Hindawi Publishing Corporation
Journal of Nanoparticles
Volume 2013, Article ID 102823, 4 pages
http://dx.doi.org/10.1155/2013/102823

Research Article

Characterization and Modification of Mesoporous Silica Nanoparticles Prepared by Sol-Gel

Meysam Keshavarz and Norhayati Ahmad

Department of Materials, Manufacturing and Industrial Engineering, Faculty of Mechanical Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Johor, Malaysia

Correspondence should be addressed to Norhayati Ahmad; nhayati@fkm.utm.my

Received 18 May 2013; Accepted 3 August 2013

Academic Editor: Vijaya Rangari

Mesoporous silica nanoparticles (MSNs) were synthesized by sol-gel reaction at normal pressure by using TEOS as a silica source and CTAB as a directing agent in ammonia solution at 323 K subsequently calcined at 823 K. Then inorganic pores were modified with metal-supported MSN with attention to the acidity, surface area, pore size, and ability of ion exchange. Crystalline size was shown to decrease up to 20 molar ratios of Si/Al followed by increasing while further adding nanoparticles-aluminium. Moreover, the XRD patterns revealed the mesostructured material for all with 2D hexagonal structure. The obtained results from the XRD patterns were confirmed by using BET and EDX. The BET surface areas revealed the spherical shape for all samples with a decrease in the pore volume and surface area for various AlMSNs which emphasized that the loading of Al and was compatible with XRD results. MSN was prepared by sol-gel methods followed by loading of Al in order to prepare AlMSN which possess strong Lewis acidic sites. This modification occurred by using various molar ratios of 0, 5, 10, 20, 50, and 100 Si/Al, respectively. The XRD patterns of various ratios of Si/Al were interpreted in terms of strain, nanocrystalline size, and distribution of the particle size by deriving Wiliamson Hall equation.

1. Introduction

More than 10 years passed since the discovery of the so-called M41S mesoporous silica materials, and the synthesis of the mesoporous materials with different characterizes has been gaining increasing attention. This study attempts to reveal the dependence effect of various ratios of Si/Al additive on nanocrystalline size, residual stress and physicochemical property of mesostructure siliceous nanoparticles (MSN) which can give a better insight of its application on petroleum refinery and petrochemical industries. Moreover, the nobility of this research might be the utilization of XRD pattern to find out nanocrystalline size, residual stress, and microstructure.

The surfactant-templating method has been extended to the synthesis of nonsilica oxide mesoporous materials [1–3]. Potential application of mesoporous transition metal oxides has been found in the fields of electromagnetic, photoelectronics, catalysis, and separation [4]. By using cationic surfactants with quaternary ammonium derivatives and then nonionic alkoxysilanes, a series of ordered mesoporous silicas had been synthesized [5–7] and the various alkaline or acidic [8–10] conditions were used. These experiments have shown better condensation of the silanol groups in mesoporous silica obtained under alkaline conditions and also a rich morphology in shapes achieved in acidic conditions [11].

Mesoporous silica nanoparticle (MSN) has been used as the ideal carrier for large quantities of biogenic agents [12]. The morphological control for a spherical shape and the reduction of particle size in the nanometer scale have made this material useful for anticancer drug delivery applications [13]. The nature of zeolites such as pore diameter (less than 2 nm) limits their catalytic performance in catalytic reactions of bulky molecules, such as pharmaceutical, biological, and some chemical reactions [14], and there is some limitation for the influence of the larger molecules into the micropore channels [15]. Due to this drawback, enhancing the pore size of zeolites and zeotype materials from micropore to mesopore is very important for both industrial applications and fundamental studying of porous structures. Therefore various mesoporous structures were synthesized by changing

the frameworks using different precursor materials, pH conditions, and temperatures [16–18]. M41S, MCM-41, MCM-48, SBA-1, SBA-2, and other samples were prepared using quaternary ammonium salts such as cetyltrimethylammonium bromide (CTAB) and polyethylene oxide as templates, TEOS and TMOS as sources of Si [19, 20]. Replacement of Al with some Si in the mesoporous silica structures alter the characteristic and acidic sites of them, and a new porous generates with modified properties and improved the Lewis or Bronsted acid sites whether alone or both of them [21]. The introduction of Al into the template of MCM-41 increased the acidity. In comparison of the other results, AlMCM-41 catalyst is more catalytically active in the condensation, Diels-Alder, Friedel-Crafts acylation, and alkylation reactions than the heterogeneous solid acids, for example, microporous H-ZSM-5, HY zeolites, mesoporous SBA-15, amorphous silica-alumina, active alumina, amberlist 15, silica gel, and homogeneous acid catalysts such as p-toluenesulfonic acid and fAlCl3 [22–24]. These researches reveal that the increase in aluminium content leads to an increase in both Lewis and Bronsted acidic sites from being moderate to strong. These materials could act as acid catalysts in the chemical reactions [25, 26].

In this study, the crystallinities, strains, and pore diameters of various aluminium containing-MSN with different molar ratios of Si/Al were measured and the calculated values from the XRD patterns were compared with experimental data. Si/Al ratios of 0, 5, 10, 20, 50, and 100 were used.

2. Materials and Methods

Cetyltrimethylammonium bromide (CTAB, 5 mmol) was dissolved in a solution containing water (10 mmol), EG (5 mmol), tetraethylorthosilicate (TEOS, 1 mmol), and 3-aminopropyl triethoxysilane (APTES, 1 mmol) with ammonia aqueous solution (25%) and stirred at 323 K for 8 h and then was kept statically at the same temperature for 20 h. Samples were collected by centrifugation (20000 rpm) and repeatedly washed with deionized water. The synthesized mesoporous were dried at 333 K. Then MSN (1 g) and NH_4NO_3 (0.3 g) were dissolved in ethanol (40 mL), heated at 333 K to remove the remained surfactant and then calcined at 823 K for 3 h. The various samples of AlMSN with 5, 10, 20, 50, 100 Si/Al molar ratios was prepared by using sodium aluminate (SA) solution via impregnation method at 340 K for 10 h, followed by filtration and drying at 383 K. The AlMSN samples were obtained by calcination at 823 K for 3 h.

In order to determine the nanocrystalline size and microstrain of Mesoporous Silica Nanoparticles with different amount of Aluminium Loaded, Williamson-Hall method was used. X-ray powder diffraction (XRD) measurements were recorded at room temperature in Bruker D8 ADVANCE diffractometer equipped with Cu-Kα radiation (λ = 1.54056 A). The intensities of diffraction lines were collected with a constant step of 0.02° of 2θ and with a constant counting time of 20 seconds at each step. X-rays diffraction line broadening profile analysis was used to analyze the crystallite size and microstrains of nanoparticles.

Table 1: Physicochemical property of catalysts and catalyst supports.

Sample	BET surface area (m^2/g)	Pore diameter (nm)	Pore volume (cm^3/g)
AlMSN0	995.3	3.4	0.84
AlMSN20	588.5	4.0	0.59

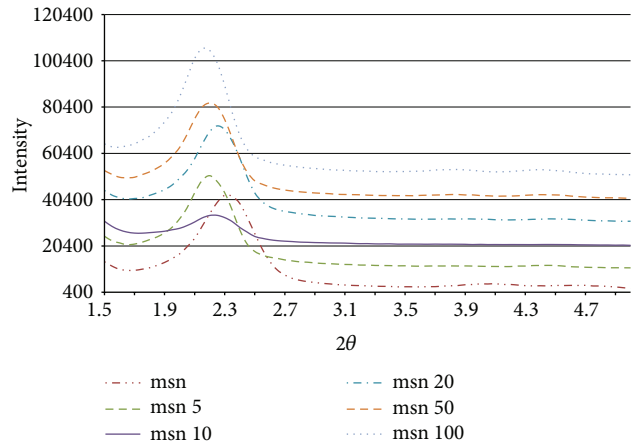

Figure 1: The XRD patterns of AlMSN 0, 5, 10, 20, 50, and 100.

3. Results and Discussion

3.1. XRD Results of AlMSN Samples. The XRD pattern of AlMSN samples is shown in Figure 1. Three intense peaks around 2θ = 2.4, 4.2 and 4.7 indexed as (100), (110), and (200) reflections were observed which confirmed the characteristic of a two-dimensional (2D) hexagonal (p 6 mm) structure with d_{10} spacing of approximately 3.8 nm.

Table 1 shows the BET results of the two samples of AlMSN0 and AlMSN20 catalysts samples.

The results cleared that after introduction of aluminium, the pore volume and surface area were decreased and pore diameter was increased which these indicated to the loading of aluminium, changing the pore wall thickness, and producing pores with smaller volumes. Then it is clear that their thickness increases after alumination that it has confirmed by the XRD pattern.

The peak breadth due to sample (strain and size), B was calculated according to Gaussian profile:

$$B2 = B2_{\text{exp}} - B2_{\text{inst}}, \tag{1}$$

where B is the FWHM at half maximum of the powder, B_{inst} is the FWHM of the standard reference materials (AlMSN0) used for calibration, and B_{exp} is the FWHM evaluated. FWHM values of the main diffraction peaks and crystalline size for mesoporous are tabulated in Table 2. The average crystallite size and internal microstrain are calculated by the Williamson-Hall method as expressed in (2).

$$B\cos\theta = \frac{K\lambda}{D} + 4\varepsilon\sin\theta, \tag{2}$$

where K is the Scherrer constant, D is crystallite size, λ is the wavelength, and ε is microstrain. The effective crystallite size

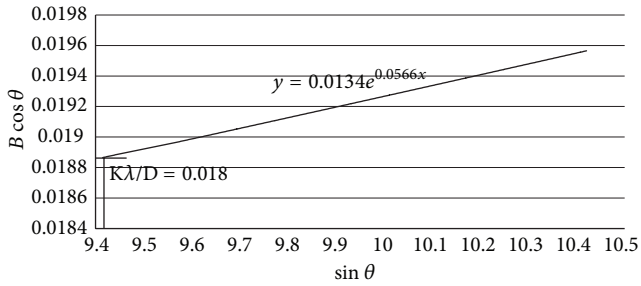

Figure 2: Microstrain and average crystalline size.

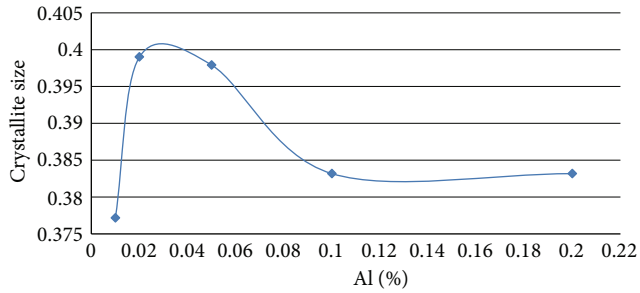

Figure 3: Variation of crystalline size and Al percentage.

Table 2: FWHM values of the main diffraction peaks and crystalline size for mesoporous.

Percentage	FWHM	Theta	Crystallite size (nm)
0	0.384	1.065	3.77181407
0.01	0.363	1.094	3.99005625
0.02	0.364	1.094	3.97909455
0.05	0.378	1.1235	3.83175886
0.1	0.378	1.1235	3.83175886
0.2	0.362	1.094	4.0010785

taking strain into account is estimated by plotting $(B\cos\theta)$ versus $(\sin\theta)$. From (2), a plot of $(B\cos\theta)$ versus $(\sin\theta)$ is a straight line with a slope of $7.0487E-04$ and an intercept of $K\lambda/D$; as shown in Figure 2 the crystallite size and microstrains nanopowders could be estimated.

3.2. XRD Profile Analysis. Figure 3 shows the data of structural parameter obtained from XRD analysis and Williamson-Hall calculation from (2). The average crystallite size of mesoporous silica nanoparticles with different amounts of loaded aluminium was calculated by measuring the value of FWHM, 2θ (angle of diffraction), and λ (wavelength) which is obtained from XRD data. The FWHM is the important value to estimate the nanocrystalline size and microstrain. Due to the loading Al into Mesoporous Silica, particle and crystalline refinement occurs and the lattice microstrain increases up to −4.44073 at 0.05% of Al loaded, the negative sign indicates compressive train of microstrain. Decreasing the portion of Al additive leads to broadening of the XRD peaks and a consequent decrease in the peak heights. The domain crystallite size of AlMSN with various

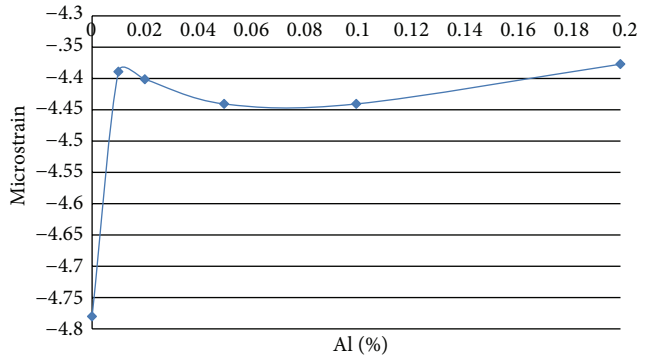

Figure 4: Relation of Al percentage and microstrain.

molar ratios of 0, 5, 10, 20, 50, and 100 Si/Al was found 0.377, 0.399, 0.398, 0.383, 0.383, and 0.4 respectively. Variation of crystalline size and Al percentage was plotted in Figure 3. The relation of Al percentage and sequentially the microstrain is revealed in Figure 4.

4. Conclusion

The mesoporous silica nanoparticles of aluminium supported (AlMSN) were synthesized by using organic-inorganic hybrid method through sol-gel reaction. The XRD pattern of the parent materials represented a higher-order structure which was a bit changed after loading of aluminium into the structures. Moreover, the XRD patterns show slight shifting of the peaks by increasing the proportion of additive which is due to changing the preferential crystalline orientation. Loading of aluminium produced the fairly strong Lewis acid sites and weak Bronsted sites. Study of XRD pattern revealed increasing in compressive strain and crystalline size from the molar ratio of Si/Al 0 to 20 and decreasing the strain and also crystalline size in low Al concentrations.

Acknowledgments

This work was sponsored by the Research University grant and University Teknologi Malaysia under Grant no. QJ130000.2524.04H74.

References

[1] M. Fröba and N. Oberender, "First synthesis of mesostructured thiogermanates," *Chemical Communications*, pp. 1729–1730, 1997.

[2] M. J. MacLachlan, N. Coombs, and G. A. Ozin, "Non-aqueous supramolecular assembly of mesostructured metal germanium sulphides from $(Ge_4S_{10})^{4-}$ clusters," *Nature*, vol. 397, no. 6721, pp. 681–684, 1999.

[3] D. M. Antonelli and J. Y. Ying, "Synthesis of a stable hexagonally packed mesoporous niobium oxide molecular sieve through a novel ligand-assisted templating mechanism," *Angewandte Chemie International Edition*, vol. 35, pp. 426–430, 1996.

[4] X. He and D. Antonelli, "Recent advances in synthesis and applications of transition metal containing mesoporous molecular

sieves," *Angewandte Chemie International Edition*, vol. 41, pp. 214–229, 2002.

[5] J. L. Blin, A. Léonard, and B. L. Su, "Well-ordered spherical mesoporous materials CMI-1 synthesized via an assembly of decaoxyethylene cetyl ether and TMOS," *Chemistry of Materials*, vol. 13, pp. 3542–3553, 2001.

[6] A. Léonard, J. L. Blin, M. Robert, P. A. Jacobs, A. K. Cheetham, and B. L. Su, "Toward a better control of internal structure and external morphology of mesoporous silicas synthesized using a nonionic surfactant," *Langmuir*, vol. 19, no. 13, pp. 5484–5490, 2003.

[7] J. L. Blin, R. Flamant, and B. L. Su, "Synthesis of nanostructured mesoporous zirconia using CTMABr-$ZrOCl_2 \cdot 8H_2O$ systems: a kinetic study of synthesis mechanism," *International Journal of Inorganic Materials*, vol. 3, no. 7, pp. 959–972, 2001.

[8] T. Yanagisawa, T. Shimizu, K. Kuroda, and C. Kato, "The preparation of alkyltrimethylammonium-kanemite complexes and their conversion to microporous materials," *Bulletin of the Chemical Society of Japan*, vol. 63, no. 4, pp. 988–992, 1990.

[9] Q. Huo, T. E. Gier, P. Sieger et al., "Generalized synthesis of periodic surfactant/inorganic composite materials," *Nature*, vol. 368, no. 6469, pp. 317–321, 1994.

[10] J. S. Beck, J. C. Vartuli, W. J. Roth et al., "A new family of mesoporous molecular sieves prepared with liquid crystal templates," *Journal of the American Chemical Society*, vol. 114, no. 27, pp. 10834–10843, 1992.

[11] H. Yang, N. Coombs, and G. A. Ozin, "Morphogenesis of shapes and surface patterns in mesoporous silica," *Nature*, vol. 386, no. 6626, pp. 692–695, 1997.

[12] I. I. Slowing, B. G. Trewyn, S. Giri, and V. S.-Y. Lin, "Mesoporous silica nanoparticles for drug delivery and biosensing applications," *Advanced Functional Materials*, vol. 17, no. 8, pp. 1225–1236, 2007.

[13] J. Gu, W. Fan, A. Shimojima, and T. Okubo, "Organic-inorganic mesoporous nanocarriers integrated with biogenic ligands," *Small*, vol. 3, no. 10, pp. 1740–1744, 2007.

[14] A. Corma, "Inorganic solid acids and their use in acid-catalyzed hydrocarbon reactions," *Chemical Reviews*, vol. 95, pp. 559–614, 1995.

[15] M. Mazaj, N.Z. Logar, G. Mali et al., "Synthesis and structural properties of titanium containing microporous/mesoporous silicate composite (Ti, Al)-Beta/MCM-48," *Microporous and Mesoporous Materials*, vol. 99, pp. 3–13, 2007.

[16] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, and J. S. Beck, "Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism," *Nature*, vol. 359, no. 6397, pp. 710–712, 1992.

[17] P. A. M. van Koppen, P. R. Kemper, and T. Michael, "Reactions of state-selected cobalt(+) with propane," *Journal of the American Chemical Society*, vol. 114, pp. 1083–1084, 1992.

[18] D. W. Lee, S.J. Parka, S. K. Ihm, and K. H. Lee, "Synthesis of Pt-containing mesoporous silica using Pt precursor as a pore-forming agent," *Journal of Non-Crystalline Solids*, vol. 353, pp. 1501–1507, 2007.

[19] J. S. Beck, J. C. Vartuli, W. J. Roth et al., "A new family of mesoporous molecularsieves prepared with liquid crystal templates," *Journal of the American Chemical Society*, vol. 114, no. 27, pp. 10834–10843, 1992.

[20] D. Zhao, J. Feng, Q. Huo et al., "Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores," *Science*, vol. 279, no. 5350, pp. 548–552, 1998.

[21] R. Ryoo, C. H. Ko, and R. F. Howe, "Imaging the distribution of framework aluminum in mesoporous molecular sieve MCM-41," *Chemistry of Materials*, vol. 9, no. 7, pp. 1607–1613, 1997.

[22] T. Kugita, S. K. Jana, T. Owada, N. Hashimoto, M. Onaka, and S. Namba, "Mesoporous Al-containing MCM-41 molecular sieves: highly active catalysts for Diels-Alder reaction of cyclopentadiene with α,β-unsaturated aldehydes," *Applied Catalysis A*, vol. 245, no. 2, pp. 353–362, 2003.

[23] X. S. Zhao, M. G. Q. Lu, and C. Song, "Immobilization of aluminum chloride on MCM-41 as a new catalyst system for liquid-phase isopropylation of naphthalene," *Journal of Molecular Catalysis A*, vol. 191, no. 1, pp. 67–74, 2003.

[24] A. Corma, M. J. Díaz-Cabañas, M. Moliner, and G. Rodriguez, "Synthesis of micro- and mesoporous molecular sieves at room temperature and neutral pH catalyzed by functional analogues of silicatein," *Chemical Communications*, no. 29, pp. 3137–3139, 2006.

[25] A. Sakthivel, S. E. Dapurkar, N. M. Gupta, S. K. Kulshreshtha, and P. Selvam, "The influence of aluminium sources on the acidic behaviour as well as on the catalytic activity of mesoporous H-AlMCM-41 molecular sieves," *Microporous and Mesoporous Materials*, vol. 65, no. 2-3, pp. 177–187, 2003.

[26] S. E. Dapurkar and P. Selvam, "Mesoporous H-AlMCM-48: highly efficient solid acid catalyst," *Applied Catalysis A*, vol. 254, no. 2, pp. 239–249, 2003.