [15,16], esterification of glycerol to glycerol carbonate [17,18] and acetalization of glycerol to cyclic products [19–21]. In these reactions, the acetalization of glycerol with acetone to solketal (five-membered cyclic product (2,2-dimethyl-1,3-dioxolan-4-yl)-methanol) and acetal (six-membered cyclic product 2,2-dimethyl-1,3-dioxan-5-ol) (as shown in Scheme 1) has attracted many attentions for petrochemical, pharmaceutical and polymer industry because the products can be used as fuel additive, solvent and plasticizer [22–26].

For the acetalization of glycerol and acetone, typical homogeneous acids such as HCl, H_2SO_4 and H_3PO_4 have been generally used. However, from the viewpoint of environmental problems, solid acid catalysts, which are easy separation, little corrosion and environmentally friendly should be encouraged. Different kinds of solid acid catalysts, such as heteropolyacids, zeolites, modified carbon materials and complex metal oxides are explored in the acetalization of glycerol. For instance, Chen et al. employed $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ heteropolyacids supported on mesoporous silica for acetalization under mild conditions [27]. Venkatesha et al. used dealuminated BEA zeolite for selective synthesis of five-membered cyclic acetal from glycerol under ambient conditions [28]. Gonçalves et al. synthesized acidic carbon-based catalysts from biodiesel waste, and about 80% of glycerol conversion and 95% of solketal selectivity were reached [29]. Titanate nanotubes and Mo and W-promoted SnO_2 solid acids were investigated as heterogeneous catalysts for the transformation of glycerol to value-added products in an eco-friendly manner [30,31].

In the field of solid acid catalyst, WO_x-ZrO_2 and MoO_x-ZrO_2 materials have been widely studied, due to their excellent catalytic property and stability. However, the formation of acid site in these two materials usually needs a high temperature calcination process, which might largely decrease the surface area of catalyst and number of active sites [32,33]. Therefore, it is important to assure the amount of active sites even treated at high temperature.

Ordered mesoporous Si-based materials have drawn many attentions in the domain of catalyst, owing to their superior textural properties and thermal stability [34,35]. For examples, the mesoporous silica-ceria-zirconia composite was employed as a support for the methane dry reforming of carbon dioxide at high temperature (700 °C). The Si-based solid acid catalysts, such as Zr-KIT-5, SO_4^{2-}/Zr-KIT-6 and WO_x/SBA-15 have been reported and used in many reactions, such as Friedel-Crafts alkylation, green diesel production from esterification of oleic acid and cellobiose hydrolysis reaction [36–38]. The abundant pore structure could provide plentiful accessible active sites for the molecules.

In this paper, we design to combine the MoO_x-ZrO_2 active sites and KIT-6 materials, and get an excellent solid acid catalyst for acetalization of glycerol with acetone. The Zr and Mo elements are directly incorporated into the KIT-6 framework through a one-pot method. In addition, the influence of Zr and Mo contents and calcination temperature in mesoporous structure are investigated systematically by small-angle X-ray diffraction (SXRD), N_2-physisorption, transmission electron microscopy (TEM) and thermogravimetric-differential scanning calorimetry (TG-DSC) characterizations, and the existing states of introduced Zr and Mo species are carefully researched by wide-angle X-ray diffraction (WXRD), elemental mapping, Raman, UV and X-ray photoelectron spectroscopy (XPS) techniques. The acidic properties of obtained materials are studied by the temperature programmed desorption of ammonia (NH_3-TPD) and FT-IR spectra of adsorbed pyridine methods. Finally, the gotten ZrMo-KIT-6 materials are taken as a solid acid catalyst in acetalization of glycerol with acetone, and the detailed results and discussion are given as follows.

2. Experimental section

2.1. Synthesis of ZrMo-KIT-6

ZrMo-KIT-6 materials with different ZrMo/Si ratios were designed and synthesized following the typical synthesis procedure described for KIT-6 material [39,40]. In a general synthesis, 2.0 g of triblock copolymer Pluronic P123 ($(EO)_{20}(PO)_{70}(EO)_{20}$, Aldrich) was dissolved in 70 mL of 0.5 M HCl solution at 35 °C. Following the complete dissolution of P123, 2.0 g of *n*-butanol was introduced and stirred for another 1 h. Finally, 8.4 g of tetraethyl orthosilicate (TEOS, Sinopharm