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

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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 $H_0 = -3 \sim -8$) 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

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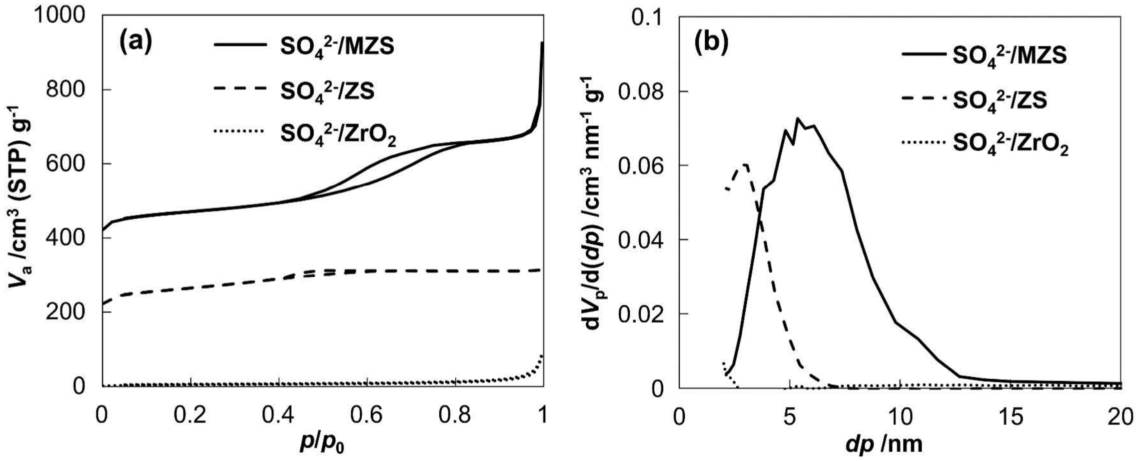

Fig. 1. N_2 adsorption isotherms (a) (baseline shifted) and BJH plots (b) of sulfated zirconia derivatives.

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 *Kα*), transmission electron microscope (TEM; JEOL, JEM-2100F), X-ray diffraction (XRD; Rigaku, MiniFlex, Cu *Kα*), 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 (m² g⁻¹)	Mesopore volume (cm³ g⁻¹)	Acid amount [a] (mmol g⁻¹)	Ratio of acid site (%)	
				$110 \le \Delta H_{des}$ [b] < 160	$160 \le \Delta H_{des}$ [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}.

than similar materials reported previously (Si/Zr = 4–5, SO_4^{2-} 5–7 wt%, 290–320 m² g⁻¹ [23]) due to higher content of SO_4^{2-} in our material (20 wt%). The Barrett-Joyner-Halenda (BJH) plot exhibited a broad distribution of pore size from 2 to 13 nm (Fig. 1(b)), which showed that the material had a non-uniform mesoporous structure. Mesopore volume of SO_4^{2-}/MZS was 0.40 $cm^3\ g^{-1}$ as shown in Table 1. SO_4^{2-}/ZS had a slightly lower surface area (180 $m^2\ g^{-1}$) than SO_4^{2-}/MZS, and the volume of mesopores (0.12 $cm^3\ g^{-1}$) was obviously smaller. Hence, this sample is useful to evaluate the effect of mesopores on other physicochemical property and catalytic performance. Surface area of SO_4^{2-}/ZrO_2 was significantly lower (45 $m^2\ g^{-1}$), but it is common for sulfated zirconia (24–98 $m^2\ g^{-1}$) [25]. As seen in the BJH plot, SO_4^{2-}/ZrO_2 had no mesopores.

Spectroscopy and microscopy further clarified the mesoporous structure of SO_4^{2-}/MZS. SAXS gave only a small peak at 0.8° with *d*-spacing of 11 nm, corresponding to (100) of *p6mm* structure (Fig. 2(a)). TEM depicted both ordered mesoporous structure and the collapsed mesopores (Fig. 3). In the ordered structure, width of zebra pattern (11 nm) was the same as the *d*-spacing of (100) plane determined by SAXS. Consequently, SO_4^{2-}/MZS is a non-uniform mesoporous material composed of ordered structure and collapsed regions.

Powder XRD pattern was measured to elucidate wall structure of SO_4^{2-}/MZS, giving a broad diffraction peak at 2θ = 20°–40° (Fig. 2(b)). In this range, silica gives a peak at 23° as confirmed by XRD analysis of mesoporous silica SBA-15. In addition, tetragonal zirconia provides peaks at 30° and 35° (JCPDS #50-1089). Assuming that the broad signal can be divided into the three diffraction peaks, deconvolution with Gauss function well reproduced the real experimental data. The Scherrer's equation gave a crystallite size of tetragonal ZrO_2 (0.7 nm) that was smaller than two unit cells, indicating very low crystallinity of the zirconia species. UV-vis diffuse reflectance spectrum (UV-DRS) of SO_4^{2-}/MZS showed a strong absorption peak at 207 nm and a weak broad peak at 300 nm (Fig. 4). The former one is derived from eight-coordinate zirconium species, which is characteristics of both amorphous and tetragonal ZrO_2 [26,27]. The latter peak is assignable to defects such as oxygen vacancies [27].

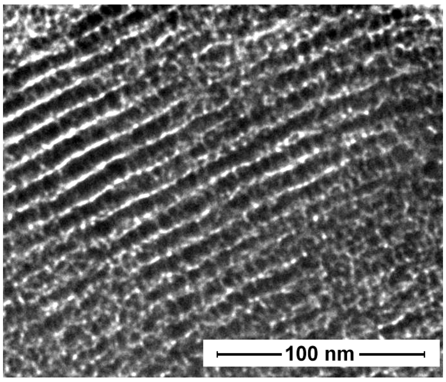

Fig. 3. TEM image of SO_4^{2-}/MZS.

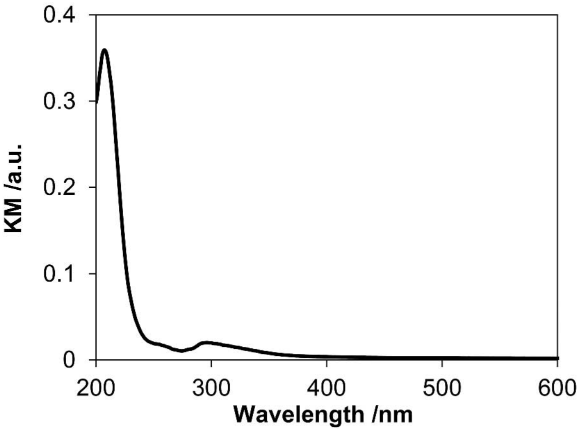

Fig. 4. UV-DRS of SO_4^{2-}/MZS.

Brønsted and Lewis acidity of the catalysts were analyzed, as it is known that Brønsted acid is more selective for the conversion of glycerol to acrolein. Pyridine adsorption with diffuse reflectance IR Fourier transform (DRIFT) spectroscopy is use-

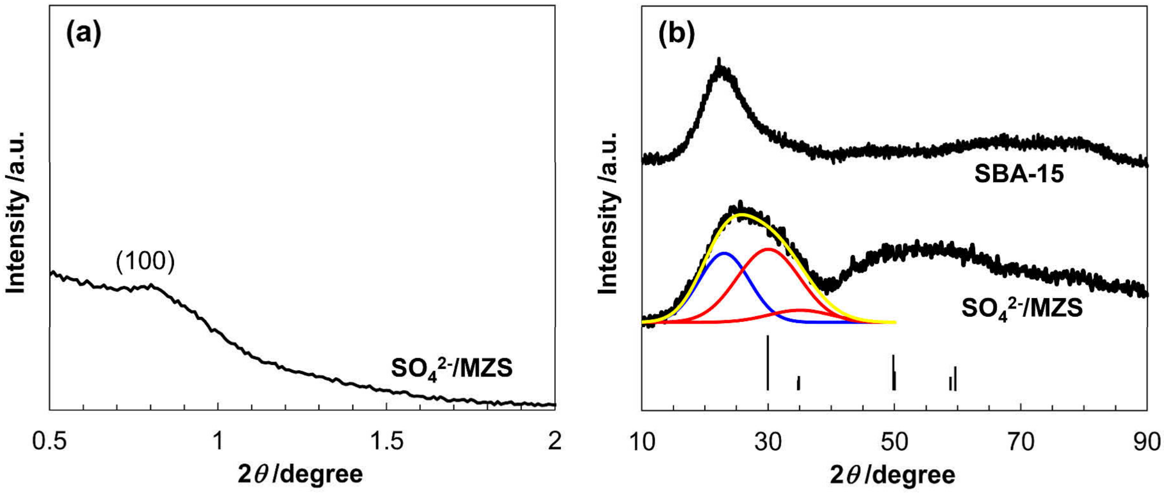

Fig. 2. SAXS (a) and XRD (b) patterns of prepared samples. Vertical lines in (b) indicate position of major diffraction peaks for tetragonal zirconia. Color lines show deconvolution.

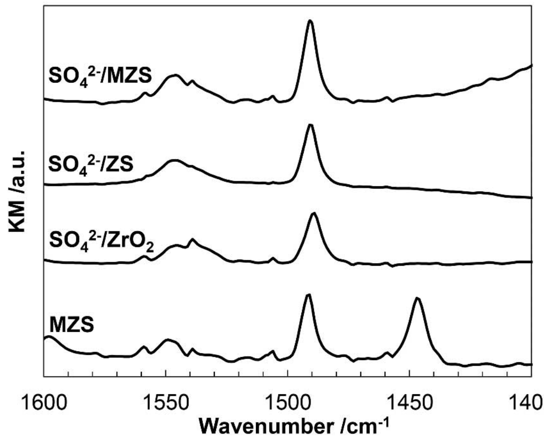

Fig. 5. DRIFT difference spectra before and after pyridine adsorption.

ful to distinguish Brønsted and Lewis acid sites. Brønsted acid sites give two absorption peaks at ca. 1550 and 1490 cm^{-1}, whereas Lewis ones at 1490 and 1450 cm^{-1} in the measurement [28]. Pyridine adsorption on SO_4^{2-}/MZS provided two peaks at ca. 1550 and 1490 cm^{-1} but not at 1450 cm^{-1} (Fig. 5), indicating that the material mainly has Brønsted acid sites. SO_4^{2-}/ZS and SO_4^{2-}/ZrO_2 also gave peaks at 1550 and 1490 cm^{-1}. The selective formation of Brønsted acid sites is due to high loading of sulfate (20 wt%), as it is known that sulfated zirconia with low loading of sulfate ($\leq$ 5 wt%) has Lewis acid sites [25]. It should be noted that MZS contains Lewis acid sites that are lost after loading of large amount of sulfate.

NH_3-TPD measurement was performed to determine acid amount and acid strength (Table 1). SO_4^{2-}/MZS gave a broad desorption profile from 390 to 800 K, which was converted to desorption enthalpy of NH_3 (ΔH_{des}) by a theoretical curve fitting method [29]. In this analysis, we focused on the acid sites with $\Delta H_{des} \geq 110$ kJ mol^{-1} (corresponding to $H_0 \leq -3$), since weaker acids ($H_0 > -3$) do not work in the conversion of glycerol at low temperature [22]. Number of acid sites with $\Delta H_{des} \geq 110$ kJ mol^{-1} was 0.34 mmol g^{-1}. The fraction of moderate acid sites (ΔH_{des} = 110-160 kJ mol^{-1}) was 85% and that of superacid sites ($\Delta H_{des} \geq 160$ kJ mol^{-1}) was 15%. SO_4^{2-}/ZS and SO_4^{2-}/ZrO_2 had similar amounts of acid sites (0.27 and 0.26 mmol g^{-1}, respectively), but fraction of superacid was increased to 22% for SO_4^{2-}/ZS and 31% for SO_4^{2-}/ZrO_2. Since formation of superacid on sulfated zirconia requires crystalline domain of zirconia [30], it is reasonable that SO_4^{2-}/ZrO_2 possesses the highest amount of superacid due to no dilution of zirconia by silica. In contrast, SO_4^{2-}/MZS has the lowest amount of superacid owing to dispersion of zirconia on a larger surface area of mesoporous structure.

Table 2
Dehydration of glycerol by solid catalysts at 523 K^a.

Catalyst	Conversion (%)	Yield of product (C%)		
		Acrolein (selec.)	Hydroxyacetone	CO and CO_2
None	11	0 (0)	0	0
SO_4^{2-}/MZS	99	81 (82)	6.4	1.3
MZS	72	29 (40)	3.0	0.9
SO_4^{2-}/ZS	91	63 (69)	0.4	0.1
SO_4^{2-}/ZrO_2	66	43 (65)	4.3	0
$FePO_4$^{b}	35	18 (51)	0	0.3

^{a} Catalyst 100 mg diluted with silica 100 mg, 10% glycerol/water LHSV = 10 mL h^{-1} g_{cat}^{-1}, carrier gas He 5 mL min^{-1}. ^{b} Prepared under hydrothermal conditions [12].

3.2. Conversion of glycerol to acrolein

Dehydration of glycerol was carried out at 523 K (Table 2), where the temperature was lower than that of previous reports (ca. 573 K). Glycerol was fed for 2 h with a syringe pump, and carrier gas flow was continued for additional 0.5 h to completely vaporize glycerol. The reaction without catalyst gave only 11% conversion of glycerol under the mild condition and no acrolein was produced. SO_4^{2-}/MZS gave 99% conversion of glycerol and 81% carbon-based yield of acrolein with 82% selectivity. This result gives one of the highest space time yields (STY; 9.0 mmol g^{-1} h^{-1}) despite the low temperature [8]. Turnover number (TON) of acid site was 53. Other identified products were hydroxyacetone (6.4%), CO (1.1%), and CO_2 (0.2%). Accordingly, the carbon balance was 90%, and the remaining 10% is unidentified products such as coke. Non-sulfated MZS was neither active nor selective for the production of acrolein (29% yield, 40% selectivity). This result shows that sulfate species are necessary for this reaction and presence of Lewis acid sites decreases selectivity. SO_4^{2-}/ZS provided 91% conversion of glycerol and 63% yield of acrolein (69% selectivity), and SO_4^{2-}/ZrO_2 provided 66% conversion of glycerol and 43% yield of acrolein (65% selectivity). We also tested $FePO_4$ as one of the best catalysts ever reported [12], which gave only 18% yield of acrolein with 51% selectivity under our mild conditions. These results show that SO_4^{2-}/MZS is a better catalyst giving high activity and selectivity at low temperature.

We hypothesize that high activity and selectivity of SO_4^{2-}/MZS is ascribed to its acidic and morphological character. The three catalysts, i.e., SO_4^{2-}/MZS, SO_4^{2-}/ZS and SO_4^{2-}/ZrO_2, have only Brønsted acid sites with similar concentration (0.26–0.34 mmol g^{-1}). However, the fraction of superacid increases in the following order: SO_4^{2-}/MZS (15%) < SO_4^{2-}/ZS (22%) < SO_4^{2-}/ZrO_2 (31%). Lower amount of superacid is beneficial for selective dehydration of glycerol [22]. Another advantage of SO_4^{2-}/MZS is mesoporous structure; SO_4^{2-}/ZS has

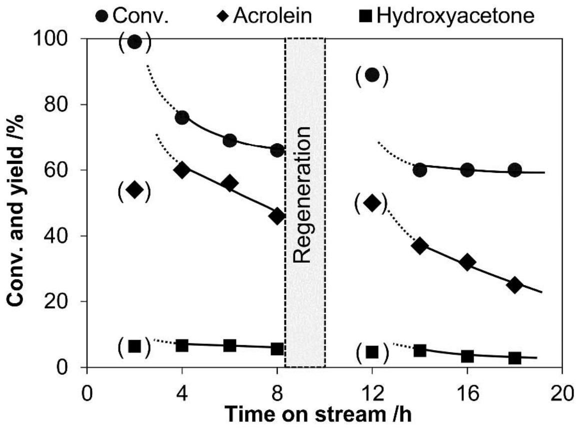

Fig. 6. Effect of time on stream and regeneration on conversion of glycerol over SO_4^{2-}/MZS.

smaller amount of mesopores and SO_4^{2-}/ZrO_2 possesses no mesopore. As a control in a literature, H-ZSM-5 predominantly has Brønsted acid sites with similar strength (ΔH_{des} = 135 kJ mol^{-1} [31]) to that of SO_4^{2-}/MZS, but the zeolite requires higher temperature to convert glycerol (588 K) [8]. Thus, we assume that good diffusion of glycerol in large pores benefits the catalytic performance.

Durability of SO_4^{2-}/MZS was studied in long time reaction (Fig. 6). Since the vaporization of glycerol takes time in this reaction, the first analysis (2 h) provides apparently higher conversion and lower yield of acrolein than real values. After the induction period, conversion of glycerol as well as yield of acrolein continuously decreased over 6 h, and color of the catalyst changed from off white to black. Therefore, the catalyst was once calcined at 673 K for 2 h in air, although coke was not completely removed. Catalytic activity was slightly recovered, but the yield of acrolein was again decreased with increasing the time on stream. The used catalyst had lower surface area (140 m^2 g^{-1}) and pore volume (0.30 cm^3 g^{-1}) than fresh one (260 m^2 g^{-1}, 0.40 cm^3 g^{-1}) due to presence of coke, while leaching of sulfur did not occur in the reaction as the trap aqueous solution was nearly neutral (pH = 4–5, corresponding to only 1% loss of S as H_2SO_4). Thus the deactivation is ascribed to covering of acid sites by coke, and we expect that complete removal of coke recovers the catalytic activity.

4. Conclusions

SO_4^{2-}/MZS catalyst selectively possesses Brønsted acid sites and converts glycerol to acrolein in 81% yield (STY = 9.0 mmol g^{-1} h^{-1}) and 82% selectivity at a low temperature of 523 K. We propose that milder acidity than sulfated zirconia and good diffusion of glycerol benefits the catalytic activity and selectivity. The catalyst is deactivated by coking without loss of sulfur, and therefore complete removal of coke may recover the catalytic activity.

Acknowledgment

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References

[1] A. Corma, S. Iborra, A. Velty, *Chem. Rev.*, **2007**, 107, 2411–2502.
[2] H. Kobayahsi, A. Fukuoka, *Green Chem.*, **2013**, 15, 1740–1763.
[3] A. F. Lee, J. A. Bennett, J. C. Manayil, K. Wilson, *Chem. Soc. Rev.*, **2014**, 43, 7887–7916.
[4] Z. Helwani, M. R. Othman, N. Aziz, J. Kim, W. J. N. Fernando, *Appl. Catal. A*, **2009**, 363, 1–10.
[5] T. M. Hsin, S. Chen, E. Guo, C. H. Tsai, M. Pruski, V. S. Y. Lin, *Top. Catal.*, **2010**, 53, 746–754.
[6] http://www.smartcatalyst.net/res/Biofuels%20smartcatalysts. pdf
[7] B. Katryniok, S. Paul, F. Dumeignil, *ACS Catal.*, **2013**, 3, 1819–1834.
[8] B. Katryniok, S. Paul, V. Bellière-Baca, P. Rey, F. Dumeignil, *Green Chem.*, **2010**, 12, 2079–2098.
[9] A. Corma, G. W. Huber, L. Sauvanaud, P. O'Connor, *J. Catal.*, **2008**, 257, 163–171.
[10] Q. B. Liu, Z. Zhang, Y. Du, J. Li, X. G. Yang, *Catal. Lett.*, **2009**, 127, 419–428.
[11] A. Alhanash, E. F. Kozhevnikova, I. V. Kozhevnikov, *Appl. Catal. A*, **2010**, 378, 11–18.
[12] J. Deleplanque, J. L. Dubios, J. F. Devaux, W. Ueda, *Catal. Today*, **2010**, 157, 351–358.
[13] L. Yang, J. B. Joo, Y. J. Kim, S. Oh, N. D. Kim, J. Yi, *Korean J. Chem. Eng.*, **2008**, 25, 1014–1017.
[14] L. Yang, J. B. Joo, N. D. Kim, K. S. Jung, J. Yi, *Korean J. Chem. Eng.*, **2010**, 27, 1695–1699.
[15] F. Cavani, S. Guidetti, L. Marinelli, M. Piccinini, E. Ghedini, M. Signoretto, *Appl. Catal. B*, **2010**, 100, 197–204.
[16] F. Cavani, S. Guidetti, C. Trevisanut, E. Ghedini, M. Signoretto, *Appl. Catal. A*, **2011**, 409–410, 267–278.
[17] G. Raju, P. S. Reddy, B. M. Reddy, *Open Catal. J.*, **2011**, 4, 83–87.
[18] C. García-Sancho, R. Moreno-Tost, J. Mérida-Robles, J. Santamaría-González, A. Jiménez-López, P. Maireles-Torres, *Appl. Catal. A*, **2012**, 433–434, 179–187.
[19] N. Pethan Rajan, G. S. Rao, V. Pavankumar, K. V. R. Chary, *Catal. Sci. Technol.*, **2014**, 4, 81–92.
[20] X. Z. Feng, Y. Yao, Q. Su, L. Zhao, W. Jiang, W. J. Ji, C. T. Au, *Appl. Catal. B*, **2015**, 164, 31–39.
[21] L. C. Liu, B. Wang, Y. H. Du, A. Borgna, *Appl. Catal. A*, **2015**, 489, 32–41.
[22] S. H. Chai, H. P. Wang, Y. Liang. B. Q. Xu, *Green Chem.*, **2007**, 9,

Graphical Abstract

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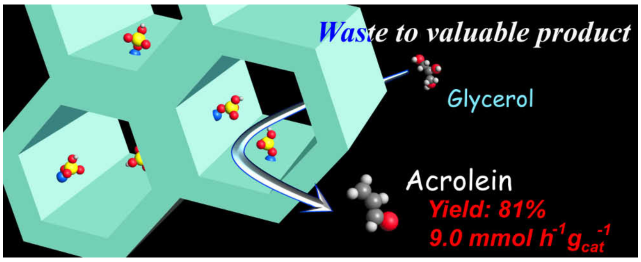

Mesoporous sulfated zirconia-silica catalyst bearing only Brønsted acid sites selectively converts glycerol to acrolein in gas phase at 523 K. Mild acid strength, absence of Lewis acid sites and large pore benefit the reaction.

1130–1136.

[23] Y. C. Du, S. Liu, Y. L. Zhang, F. Nawaz, Y. Y. Ji, F. S. Xiao, *Microporous Mesoporous Mater.*, **2009**, 121, 185–193.

[24] F. R. Chen, G. Coudurier, J. F. Joly, J. C. Vedrine, *J. Catal.*, **1993**, 143, 616–626.

[25] H. Matsuhashi, H. Nakamura, T. Ishihara, S. Iwamoto, Y. Kamiya, J. Kobayashi, Y. Kubota, T. Yamada, T. Matsuda, K. Matsushita, K. Nakai, H. Nishiguchi, M. Ogura, N. Okazaki, S. Sato, K. Shimizu, T. Shishido, S. Yamazoe, T. Takeguchi, K. Tomishige, H. Yamashita, M. Niwa, N. Katada, *Appl. Catal. A*, **2009**, 360, 89–97.

[26] E. Fernandez-López, V. Sanchez Escribano, M. Panizza, M. M. Carnasciali. G. Busca, *J. Mater. Chem.*, **2001**, 11, 1891–1897.

[27] D. Ciuparu, A. Ensuque, G. Shafeev, F. Bozon-Verduraz, *J. Mater. Sci. Lett.*, **2000**, 19, 931–933.

[28] G. Busca, *Phys. Chem. Chem. Phys.*, **1999**, 1, 723–736.

[29] N. Katada, T. Tsubaki, M. Niwa, *Appl. Catal. A*, **2008**, 340, 76–86.

[30] B. M. Reddy, M. K. Patil, *Chem. Rev.*, **2009**, 109, 2185–2208.

[31] K. Suzuki, T. Noda, N. Katada, M. Niwa, *J. Catal.*, **2007**, 250, 151–160.