Influence of Ionic Liquid as a Template on Preparation of Porous η -Al₂O₃ to DME Synthesis from Methanol

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Porous η -Al₂O₃ was synthesized by modified sol-gel method using ionic liquid as a templating material. The addition of ionic liquid assisted to increase the surface area of alumina. However, the acidity of aluminas prepared with ionic liquids was hardly affected regardless the change of its structural properties. Among the ionic liquids used in this study, 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆]) was the most effective ionic liquid to produce porous η -Al₂O₃ particles. The catalytic performance of these aluminas has been investigated in dehydration of methanol to produce dimethyl ether. The alumina prepared with [Bmim][PF₆] outperformed the other aluminas except η -Al₂O₃ without modification in this reaction.

Key Words: Porous η -Al₂O₃, Ionic liquid, Surface area, DME synthesis

Introduction

Since the development of clean fuel has been one of major worldwide issues, synthesis of dimethyl ether (DME) from synthesis gas has significantly received attention. DME is well known as a useful chemical intermediate for the production of gasoline, ethylene and aromatics.¹⁻⁵ Especially DME could be utilized as a clean alternative fuel for diesel engine automobiles because of its desirable properties, such as high cetane number, thermal efficiency, and so on.^{6,7} So far, DME has been produced from synthesis gas by two mechanisms. The first is a two-step process with a methanol synthesis and dehydration. The second is a one step process with bifunctional catalyst^{7,8} or physically admixed catalysts⁹⁻¹² to produce DME from synthesis gas directly. Hence, the proper use of solid acid catalyst is one of key technologies in DME synthesis. Up to date, solid acid catalysts have been studied to develop a desirable process for methanol dehydration.²⁻¹² Among the catalysts, alumina has been considered a good candidate in this reaction. It have been known that the moderate acid site strength of alumina could enhance the formation of DME from methanol.¹³

In our previous work,¹⁴ η -Al₂O₃ showed significant performance for methanol dehydration to produce DME. Moreover, it was found that the structure of alumina is more crucial factor than acidity properties to determine catalytic performance. However, it is still uncertain to conclude the essential factor in this reaction. For the reason, modification of η -Al₂O₃ was carried out to investigate the effect of catalyst structure in this reaction. The modification presented in this study is to use an ionic liquid as a template material. Ionic liquids are a unique type of solvent consisting practically only of ions. They have almost no vapor pressure and possess tunable solvent properties.^{15,16} In this study, various ionic liquids were used as templates to prepare porous η -Al₂O₃ particles. The low vapor pressure of an ionic liquid could assist in reducing the shrinkage problem for drying, which could avoid reduction of surface area. Here porous η -Al₂O₃ particles with high surface area were successfully syn-

thesized using ionic liquids. The prepared samples have been characterized to identify their properties. Moreover, the methanol dehydration reaction was performed under identical conditions to investigate the effect of structure phase on catalytic performance.

Experimental Section

The η -Al₂O₃ was prepared by modified Yoldas method. The sample was initially prepared by mixing 124 g of aluminum tri-sec-butoxide (ATSB, 97%, Acros Organics) and 1800 mL of water (at 25 °C). After stirring for 1 h, the solution was aged for 24 h. After filtration, the obtained solid was dried at 110 °C for 12 h and then calcined at 600 °C for 5 h in air. This catalyst named as "pure" was used as the control sample for comparison with other catalysts. For the modification, one of the ionic liquids (C-TRY, Korea) presented in Table 1 was added to the mixed solution of ATSB and water with an ionic liquid/mixed oxide molar ratio of 3 at room temperature. After stirring for 1 h, the solution was aged for 24 h. After filtration and washing with distilled water, the excess ionic liquid was extracted using acetonitrile (CH₃CN) and filtrated. The obtained solid was dried and then calcined at 600 °C with same procedure mentioned above.

The powder X-ray diffraction (XRD) patterns of the catalysts were recorded using a X-ray diffractometer (Shimadzu XRD-6000) that was operated at 40 kV and 30 mA, using Cu K α (λ =

Table 1. List of ionic liquids as a template polymers

Symbol*	Full name
BPF6	1-Butyl-3-methylimidazolium hexafluorophosphate
BBF4	1-Butyl-3-methylimidazolium tetrafluoroborate
BCF3	1-Butyl-3-methylimidazolium trifluoromethanesulfonate
HPF6	1-Hexyl-3-methylimidazolium hexafluorophosphate
OPF6	1-Octyl-3-methylimidazolium hexafluorophosphate

*used in this paper

0.15418 nm) radiation to determine the crystal structure. The surface area of sample was measured using the N₂ sorption method with a Micromeritics ASAP 2010 instrument. The sample images were confirmed using scanning electron microscopy (SEM, Hitachi, Model S-4100). Acidity measurements were performed by the temperature-programmed adsorption of ammonia with a quadrupole mass spectrometer (QMS) (Pfeiffer Vacuum) in the temperature range from room temperature to 800 °C, with a heating rate of 5 °C/min. The catalysts were purged at 350 °C for 3 h under helium flow (65 mL/min) prior to ammonia adsorption at room temperature for 1 h and then the physisorbed NH₃ on the surface of the catalyst was desorbed by heating at 120 °C for 2 h. The amount of NH₃ desorbed from the catalyst was determined by comparing the peak area ($m/z = 15$) of known amount of NH₃ to avoid any confusion with the peak of H₂O.

Catalytic reaction was performed in a fixed-bed high-pressure reactor with an inner diameter of 0.95 cm. The products were analyzed using an online gas chromatograph that was equipped for thermal conductivity detection (TCD). The methanol dehydration was carried out at atmospheric pressure and a gas hourly space velocity (GHSV) of 6000 h⁻¹. The details of the procedure can be found elsewhere.^{9,14,18}

Results and Discussion

XRD patterns of samples prepared with ionic liquids and without ionic liquid were shown in Fig. 1. The samples possessed the η -Al₂O₃ phase except BCF3 and OPF6 samples. Small peak at 77° was observed over the both samples. This means both samples were formed η -Al₂O₃ with tiny impurity phase.

The effect of ionic liquids on surface area of samples was investigated with N₂ physisorption. The surface area of η -Al₂O₃ prepared with ionic liquids was greater than that of the catalyst prepared without ionic liquid. The effect of anion part in the ionic liquid on the surface area is illustrated in Fig. 2. The η -Al₂O₃ particle prepared with ionic liquid containing [PF₆]⁻ showed the highest surface area while BCF3 particles possessed the lowest surface area. This means that anion part in ionic liquid has significant effect on the formation of η -Al₂O₃ particle. This tendency could be occurring possibly due to the hydrogen bond-co- π - π stack mechanism proposed by Zhou's research group.¹⁹ The formation mechanism is based on the special molecular structure and property of the ionic liquid. Water molecules in the ionic liquid interact with anion part by hydrogen bonding. However, the cation part including imidazolium ring does not interact with water. Thus, the property of ionic liquid is comparable to the surfactant forming micelle. For this reason, the interaction balance between hydrogen bond and π - π interaction causing stack of cation part is crucial to form effective template material. The strength of the hydrogen bonds between anion part and water increases in the order [PF₆]⁻ < [BF₄]⁻ < [CF₃SO₃]⁻.²⁰ In this case, the weaker hydrogen bonds can assist to the formation of templating materials by balancing with π - π interaction of imidazolium rings.

The effect of cation part in the ionic liquid on the surface area is shown in Fig. 3. The smaller surface area was obtained with the larger cation parts of ionic liquid. This is mainly attributed to

the fact that the stacks of cation part with longer chain were not formed completely. Indeed, no templating effect was observed over OPF6 sample. Thus, it was found that BPF6 is the most effective template to reduce the shrinkage problem during ageing and drying of precipitates, therefore a reduction of surface area can be avoided.

SEM image of the samples was shown in Fig. 4. The shape of particle was different significantly with ionic liquid as a templating material. It clearly reveals that BPF6 has an excellent effect on the control of particle size and uniformly distributed during the synthesis. An irregular shape of particles was observed over OPF6 sample. This is mainly attributed to less templating effect of the ionic liquid. The pore size distributions of the samples were shown in Fig. 5. Among the samples, BPF6 possessed the smallest pore size and narrow pore size distribution. However, OPF6 and BCF3 samples showed relatively poor pore size distribution. The result is in a good agreement with the characterization results of SEM analysis.

The N₂ adsorption-desorption isotherm of selected samples are illustrated in Fig. 6. The effect of ionic liquid as a template material to produce porous particle was clearly observed from

Figure 1. XRD patterns of η -Al₂O₃ samples prepared with various ionic liquids.

Figure 2. The effect of anion parts in ionic liquid with [Bmim]⁺ on surface area of particles.

Figure 3. The effect of cation parts in ionic liquid with $[PF_6]^-$ on surface area of particles.

Figure 4. SEM images of η - Al_2O_3 samples prepared with various ionic liquids.

isotherm of BPF6 samples (see Fig. 6(b)). This isotherm pattern exhibited type IV-like behaviour which is a characteristic of porous materials based on the IUPAC classification.²¹ A sharp inflection of adsorbed volume at $P/P_0 = 0.65$ (hysteresis loop) and a relatively steep desorption branch. This means the existence of mesoporosity in the particle.

The acidity of samples was determined by NH_3 -temperature programmed desorption (NH_3 -TPD) with mass spectroscopy to measure desorption of pure ammonia without any impurity.

Figure 5. Pore size distribution of the samples calcined at 600 °C.

Figure 6. Nitrogen adsorption-desorption isotherms of η - Al_2O_3 prepared (a) without ionic liquid and (b) with $([Bmin][PF_6])$.

Especially, the effect of water desorption from the surface of aluminas can be avoided completely. Thus, the intrinsic properties of acid site over sample could be measured. The ammonia desorp-

Figure 7. Deconvolution of NH₃-TPD profile of "Pure" sample with temperature.

Table 2. The properties of acidity over η -Al₂O₃ samples

Catalyst	Total Acidity ($\mu\text{mol/g}$)	Acid strength distribution (%)			
		Weak	Moderate	Strong	Very strong
Pure	61.6	12.5	25.4	30.2	31.9
BPF6	60.2	13.8	26.1	29.8	30.3
BBF4	59.8	14.5	25.1	30.4	30
BCF3	58.3	16.2	24.1	31.6	28.1
HPF6	59.2	14.2	25.8	28.9	31.1
OPF6	56.3	17.5	24.7	30.5	27.3

tion profile with temperature was used to determine the total acidity and acid strength distribution as shown in Fig. 7. The area of entire peak was corresponded to the total acidity of the sample. However, the acid strength distribution couldn't be calculated directly from the peak profile. Therefore, a deconvolution procedure was used to separate the peak for acid site distribution. The four peaks indicating weak, moderate, strong, and very strong acid site were separated from deconvolution. The total acidity and acid strength distribution of samples were presented in Table 2. Interestingly, all samples showed comparable properties of acid sites, even though the structure properties of samples were different significantly. This means that the effect of acidity was little to determine catalytic performance.

The methanol dehydration reaction was carried out over the samples to investigate catalytic performance at various reaction temperatures. Generally, methanol is converted over solid acid catalyst to either DME by simple dehydration or hydrocarbons by deep dehydration.²² It should be noted that hydrocarbon products were not produced by deep dehydration in the reaction conditions. The catalytic performances of these catalysts with reaction temperatures are presented in Fig. 8. Even though all catalysts possessed comparable acidity properties, the catalytic activity was quite different. BPF6 sample with relatively uniform pore structure outperformed the other samples prepared with ionic liquid at entire reaction temperature range. However, both samples (BCF3 and OPF6) formed by less templating effect

Figure 8. The effect of reaction temperature on catalytic activity of η -Al₂O₃ samples at various temperatures (GHSV = 6000 h⁻¹).

Figure 9. Correlation of acid site density of the catalysts except pure sample with DME yield performed at 260 °C.

showed the lowest catalytic performance.

It was reported that acid site density was crucial factor to determine the catalytic performance in this reaction.²³⁻²⁵ Especially, DME yield was increased with acid site density among the alumina catalysts possessing identical crystal phase. However, opposite trend was found among the samples prepared using ionic liquids as shown in Fig. 9. In the sample reaction conditions, DME yield was decreased with increasing the acid site density of the catalyst. In this case, the catalysts possessed different smaller particle size and better size distribution leading to higher surface areas even though the total acidity of those samples was comparable. Thus, intricate properties of alumina might give an effect on the catalytic activity in methanol dehydration to DME yield. This means structure properties of alumina is more important than acidity properties to determine catalytic performance in the reaction.

Conclusions

Synthesis of porous η -Al₂O₃ particles was investigated by

sol-gel method using ionic liquid. The prepared η -Al₂O₃ particles using [Bmim][PF₆] as an effective templating material had good structural properties including high surface area. Especially, the strength of the hydrogen bonds on the anion part of ionic liquid with water was crucial factor produce mesoporous structure of η -Al₂O₃ particles. The mechanism of porous η -Al₂O₃ formation is an effective aggregation of the particles with a self-assembled ionic liquid. Among the ionic liquids, it was found that 1-butyl-3-methylimidazolium hexafluorophosphate ([Bmim][PF₆]) was the most effective ionic liquid to prepare porous η -Al₂O₃ particles. However, the properties of acid sites of all samples were comparable. The catalytic perform of the sample were investigated by dehydration of methanol to produce DME. Among the η -Al₂O₃ particles except sample prepared without ionic liquid, the sample prepared by [Bmim][PF₆] showed the highest catalytic activity, even though all catalysts possessed comparable acidity properties. Consequently, the structure of η -Al₂O₃ catalyst is crucial factor to enhance the DME synthesis by methanol dehydration.

References

- Vishwanathan, V.; Jun, K. W.; Kim, J. W.; Roh, H. S. *Appl. Catal. A* **2004**, 276, 251.
- Vishwanathan, V.; Rho, H. S.; Kim, J. W.; Jun, K. W. *Catal. lett.* **2004**, 96, 23.
- Yaripour, F.; Baghaei, F.; Schmidt, I.; Perregaard, J. *Chem. Commun.* **2005**, 6, 147.
- Fu, Y.; Hong, T.; Chen, J.; Auroux, A.; Shen, J. *Thermochim. Acta* **2005**, 434, 22.
- Siva Kumar, V.; Padmasri, A. H.; Satyanarayana, C. V. V.; I.; Reddy, A. K.; Raju, B. D.; Rama Rao, K. S. *Catal. Commun.* **2006**, 7, 745.
- Jiang, S.; Hwang, J. S.; Jin, T. *Bull. Korean Chem. Soc.* **2004**, 2, 185.
- Xu, M.; Lunsford, J. H.; Goodman, W. D.; Bhattacharyya, A. *Appl. Catal. A* **1997**, 149, 303.
- Mao, Y.; Yang, W. *J. Mol. Catal. A: Chem.* **2006**, 250, 138.
- Kim, J. H.; Park, M. J.; Kim, S. J.; Joo, O. S.; Jung, K. D. *Appl. Catal. A* **2004**, 264, 37.
- Ge, Q.; Huang, Y.; Qiu, F.; Li, S. *Appl. Catal. A* **1998**, 167, 23.
- Jun, K. W.; Lee, H. S.; Rho, H. S.; Park, S. E. *Bull. Korean Chem. Soc.* **2002**, 23, 803.
- Yaripour, F.; Baghaei, F.; Schmidt, I.; Perregaard, J. *Catal. Commun.* **2005**, 6, 542.
- Spivey, J. J. *Chem. Eng. Comm.* **1991**, 110, 123.
- Seo, C. W.; Jung, K. D.; Lee, K. Y.; Yoo, K. S. *Ind. Eng. Chem. Res.* **2008**, 47, 6573.
- Wasserscheid, P.; Keim, W. *Angew. Chem. Int. Ed. Engl.* **2000**, 39, 3772.
- Welton, T. *Chem. Rev.* **1999**, 99, 2071.
- Brinker, C. J. *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*; Academic Press: San Diego, 1990.
- Yoo, K. S.; Kim, J. H.; Park, M. J.; Kim, S. J.; Joo, O. S.; Jung, K. D. *Appl. Catal. A* **2007**, 330, 57.
- Zhou, Y.; Schattka, J. H.; Antonietti, M. *Nano Lett.* **2004**, 3, 477.
- Cammarata, L.; Kazarian, S. G.; Salter, P. A.; Welton, T. *Phys. Chem. Chem. Phys.* **2001**, 3, 5192.
- Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscow, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniowska, T. *Pure Appl. Chem.* **1985**, 57, 603.
- Venuto, P. B. *Microporous Mater.* **1994**, 2, 297.
- Youssef, A. M.; Ahmed, A. I.; Samra, S. E. *Mater. Lett.* **1990**, 10, 175.
- Youssef, A. M.; Alaya, M. N.; Hamada, M. A. *Thermochim. Acta* **1994**, 235, 91.
- Kim, S.-M.; Lee, Y.-J.; Bae, J. W.; Potdar, H. S.; Jun K.-W. *Appl. Catal. A* **2008**, 348, 113.