Journal of Applied Sciences

ISSN 1812-5654

science alert

ANSInet
an open access publisher
http://ansinet.com

Journal of Applied Sciences 11 (20): 3510-3514, 2011
ISSN 1812-5654 / DOI: 10.3923/jas.2011.3510.3514

Instability of SBA-15 to Strong Base: Effects of LiOH Impregnation on its Surface Characteristics and Mesoporous Structure

Muhammad Ayoub and Ahmad Zuhairi Abdullah
School of Chemical Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

Abstract: Effects of strong base impregnation on surface characteristics of SBA-15 were investigated. LiOH (5-20 w/w %) was impregnated on SBA-15 with the objective of increasing the basicity of the material. The structure, surface area and basicity of the prepared materials were studied using Scanning Electron Microscope (SEM), Energy-Dispersive X-ray spectroscope (EDX), Transmission Electron Microscope (TEM), small-angle X-ray diffractometer and surface analyzer. Basicity increased with increasing LiOH loading but significant structural collapse was observed. About 20%w/w LiOH loading totally destroyed the porous structure of SBA-15 due to alkali-silica reaction. A new fluffy type with sharp edge structure resulted. Thus, SBA-15 showed poor resistance against LiOH and converted into a completely new structure.

Key words: LiOH impregnation, mesoporous SBA-15, structural destruction, alkali-silica reaction, basicity

INTRODUCTION

Most studies involving the catalytic activity of basic catalysts make us of either alkali-exchanged zeolites or zeolites impregnated with sodium metal clusters or alkali oxides (Dartt and Davis, 1994). Ordered mesoporous silicas such as MCM-41 (Kresge *et al*., 1992; Qi *et al*., 2011), SBA-15 (Zhao *et al*., 1998; Thielemann *et al*., 2011) and zeolite-MCM-41 composite (Li *et al*., 2011) are attractive materials due to their high surface area and ordered arrays of uniform channels. SBA-15 has ordered straight mesopores as well as disordered interchannel micropores in the mesopore wall (Zhang *et al*., 2006; Yang *et al*., 2003). Recent research focus is directed towards the design of basic mesoporous materials for various reactions (Rymsa *et al*., 1999). In this respect, SBA-15 is one of the most widely investigated for use as catalysts in many reactions.

Alkaline metal oxides are often used to improve the basic strength of a solid catalyst due to their strong basic behavior. Mesoporous strong solid bases can be prepared through impregnation of mesoporous material with alkali metals or alkaline earth metals. For example, lithium can be used as the guest component to generate strong basicity in various porous hosts such as MCM-41 and zeolites (Clacens *et al*., 2002). Kloetstra and van Bekkum (1997) successfully demonstrated the preparation of strong basic mesoporous solid, especially MCM-41 using cesium acetate solution. The prepared basic materials showed rather poor stability because cesium oxide could react with the silica host and damaged the mesoporous frame works (Kloetstra and van Bekkum, 1997; Zhao *et al*., 1998). With relatively thicker pore walls , SBA-15 is reported to be more stable than MCM-41. However, limited result on its stability to strong base is available in the literature.

There are two main factors which are considered as the obstacles to the successful generation of strong basicity in mesoporous silicas. Firstly, weak host-guest interaction between silica and the base precursors can lead to the difficulty in the decomposition of the base precursors to their basic forms. It was reported that only a small amount of alkali salt could be decomposed on silica, even when the sample was activated at the high temperature of 600°C (Sun *et al*., 2008a). The second factor is the poor resistance of mesoporous silicas against alkali. It is due to the reaction between alkali hydroxides with silica hydroxylsilicates. This can result in the collapse of the mesoporous structure after the formation of this strongly basic species (Sun *et al*., 2008b).

The objective of this study is to demonstrate the effects of strong metal hydroxide on the porous structures of SBA-15. Detail study on this topic is rarely reported and understanding on the surface and structural phenomena is yet to be established. Thus, through several surface analysis method, specific changes that occur upon exposure to strong metal hydroxide can be elucidated.

MATERIALS AND METHODS

Material preparation: Mesoporous silica (SBA-15) was synthesized according to areported method by Zhao *et al.* (1998). Briefly, 4 g of triblock copolymer

Corresponding Author: Ahmad Zuhairi Abdullah, School of Chemical Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia Tel: +604-599 6411, +604-594 1013

P123 ($EO_{20}PO_{70}EO_{20}$, M = 5800, Aldrich) as the templating agent was dissolved in 90 mL of water and 60 mL of 4 M HCl aqueous solution with stirring at 40°C for 2 h. Next, 8.5 g of tetraethyl orthosilicate (TEOS) was then added to the homogeneous solution and stirred at this temperature for 22 h. Finally, the temperature was heated to 100°C and held at this temperature for 24 h under static condition. The prepared sample was recovered by Filtration washed with water and air-dried at room temperature. The removal of the template was carried out at 550°C in air for 6 h. Alkali metal LiOH was introduced through wet impregnation process. An identical amounts of LiOH (namely 5, 10 and 20 wt. %) were used for all samples. The required amount of LiOH was dissolved in deionized water followed by the addition of the host (SBA-15). After stirring at room temperature for 24 h, the mixture was evaporated at 80°C and subsequently dried at 100°C for 4 h. The obtained solid was then calcined at 550°C for 5 h in air.

Material characterization: The materials obtained were characterized using XRD, surface analyzer, SEM and TEM. The N_2 adsorption-desorption isotherms were measured using a Belsorp II system at-196°C. Those samples were degassed at 300°C for 4 h prior to analysis. The Brunauer-Emmett-Teller (BET) surface area was calculated using adsorption data at relative pressures ranging from 0.04 to 0.20. The total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure of about 0.99. The pore diameter was calculated from the adsorption branch by using the Barrett-Joyner-Halenda (BJH) method. Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray (EDX) analyses were performed using a Zeiss Supra 35VP equipment operated at 3.00 kV. The TEM images of the prepared samples were analyzed using a Phillips CM 12 transmission electron microscope equipped with an image analyzer and operated at 120 kV. The basic strengths of materials (H-) were determined using Hammett indicators method. About 25 mg of the sample was shaken with 5.0 mL of a solution of Hammett indicators diluted with methanol and left to equilibrate for 2 h. After the equilibration, the color on the catalyst was observed. The following Hammett indicators were used: methyl red (H_ = 4.8), neutral red (H_ = 6.8), bromthymol blue (H_ = 7.2), phenolphthalein (H_ = 9.3), 2, 4-dinitroaniline (H_ = 15.0) and 4-nitroaniline (H_ = 18.4).

RESULTS AND DISCUSSION

Effects on surface characteristics: The basic strength and surface characteristics of the catalysts used in this work are shown in Table 1. It is noted that the basic strength of the prepared samples increased after loading with LiOH from 5 to 20 wt. %. The basic strength of SBA-15 was found at H_<4.8. However, after loading 20 wt% LiOH, it was noted that basic strength was significantly increased to 9.3<H_<15. This observation suggested that alkali metal loading directly involved in the basicity of the materials, regardless of their surface or structural properties.

It could be deduced from the sharp decrease in the area of alkali metal loaded samples that structure of SBA-15 might collapse due to the reaction with alkali metal (LiOH). This was also proven by changes in the mesoporous area of these samples as shown in the same table. It was found that the mesoporous area and pore volume also sharply decreased in agreement with the decreasing surface area of these samples. Obviously, it was an indication of major loss of mesoporous structure that presented in these samples.

Data in the same table proved that the surface area of the prepared SBA-15 samples sharply decreased after loading with alkali metal. These results suggested that major destruction must have occurred with the corresponding loss of porosity and surface area. Clearly, the mesoporous channels in the SBA-15 should have collapsed to form non-porous mass of silica due to the reaction with the alkali metals. The solid evidently consisted of small particles that were readily dispersible in water or aqueous solution during basicity test as the basicity was found to increase with metal loading.

Nitrogen adsorption-desorption isotherms of SBA-15 and SBA-15 with different LiOH loadings are given in Fig. 1. Parent SBA-15 showed the isotherm and hysteresis loop which are generally associated with mesoporous materials (Zhao *et al*., 1998). However, for LiOH/SBA-15 sample (5) with small loading of LiOH, the hysteresis loop sharply decreases along with a decrease in surface area and pore volume. The shapes of the curves for sample LiOH/SBA-15 (10) and LiOH/SBA-15 (20) generally agree with the Type I isotherm according to the IUPAC nomenclature which is a characteristic of microporous materials. This result was in agreement with data in Table 1 that show loss of mesoporousity.

In addition, according to further classified shapes of the hysteresis loops, these three metal loaded SBA-15 samples exhibited the type H_3 hysteresis loops. This type of hysteresis is usually shown by aggregates or agglomerates of particle forming slit shaped pores (plates or edged particles like cubes). Thus, in agreement with previous study on titania (Sun *et al*., 2008a), the incorporation of high loading of alkali metals led to the collapse of some mesostructures leading to a severe drop

Table 1: Characteristics of LiOH/SBA-15 samples prepared with different LiOH loadings

Sample	Metal loading(wt. %)	Basic Strength(H_)	S_{BET} (m^2/g)	Mesopore area(m^2/g)	Micropore area(m^2/g)	Pore volume(cc/g)
LiOH/SBA-15(0)	0	H_<4.0	746	699	46	1.10
LiOH/SBA-15(5)	5	4.0<H_<6.8	230	155	75	0.52
LiOH/SBA-15(10)	10	6.8<H_<9.3	65	45	20	0.25
LiOH/SBA-15(20)	20	9.3<H_<15	29	28	1	0.15

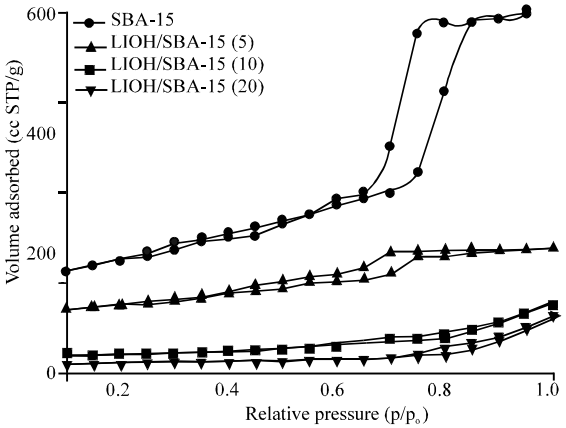

Fig. 1: Nitrogen adsorption-desorption isotherms for LiOH/SBA-15 samples with different LiOH loadings

in porosity. As such, the synthesis of alkali metal loaded porous silica materials through simple wet impregnation was indeed a challenging task.

The collapse of porous structure of SBA-15 was deemed to be directly caused by the alkali-silica reaction between the loaded metal and the silica matrix in aqueous condition. This reaction led to the formation of lithium silicate hydrates. This reaction caused the expansion of the altered aggregate by the formation of a swelling gel of these hydrates. This gel increased in volume with water and exerts an expansive pressure inside the SBA-15 material, causing spalling and loss of its mesoporous structure.

Another strong possibility which might be involved in the destruction the porous silica structure of SBA-15 is the change in media pH. According to Zhao *et al*. (1998), the mesoporous SBA-15 structure is formed and stable under a strong acidic media (pH<3). Therefore, when trying to load a strong alkali LiOH, its media changed from strong acidic to week acidic (pH>3). As silica structure could not be stable under this media, it might collapse badly leading to the major loss of porosity.

Effects on particle structure: Based on the XRD pattern (result not shown), SBA-15 exhibited regular XRD patterns, with an intense (100) diffraction peak and two or more well-resolved peaks (100, 110, 200) which were indexed as 2D hexagonal symmetry (Yang *et al*., 2003). Compared to the SBA-15 sample, the intensity of the

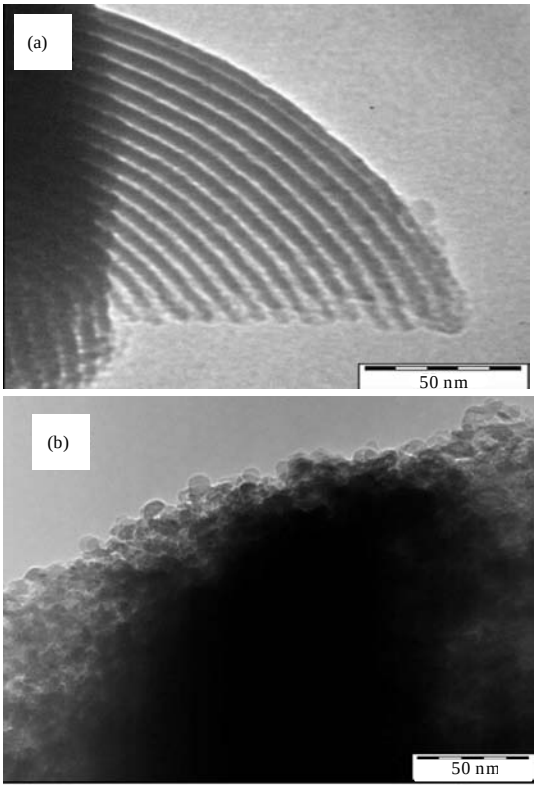

Fig. 2(a-b): TEM images of, (a) pure SBA-15 and (b) SBA-15 loaded with 20 wt % of LiOH

peaks for LiOH loaded SBA-15 samples were very weak and their positions were not clear. This observation suggested that the original mesoporous structure of SBA-15 was not sustained.

Similar characteristics of the prepared samples were also observed in TEM images. TEM images of sample SBA-15 and LiOH/SBA-15 prepared by impregnation method with 20 wt. % of LiOH loadings are shown in Fig. 2a and b, respectively. SBA-15 showed well-ordered hexagonal pores with clear channel tubing inside the structure. However, with 20 wt. % of LiOH loading, the ordering of the SBA-15 support was observed to disappear.

Figure 3 shows SEM images of the prepared SBA-15, LiOH/SBA-15 (5 wt. %) and LiOH/SBA-15 (20 wt. %). In Fig. 3a, the microscopic morphology of prepared

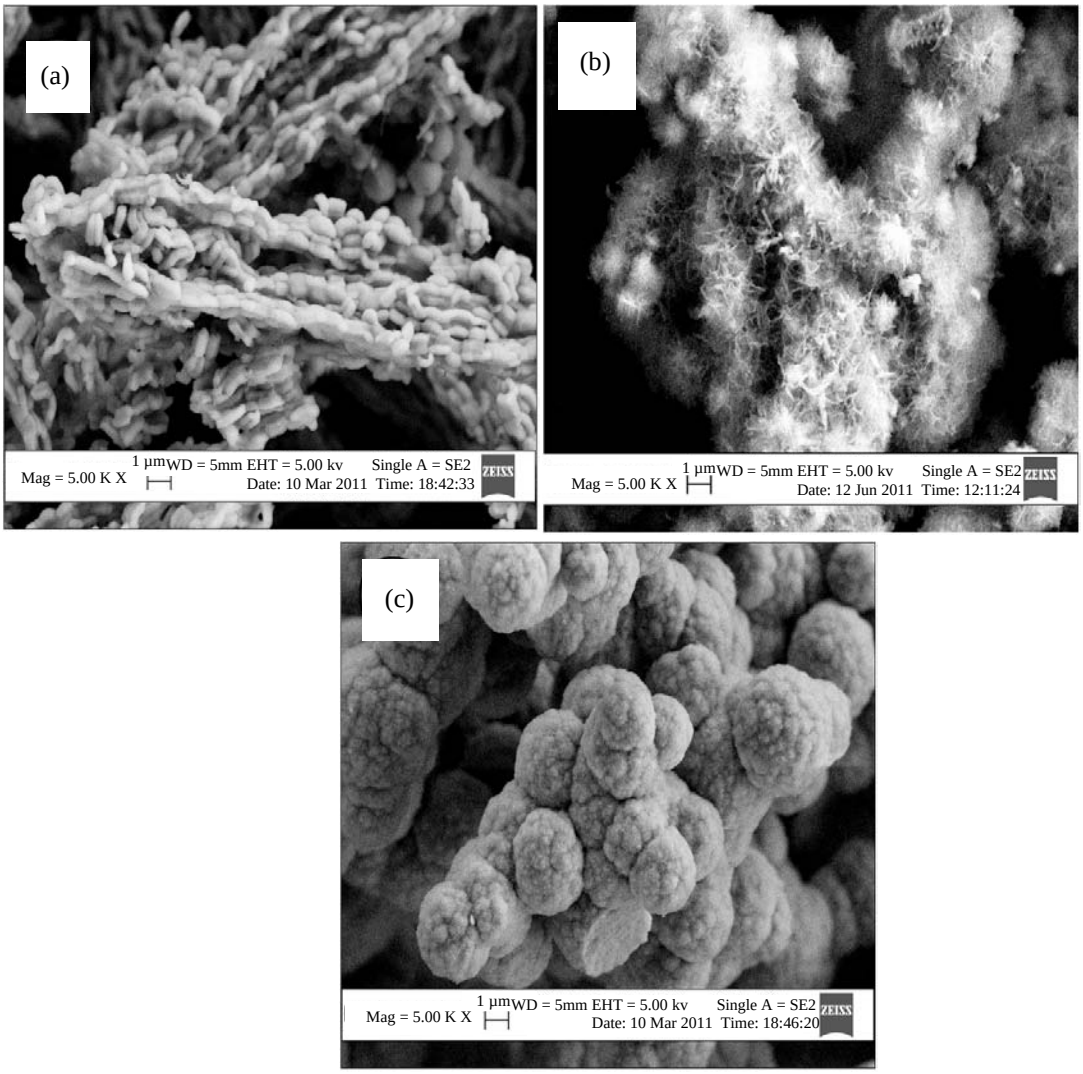

Fig. 3(a-c): SEM images at a magnification of 5000 X, (a) SBA-15, (b) 5% LiOH/SBA-15 and (c) 20% LiOH/SBA-15

SBA-15 is similar to generally published mesoporous structure of SBA-15 (Rymsa *et al*., 1999; Li *et al*., 2011). As observed in Fig. 3b, 5 wt. % LiOH loading over SBA-15 consisted of a large amount of small spherical particles with spiky structures on the surface, evidently contributed by the loaded metal. When the LiOH loading was increased to 20%, the shape of SBA-15 structure had entirely different looks with a fluffy type and sharp edges. No specific SBA-5 morphology that can be seen in Fig. 3b and c, they were generally irregular in shape. This was an evidence of mesoporous structure collapse.

As reported by different researchers (Sun *et al*., 2008b; Thielemann *et al*., 2011), mesoporous SBA-15 could have weak resistance to strong alkali. In this work, its structure could be destroyed in the presence of alkali metals. The morphology of 20 wt. % LiOH loaded over SBA-15 materials (Fig. 3c) was seen to be made up of more fluffy fibers with large circular ball shape. Thus, the analysis of TEM and SEM images of prepared LiOH loaded samples showed that LiOH well-dispersed over the surface of SBA-15. It could be concluded that the morphology of SBA-15 structure underwent significant changes after loading with this strong alkali metal. The

newly prepared structures of these samples seemed to be fluffier and denser than the parent SBA-15. This type of material is unlikely to act as good basic catalyst due to its non-porous characteristics.

CONCLUSIONS

Increasing severity of mesoporous structure destruction was detected when SBA-15 was impregnated with LiOH with increasing LiOH loading. This destruction was ascribed to the chemical reaction between strong alkali metal and mesoporous matrices to form metal hydrosilicates. The new structure of alkali-loaded SBA-15 was found to be fluffier and lighter than the parent material. The new structure was neither microporous nor mesoporous and was entirely different from parent structure of SBA-15. However, the basic strength of the prepared material was found to increase with increasing lithium loading. Thus, despite having thicker pore walls compared to other mesoporous materials, SBA-15 still shows poor resistance to strong basic metals.

REFERENCES

Clacens, J.M., Y. Pouilloux and Barrault, 2002. Selective etherification of glycerol to polyglycerols over impregnated basic MCM-41 type mesoporous catalysts. Applied Catal. A: Gen., 227: 181-190.

Dartt, C.B. and M.E. Davis, 1994. Applications of zeolites to fine chemicals synthesis. Catal. Today, 19: 151-186.

Kloetstra, K.R. and H. van Bekkum, 1997. Solid mesoporous base catalysts comprising of MCM-41 supported intraporous cesium oxide. Stud. Surf. Sci. Catal., 105: 431-438.

Kresge, C.T., M.E. Leonowicz, W.J. Roth, J.C. Vartuli and J.S. Beck, 1992. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. Nature, 359: 710-712.

Li, P., L. Liu and G. Xiong, 2011. Effect of zeolite precursor on the formation of MCM-41 molecular sieve containing zeolite Y building units. Phys. Chem. Chem. Phys., 13: 11248-11255.

Qi, J., B. Qin, J. Liu, Y. Yu and Z. Zhang *et al*., 2011. MCM-41 single crystal of hexagonal circular bicone with pseudo-singular surface and morphogenesis. Cryst. Eng. Commun., 13: 4666-4675.

Rymsa, U., M. Hunger, H. Knozinger and J. Weitkamp, 1999. Spectroscopic and catalytic characterization of basic zeolites and related porous materials. Stud. Surf. Sci. Catal., 125: 197-204.

Sun, L.B., F.N. Gu, Y. Chun, J. Yang, Y. Wang and J.H. Zhu, 2008a. Attempt to generate strong basicity on silica and titania. J. Phys. Chem. C, 112: 4978-4985.

Sun, L.B., J.H. Kou, Y. Chun, J. Yang and F.N. Gu *et al*., 2008b. New attempt at directly generating superbasicity on mesoporous silica SBA-15. Inorg. Chem., 47: 4199-4208.

Thielemann, J.P., F. Girgsdies, R. Schlogl and C. Hess, 2011. Pore structure and surface area of silica SBA-15: Influence of washing and scale-up. J. Nanotechnol., 2: 110-118.

Yang, C.M., B. Zibrowius, W. Schmidt and F. Schuth, 2003. Consecutive generation of mesopores and micropores in SBA-15. Chem. Mater., 15: 3739-3741.

Zhang, W.H., L. Zhang, J. Xiu, Z. Shen, Y. Li, P. Ying and C. Li, 2006. Pore size design of ordered mesoporous silicas by controlling micellar properties of triblock copolymer $EO_{20}PO_{70}EO_{20}$. Microporous Mesoporous Mater., 89: 179-185.

Zhao, D., J. Feng, Q. Huo, N. Melosh, G.H. Fredrickson and B.F. Chmelka, 1998. Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. Sci., 279: 548-552.