

Comparison of Mesoporous Aluminas Synthesized using Stearic Acid and Its Salts

Younghun Kim, Pil Kim, Changmook Kim and Jongheop Yi[†]

School of Chemical and Biological Engineering, Institute of Chemical Processes, Seoul National University,
San 56-1, Shillim, Kwanak, Seoul 151-742, Korea

(Received 3 November 2004 • accepted 24 December 2004)

Abstract—Mesoporous aluminas, X-MAs (X=Na, Mg, and Ni) were prepared using stearic acid and its salts as templates. Sodium stearate, which is more soluble than stearic acid, was an effective template for preparing Na-MA. The characteristics of Mg-MA prepared using cost-effective template (magnesium stearate) were similar to those for an MA prepared using stearic acid. Mg ions were easily exchanged with Ni ion by treatment with an acid or base. Thus, nickel incorporated alumina (Ni-MA) could be directly prepared using nickel stearate, which was acting as a chemical template and a metal source. The MA and X-MAs had a similar pore size (3.6 nm), a narrow pore size distribution ($D_{FWHM} \sim 1$ nm), and a γ -alumina phase. In addition, bimetallic Ni-MAN catalysts were prepared and applied to the partial oxidation methane as a potential application.

Key words: Mesoporous Alumina, Stearic Acid, Stearic Acid Salts, ^{27}Al MAS NMR

INTRODUCTION

Activated alumina (AA) is frequently used as a catalyst support or adsorbent in industrial applications. The discovery of mesoporous silica led to intensive research on the design of mesoporous materials and its applications [Coma, 1997]. Because mesoporous alumina (MA) has sponge-like pore structure and uniform pore size, it is preferred to AA for use in catalytic reactions and adsorption process [Kim and Yi, 2004].

Ionic surfactants (carboxylic acid and sodium dodecyl sulfate) [Yada et al., 1997; Carbrera et al., 1999] or neutral surfactants (Tergitol and Pluronic) [Bagshaw and Pinnavaia, 1996] are normally used as chemical templates in the preparation of MA. In this study, MA was prepared using stearic acid, and the pore properties of the product were controlled by the water content, calcination conditions, the molar ratio of surfactant to precursor, and the use of either a pre- or post-hydrolysis [Kim et al., 2002]. MA prepared via the post-hydrolysis method showed a large surface area (300–500 m^2/g) and the pore size distribution was highly uniform ($D_{FWHM} < 1$ nm). Nickel catalysts supported on MA had a low deactivation and high selectivity compared with those for AA in a HDC reaction (hydrodechlorination) [Kim et al., 2003b] and POM (partial oxidation of methane) [Kim et al., 2004a]. In addition, calcined MA proved to be a very effective adsorbent for the removal of arsenic from aqueous solutions [Kim et al., 2004b].

Sodium hydroxide is used to dissolve the stearic acid in the preparation of MA, since stearic acid is insoluble in the alcohol phase at room temperature. However, sodium stearate, in which the carboxyl group is in the sodium salt form, has a greater solubility. To examine the possibility of using stearic acid salts as a template, sodium stearate was used in the preparation of Na-MA. Whereas its solubility is excellent compared with that of stearic acid, the cost of raw material is approximately double that of stearic acid. Magne-

sium stearate is very low in cost and its solubility is similar to that for sodium stearate. Because of this, Mg-MA was prepared by using this salt as well [Kim et al., 2003a]. It is noteworthy that other stearic acid salts might also be useful as chemical templates for preparing X-MAs. When magnesium stearate was treated with the target metal precursor in either acidic or basic solution, magnesium ions were exchanged with precursor metal ions due to the difference in the formation energies of chloride or hydroxide salts. For example, nickel stearate could be prepared by exchanging nickel for magnesium, and was used to prepare Ni-MA. After reduction in the presence of hydrogen, reduced Ni-MA catalyst could be used in POM reaction.

EXPERIMENTAL

1. Preparation of MA using Stearic Acid

In previous studies, we reported on some synthetic strategies for preparing MA using pre- and post-hydrolysis procedures [Kim et al., 2002, 2003c]. The pre-hydrolyzed aluminum precursor in the pre-hydrolysis method formed an aggregated aluminum sol, leading to the production of a poorly organized MA [Valange et al., 2000]. Whereas the post-hydrolyzed aluminum precursor, produced by post-hydrolysis, resulted in well ordered MA. Thus, the post-hydrolysis method was selected for preparing the MA. Stearic acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$, Sigma) was used as an anionic surfactant, and aluminum *sec*-butoxide (Fluka) was used as the aluminum precursor. To enhance the solubility of stearic acid in alcohol phase, sodium hydroxide was used. The aluminum precursor and surfactant were dissolved in *sec*-butyl alcohol and one with sodium hydroxide, respectively, and the two solutions were then mixed.

Small amounts of water were slowly added dropwise to the mixture at a rate of 1 ml/min. This resulting suspension was stirred for an additional 24 hr. The pH of the reactant solution was adjusted by the addition of 1 M HNO_3 solution. The product was dried at room temperature for 48 hr. The resulting materials were calcined for 3 hr at 450 $^\circ\text{C}$ in air. The molar ratio of the mixture was 1 Al(*sec*-

[†]To whom correspondence should be addressed.

E-mail: jyi@snu.ac.kr

$\text{BuO})_3 : 0.2 \text{ C}_{17}\text{H}_{35}\text{COOH} : 0.04 \text{ NaOH} : 5 \text{ sec-BuOH} : 4\text{-}8 \text{ H}_2\text{O}$.

2. Preparation Na-MA using Sodium Stearate

The procedure was the same as that used in the preparation of MA except sodium stearate ($\text{C}_{17}\text{H}_{35}\text{COONa}$, Fluka) was used in the organic phase. The molar ratio of the mixtures were $1 \text{ Al}(\text{sec-BuO})_3 : 0.2 \text{ C}_{17}\text{H}_{35}\text{COONa} : 5 \text{ sec-BuOH} : 4\text{-}8 \text{ H}_2\text{O}$.

3. Preparation of Mg-MA using Magnesium Stearate

The magnesium salt of stearic acid ($(\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Mg}$, Riedel-De-Häen) has one head group with two tail groups and is 125 times cheaper than stearic acid. The molar ratio of the mixture was $1 \text{ Al}(\text{sec-BuO})_3 : 0.1 (\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Mg} : 5 \text{ sec-BuOH} : 4\text{-}8 \text{ H}_2\text{O}$.

4. Preparation of Ni-MA using Nickel Stearate

The magnesium ion of magnesium stearate can be used as a substitute for the nickel ion of nickel nitrate by treatment with NH_4OH , resulting in the formation of nickel stearate $(\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Ni}$. The product was then separated by centrifugation at 4,500 rpm. The solid fraction, isolated from the NH_4OH -treated reactant by filtration, was used as both a chemical template and a metal source. The molar ratio of this reaction mixture was $1 (\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Mg} : 1 \text{ Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} : 1\text{-}8 \text{ NH}_4\text{OH} : 40 \text{ sec-BuOH}$. The procedure for the preparation of Ni-MA was the same as that of MA. The molar ratio of this reaction mixture was $1 \text{ Al}(\text{sec-BuO})_3 : 0.1 (\text{C}_{17}\text{H}_{35}\text{COO})_2\text{Ni} : 5 \text{ sec-BuOH} : 4\text{-}8 \text{ H}_2\text{O}$.

5. Potential Application: Partial Oxidation of Methane

The catalytic activities of the Ni-MA catalysts were examined in a fixed-bed apparatus at atmospheric pressure. Each calcined catalyst (200 mg) was charged in a tubular quartz reactor and pre-reduced with a mixed stream of hydrogen (10 ml/min) and nitrogen (20 ml/min) as the carrier gas at 700 °C for 4 hr. A mixed feed of CH_4 (10 min^{-1}) and O_2 (5 min^{-1}) was then continuously fed into the reactor together with the N_2 carrier gas (20 min^{-1}). The feed ratio of the CH_4/O_2 was maintained at a stoichiometric ratio of 2. The products were analyzed by gas chromatography using a TCD detector. Argon and Carbosphere (60/80 mesh) were used as a carrier gas and as a column material, respectively.

6. Characterizations

N_2 adsorption/desorption analyses were carried out with a Micromeritics ASAP 2010 analyzer, and powder X-ray diffraction (XRD, M18XHF-SRA, MAC/Science) patterns were recorded to determine the degree of crystallinity of prepared samples. The porosity of the MA was characterized by transmission electron microscopy on a JEM-2000EXII instrument. ^{27}Al MAS NMR spectra were obtained on a Varian-Inova spectrometer (300 MHz) at a MAS frequency of 6 kHz.

RESULTS AND DISCUSSION

1. Template Effects of X-MAs

Stearic acid and its salts have different solubility in an alcohol phase. Stearic acid salts such as sodium stearate are easily dissolved in an alcohol. Thus, a variety of stearic acid salts (*i.e.*, sodium stearate, magnesium stearate, and nickel stearate) was selected as templates in this study. As shown in Fig. 1, FT-IR results suggest that the mechanism of formation of the product is the same, irrespective of whether stearic acid or salt is used. The as-made MA showed a strong band at 1,335-1,440 cm^{-1} assigned to symmetric $-\text{COO}^-$ stretching, and a band at 1,550-1,650 cm^{-1} assigned to asymmetric

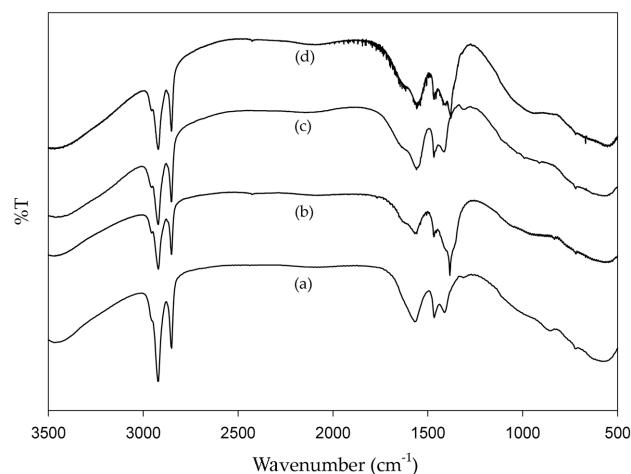


Fig. 1. FT-IR spectra of non-calcined (a) MA, (b) Na-MA, (c) Mg-MA, and (d) Ni-MA.

$-\text{COO}^-$ stretching (Fig. 1(a)). This spectrum was almost the same as that for as-made Na-MA (Fig. 1(b)). This indicates that the carboxyl group ($-\text{COOH}$, 1,700 cm^{-1}) of stearic acid was transformed into a carboxylic salt ($-\text{COO}^-$) in the solvent, after which the salts might have been combined with the aluminum precursor. The mechanism involved is similar to the mediated pathway through charge matching (S⁻M⁺T) when mesoporous silica is prepared using an ionic surfactant [Huo et al., 1994]. Therefore, different salts, such as magnesium stearate and nickel stearate, can be used equally as well as chemical templates for MA via a charge matching pathway as evidenced by FT-IR. In fact, the FT-IR spectra of as-made Mg-MA and Ni-MA were the same as those of as-made MA and Na-MA.

However, the cost of sodium stearate is twice that of stearic acid. This high cost of templates is undesirable in terms of industrial applications. Magnesium stearate is 125 times cheaper as well as more soluble than stearic acid. The mechanism of formation of Mg-MA appears to be similar to that of Na-MA, and an Mg-MA sample with 3.5 nm pores could be successfully synthesized. It should be noted that the preparation of Mg-MA using an inexpensive template is feasible for mass production for industrial applications.

In a catalytic reaction such as HDC and POM, a nickel catalyst supported on MA was used [Kim et al., 2003b, 2004a]. When nickel stearate was used as a chemical template as well as a nickel source, a Ni/ Al_2O_3 catalyst could be easily produced without any additional metal impregnation step. Because the heat energy of $\text{Mg}(\text{OH})_2$ is higher than that of $\text{Ni}(\text{OH})_2$ (Table 1), nickel stearate was prepared by the exchange of magnesium ions in magnesium stearate with nickel ions, using an NH_4OH treatment. In addition, nickel stearate was obtained by treatment with HCl due to the low heat of formation energies of MgCl_2 compared to NiCl_2 [Kim et al., 2003d]. Ni-MA with a slightly increased pore (3.8 nm) was prepared by using this procedure. The nickel in Ni-MA was directly incorporated into the alumina framework. The nickel and magnesium contents of Ni-MA were dependent on the initial metal contents, and, in a typical sample, were 8 and 2 wt%, respectively. The magnesium content could be decreased to below 1 wt% by repeated purification. The ratio of nickel and magnesium was adjusted by altering the initial

Table 1. Heat of formation data for chloride and hydroxide salts

Chloride form salts	MgCl ₂	NiCl ₂	CoCl ₂	CuCl ₂	PtCl ₂
Hydroxide form salts	Mg(OH) ₂	Ni(OH) ₂	Co(OH) ₂	Cu(OH) ₂	Pt(OH) ₂
ΔH (kcal/mol)	-153	-75	-76	-48	-34
	-221	-129	-131	-108	-87

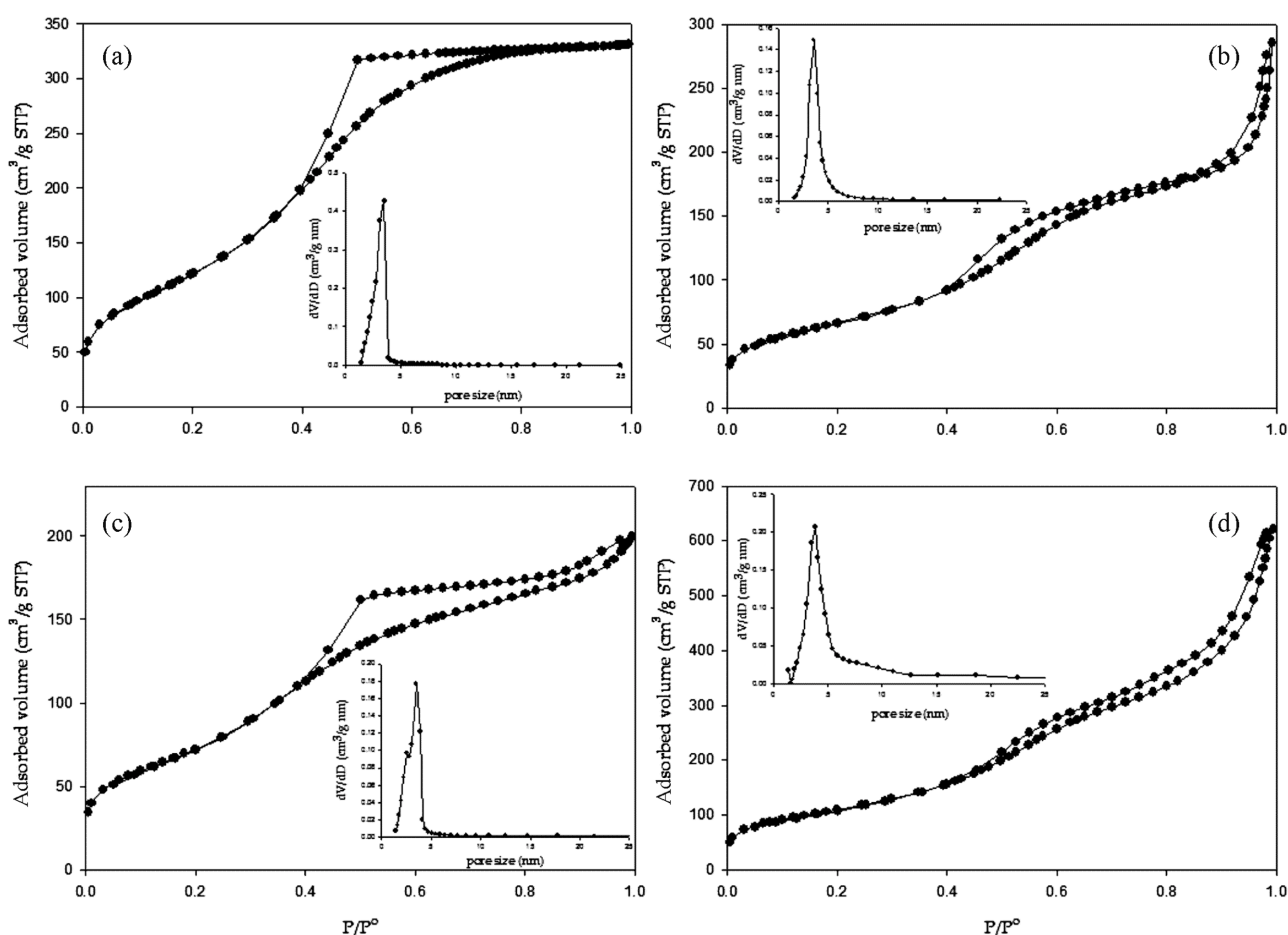
molar ratio of magnesium stearate to the nickel precursor. Ni-MA_n with different metal ion ratios (Ni/Mg=7.4/2.3, 7.6/7.1 and 7.8/15.8 for Ni-MA1, Ni-MA2, and Ni-MA3, respectively) were tested in the POM reaction as a potential application.

Other stearic acid salts could also be prepared by the exchange of metal ions with magnesium ions based on thermodynamic data

(Table 1). Namely, Co-MA, Cu-MA, and Pt-MA could be prepared using cobalt, copper, and platinum stearate, respectively.

2. Pore Properties of MA and X-MAs

As shown in Fig. 2 and Table 2, the mesostructures of the MA and X-MAs (X=Na, Mg, and Ni) prepared with stearic acid and its salts were somewhat different. The N₂ adsorption/desorption iso-

**Fig. 2. N₂ adsorption/desorption isotherms of (a) MA, (b) Na-MA, (c) Mg-MA, and (d) Ni-MA.****Table 2. Pore properties of the prepared mesoporous aluminas**

Sample	Template/cost ratio	D (nm)	D_{FWHM}^b (nm)	S_{BET} (m^2/g)	V_p (cm^3/g)
MA	C ₁₇ H ₃₅ COOH/1	3.49	0.89	485	0.50
Na-MA	C ₁₇ H ₃₅ COONa/2	3.59	1.09	241	0.29
Mg-MA	(C ₁₇ H ₃₅ COO) ₂ Mg/0.008	3.56	1.03	311	0.31
Ni-MA	(C ₁₇ H ₃₅ COO) ₂ Ni/0.015 ^a	3.80	0.78	399	0.64

^aPrice of nickel stearate=price of (magnesium stearate+nickel nitrate).

^bFull width at half maximum of pore size distribution.

therm was a typical type of IV isotherm and an H_2 hysteresis loop, indicating mesoporous porosity. The framework porosity at 0.4–0.7 P/P^0 in the N_2 isotherm indicates that the porosity is contained within the uniform channels of the templated framework, while the textural porosity at 0.8–1 P/P^0 is indicative of a porosity arising from non-crystalline intra-aggregate voids and spaces formed by inter-particle contacts. MA and Mg-MA had a mainly framework porosity, while Na-MA and Ni-MA showed both framework and textural porosity. It might be due to the effect of different cations in head group of templates. Therefore, the pore properties of MA and X-MAs are affected slightly by the type of surfactant used (Table 2). However, both MA and X-MAs have a similar pore size (3.6 nm) and narrow pore size distribution ($D_{FWHM} \sim 1.0$ nm). Because the alkyl chain length of the surfactants is identical, the pore sizes are essentially the same. In addition, the pore uniformity and the surface area of the X-MAs are superior to that for AA, which shows an irregular pore distribution and a small surface area (*ca* 100 m²/g).

In low angle XRD patterns for mesoporous aluminas, only one peak appeared at 2θ between 0.5–3° (Fig. 3). The generation of X-ray peaks results from a difference in the scattering power (or scattering contrast) between two building blocks (amorphous wall, and pore channel contained with air and helium) of mesoporous materials. This indicates that the mesoporous aluminas have different

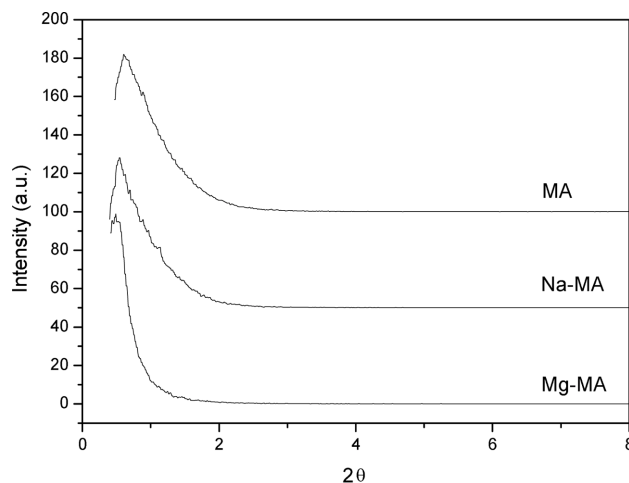


Fig. 3. Low angle XRD patterns of mesoporous aluminas.

pore structures compared to hexagonal mesoporous silicas such as MCM-41 or SBA-15, which exhibit three peaks at 2θ between 0.5–5°. Thus, the mesoporous aluminas prepared here have a sponge-like pore channel structure with a random pore distribution, whereas MCM-41 has a 1D cylindrical pore structure with a highly regular

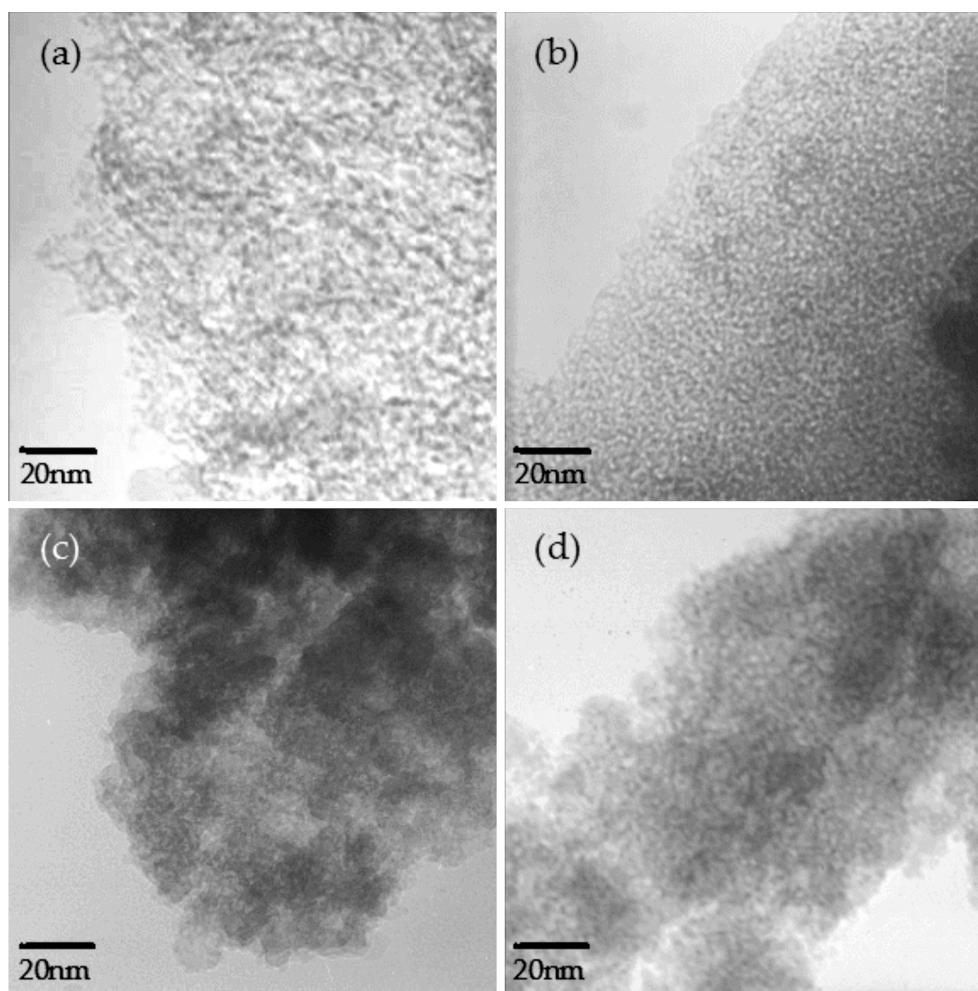


Fig. 4. TEM images of (a) MA, (b) Na-MA, (c) Mg-MA, and (d) Ni-MA.

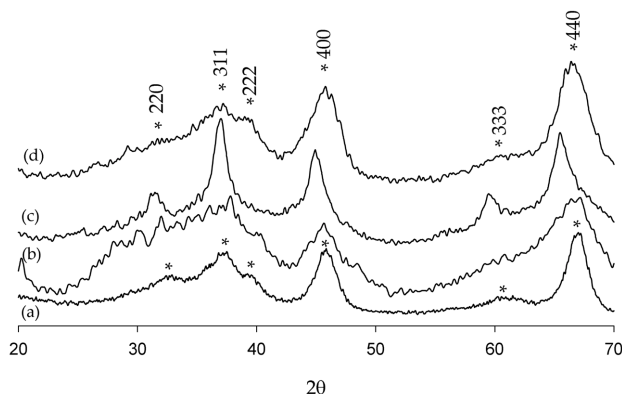


Fig. 5. XRD patterns of (a) MA, (b) Na-MA, (c) Mg-MA, and (d) Ni-MA.

pore distribution. These results are consistent with the following TEM data as shown in Fig. 4.

In all of the MA and X-MAs, the developed framework pores had a sponge-like appearance, which confirms the advantage of having an interconnected pore system. A similar pore morphology was found for disordered mesoporous silica (*i.e.*, HMS type) and aluminas when ionic or neutral surfactants were used in their preparation. An interconnected pore structure has the advantage of a reduced diffusion limitation and an enhanced molecular accessibility to active sites on the inner surface [Kim et al., 2004c].

3. Phase Determination of MA and X-MAs

Aluminas have a variety of crystalline structures and show three major peaks in the spinel structure of MA, as shown in Fig. 5. The cubic spinel structure (space group, $Fd\bar{3}m$), usually denoted as AB_2O_4 , possesses an *fcc* sublattice of oxygen ions with A and B cations occupying the tetrahedral (Al^{IV}) and octahedral (Al^{VI}) interstices [Wolverton and Hass, 2001]. In addition, unoccupied tetrahedral and octahedral interstices of the oxygen sublattice are present. The total ratio of cation to anion for the spinel structures is 3 : 4, and thus creating an Al_2O_3 phase (cation : anion = 2 : 3) in the spinel structure that necessitates the creation of vacancy defects on the cation sublattice. Among the various alumina phases, γ , η - and δ -aluminas have spinel structures.

XRD patterns of MA and X-MAs typically show the characteristic peaks of activated alumina. The pattern for Mg-MA was similar to that of MA, while the peaks were left-shifted and the width of the peaks became narrow without any magnesium peaks. This was due to the different ionic radius of magnesium ions and the characteristic peaks of the magnesium spinel structure, which were overlapped with those of the activated alumina phase. The ionic radii of sodium (Na^+) and magnesium (Mg^{2+}) are 0.97 Å and 0.66 Å, respectively. In Na-MA, no sodium ions penetrate into the interior of the

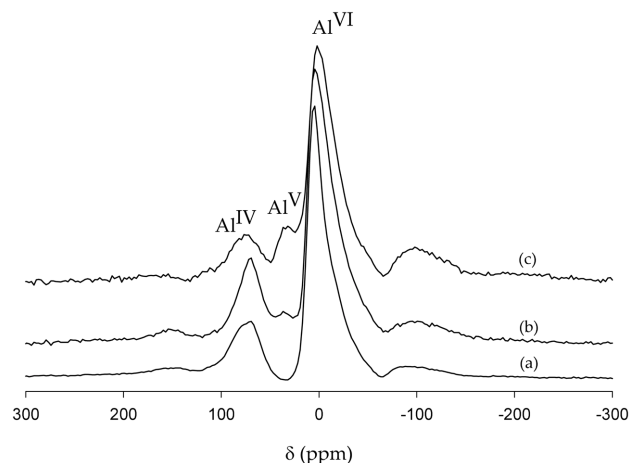


Fig. 6. ^{27}Al MAS NMR spectra of (a) MA, (b) Mg-MA, and (c) Ni-MA.

structure, namely, the cation vacancy of the surface, because of its large ionic radius. As a result, it was likely that sodium was present only on the surface of the Na-MA, and not on the inside of the crystal. Because of this, sodium ions were easily removed by washing, while magnesium ions were able to penetrate into the interior of the structure. Mg-MA forms a crystalline structure that contains magnesium. Because the ionic radius of magnesium is larger than that of aluminum, magnesium within an alumina structure expands the lattice parameter of Mg-MA, followed by a left-shift in the XRD peak. In addition, magnesium ions occupy the cation vacancy and reinforce the structure of alumina, and, as a result, the peak width is narrowed.

The γ and η -aluminas generally exist as spinel alumina because their structures are very closely related to that of Mg spinel ($MgAl_2O_4$). The XRD patterns of both activated aluminas are similar, and it is not easy to distinguish the phase. Therefore, the coordination of Al atoms to the activated alumina was investigated by ^{27}Al MAS NMR (Fig. 6).

In general, as-made aluminas mainly have 6-coordinated Al atoms, in the form of layered aluminum hydroxide. After calcination, tetrahedral (Al^{IV}) and octahedral (Al^{VI}) coordinated Al are produced as the result of dehydration and the dehydroxylation of aluminum hydroxide, and pentahedral (Al^V) coordinated Al is produced by migration toward the tetrahedral and/or octahedral sites. ^{27}Al NMR studies indicate $75 \pm 4\%$ Al^{VI} in γ -alumina and $65 \pm 4\%$ Al^{VI} in η -alumina, respectively [Sohlberg et al., 2001]. As shown in Table 3 and Fig. 6, the calculated ratios of $Al^{IV} : Al^V : Al^{VI}$ of MA, Mg-MA, and Ni-MA are 28.2 : 0.0 : 71.8, 23.2 : 0.7 : 76.1, and 17.0 : 5.0 : 78.0, respectively, and the phase of all the aluminas is close to γ -alumina.

Table 3. ^{27}Al MAS NMR data for mesoporous alumina

Sample	Population (%)				Position (ppm)		
	Al^{IV}	Al^V	Al^{VI}	Al^{VI}/Al^{IV}	Al^{IV}	Al^V	Al^{VI}
MA	28.2	0.0	71.8	2.55	69.289	-	4.315
Mg-MA	23.2	0.7	76.1	3.28	69.289	36.802	4.315
Ni-MA	17.0	5.0	78.0	4.58	76.788	31.804	1.816

However, the chemical shift position of Ni-MA was slightly different to that for MA (Table 3). In the case of inverse bimetallic spinels such as NiAl_2O_4 , nickel oxide, supported on the active alumina, allows Ni^{2+} ions to diffuse into the surface lattice vacancies of the alumina spinel structure [Chokkaram et al., 1997]. The surface lattice vacancies of the tetrahedral coordinated Al are occupied by Ni^{2+} ions that diffused in during dehydroxylation and dehydration, and, as a result, the electron field of Al^{IV} is deshielded compared to that of Al^{IV} with vacancies. Therefore, the position of the chemical shift (δ) of tetrahedral Al atoms in Ni-MA ($\text{Al}_\delta^{\text{IV}}=76.788$) was shifted to the left (deshielding), compared to that in MA ($\text{Al}_\delta^{\text{IV}}=69.289$). This migration of nickel ions into the alumina matrix is a common phenomenon associated with metal supported catalysts and may be limited to the first few layers of the support [Kim et al., 2003d]. For pentahedral Al, unsaturated Al is produced due to the formation of oxygen vacancies as the result of the dehydroxylation of precursors. This Al^{V} coordinated Al serves as an electron acceptor and functions as Lewis acid sites.

4. Potential Applications of MA and X-MAs

In this study, bimetallic Ni-MAN ($n=1, 2, 3$) with different metal ratios ($\text{Ni/Mg}=7.4/2.3, 7.6/7.1$ and $7.8/15.8$ for Ni-MA1, Ni-MA2, and Ni-MA3, respectively) were evaluated for use in the POM reaction as a potential application. The reaction was performed at a high temperature (700°C). Thus, as-made Ni-MAN was thermally treated at 800°C , and calcined Ni-MAN was then reduced at 750°C . While the surface area of Ni-MAN was decreased to $110\text{ m}^2/\text{g}$ due to the sintering effect, mesoporosity was maintained. In XRD data, Ni-MA catalyst treated at 800°C maintained the same characteristic peaks of γ -alumina, which calcined at $400\text{--}550^\circ\text{C}$. It should be noted that a bimetallic catalyst has a high thermal stability. As shown in Fig. 7, methane conversion for Ni-MAN changed with the metal ratio. Ni-MA2 and Ni-MA3 showed a higher conversion and was more stable than Ni-MA1 during an 11 hr reaction. In POM reaction as a potential application, there existed the optimum metal ratio of nickel to magnesium, and its ratio was about 1. While nickel metal mainly acted as an active site, magnesium enhanced the thermal stability of framework and suppressed the deactivation of POM.

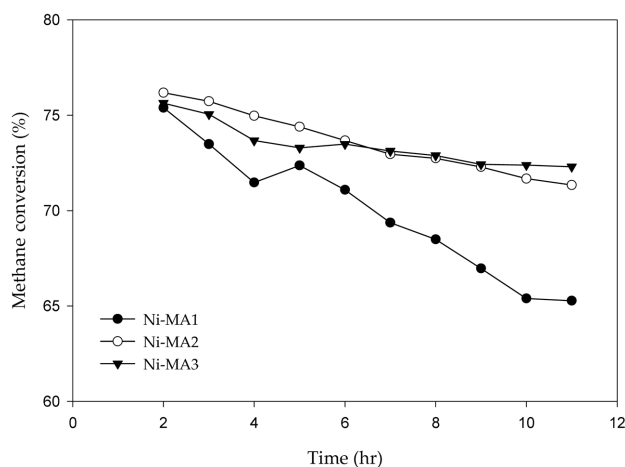


Fig. 7. Catalytic activity of Ni-MAN catalysts in the POM reaction over an 11 hr period.

CONCLUSIONS

MA and X-MAs ($X=\text{Na}, \text{Mg}$, and Ni) were prepared by using four different templates, including stearic acid, sodium stearate, magnesium stearate, and nickel stearate. The pore properties of the X-MAs were similar to those of MA. This clearly shows that stearic acid salts could be used as templates for the preparation of X-MAs. The preparation of Mg-MA using an inexpensive template was feasible for mass production in industrial applications. By treatment with an acid or base, magnesium ions in magnesium stearate were readily exchanged with other metal ions. Thus metal incorporated alumina could be easily and directly prepared using metal stearate as a chemical template and a metal source. The POM reaction, as a potential application, was conducted using bimetallic Ni-MAN catalysts, and showed a high thermal stability and a low deactivation.

ACKNOWLEDGMENTS

This work was supported by National Research Laboratory (NRL) of the Korean Science and Engineering Foundation (KOSEF).

REFERENCES

- Bagshaw, S. A. and Pinnavaia, T. J., "Mesoporous Alumina Molecular Sieves," *Angew. Chem. Int. Ed.*, **35**(10), 1102 (1996).
- Cabrera, S., Haskouri, J. E., Alamo, J., Beltran, A., Mendioroz, S., Marcos, M. D. and Amoros, P., "Surfactant-Assisted Synthesis of Mesoporous Alumina Showing Continuously Adjustable Pore Size," *Adv. Mater.*, **11**(5), 379 (1999).
- Chokkaram, S., Srinivasan, R., Milburn, D. R. and Davis, B. H., "Conversion of 2-Octanol over Nickel-Alumina, Cobalt-Alumina, and Alumina Catalysts," *J. Mol. Catal. A*, **121**(2-3), 157 (1997).
- Corma, A., "From Microporous to Mesoporous Molecular Sieve Materials and Their Use in Catalysis," *Chem. Rev.*, **97**(6), 2373 (1997).
- Huo, Q., Margolese, D. I., Ciesla, U., Feng, P., Gier, T. E., Sieger, P., Leon, R., Petroff, P. M., Schuth, F. and Stucky, G. D., "Generalized Synthesis of Periodic Surfactant/Inorganic Composite Materials," *Nature*, **368**(24), 317 (1994).
- Kim, C., Kim, Y., Kim, P. and Yi, J., "Synthesis of Mesoporous Alumina Using a Cost-Effective Template," *Korean J. Chem. Eng.*, **20**(6), 1142 (2003a).
- Kim, P., Kim, Y., Kim, C., Kim, H., Park, Y., Lee, J. H., Song, I. K. and Yi, J., "Synthesis and Characterization of Mesoporous Alumina as a Catalyst Support for Hydrodechlorination of 1,2-Dichloropropane: Effect of Catalyst Preparation Method," *Catal. Lett.*, **89**(3-4), 185 (2003b).
- Kim, P., Kim, H., Kim, Y., Song, I. K. and Yi, J., "Synthesis and Characterization of Mesoporous Alumina with Nickel Incorporated for Use in the Partial Oxidation of Methane into Synthesis Gas," *Appl. Catal. A*, **272**(1-2), 157 (2004a).
- Kim, Y., Lee, B. and Yi, J., "Synthesis of Mesoporous γ -Alumina through Pre- and Post-Hydrolysis Methods," *Korean J. Chem. Eng.*, **19**(5), 908 (2002).
- Kim, Y., Kim, C., Choi, J. W., Kim, P. and Yi, J., "Synthesis of Mesoporous γ -Aluminas of Controlled Pore Properties Using Alkyl Carboxylate Assisted Method," *Stud. Surf. Sci. Catal.*, **146**, 209 (2003c).
- Kim, Y., Kim, P., Kim, C. and Yi, J., "A Novel Method for Synthesis of

- a Ni/Al₂O₃ Catalyst with a Mesoporous Structure Using Stearic Acid Salts," *J. Mater. Chem.*, **13**(9), 2353 (2003d).
- Kim, Y., Kim, C., Choi, I., Rengaraj, S. and Yi, J., "Arsenic Removal Using Mesoporous Alumina Prepared via a Templating Method," *Environ. Sci. Technol.*, **38**(3), 924 (2004b).
- Kim, Y., Kim, C. and Yi, J., "Synthesis of Tailored Porous Alumina with A Bimodal Pore Size Distribution," *Mater. Res. Bull.*, **39**(13), 2103 (2004c).
- Kim, Y. and Yi, J., "Advances in Environmental Technologies via the Application of Mesoporous Materials," *J. Ind. Eng. Chem.*, **10**(1), 41 (2004).
- Sohlberg, K., Pantelides, S. T. and Pennnycook, S. J., "Surface Reconstruction and the Difference in Surface Acidity between γ - and η -Alumina," *J. Am. Chem. Soc.*, **123**(1), 26 (2001).
- Valange, S., Cuth, J.-L., Kolenda, F., Lacombe, S. and Gabelica, Z., "Synthesis Strategies Leading to Surfactant-Assisted Aluminas with Controlled Mesoporosity in Aqueous Media," *Micropor. Mesopor. Mat.*, **35-36**, 597 (2000).
- Wolverton, C. and Hass, K. C., "Phase Stability and Structure of Spinel-Based Transition Aluminas," *Phys. Rev. B*, **63**, 024102 (2001).
- Yada, M., Hiyoshi, H., Ohe, K., Machida, M. and Kijima, T., "Synthesis of Aluminum-Based Surfactant Mesophases Morphologically Controlled through a Layer to Hexagonal Transition," *Inorg. Chem.*, **36**(24), 5565 (1997).