Chinese Journal of Catalysis 38 (2017) 420–425

available at www.sciencedirect.com

ScienceDirect

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

Article (Special Column on Novel Catalysts for Energy and Environmental Issues)

Conversion of glycerol to acrolein by mesoporous sulfated zirconia-silica catalyst

Hirokazu Kobayashi [a], Shogo Ito [a,b], Kenji Hara [c], Atsushi Fukuoka [a,*]

[a] *Institute for Catalysis, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan*

[b] *Graduate School of Chemical Sciences and Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, Hokkaido 060-8628, Japan*

[c] *School of Engineering, Tokyo University of Technology, Hachioji, Tokyo 192-0982, Japan*

ARTICLE INFO

Article history:
Received 27 July 2016
Accepted 5 September 2016
Published 5 March 2017

Keywords:
Acrolein
Glycerol
Mesopore
Sulfated zirconia

ABSTRACT

A mesoporous sulfated zirconia-silica catalyst bearing only Brønsted acid sites converted glycerol to acrolein in 81% yield with 82% selectivity. Space time yield as high as 9.0 mmol h^{-1} g_{cat}^{-1} was achieved even at a low reaction temperature of 523 K. The catalytic activity and selectivity were higher than those of typical sulfated zirconia. It is proposed that the milder acidity due to dilution of zirconium species by silica and large pore size for faster diffusion contributed towards the better catalytic performance.

1. Introduction

Catalytic conversion of renewable biomass has attracted great attention for sustaining future demands of fuels and chemicals [1,2]. Triglyceride is a typical biomass resource, and its transesterification with methanol produces fatty acid methyl esters and glycerol [3–5]. The ester serves as a practical diesel fuel, whereas glycerol is so far a less valuable compound. Accordingly, the valorization of glycerol is essential to improve the overall efficiency of the process. A difficulty in glycerol utilization is the contamination of glycerol with the base used in transesterification process, but recently production of base-free glycerol has been realized using solid catalysts such as SCRO-80 [6]. Thus, base-free glycerol will become an attractive feedstock in chemical industry.

A promising derivative of glycerol is acrolein [7,8], which is a precursor to polyacrylate, pyridine, and pharmaceuticals. Solid acid catalysts can convert base-free glycerol to acrolein [7–21], and statistical analysis of the catalytic performance concludes that Brønsted acid site with moderate acid strength (typically H_0 = –3 ~ –8) is suitable for this reaction [22]. Therefore, it is reasonable that sulfated zirconia, a super acid (H_0 < –12), provides low yield of acrolein (in most cases less than 30%) [13–17]. Nonetheless, in this work, we have found that a non-uniform mesoporous sulfated zirconia-silica catalyst not only gives good yield of acrolein, but also works at relatively low temperature (523 K) among reported values (typically 573 K) [7,8].

2. Experimental

2.1. Preparation of catalysts

A mesoporous zirconia-silica, denoted MZS, was prepared

* Corresponding author. Fax: +81-11-706 9139; E-mail: fukuoka@cat.hokudai.ac.jp

This work was supported by Grant-in-Aid for Research Activity Start-up (KAKENHI, 21860004) and for Young Scientists (KAKENHI, 26709060) from Japan Society for the Promotion of Science (JSPS).
DOI: 10.1016/S1872-2067(16)62564-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 3, March 2017

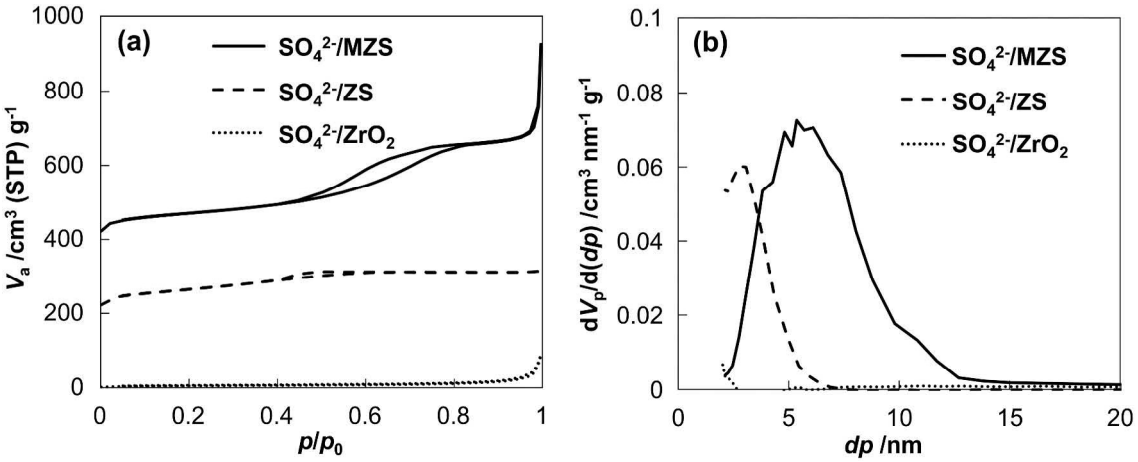

Fig. 1. N_2 adsorption isotherms (a) (baseline shifted) and BJH plots (b) of sulfated zirconia derivatives.

by following the literature procedure [23]. Si/Zr atomic ratio was set at the lowest value (4.5) necessary to obtain a mesoporous structure. MZS (1.00 g) was dispersed in 10 mL of water, and 10 mL of 260 mmol L^{-1} $(NH_4)_2SO_4$ aq. (corresponding to 20 wt% SO_4^{2-} in the catalyst, molar ratio of SO_4^{2-}/Zr = 1.02) was added to the mixture. After drying up the mixture in vacuo for 18 h, the resulting white solid was calcined in air at 773 K for 4 h to obtain sulfated MZS (SO_4^{2-}/MZS). The lower than usual calcination temperature (ca. 873 K) was employed to gain surface area and to decrease the acid strength [24]. Energy dispersive X-ray (EDX, Shimadzu EDX-720) analysis gave an atomic ratio of S:Zr:Si = 18:14:68, which was similar to that used in the preparation (16:15:69). Other instruments used for characterization were N_2 adsorption (Bel, Belsorp mini), small angle X-ray scattering (SAXS; Rigaku, RINT, Cu K_α), transmission electron microscope (TEM; JEOL, JEM-2100F), X-ray diffraction (XRD; Rigaku, MiniFlex, Cu K_α), UV-visible spectrometer (JASCO, V-650), infrared spectrometer (IR, Perkin-Elmer, Spectrum 100, mercury cadmium telluride detector), and ammonia temperature programmed desorption (NH_3-TPD; Bel, BELCAT A, mass spectrometer).

Sulfated zirconia-silica (SO_4^{2-}/ZS) was prepared by a similar manner but in the absence of surfactant to avoid formation of mesopores. We also prepared simple sulfated zirconia (SO_4^{2-}/ZrO_2) using a reference zirconia catalyst from the Catalysis Society of Japan (JRC-ZRO-2).

2.2. Catalytic dehydration of glycerol

Conversion of glycerol to acrolein was conducted in a Pyrex vertical fixed-bed flow reactor with an internal diameter of 7 mm under atmospheric pressure. Catalyst (100 mg) mixed with inactive silica (100 mg) was suspended by quartz sand on quartz wool in the reactor. The reactor was heated to 523 K under He flow (5 mL min^{-1}). Aqueous solution of glycerol (10 wt%, d = 1.02 g cm^{-3}, LHSV = 10 mL h^{-1} g_{cat}^{-1}) was fed for 2 h into quartz wool fixed at upper part of the catalyst bed to be vaporized steadily. After finishing the feed, He gas was further streamed for 0.5 h to completely vaporize glycerol remaining in the reactor. Unreacted glycerol and water-soluble products were collected in a cold trap containing aqueous hydroquinone (30 mmol L^{-1}) attached at bottom of the reactor, where collection efficiency of acrolein was over 95% in our test. The solution was analyzed with a high-performance liquid chromatograph (HPLC; Shimadzu, LC10-AT*VP*, Shodex Sugar SH-1011 column) equipped with a reflective index detector and a UV detector. Gas chromatographs equipped with thermal conductivity detector (GC-TCD; Shimadzu, GC-8A, Gaskuropack 54 column) and flame ionization detector (GC-FID; Shimadzu, GC-14B, DB-WAX column) were also used to quantify the products.

3. Results and discussion

3.1. Characterization of catalysts

Textural property of catalysts was characterized by N_2 adsorption at 77 K. The isotherm of SO_4^{2-}/MZS was type-IV curve with a hysteresis loop (Fig. 1(a)), indicating a bottleneck shaped mesoporous structure. Brunauer-Emmet-Teller (BET) specific surface area (260 m^2 g^{-1}, Table 1) was slightly lower

Table 1
Characterization of catalysts.

Catalyst	BET specific surface area (m^2 g^{-1})	Mesopore volume (cm^3 g^{-1})	Acid amount [a] (mmol g^{-1})	Ratio of acid site (%)	
				$110 \leq \Delta H_{des}$ [b] < 160	$160 \leq \Delta H_{des}$ [b]
SO_4^{2-}/MZS	260	0.40	0.34	85	15
SO_4^{2-}/ZS	180	0.12	0.27	78	22
SO_4^{2-}/ZrO_2	45	0.02	0.26	69	31

[a] Acid site with ΔH_{des} [b] of 110–200 kJ mol^{-1}. [b] Ammonia desorption enthalpy /kJ mol^{-1}.