



Room temperature synthesis of solketal from acetalization of glycerol with acetone: Effect of crystallite size and the role of acidity of beta zeolite



Pandian Manjunathan, Sanjeev P. Maradur, A.B. Halgeri, Ganapati V. Shanbhag*

Materials Science Division, Poornaprajna Institute of Scientific Research (PPISR), Bidalur Post, Devanahalli, Bangalore 562110, Karnataka State, India

ARTICLE INFO

Article history:

Received 21 July 2014

Received in revised form

16 September 2014

Accepted 21 September 2014

Available online 30 September 2014

Keywords:

H-Beta zeolite

Crystallite size

Acidity

Glycerol

Solketal

ABSTRACT

Room temperature synthesis of solketal from acetalization of glycerol with acetone was carried out over various types of Brønsted solid acid catalysts in the liquid phase. Among the catalysts screened, H-Beta zeolite showed the best performance in less time period with 86% glycerol conversion and 98.5% selectivity to solketal. The chemical and structural properties of modified and unmodified beta catalysts were studied by X-ray diffraction, AAS, SEM, NH₃-TPD and FTIR-pyridine adsorption. The H-Beta catalyst with lower crystallite size gave better conversion and solketal selectivity compared to H-Beta with higher crystallite size. The effect of acidity of the catalyst on acetalization of glycerol was studied by modified beta catalysts of varying acidities. Glycerol conversion decreased with decrease in total acidity of beta catalysts. Strong to weak acidity ratio of the catalysts was found to have a direct correlation with catalyst performance.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Due to medium-term depletion of fossil fuel reserves and growing scarcity of fossil hydrocarbon, researchers around the world are motivated to search for an alternative source of energy. Experts considered biomass as the only sustainable source of future energy and it has the potential to displace the petroleum feedstock. Among which vegetable oil is one such source used for the synthesis of biodiesel from transesterification reaction. Glycerol is obtained as a byproduct during transesterification of vegetable oil which accounts for one tenth of every gallon of biodiesel produced. Increasing availability of glycerol has made it an inexpensive and abundant raw material to synthesize value-added chemicals and hence it is a challenge for researchers to utilize this waste glycerol to transform into commercially important products. The major direct utilities of this compound are in cosmetics, personal care products and soaps. However, these sectors may not be able to consume tons of glycerol produced from biodiesel plants. Moreover, it is well known that glycerol can be converted into chemicals by catalytic processes namely, acetalization, oxidation, hydrogenation, esterification, etherification, transesterification, dehydration, oligomerization and pyrolysis. Hence, there is a great

commercial interest to design green and chemoselective catalysts for these processes. Due to the presence of three hydroxyl groups, glycerol exhibits versatile and high chemical reactivity, and can be converted into value-added chemicals and fuel additives [1–4].

Glycerol reacts with ketone, aldehyde and alcohol forming ketals, acetals and ethers respectively. These products can be used as fuel additives which improve the quality of diesel by reducing the emission of carbon monoxide and unregulated aldehydes [5]. Glycerol reacts with benzaldehyde to produce 5-hydroxyl-2-phenyl-1,3-dioxane which can be used as a starting material for the production of 1,3-propanediol [6]. The ketalization of glycerol with acetone yields solketal and acetal. Solketal can be used as a cold flow improver to enhance cold weather performance of diesel fuel which also reduces its viscosity. Solketal blended with regular gasoline in 1, 3 or 5 vol% decreases the gum formation and also it enhances the octane number up to 2.5 points [7,8].

Heterogeneous catalysts are preferred for these reactions due to several advantages over conventional homogeneous catalysts like high recyclability, thermal stability and process friendly nature. Among which, zeolites [9], supported metal oxides [10], hydrotalcite [11], sulphonic functionalized resins and mesoporous silica [9,12] are used for glycerol transformation reactions. Zeolite is an aluminosilicate which plays an important role in petrochemical industries due to its acidic sites, high thermal stability and shape selectivity toward desired molecules with tunable pore size [13]. Among different forms of zeolite, nanocrystalline

* Corresponding author. Tel.: +91 27408552; fax: +91 23619034.
E-mail address: shanbhag@poornaprajna.org (G.V. Shanbhag).

zeolite plays a vital role in catalytic reactions because of high surface area, lower diffusion path length and more exposed active sites. Nanocrystalline zeolite beta and Y showed higher activity than microcrystalline zeolite beta and Y toward palm oil cracking for the production of biofuels [14]. N-alkylation of amines with alcohols over nanosized zeolite beta was found to be more active than bulk beta due to shorter path length in nanosized form [15].

Acetalization of glycerol with acetone was studied with various acid catalysts such as amberlyst-15, montmorillonite K-10, zeolite beta, HUSY, zeolite ZSM-5, *p*-toluenesulfonic acid [9], SO₃H-SBA-15 [12], sulphonated carbon-silica composite [16] and silica-induced heteropolyacids [17]. However, these catalysts are reported to be active at reaction temperatures higher than 65 °C. Among them, amberlyst-15 was found to be more active than all the other solid acid catalysts because of the presence of sulphonic functionality and high amount of acidity. Silva et al. reported acetalization of glycerol with acetone using beta zeolite at 70 °C with high catalyst concentration of 37.5 wt% with respect to glycerol which gave glycerol conversion of 95% in 60 min [9].

The aim of this work is to explore a suitable solid acid catalyst for room temperature synthesis of solketal from acetalization of glycerol with acetone. Solid acid catalysts differing in properties (nature of acidity, porosity, etc.) are screened to find out an efficient catalyst for this reaction. Two decisive catalyst properties *viz.* crystallite size and acidity of zeolite beta are correlated with catalytic activity. Reaction parameters such as catalyst concentration and mole ratio are also optimized.

2. Experimental

2.1. Materials

Glycerol, acetone, methanol, isopropanol, sodium nitrate, sodium hydroxide and copper nitrate trihydrate were purchased from Merck India Ltd. NH₄-Beta zeolite (SAR=25) was obtained from Nankai, China (here onwards Beta-1). NH₄-ZSM-5 zeolite (SAR=23) and H-Y zeolite (SAR=30) were purchased from Zeolyst International. H-Mordenite zeolite (SAR=16) was kindly donated by Sud-Chemie India Pvt. Ltd. Montmorillonite-K10, tetraethylorthosilicate and solketal (as a GC standard) were purchased from Sigma-Aldrich. Amberlyst-15, ammonium molybdate and fumed silica were purchased from Alfa Aesar. Oxalic acid was purchased from Nice Chemicals, Kochi, India.

2.2. Catalyst preparation

The ammonium form of zeolites were calcined in flowing air at 540 °C for 4 h with the ramp rate of 5 °C min⁻¹ to convert ammonium form into protonic form. The obtained samples were labeled as H-Beta-1, H-ZSM-5 and H-Mordenite.

2.2.1. Preparation of dealuminated H-Beta-1 zeolite

Mild dealumination was performed by stirring 4 g of H-Beta-1 with 80 ml of two different concentrations (0.01 M and 0.05 M) of oxalic acid solution at room temperature for 1 h and the samples were filtered, washed with distilled water and dried at 120 °C for 12 h. Then the dealuminated samples were calcined in flowing air at 540 °C for 4 h at a heating rate of 1 °C min⁻¹ [18]. The obtained samples were labeled as H-Beta-1-A and H-Beta-1-B respectively.

2.2.2. Preparation of copper ion exchanged Beta-1 zeolite

The copper ion exchanged H-Beta-1 zeolite was prepared by refluxing 4 g of H-Beta-1 with 60 ml of 0.1 M aqueous copper nitrate trihydrate solution for 12 h. It was then filtered, washed with distilled water and dried at 120 °C for 12 h. The obtained zeolite was

calcined at 540 °C for 4 h under static air at a heating rate of ramp 5 °C min⁻¹. The obtained sample was labeled as Cu/H-Beta [19].

The Na form of beta catalyst was prepared by stirring 10 g of H-Beta-1 with 100 ml of 0.5 M aqueous sodium nitrate solution at 80 °C for 4 h, followed by filtration, washing with distilled water and drying at 120 °C for 2 h. The above procedure was repeated to convert the protonic form into Na-form of beta zeolite. Furthermore, copper ion exchange of Na-Beta was carried out by stirring 5 g of Na-Beta with 75 ml of 0.1 M aqueous copper nitrate trihydrate solution at 80 °C for 4 h and then it was filtered, washed with distilled water and dried at 120 °C for 2 h. The above procedure was repeated twice for maximum copper ion exchange. The obtained catalyst was calcined at 540 °C for 4 h under static air at a heating rate of 5 °C min⁻¹ and was designated as Cu-Beta.

2.2.3. Synthesis of H-Beta zeolite of higher crystallite size

H-Beta zeolite of higher crystallite size (Beta-2) was synthesized under template free condition with modification of the reported method [20]. The synthesis was carried out in a 100 ml teflon-lined stainless-steel autoclave with the following procedure. A 0.18 g of sodium aluminum oxide was dissolved in 37.8 ml of distilled water, followed by the addition of 1.56 g of sodium hydroxide. After stirring for 30 min, 3.6 g of fumed silica was added to the above solution followed by the addition of 12.2 ml distilled water into the mixture with continued stirring. After stirring for 10 min, 0.18 g of H-Beta-1 zeolite was added into the mixture for seeding and stirred for 5 min. The resulted mixture was then sealed and allowed to crystallize in an oven at 120 °C for 7 days. The obtained solid product was filtered, washed with distilled water and dried at 80 °C for 12 h. The obtained Na-form of beta zeolite was converted to H-form by ion exchange treatment using 0.5 M NH₄NO₃ (20 ml of 0.5 M NH₄NO₃ solution/g of zeolite) under reflux condition for 12 h. Then the sample was filtered, washed with distilled water, dried at 80 °C and calcined at 450 °C for 5 h at a heating rate of 1 °C min⁻¹. The ion exchange procedure was further repeated twice to remove the sodium ions present in beta zeolite. The obtained sample was labeled as H-Beta-2.

Other Brønsted solid acid catalysts like 10 wt% molybdenum oxide supported on silica (MoO₃/SiO₂) and cesium salt of phosphotungstic acid Cs_{2.5}H_{0.5}PW₁₂O₄₀ (CsHPW) were prepared from the reported literature [21,22].

2.3. Catalyst characterization

Powder X-ray diffraction patterns of unmodified and modified beta catalysts were recorded with Bruker D2 phaser X-ray diffractometer using Cu K α radiation ($\lambda = 1.542 \text{ \AA}$) with high resolution Lynxeye detector. All the samples were scanned in the 2 θ range of 5–60° with step size of 0.02°/s. Crystallinity of unmodified and modified beta catalysts was evaluated from the integrated intensity of the signal at 2 $\theta = 22.4^\circ$ [23].

The Brønsted and Lewis acidic sites of unmodified and modified beta catalysts were investigated by pyridine adsorption study using FT-IR (alpha-T, Bruker). The self supported wafers of the catalysts were prepared by a pellet press instrument. The wafer was then calcined at 500 °C for 1 h, cooled and placed in a desiccator to maintain moisture free condition. Then the samples were saturated with pyridine and heated at 150 °C for 1 h to remove physisorbed pyridine. FTIR spectra were recorded in absorbance mode in the wavelength range from 1400 to 1600 cm⁻¹. The spectrum obtained after pyridine treatment was subtracted with that of pyridine untreated sample to get the peaks only due to pyridine–acid interaction.

The acidity of unmodified and modified beta catalysts were determined by temperature programmed desorption of ammonia

Download English Version:

<https://daneshyari.com/en/article/65249>

Download Persian Version:

<https://daneshyari.com/article/65249>

[Daneshyari.com](https://daneshyari.com)