



Solvent-free aminolysis of aliphatic and aryloxy epoxides with sulfated zirconia as solid acid catalyst

Arpan K. Shah^{a,b}, Manish Kumar^{a,b}, Sayed H.R. Abdi^{a,b,*}, Rukhsana I. Kureshy^{a,b}, Noor-ul H. Khan^{a,b}, Hari C. Bajaj^{a,b}

^a Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), A Unit of Council of Scientific and Industrial Research (CSIR), G. B. Marg, Bhavnagar 364021, Gujarat, India

^b Academy of Scientific and Innovative Research (AcSIR), CSIR-CSMCRI, Bhavnagar, Gujarat, India

ARTICLE INFO

Article history:

Received 10 February 2014

Received in revised form 16 August 2014

Accepted 19 August 2014

Available online 30 August 2014

Keywords:

Sulfated zirconia

Aminolysis of epoxide

Solid acid catalyst

β -Amino alcohols

Aryloxy and aliphatic epoxides

ABSTRACT

Single-step and two-steps synthetic procedure for the synthesis of sulfated zirconia (SZ) was developed, which were calcined at 500, 600 and 700 °C and characterized by various physico-chemical methods such as PXRD, FTIR, surface area, microanalysis, NH₃-TPD and DRIFT analysis. These SZ materials were then employed as solid acid catalysts for the aminolysis of different aliphatic/aromatic terminal, aryloxy and meso epoxides with aromatic and aliphatic amines under ambient conditions. Amongst the catalyst prepared, **SZ-2-600** prepared in two-steps and 600 °C calcined was found to be the most efficient catalyst to give β -amino alcohols in up to 98% yield and >99% regioselectivity. The SZ catalyst was successfully recycled and reused up to six catalytic runs with intact efficiency.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Aminolysis of epoxide (AoE) is one among the most atom efficient methods to produce racemic and non-racemic β -amino alcohols, which are commonly found in natural and synthetic molecules of commercial importance [1–6]. A real issue with AoE is regioselectivity, as either carbon of a non-symmetric epoxide can react with the nucleophile to produce regioisomers (Fig. 1). Plenty of literature is available on AoE that include non-catalytic [7–10] and catalytic approaches [5,6,11–43] with moderate to high success. Noticeable results in AoE were achieved with Brønsted [11–15] and Lewis acids [16–21] under homogeneous condition and with solid acid materials [21–42] under heterogeneous condition with moderate to excellent yield and selectivity of β -amino alcohols. A closer look into the structure of β -amino alcohol of commercial importance would reveal that structural variations (substituents) on motifs (Fig. 1) originating from epoxide as well as amine are prevalent. Therefore, a catalyst which can perform

AoE effectively for variety of aliphatic and aryloxy epoxides with variety of aromatic and aliphatic amines is highly desirable and such efforts have been reported in the past with mixed success [5,6,9,14,18–21]. Here we report, synthesis of nano-sized sulfated zirconia (SZ) [40–51] having super acidity/high acid strength, hydrothermal stability as solid acid catalyst for AoE. As such SZ is a well-known solid acid catalyst for various commercially important organic transformations [40–47]. In fact SZ has been used in the AoE under solvent free condition by Negrón-Silva et al. [40] and under microwave irradiation and by Reddy et al. [41] in high yields but in later case the reaction took longer time. Das et al. [42] efficiently opened the epoxide ring with substituted indoles via C–C bond forming reaction using SZ catalyst. Recently, Pathare et al. [6] reported sulfated tungstate as potential solid acid catalyst for AoE of various epoxides with amines. However, in this case, catalyst preparation method required hazardous sulfonation source–ClSO₃H, chlorinated organic solvent and subambient reaction temperature (0–5 °C). Therefore, still there is a room to improve overall AoE process particularly in exploring wide variety substrate ranges, developing easily synthesizable and recyclable catalysts for commercial applications. It is well known in the literature that catalytic activity of SZ significantly depends upon its texture properties, use of zirconium precursor, sulfating agent, types of preparation method and activating temperature [43–51]. With this backdrop, we present here the synthesis of

* Corresponding author at: Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSIR-CSMCRI), A Unit of Council of Scientific and Industrial Research (CSIR), G. B. Marg, Bhavnagar 364021, Gujarat, India. Tel.: +91 0278 2567760; fax: +91 0278 2566970.

E-mail addresses: shrabdi@csmcri.org, raziabdi56@gmail.com (S.H.R. Abdi).

sulfated zirconia catalyst by single-step and two-steps preparation methods using zirconium *n*-propoxide ($Zr(OC_3H_7)_4$) as a source of zirconium and sulfuric acid as a sulfating agent. The resultant zirconia materials were calcined at different temperatures in order to achieve optimum catalytic activity. In single-step method, SZ materials were prepared by sol–gel process of Oh. et al. [46] with some modifications, where initially zirconium precursor was hydrolyzed followed by in situ sulfation of the sol–gel obtained was carried out by the addition of sulfuric acid. The solid obtained was dried at 120 °C to give solid sulfated zirconia catalyst henceforth known as **SZ-1-120**, which was further calcined at 500, 600 and 700 °C temperatures giving catalysts **SZ-1-500**, **SZ-1-600** and **SZ-1-700** respectively. In two-steps process, the method of Mishra et al. [47] was used, where in first step zirconium hydroxide was prepared by the hydrolysis of ($Zr(OC_3H_7)_4$) with ammonia followed by sulfation of zirconium hydroxide with sulphuric acid in second step. Drying of the resultant powder at 120 °C (**SZ-2-120**) and subsequent calcination at 500, 600 and 700 °C temperatures furnished catalysts **SZ-2-500**, **SZ-2-600** and **SZ-2-700** respectively. As synthesized SZ materials were then employed as catalyst in AoE under solvent free condition at RT. Among the SZ materials used, **SZ-2-600**, prepared in two steps was found to have the best catalytic activity in terms of yield and selectivity of β -amino alcohols in short reaction time under solvent free condition at RT. The catalyst, **SZ-2-600** was also found to be effective for a variety of aliphatic cyclic or acyclic, aromatic and aryloxy epoxides with aliphatic/aromatic primary and secondary amines. Since in most of the cases product is either viscous liquid or solid, the catalyst after each catalytic cycle was easily recovered by filtration/centrifugation with an appropriate solvent then dried for reuse. The recovered catalyst showed no signs of loss in its performance even after six catalytic runs studied.

2. Experimental

2.1. Materials and methods

X-ray Powder Diffraction studies were carried out using X'pert Mpd, PHILIPS and Empyrean XRD systems from PANAnalytical (Japan) within 2θ range of 10–65° using $CuK\alpha_1$ ($\lambda = 1.54060 \text{ \AA}$) at ambient temperature. Surface area and pore size distribution of SZ materials were determined by nitrogen adsorption–desorption method at 77.35 K by using ASAP 2020 instrument, Micromeritics Inc., USA. All SZ samples were activated at 393 K under vacuum just prior to measurements. FT-IR spectra were recorded on Perkin Elmer Spectrum GX spectrophotometer (USA) using KBr window. JEOL, JEM-2100 microscope (Japan) was used for transmission electron microscopic (TEM) analysis at 200 kV using carbon coated copper grid. For this SZ material was dispersed in ethanol and a drop of the dispersion was placed on copper grid to determine the textural properties of the materials. Elemental analysis was done on CHNS analyzer “ElementarVario MICRO Cube (Germany)”. Diffuse Reflectance FT-IR spectroscopy (DRIFT) was used to determine the Brønsted/Lewis (B/L) acid ratio of pyridine adsorbed SZ samples using Perkin Elmer GX equipped with DRIFT Selector accessory (Graseby Specac, P/N 19900 series). The spectra were recorded at room temperature (27 °C), 150 °C and 250 °C after holding at each temperature for 10 min, thus allowing sufficient time for pyridine desorption. NMR spectra were recorded on a Bruker F113V spectrometer (200 MHz and 500 MHz, Switzerland) using TMS as an internal standard. GC analysis was done on GC-2010AF APC instrument (Shimadzu, Japan) using BP-5 capillary column (SGE, USA). The aminolysis products were purified by flash chromatography using silica gel 60–120 and 100–200 mesh purchased from s. d. Fine Chem. Ltd., India. Zirconium *n*-propoxide and various cyclic, acyclic, aryloxy and *meso* epoxides, aromatic and aliphatic amines

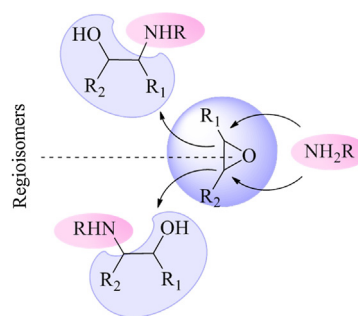


Fig. 1. Regioselectivity in AoE reaction.

(substituted amines) were purchased from Aldrich chemicals and used as received (USA).

2.2. Synthesis of sulfated zirconia (SZ) catalysts

Sulfated zirconia materials were synthesized by using single-step and two-step processes as follows.

2.2.1. Single-step process for the synthesis of SZ catalysts

The single-step process [46] was slightly modified wherein $Zr(OC_3H_7)_4$ (10 mL, 70% in *n*-propanol) was diluted with 12.5 mL of *n*-propanol (up to 30%) to which 1 N aqueous solution of H_2SO_4 (20 mL) was added drop-wise under vigorous stirring within 30 min and the resultant reaction mixture was stirred for another 6 h. The white solid thus obtained was filtered and dried at 120 °C (**SZ-1-120**) followed by calcination at 500, 600 and 700 °C for 4 h giving catalysts **SZ-1-500**, **SZ-1-600** and **SZ-1-700** respectively.

2.2.2. Two-steps synthesis of SZ catalysts

In the two-steps process [47], hydrolysis of ($Zr(OC_3H_7)_4$) (30 wt.% solution in *n*-propanol) was carried out by using aqueous ammonia. At pH 9–10 $Zr(OH)_4$ gel was formed which was dried at 110 °C. In the second step, sulfation of $Zr(OH)_4$ dried powder was carried out by using 15 mL/g solution of 1 N H_2SO_4 . White solid thus obtained was filtered and dried at 120 °C (**SZ-2-120**) overnight and calcined at 500, 600 and 700 °C giving catalysts **SZ-2-500**, **SZ-2-600** and **SZ-2-700** respectively.

2.2.3. Synthesis of zirconia- ZrO_2

For the sake of comparison, unpromoted zirconia- ZrO_2 was prepared by the calcination of zirconium hydroxide at 350 °C for 4 h.

2.3. Catalytic procedure for aminolysis of epoxide (AoE) using SZ catalyst

A solid SZ catalyst (20 mg), an epoxide (1 mmol) and an amine (1 mmol) were taken in a 5 mL screw capped vial and stirred magnetically for a given time period (monitored by GC or TLC) under solvent free condition at RT. On completion of the reaction, viscous liquid or solid product obtained was treated with methanol ($2 \times 3 \text{ mL}$) and centrifuged for the complete removal of organic compounds from the solid catalyst. The evaporation of solvent from the combined organic layers furnished the crude product. A small fraction of the crude product was directly injected to HPLC to find out the regioselectivity. The remaining portion of the crude mixture was purified by flash column chromatography (hexane/ethyl acetate, 80:20) to get the major regioisomer in pure form. The purified product was characterized by 1H and ^{13}C NMR analysis. The residue thus obtained from centrifugation was dried in air (2 h) and then at 200 °C for 3 h to get back the active catalyst (>97% recovery) for the next catalytic run.

Download English Version:

<https://daneshyari.com/en/article/39437>

Download Persian Version:

<https://daneshyari.com/article/39437>

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