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Simple one-pot synthesis of a mesoporous superacidic catalyst for the dehydration of glycerol to acrolein

Lina Yang*,‡, Ji Bong Joo,‡, Nam Dong Kim**, Kwang Seop Jung***, and Jongheop Yi**,†**

*Department of Petrochemical Engineering, Liaoning Shihua University, Fushun 113001, China
**School of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University, 599 Gwanak-ro, Gwanak-gu, Seoul 151-744, Korea
***GS Caltex Corporation, 104-4, Munji-dong, Yusung-gu, Daejeon 305-380, Korea
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Abstract−Mesoporous silica containing a ZrO_2/SO_4^{2-} superacid catalyst (SZS) was synthesized via a simple one-pot process. ZrO_2/SO_4^{2-} (SZ) was introduced during the synthesis of the SBA-15. When the molar ratio of Zr to Si was less than 0.37 : 1, a 2D-hexagonal pore structure was maintained. The superacidic SZ was successfully supported on mesoporous silica resulting in superacidity. The prepared SZS catalysts were applied to the conversion of glycerol to acrolein by dehydration and had considerable catalytic activity. The present study describes the first attempt to utilize mesoporous silica-supported superacid catalysts in the dehydration of glycerol to produce acrolein.

Key words: Mesoporous Silica, ZrO_2/SO_4^{2-}, One-pot Synthesis, Superacid, Acrolein

INTRODUCTION

Solid superacids are potentially useful as solid catalysts for chemical reactions that require very strong acid sites under mild conditions. Acidic sulfated zirconia (ZrO_2/SO_4^{2-}), a well known superacid, has attracted a great deal of attention because of its excellent catalytic activity and strong acidic properties [1,2]. Sulfated zirconia is highly useful in that it can be used to promote chemical reactions that involve proton transfer. However, its low surface area limits its applications [3].

An effective solution to the problem of the low surface area of sulfated zirconia would be to synthesize a supported catalyst using support materials which have a high surface area. For this purpose, a number of materials, including silica, alumina and a microporous zeolite, have been investigated as possible substrates [4-10]. Mesoporous materials such as MCM-x, SBA-x and CMK-x have advantageous characteristics, which include a high surface area, relatively large mesopores and a uniform pore structure resulting in low hindrance to diffusion. The use of mesoporous materials in supported ZrO_2/SO_4^{2-} catalysts would greatly expand the scope of applications of this superacid catalyst [3,11-16].

Hua et al. [14] demonstrated the use of mesoporous silica SBA-15 as a supporting material for a supported superacid catalyst. Other researchers also have reported the introduction of zirconia during the SBA-15 synthesis using a two-step procedure that requires two types of inorganic-organic complexes [17]. Although substantial progress has been made in the synthesis of a sulfated zirconia (ZrO_2/SO_4^{2-}) catalyst on a mesoporous silica support, the development of a new straightforward route is needed, because existing synthetic processes are complicated and time-consuming.

Glycerol is the one of the main by-products produced during the production of bio-diesel and it promises to become more widely available as the biodiesel industry continues to develop [18]. It is expected that the cost of glycerol will decrease soon with the current increase in biodiesel production. Thus, glycerol could be converted to high-value chemicals such as propandiols, glycerolcarbonate, acrolein and other compounds. Among the above chemicals, acrolein constitutes an important intermediate in the chemical industry, as it is frequently used as a raw material in the synthesis of acrylic acid and pharmaceuticals. The catalytic conversion of glycerol to acrolein via dehydration might be an important route to achieving the complete utilization of available glycerol [19]. Various acidic catalysts have been investigated in homogeneous and heterogeneous systems for the production of acrolein by the dehydration of glycerol [19-21]. Although many studies have investigated the use of various acidic catalysts in dehydration reactions, the activities of such catalysts are insufficient for the practical dehydration of glycerol. Thus, more efficient acidic catalysts, which function under mild conditions, are needed for this reaction.

In this work, we describe a method for the simple synthesis of superacid catalysts supported on mesoporous silica (SZS). The method is much simpler and less time-consuming than either the conventional impregnation method or the introduction method in which two types of inorganic-organic complexes are employed. The prepared catalysts (SZS-x) were examined as acidic catalysts for the dehydration of glycerol to acrolein. To our knowledge, this is the first report of the use of a mesoporous silica-supported superacid catalyst in the conversion of glycerol to acrolein.

EXPERIMENTAL

1. Catalyst Preparation

The unsupported superacid catalyst was synthesized by precipitation, followed by sulfated treatment as previously reported [14,22-

†To whom correspondence should be addressed.
E-mail: jyi@snu.ac.kr
‡The authors (Lina Yang and Ji Bong Joo) contributed equally to this work.

25]. The detailed procedure is as follows. $ZrOCl_2 \cdot 8H_2O$ was dissolved in D.I. water and precipitated with ammonia solution until the pH reached approximately ca. 9.5. The precipitate was washed with copious amount of D.I. water for the elimination of Cl^- ion. Then, the sample was treated with 1.0 N sulfuric acid, and filtered. The resulting precipitate was dried and calcined at 650 °C to give superacid catalyst (SZ).

The superacid catalyst supported on mesoporous silica was synthesized by a simple one-pot synthetic procedure. The detailed procedure is as follows: 8.48 g of tetraethoxysilane (TEOS, Fluka) was dissolved in a solution containing 4.0 g of P123 ($EO_{20}PO_{70}EO_{20}$, BASF) and 25.1 g of hydrochloric acid (35.0-37.0 wt%, Aldrich). The resulting mixture was stirred at 40 °C for 20 h and the calculated amount of $ZrOCl_2 \cdot 8H_2O$ was then added. The resulting solution was held at 100 °C for 24 h. and then neutralized by adding an ammonia solution until the pH reached approximately 9.5. The as-synthesized mesoporous silica containing Zr was treated with sulfuric acid (1.0 N). The resulting solid was isolated, dried at 100 °C and calcined at 650 °C to give a superacid catalyst supported on mesoporous silica (SZS). The samples are designated as SZS-(x), where x is the calculated molar ratio of Zr to Si in the samples (Zr : Si).

2. Characterization

Small angle X-ray scattering (SAXS) patterns were collected on a Bruker GADDS diffractometer. Large-angle powder X-ray diffraction (XRD) patterns were obtained using an X-ray diffractometer with Cu Kα radiation (MAC Science, M18XHF-SRA). N_2 adsorption-desorption isotherms were obtained with an ASAP 2010 sorption instrument. Pore size distributions were calculated by using the adsorption branch by the BJH method. Transmission electron microscopy (TEM) images were obtained on a JEM-2000EXII instrument. Fourier transform infrared spectra (FT-IR) were obtained on a MIDAC-M4000 spectrometer.

The temperature-programmed desorption of ammonia (NH_3-TPD) was carried out to investigate the acidic nature of the prepared catalysts. The samples were pretreated at 300 °C under an inert atmosphere for 1 h, then cooled to 30 °C and finally flushed with several pulses of ammonia. After saturation, the weakly adsorbed NH_3 was eliminated at 50 °C under vacuum for 1 h. The temperature was then increased linearly to 650 °C at a rate of 5 °C/min under an atmosphere of dry helium. The amount of NH_3 evolved from the sample was observed with a TCD detector.

3. Catalytic Activity

The test of the conversion of glycerol to acrolein was performed by reactive distillation under ambient pressure. The prepared catalyst (1.0 g) and glycerol (50 g, 99.0 wt%, Aldrich) were added to a flask equipped with a condenser. The reactor was heated to the desired temperature and a magnetic stirrer, operated at an agitation speed of 200 rpm, was used to create a slurry-type reaction mixture. The reaction products were analyzed by gas chromatography (GC, HP 5890) using an FID detector and a BP20 capillary column.

RESULTS AND DISCUSSION

SAXS patterns of the SZS catalysts are shown in Fig. 1(a). The SZS (0.19 : 1) and SZS (0.37 : 1) catalysts showed a single intense peak indicating a (100) diffraction. In addition, a weak (110) peak was present, indicating the presence of a highly ordered pore structure. These results constitute typical characteristics of the hexagonal pore arrangement of SBA-15 [14]. They also indicate that the SZS (0.19 : 1) and SZS (0.37 : 1) catalysts have hexagonal pore structure with a high orderness and that the pore structure could be maintained during the catalyst preparation process using the simple one-pot synthesis procedure. As the Zr : Si molar ratio increased, the intensity of the peaks decreased and eventually disappeared. These results indicate that the long-range pore orderness of the SZS samples was gradually destroyed with increasing amounts of Zr. However, the (100) and (110) peaks were most clearly observed when the molar ratio of Zr to Si was 0.37. This indicates that the mesostructure is not lost until the ratio of Zr to Si exceeds 0.37.

The large-angle XRD patterns of the prepared SZS (x) are shown in Fig. 1(b). In all catalysts, a broad diffraction peak at ca. 2θ=25° was observed indicating that the prepared mesoporous silica support is amorphous. Zirconia is known to exist in monoclinic, tetragonal, cubic phases or as an amorphous solid. The SZS (x) samples showed typical diffraction peaks for (111), (202) and (131) at 2θ= 30.4, 50.9 and 60.7°, respectively. This indicates presence of tetragonal zirconia on the prepared SZS (x) catalysts, which is required for superacid formation [26]. SZS (0.19 : 1), which contains a small amount of Zr species, showed the broadest and smallest diffraction peaks. The intensities of these peaks increased slightly with increas-

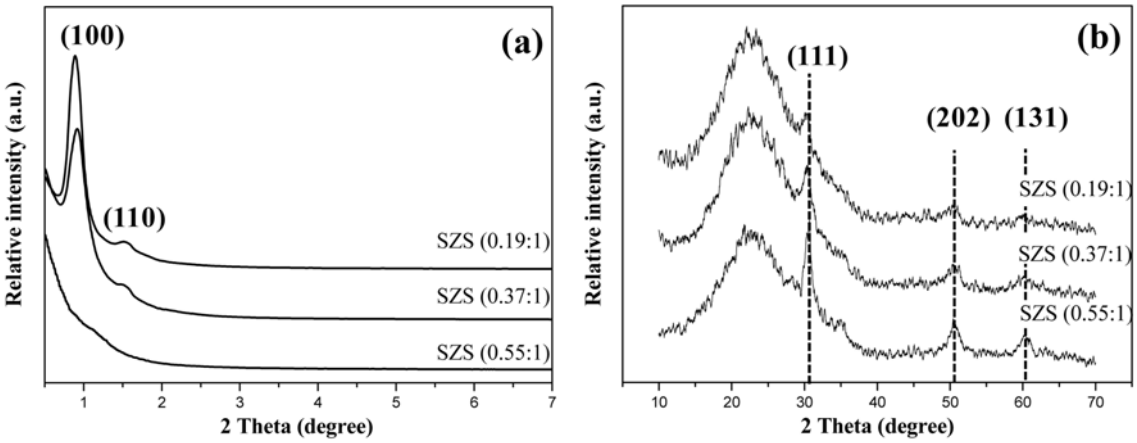

Fig. 1. (a) SAXS and (b) large angle XRD patterns of the prepared SZS (x) catalysts.

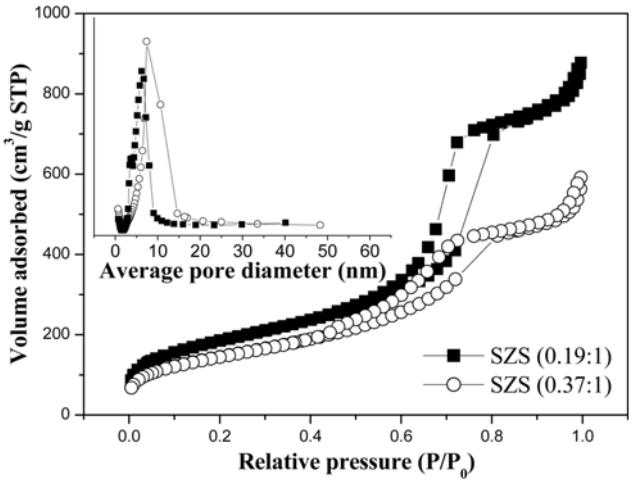

Fig. 2. N_2 adsorption-desorption isotherms and BJH pore distributions (inset image) of the prepared SZS (x) catalysts.

ing Zr : Si molar ratios. This indicates that the supported ZrO_2 crystals were conglomerated due to the presence of a high amount of Zr species on the support materials.

The pore structures of the SZS samples were investigated using N_2-adsorption techniques. N_2 adsorption-desorption isotherms and the corresponding pore size distributions for SZS (0.19 : 1) and SZS (0.37 : 1) are shown in Fig. 2. They show typical type IV isotherms with a hysteresis loop, indicating well-developed mesoporous structures that are similar to conventional mesoporous silica (MS). In addition, the prepared SZS (x) catalysts showed relatively narrow pore size distributions in the mesopore range (Fig. 2 inset image). SZS (0.19 : 1) in particular has well-developed box-type isotherm with an H1 hysteresis loop and a sharp pore size distribution peak centered at 6.2 nm. Its properties are almost identical to those of conventional mesoporous silica SBA-15. The detailed textural properties are listed in Table 1. The prepared SZS catalysts have relatively high surface area, pore volume and pore diameter in the mesopore range. SZS (0.19 : 1) exhibited a larger pore diameter, pore volume and surface area than SZS (0.37 : 1).

During the preparation of the SZS catalysts, the zirconia precursor causes the formation of a complex comprised of silica and the template to reorganize. This reorganization could suppress the formation of micropores and expand the mesopores. Therefore, it is possible that the large pore and partial deformation of pore structure would occur during the SZS preparation. In addition, a large amount of zirconia precursor could induce a larger-sized crystalline SZ on the surface or in the channel of the mesoporous silica

Table 1. Textural properties of the prepared SZS (x) catalysts

Samples	S_{BET} (m^2/g)	d_{pore} (Å)	V_{total} (cm^3/g)	a_0[a] (Å)	t[b] (Å)
SZS (0.19 : 1)	676.08	72.71	1.23	114.71	42.00
SZS (0.37 : 1)	529.51	59.10	0.78	110.68	51.58
SZ	113.00 [14]	-	-	-	

[a] a_0 was determined from the d_{100}, where $a_0=2/(3)^{1/2}d_{100}$
[b] $t=a_0-d_{pore}$

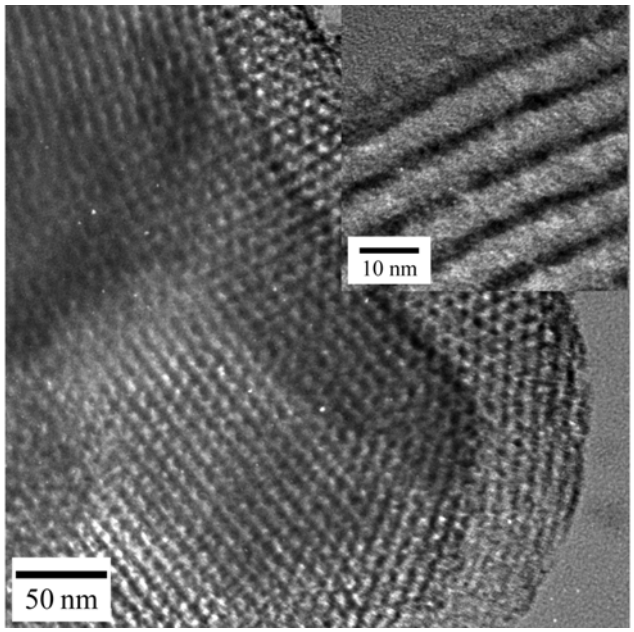

Fig. 3. TEM image of representative SZS (0.19 : 1) catalyst: (inset image: parallel image to the channel).

support. In the case of SZS (0.37 : 1), all values related to textural properties such as pore volume and surface area were less than those obtained for SZS (0.19 : 1) because of the bulky SZ crystalline nature of SZS (0.37 : 1), as evidenced by the XRD analysis shown in Fig. 1(b).

The size and shape of the pores in SZS (0.19 : 1) can be readily observed in TEM micrographs (Fig. 3). SZS (0.19 : 1) exhibited a regular, two-dimensional hexagonal array of uniform pores. The pore size was determined to be approximately 7.0 nm, consistent with values obtained from the BET measurements (Fig. 3 inset image). In contrast, SZS (0.55 : 1) did not show any ordered mesopore structure from other analysis and it would be difficult to observe ordered cylindrical pore structure. From the TEM analysis, it is noticed that the ordered mesoporous structure of mesoporous silica SBA-15 was

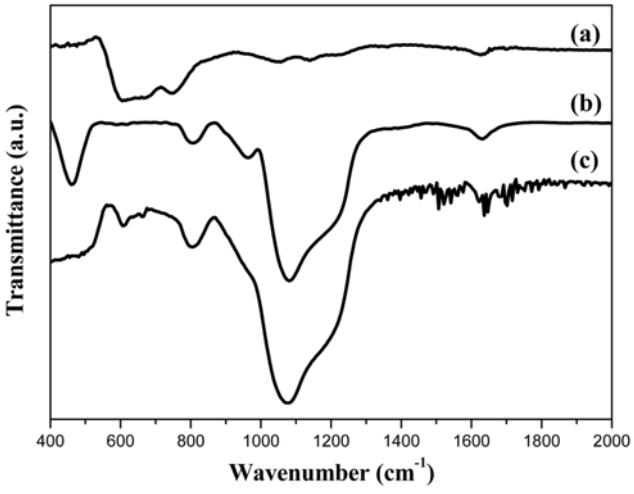

Fig. 4. FT-IR spectra of (a) unsupported bulk SZ, (b) mesoporous silica (MS) and (c) SZS (0.19 : 1).

maintained in spite of the presence of a zirconia precursor in case of SZS (0.19 : 1) catalyst. In addition, bulk ZrO_2/SO_4^{2-} particles were not observed in nano-channels during the TEM analysis, indicating that the crystalline, superacidic ZrO_2/SO_4^{2-} particles were highly dispersed on the support material. Based on the XRD and TEM results, it appears likely that the superacid ZrO_2/SO_4^{2-} (SZ) was well-dispersed in the mesoporous structure of the SZS (0.19 : 1) catalyst.

Fig. 4 shows representative FT-IR spectra of samples including (a) unsupported bulk SZ, (b) mesoporous silica (MS) and (c) SZS (0.19 : 1) in the region of 400-2,000 cm^{-1}. SZ showed the absorption peak in the range of 550-680 cm^{-1}, which is assigned to Zr-O stretching [27]. In addition, the IR spectrum of bulk SZ shows a pattern of three small bands related to SO_4^{2-} ions in a C_{2v} symmetry with $\nu 3$ at ca. 1,045, 1,137 and 1,220 cm^{-1} coordinated to zirconia [28]. An additional broad band at ca. 1,620 cm^{-1} was observed and can be attributed to O-H bonds of water molecules. MS has typical features of silica-based materials with a prominent shoulder at ca. 1,215 cm^{-1} and a main peak at ca. 1,075 cm^{-1}. In addition, there are two small peaks at ca. 955 and 800 cm^{-1}, and strong band at ca. 460 cm^{-1}, respectively. The strong band peaks at ca. 1,075 cm^{-1} are closely related to Si-O-Si asymmetric stretching vibration. Two small peaks at ca. 955 and 800 cm^{-1} are due to Si-(OH) stretching of terminal silanols and the symmetric stretching/in plane deformation of Si-O-Si bridges, respectively. The strong band at ca. 460 cm^{-1} is closely associated with the rocking of the Si-O-Si bridges [27]. SZS has similar IR spectrum to that of MS. A new adsorption band in the range of 550-680 cm^{-1} is also observed. It is noticed that this band is assigned to Zr-O stretching, which has identical properties with SZS. This provides a clear demonstration indicating that the ZrO_2/SO_4^{2-} was successfully supported on the mesoporous silica surface. However, other peaks related to the vibration of supported SO_4^{2-} ions could not be observed due to the strong band of Si-O-Si asymmetric stretching vibration in the range of 900-1,300 cm^{-1}.

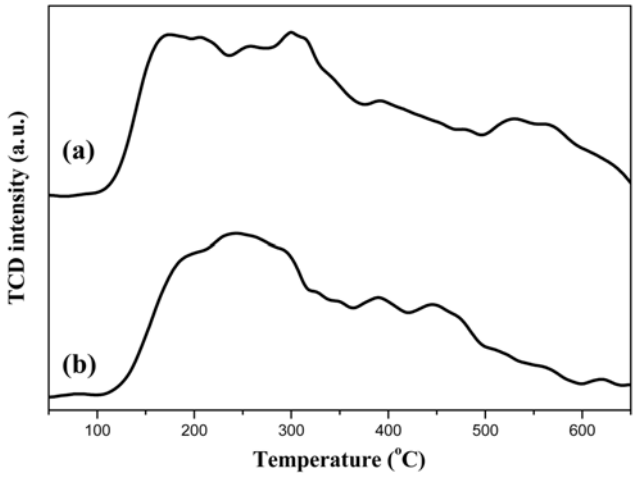

Fig. 5. NH_3-TPD data of (a) unsupported bulk SZ and (b) SZS (0.19 : 1).

NH_3-TPD was used to characterize the acidic properties of the prepared catalysts. NH_3-TPD spectra of unsupported bulk SZ and SZS (0.19 : 1) are shown in Fig. 5. The SZ and SZS (0.19 : 1) catalysts afforded broad desorption profiles over the range from 100 to 650 °C. This indicates that the two catalysts have a broad distribution of heterogeneous acid sites [29]. In the literature, the acid sites present on a superacid are artificially divided into three categories: weak, middle and strong acidity [29,30]. In the TPD pattern of SZ, it could be divided into two groups. The first peak (120-350 °C) can be assigned to SZ with large number of acid sites with relatively weak and middle acidity. The shoulder between 350 and 600 °C suggests strong acidity, which is a typical characteristic of a superacid [30]. The SZS (0.19 : 1) catalyst also showed similar TPD patterns. This result implies that superacidic sites were successfully supported on mesoporous silica, which is consistent with the results of FT-IR analyses.

The prepared SZS catalysts were used in the synthesis of acrolein from glycerol as a model reaction. To the best of our knowledge, the use of a superacid catalyst in this reaction has not been reported previously. The yields of acrolein from glycerol were compared and are listed in Table 2. For purposes of comparison, several soluble acidic catalysts such as $AlCl_3$ and phosphotungstic acid (HPWA) were also tested under identical reaction conditions. As shown in Table 2, mesoporous silica (MS) and ZrO_2 were not catalytically active in this reaction, indicating that the acidity of these samples was inadequate for glycerol dehydration. HPWA showed considerably high catalytic activity in terms of acrolein yield per mass of catalyst. Among the samples tested, the unsupported SZ showed the highest catalytic activity, indicating that the SZ have the strong acidic sites enough to dehydrate two H_2O molecules from glycerol. The SZS (0.19 : 1) and SZS (0.37 : 1) also showed considerable catalytic activity. The acrolein yields of the supported SZS samples were much better than that obtained using pure mesoporous silica (MS). This indicates that the mesoporous silica molecular sieve was effectively modified by the suggested method. However, the supported SZS (0.19 :1) catalyst showed slightly less catalytic activity than SZ and HPWA. During the reactions, the calculated amounts of sulfated zirconia in SZS (0.19 : 1) and SZS (0.37 : 1) were much smaller than that of unsupported SZ. Based on the calculated composition of sulfated zirconia, the order of catalytic activity, however, is as follows: SZS (0.19 : 1)≥SZS (0.37 : 1)>SZ. In addition, the reactions were carried out using a batch-type reactor. In such a reaction system, conventional soluble acid catalysts such as HPWA may have a higher catalytic activity because the reaction would occur on the molecular level. Thus, the yield of acrolein using the supported SZS catalysts could be less than that for SZ and HPWA catalysts. Although the catalytic activity of the supported SZS is slightly low, the separation of the catalyst from reaction media is much easier. In practical reaction tests, the supported SZS catalysts can be easily separated and recovered from the reaction media by a simple filtration.

In this work, a supported super acid catalyst was easily prepared

Table 2. Reaction results of glycerol dehydration to acrolein over the prepared materials

Sample	Blank	MS	$AlCl_3$	HPWA	SZ	SZS (0.19 : 1)	SZS (0.37 : 1)
Yield (%)	0.00	0.00	2.00	11.24	16.73	6.49	9.87

via a simple one-pot synthesis and the prepared SZS showed superacidic properties with an ordered mesostructure. In addition, we first attempted to apply the SZS catalyst to the dehydration of glycerol to acrolein. From the experimental results, although SZS has superacidic characteristics and considerable catalytic activity as a heterogeneous acidic catalyst, it is still insufficient for practical use in terms of acrolein productive yields and catalyst reusability. Detailed investigations on the above results of mesoporous superacid catalysts are currently underway.

CONCLUSIONS

Mesoporous superacid catalysts (SZS) with highly ordered mesostructures were synthesized by a one-pot synthetic procedure during the synthesis of mesoporous silica. When the molar ratio of Zr to Si is less than 0.37 : 1, the prepared SZS samples have the typical mesoporous structure with a regular 2D hexagonal array of channels and a uniform pore size. The active SZ was highly dispersed on the mesoporous silica support. The prepared SZS also showed superacidic characteristics that are similar to bulk SZ. The prepared SZS catalyst was applied to the dehydration of glycerol to produce acrolein. In the production of acrolein from glycerol, the supported SZS (0.19 : 1) catalyst showed considerable catalytic activities and the SZS (0.19 : 1) catalyst could be easily separated from the reaction media at the end of the reaction. Detailed investigations dealing with enhancing of acrolein production and evaluating catalyst stability using mesoporous superacid catalysts are currently underway.

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