

## Synthesis of Mesoporous Alumina by using a Cost-effective Template

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**Abstract**—A salt of stearic acid, i.e., magnesium stearate [(C<sub>17</sub>H<sub>35</sub>COO)<sub>2</sub>Mg], can be used as a chemical template for the formation of mesoporous alumina, and is a less expensive reagent than stearic acid. Mesoporous alumina prepared using this cost-effective surfactant shows similar pore properties with respect to pore size (3.5 nm) and surface area (above 300 m<sup>2</sup>/g) to that prepared using stearic acid. In addition, textural porosity, arising from non-crystalline intra-aggregate voids and spaces, was effectively removed by the addition of magnesium nitrate. The entire transformation from aluminum hydroxide to active alumina was performed at 550 °C, and the crystallinity of the product was confirmed by powder XRD analysis. <sup>27</sup>Al MAS NMR result shows the phase of mesoporous alumina is the  $\gamma$ -alumina form.

Key words: Cost-effective Template, Magnesium Stearate, Mesoporous Alumina, Stearic Acid

### INTRODUCTION

Activated aluminas have been used as catalysts and catalyst supports for reactions such as hydrodesulfurization, the Claus reaction, dehydrogenation and dehydration. Alumina is superior to silica because of the higher hydrolytic stability and the different point of zero charge, which makes it easier to be loaded with different metal species. The performance of conventional alumina, however, is frequently limited due to its uncontrolled porosity, deactivation by coking and plugging that hinders the diffusion of reactants and products. Thus, alumina supports with a narrow pore size distribution, uniform pore structure and high surface area are required for use in practical industrial applications [Schüth et al., 1996].

Beginning in 1996, the synthesis of mesoporous alumina was reported by several groups. Davis and Coworkers [1996] prepared mesoporous alumina using an alkyl carboxylate as a surfactant. The resulting materials, however, had an approximately constant pore size (*ca.* 20 Å) that could not be tailored by changing the length of the surfactant chains. Yada et al. [1996] prepared hexagonally mesostructured alumina using dedecyl sulfate and aluminum nitrate, and the mesostructure was destroyed when it was calcined. Bagshaw et al. [1996] obtained mesoporous aluminas from electrically neutral assemblies of poly(ethylene oxide) and aluminum alkoxides. Kim et al. [2002, 2003] prepared mesoporous alumina based on a post-hydrolysis method, which showed superior pore characteristics to the above mentioned methods, in ambient conditions. However, alumina prepared by the above methods entails a very high production cost due to the high cost of raw materials, and thus it has disadvantages in terms of application to industrial catalysis.

In this study, mesoporous alumina was prepared by using magnesium stearate, a salt of stearic acid and a cost-effective material.

### EXPERIMENTAL

Magnesium stearate (Riedel-De Häen) and aluminum *sec*-butox-

ide (Fluka) were used as a surfactant and an aluminum precursor, respectively. Magnesium nitrate (Riedel-De Häen) and *sec*-butyl alcohol (Fluka) were used as an additive and solvent, respectively.

The aluminum source and surfactant were dissolved separately in *sec*-butyl alcohol, after which the two solutions were then mixed. Appropriate amount of additive was added to the mixture. Small amounts of water were slowly added dropwise to the mixture at a rate of 1 ml/min generating a white precipitate. This resulting suspension was further stirred for 24 hr. The product was then dried at room temperature for 24 hr. The resulting materials were calcined for 3 hr at 550 °C in air. The molar ratio of this reaction mixture was 1 Al(*sec*-BuO)<sub>3</sub> : 0.2 (C<sub>17</sub>H<sub>35</sub>COO)<sub>2</sub>Mg : 5 C<sub>4</sub>H<sub>7</sub>OH : 4 H<sub>2</sub>O : 0-0.4 Mg(NO<sub>3</sub>)<sub>2</sub>. N<sub>2</sub> adsorption/desorption experiments were carried out by using a Micromeritics ASAP 2010 analyzer, and powder X-ray diffraction (XRD, M18XHF-SRA, MAC/Science) patterns were recorded to determine the crystallinity of the prepared samples. NMR spectra were obtained on a Varian-Inova spectrometer (300 MHz) at an MAS frequency of 6 KHz.

### RESULTS AND DISCUSSION

As shown in Table 1, the pore properties of the mesoporous aluminas are dependent on the synthesis conditions, that is, the ratio of magnesium nitrate to surfactant. Aluminas prepared without the addition of magnesium nitrate show a uniform pore size distribution ( $D_{FWHM} \sim 1$  nm), but a poorly organized framework porosity due

**Table 1. Pore properties of the mesoporous aluminas**

[Mg(NO <sub>3</sub> ) <sub>2</sub> ]/[surfactant]	$S_{BET}/m^2g^{-1}$	$V_p/cm^3g^{-1}$	$D_{mode}/nm$
0.0	219	0.26	3.69
0.5	271	0.30	3.57
1.0	311	0.31	3.56
1.5	238	0.22	3.53
2.0	219	0.20	3.56

$S_{BET}$ : BET surface area,  $V_p$ : Pore volume,  $D_{mode}$ : pore size at maximum of pore size distribution.

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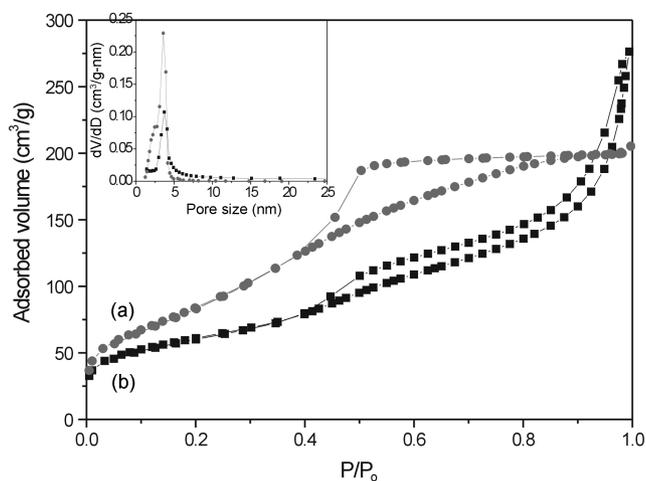


Fig. 1.  $N_2$  isotherms of mesoporous alumina prepared (a) with and (b) without the use of magnesium nitrate.

to its textural porosity (Fig. 1). Using various ratios of magnesium nitrate to surfactant, the surface area and pore volume of mesoporous alumina can be controlled from 219  $m^2/g$  and 0.20  $cm^3/g$  to 311  $m^2/g$  and 0.31  $cm^3/g$ , respectively. The pore size, however, remained unchanged. It should be noted that the addition of magnesium nitrate has no effect on the size of the micelle structure, which is used as a template for the formation of mesoporous aluminas. As shown in Fig. 1, alumina prepared at the ratio (magnesium nitrate/surfactant) of 1 shows larger surface area and pore volume than those of the other aluminas, and has a uniquely well-developed framework porosity. This phenomenon occurs due to the self-assembled pathway via virtue of electrostatic force between the surfactant and precursor. The appropriate amount of the magnesium nitrate might act as an intermediate ion, and enhances the interaction between the surfactant and precursor. An excess, however, weakened the structure, leading to a poor textural porosity, the origin of which are the non-crystalline intra-aggregate voids and spaces formed as a result of interparticle contacts.

In low angle XRD patterns (not shown here) of mesoporous alumina, only one peak appears at  $2\theta$  between  $0.5-3^\circ$ . This indicates that the prepared aluminas have different pore structures compared to hexagonal mesoporous silica such as MCM-41 or SBA-15, which exhibits three peaks at  $2\theta$  between  $0.5-5^\circ$ . Thus, MCM-41 has a 1D cylindrical pore structure with a highly regular pore distribution, whereas the aluminas prepared here have a 3D interconnected pore channel structure with a random pore distribution. These results are consistent with the TEM data. The TEM analysis (not shown) of the pore structure of alumina prepared at ratio 1 indicated a sponge-like appearance, clearly demonstrating the advantage of a highly inter-connected pore system. Similar pore morphology was found for alumina when cationic or neutral surfactants were used in their preparation [Bagshaw et al., 1996; Kim et al., 2002].

The crystalline phase of as-made and calcined mesoporous alumina prepared at ratio 1 was confirmed by XRD and  $^{27}Al$  MAS NMR analysis. The phase of the alumina was generally dependent on the temperature used in the heat treatment. The phase transformation from bayerite to  $\eta$ -alumina is  $230^\circ C$ , and from boehmite to  $\gamma$ -alumina is  $450^\circ C$  [Digne et al., 2002]. When stearic acid was used as

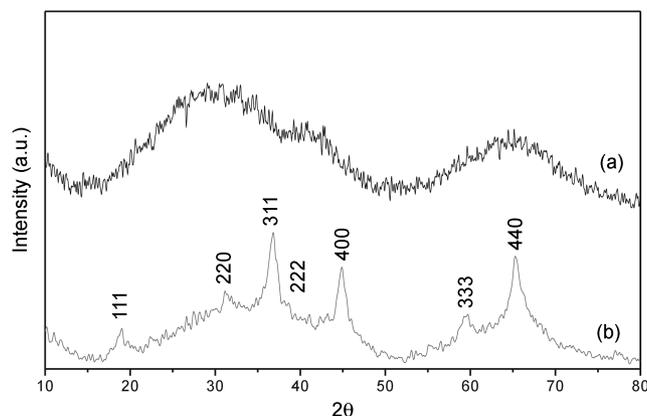


Fig. 2. XRD results of mesoporous alumina (the ratio of magnesium nitrate to surfactant of 1) calcined at temperatures of (a)  $450^\circ C$  and (b)  $550^\circ C$ .

a template [Kim et al., 2002], the phase transformation from boehmite to  $\gamma$ -alumina occurred after heat treatment at  $420^\circ C$  for 3 hr. In the case where magnesium stearate was used as a template, the entire transformation to activated alumina occurred at  $550^\circ C$  (Fig. 2). Typically, active alumina is  $\gamma$  and  $\eta$ -alumina, generally known as spinel aluminas because their structures are very closely related to that of an Mg spinel [Wolverton et al., 2000]. XRD patterns of both active aluminas are similar, and it is not easy to distinguish the phase. Therefore, the coordination of Al atoms to the active alumina was investigated by  $^{27}Al$  MAS NMR.

As-made alumina has mainly 6-coordinated Al atoms, in the form of layered aluminum hydroxide. After calcination, 4, 5, and 6-coordinated Al atoms are present (Fig. 3). Tetrahedral ( $Al^{IV}$ ) and octahedral ( $Al^{VI}$ ) coordinated Al are produced as the result of dehydration and dehydroxylation of aluminum hydroxide, and pentahedral ( $Al^V$ ) coordinated Al is produced by migration toward the tetrahedral and/or octahedral sites [Krokidis et al., 2001]. As shown in Fig. 3, the ratio of  $Al^{VI}$  to  $Al^{IV}$  for calcined mesoporous alumina is 3.28.

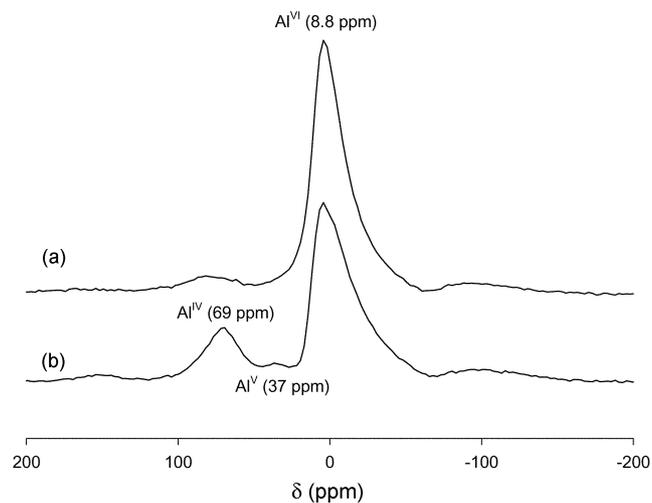


Fig. 3.  $^{27}Al$  MAS NMR spectra of (a) as-made alumina, and (b) calcined alumina (the ratio of magnesium nitrate to surfactant of 1).

From the literature, the percentage of 6-coordinated Al present is reported to be  $75\pm 4\%$  Al<sup>VI</sup> for  $\gamma$ -alumina and  $65\pm 4\%$  Al<sup>VI</sup> for  $\eta$ -alumina [Sohlberg et al., 1999]. Namely, the Al<sup>VI</sup>/Al<sup>IV</sup> value is 2.4-3.8 in  $\gamma$ -alumina and 1.6-2.3 in  $\eta$ -alumina. Therefore, mesoporous alumina prepared in this study is almost ideal  $\gamma$ -alumina.

In conclusion, mesoporous aluminas with a high surface area and an uniform pore size were synthesized by using a cost-effective template, i.e., magnesium stearate. N<sub>2</sub> adsorption/desorption isotherms show similar properties to previously reported alumina, but the textural porosity is retained. This textural porosity can be removed by adding magnesium nitrate. XRD and <sup>27</sup>Al MAS NMR results show that the prepared alumina was  $\gamma$ -alumina with a spinel structure.

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#### REFERENCES

- Bagshaw, S. A. and Pinnavaia, T. J., "Mesoporous Alumina Molecular Sieves," *Angew. Chem. Int. Ed. Engl.*, **35**, 1102 (1996).
- Digne, M., Sautet, P., Raybaud, P., Toulhoat, H. and Artacho, E., "Structure and Stability of Aluminum Hydroxide: A Theoretical Study," *J. Phys. Chem. B*, **106**, 5155 (2002).
- Kim, Y., Lee, B. and Yi, J., "Synthesis of Mesoporous  $\gamma$ -Alumina through Pre- and Post-hydrolysis Methods," *Korean J. Chem. Eng.*, **19**, 908 (2002).
- Kim, Y., Kim, P., Kim, C. and Yi, J., "A Novel Method for Synthesis of a Ni/Al<sub>2</sub>O<sub>3</sub> Catalyst with a Mesoporous Structure using Stearic Acid Salts," *J. Mater. Chem.*, **13** (2003)
- Krokidis, X., Raybaud, P., Gobichon, A.-E., Rebours, B., Euzen, R. and Toulhoat, H., "Theoretical Study of the Dehydration Process of Boehmite to  $\gamma$ -Alumina," *J. Phys. Chem. B*, **105**, 5121 (2001).
- Schüth, F., "Non-silicious Mesostructured and Mesoporous Materials," *Chem. Mater.*, **13**, 3184 (1996).
- Sohlberg, K., Pennycook, S. J. and Pantelides, S. T., "Hydrogen and the Structure of the Transition Aluminas," *J. Am. Chem. Soc.*, **121**, 7493 (1999).
- Vaudry, F., Kohdabandeh, S. and Davis, M. E., "Synthesis of Pure Aluminas Mesoporous Materials," *Chem. Mater.*, **8**, 1451 (1996).
- Wolverton, C. and Hass, K. C., "Phase Stability and Structure of Spinel-based Transition Aluminas," *Phys. Rev. B*, **63**, 024102 (2000).
- Yada, M., Machida, M. and Kijima, T., "Synthesis and Deorganization of an Aluminum-based Dodecyl Sulfate Mesophase with a Hexagonal Structure," *Chem. Commun.*, 769 (1996).