

Synthesis of superacidic mesoporous alumina and its application in the dehydration of glycerol

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Abstract—Superacid $\text{ZrO}_2/\text{SO}_4^{2-}$ (SZ) was supported on mesoporous alumina (MA) to synthesize a novel superacid catalyst (SZMAP) with high active surface area. The synthesized catalyst was characterized by both physical and chemical methods, including XRD, BET, NH_3 -TPD and TEM. The prepared superacidic mesoporous alumina (SZMAP) showed typical gamma-alumina phase patterns and uniform mesoporous structures with a regular channel arrangement. NH_3 -TPD analysis indicated that SZMAP has superacidic characteristics. The SZMAP catalyst was used in the dehydration of glycerol to acrolein. Results showed that SZMAP showed much higher catalytic activity than the bulk superacid, $\text{ZrO}_2/\text{SO}_4^{2-}$ (SZ), and MA due to the high dispersion of active SZ molecules, which results from a large surface area and uniform mesopores of mesoporous alumina.

Key words: Mesopore, γ -Alumina, $\text{ZrO}_2/\text{SO}_4^{2-}$, Super Acid, Acrolein

INTRODUCTION

Solid superacids are promising solid catalysts in many reactions that involve very strong acid sites under mild conditions. Remarkably, $\text{ZrO}_2/\text{SO}_4^{2-}$ has been the focus of considerable research due to its excellent acidity [1,2]. The high acidity of sulfated zirconium dioxide gives rise to high activity in reactions involving proton transfer. Therefore, $\text{ZrO}_2/\text{SO}_4^{2-}$ is regarded as a suitable catalyst for alkylation, esterification, cyclization, oligomerization, etc. [3]. However, the low surface area of $\text{ZrO}_2/\text{SO}_4^{2-}$ limits its commercial applicability [4].

An effective solution to this problem is to prepare a supported catalyst by using a supporting material that has a high surface area and a narrow pore size distribution. Many mesoporous materials, including MCM-41, SBA-15, HMS, and FSM-16, have been used in the preparation of supported superacid catalysts.

γ -alumina ($\gamma\text{-Al}_2\text{O}_3$) has greater applicability in many catalytic reactions compared with silica-based materials. The distinctive chemical, mechanical and thermal properties of γ -alumina make the compound one of the most promising advanced materials for various applications, such as catalysts, supports, and adsorbents [5]. However, traditional materials, such as γ -alumina, are easily deactivated during catalysis due to coke formation in micropores [6]. Thus, production of alumina with mesopores and narrow pore size distribution are desirable. Mesoporous alumina would also be an effective supporting material for a highly active $\text{ZrO}_2/\text{SO}_4^{2-}$ superacid catalyst. Thus, synthesis of mesoporous alumina with controlled porosity and high thermal stability has been actively pursued [7].

In the present study, a novel superacid mesoporous alumina was prepared and characterized. The prepared catalyst was used in the synthesis of acrolein from glycerol via a dehydration reaction. To

the best of our knowledge, this study is the first to prepare superacid mesoporous alumina and to use a mesoporous superacidic catalyst in glycerol dehydration.

EXPERIMENTAL

1. Synthesis of Mesoporous Alumina

Mesoporous alumina (MA) was synthesized by using the post-hydrolysis method reported by Kim et al. [8]. Aluminum *sec*-butoxide (Fluka) was used as the alumina precursor and lauric acid (Fluka) was chosen as the template. For comparison purposes, NPA (Alumina from no-pore directing agent) was synthesized by the same procedure for MA with the exception of a template.

Solutions of aluminum *sec*-butoxide and lauric acid in *sec*-butyl alcohol (Aldrich) were prepared, and then mixed. A small amount of water was dropped into the mixture at a rate of 1 ml/min, resulting in the formation of a white precipitate. This suspension was stirred for an additional 24 h at room temperature. The product was washed with de-ionized water, dried at room temperature, and calcined at 550 °C for 6 h in air.

Supported catalyst was synthesized by using an impregnation method, as follows: mesoporous alumina was impregnated with 6.0 wt% ZrOCl_2 (Kanto) solution and precalcined at 300 °C for 2 h. The calcined sample was treated with 0.5 N sulfuric acid for 0.5 h, and a second calcination at 650 °C for 3 h gave the mesoporous superacid catalyst (SZMAP). When 0.3 N sulfuric acid was used, the resulting sample was abbreviated, SZMAP-3.

2. Characterizations

Large-angle powder X-ray diffraction (XRD) patterns were obtained with an X-ray diffraction MAC Science M18XHF-SRA diffractometer at 40 kV, 100 mA by using nickel-filtered $\text{CuK}\alpha$ radiation ($\lambda=0.15404$ nm).

N_2 adsorption-desorption data were obtained with a Brunauer-Emmett-Teller instrument (BET; ASAP 2010, Micrometrics) using a

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static method.

The acidities of samples were determined by temperature programmed desorption of ammonia (NH₃-TPD). A 0.5 g sample was introduced into a quartz glass tube and pretreated at 300 °C under vacuum for 1 h. The sample was cooled to 30 °C and several ammonia pulses were flushed through the sample tube. After saturation, weakly adsorbed NH₃ was eliminated by treatment with dry helium at the same temperature. Subsequently, the temperature was increased to 600 °C at a linear rate of 10 °C/min with a dry helium purge. The amount of NH₃ evolved from the sample was determined with a TCD detector. The helium flow rate was held constant at 30 ml/min.

Transmission electron microscopy (TEM) images were obtained with a JEM-2000EXII electron microscope operated at an accelerating voltage of 200 kV.

3. Catalytic Activities

The reaction was carried out by using batch reactive distillation in a fully agitated 250 ml glass reactor with a condenser on the top of it. A magnetic stirrer with an agitation speed of 300 rpm was used to create a slurry-type reaction mixture. The glass reactor was immersed in an oil bath at constant temperature. The temperature difference was controlled within ± 1 °C. A mixture containing the desired amount of catalyst and 50 g of glycerol was heated to 240 °C in the

glass reactor and the distillate was collected in a round flask. After one hour the products were analyzed by a GC equipped with an FID detector and a BP20 capillary column.

RESULTS AND DISCUSSION

1. Characteristics of SZMAP

XRD patterns of SZ, SZMAP-3, MA and SZMAP samples within the range of 10.0–80.0° are depicted in Fig. 1. When the γ -Al₂O₃ support was treated with 0.5 N H₂SO₄, the characteristic peaks of γ -Al₂O₃ ($2\theta=45.7^\circ$ and 66.7°) were clearly observed in Fig. 1B, which reflects that the crystal structure of γ -Al₂O₃ has been preserved throughout the synthesis and subsequent calcinations. However, when 3.0 N sulfuric acid was used, γ -Al₂O₃ reacted with sulfuric acid, and the corresponding crystal phase of Al₂(SO₄)₃ salt was observed in Fig. 1A. Therefore, the concentration of sulfuric acid should be carefully controlled to obtain the superacidic mesoporous alumina. No characteristic ZrO₂ peaks were found in XRD patterns for SZMAP. This result indicates that SZ was well-dispersed on the outer and inner MA surfaces.

The N₂ adsorption-desorption isotherms and BJH pore size distributions for MA, SZMAP and NPA are shown in Fig. 2. MA showed the typical type IV isotherm with an H2 hysteresis loop, indicating

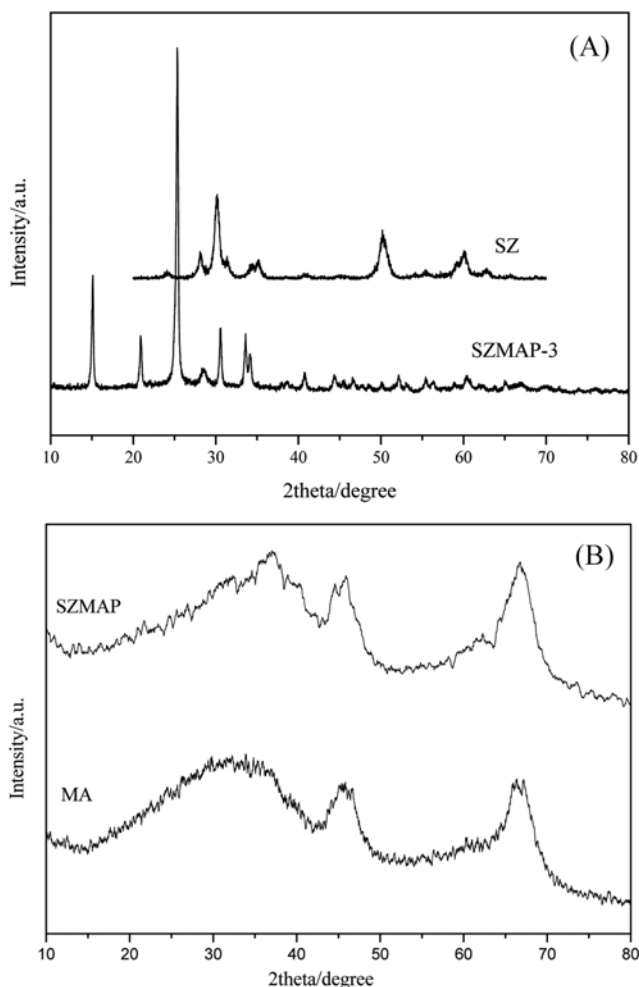


Fig. 1. XRD patterns: (A) SZ, SZMAP-3 and (B) MA, SZMAP.

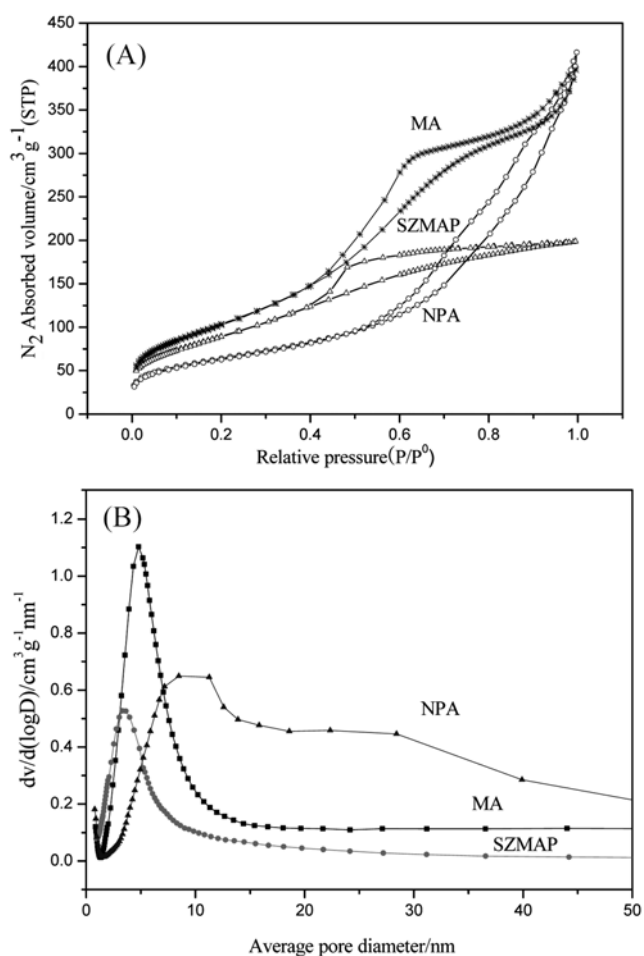


Fig. 2. (A) N₂ isothermal curve and (B) BJH pore size distribution of MA, SZMAP and NPA.

well-developed mesoporous characteristics. After impregnation of mesoporous alumina with superacid (SZ), the SZMAP showed similar nitrogen adsorption isotherms. This indicates that the mesoporous structure of MA was maintained. However, the NPA showed different nitrogen adsorption isotherm and capillary condensation occurred at higher relative pressure compared to MA and SZMAP (Fig. 2A).

The difference in pore size distributions between MA and NPA was significant (Fig. 2B). Both MA and SZMAP had narrow pore-size distribution peaks at ca. 4 nm. However, NPA, which is prepared without template, exhibited a wide pore size distribution implying irregular pore structure with non-uniform mesopores. As described in the experiment section, the MA and SZMAP were prepared by using lauric acid as a pore forming template. Micelles were formed by templating agent in synthetic solution, and then hydrolysis and condensation reaction of alumina precursor occurred around the micelles to form uniform mesopores. However, in the case of NPA, the hydrolysis and condensation reaction occurred randomly in the synthetic solution and the resulting alumina had irregular pore structure with wide pore size distribution.

SZMAP pore size and shape were readily apparent in the TEM micrographs (Fig. 3). SZMAP showed a sponge-type pore structure and the pore size was observed approximately 3.8 nm, consistent with the BET results. According to XRD, BET and TEM results, the mesoporous structure and γ - Al_2O_3 crystal structure were well preserved after impregnation and the superacid was highly dispersed on mesoporous alumina support.

In order to study the acidity properties of samples, NH_3 -TPD was used. The NH_3 -TPD spectra of SZ and SZMAP are shown in Fig. 4. These two materials had similar desorption peaks at temperatures of less than 150 °C due to physical absorption of ammonia, such peaks are caused by the weak acid sites. At temperatures in excess of 400 °C, broad peaks were observed due to chemical absorption of ammonia, which confirmed the presence of superacid sites in samples with a wide range of acid strength.

2. Reactivity of SZMAP

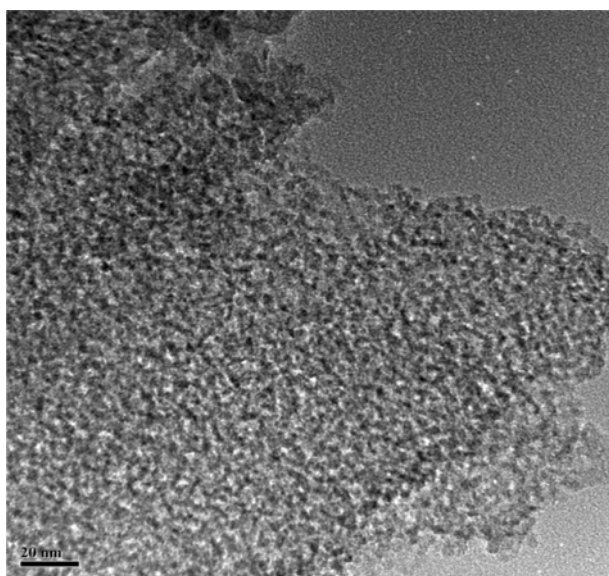


Fig. 3. HR-TEM image of SZMAP calcined at 650 °C.

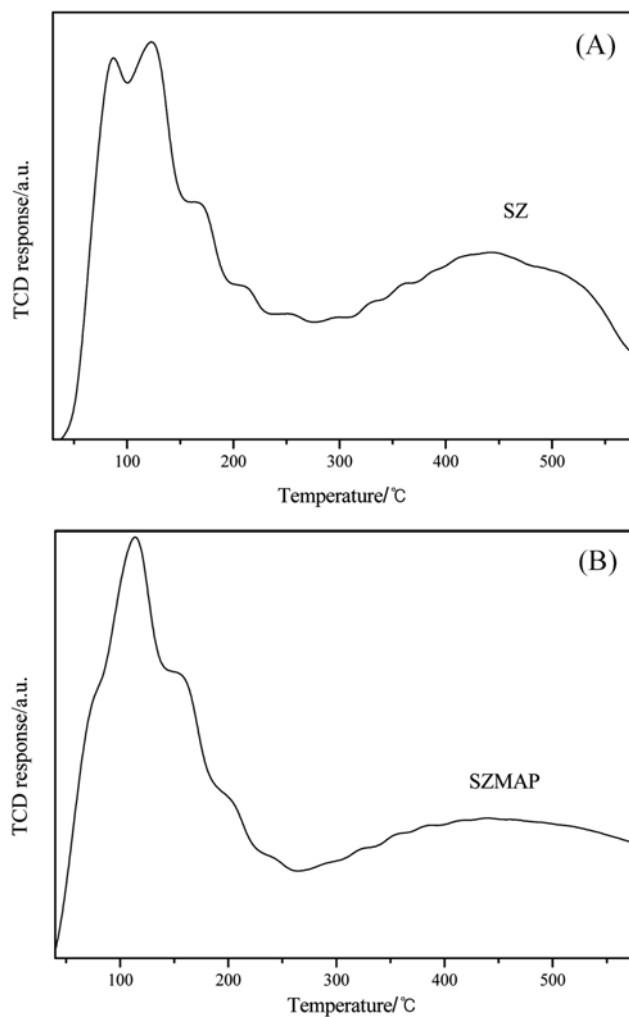


Fig. 4. NH_3 -TPD results: (A) SZ and (B) SZMAP.

Table 1. Results of glycerol dehydration to acrolein over prepared materials

Sample	Blank	MA	SZ	ZrO_2	SZMAP
Yield/%	0.00	0.00	2.74	0.00	4.21

The catalytic activity of SZMAP in the dehydration of glycerol was studied. Based on the calculated composition of SZMAP, the catalytic activity of similar amounts of MA, SZ and ZrO_2 was also studied in the glycerol dehydration reaction (Table 1). MA and ZrO_2 were ineffective catalysts, implying that the acid strength of MA and ZrO_2 was insufficient for glycerol dehydration under such moderate reaction conditions. The acrolein yield of SZMAP was much higher than that of bulk SZ. In a reaction test, the same amount of $\text{ZrO}_2/\text{SO}_4^{2-}$ (SZ) was used in a batch. Thus, it is reasonable that SAMAP has higher catalytic activity than bulk SZ. From the characterization results of SAMAP, the superacid $\text{ZrO}_2/\text{SO}_4^{2-}$ components were highly dispersed on ordered mesoporous alumina. Generally, the highly dispersed active components are advantageous in catalytic reactions. In this work, we prepared the highly dispersed superacid catalyst on mesoporous alumina. Based on the results, the enhanced cata-

lytic activity of SZMAP would result from a high SZ dispersion for mesoporous alumina, which has a high surface area and uniform mesopores.

CONCLUSIONS

A superacid mesoporous alumina catalyst was successfully synthesized. The synthesized catalyst exhibited a crystal structure typical of γ -Al₂O₃. SZ was very well-dispersed on MA. Under mild conditions, the activity of SZMAP was much greater than the activities of MA, ZrO₂ and even of the bulk superacid. Therefore, the SZMAP synthesized in the present study is a promising superacid catalyst.

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