

A Review: Mesoporous Santa Barbara Amorphous-15, Types, Synthesis and Its Applications towards Biorefinery Production

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Abstract: Problem statement: Santa Barbara Amorphous (SBA-15) is significant mesoporous silica with exclusive and important properties of highly ordered mesopores, hydrothermally stable and thick wall, profusely large surface area and huge pore volume which render it as promising catalyst for wide applications. However, the purely siliceous SBA-15 which lacks of acidity characteristic hinders its ideal capabilities as catalyst. Moreover, functionalization and modification of SBA-15 could enhance and optimize its catalytic activity. **Conclusion/Recommendations:** Thus, in this review, the various types and different synthesis of modifying SBA-15 are discussed in detail towards its application in biorefinery production. The catalytic activities in various operating conditions and reactions are also reviewed for future reference and scope of studies.

Key words: Mesoporous materials, biorefinery production, Santa Barbara amorphous, Tetramethyl Orthosilicate (TMOS), catalytic activity, mesoporous structure

INTRODUCTION

Mesoporous material, as defined by IUPAC nomenclature, is material with pore of free diameters in the range of 2-50 nm (McCusker *et al.*, 2003). Generally, mesoporous materials is defined with the term of host, pores and chemical composition of its host and guests (Liebau, 2003). Mesoporous materials is more preferred for its highly ordered mesostructure, apart from high surface area, which allows diffusion and adsorption of larger molecules for wide applications than that of microstructure which only limits to separation and fine chemical catalysis (Fedeyko *et al.*, 2006). Moreover, microporous material has selective thermal stability based on size and shape of cage or channel within lattice of selected organic moieties during synthesis, which restricts its potentiality to limited applications (Morey *et al.*, 1998). Mesoporous materials are widely applied in catalysis (Abdalla *et al.*, 2009), drug control delivery (Pasqua *et al.*, 2009), biosensors (Xu *et al.*, 2009b), biofuel (Ooi and Bhatia, 2007), sorption (Chang *et al.*, 2008) and membrane separation (Zornoza *et al.*, 2009). Typical compounds of mesoporous material include

silica (Xia and Mokaya, 2003), alumina (Xu *et al.*, 2009a), carbon (Chen *et al.*, 2009) and transition metal oxides (Rao and Antonelli, 2009).

Silica is widely employed as main building block of mesoporous materials because it is inexpensive, thermally stable, chemically inert, harmless (Nandiyanto *et al.*, 2009) and abundantly available in the Earth's crust (Draggan, 2008). Unlike zeolitic materials which are silica self-assembles reliance upon heating, mesoporous silica is formed in the presence of self-associating molecules such as cationic surfactant for MCM-41 synthesis and block copolymers for synthesis of SBA-15 (Liebau, 2003). Figure 1 shows typical synthesis of mesoporous silica MCM-41.

Mesoporous silica was first discovered in 1990 by researchers in Japan (Yanagisawa *et al.*, 1990) and later was produced in Mobil Corporation Laboratories (Chen *et al.*, 2009) and named as M41S. MCM-41, MCM-48 and MCM-50 are among the widely known mesoporous silica in M41S family (Vartuli *et al.*, 2008) which have different methods of synthesis and applications based on instability and limitation of mesoporous structure (Tatsumi *et al.*, 1999, Zhang *et al.*, 2007).

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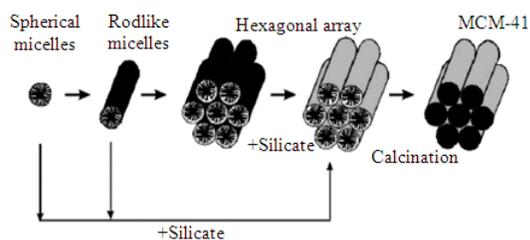


Fig. 1: Liquid crystal templating mechanism of formation of the mesoporous silica material MCM-41 (Brady *et al.*, 2008)



Fig. 2: The M41S family of materials including MCM-41, MCM-48 and MCM-50 (Vartuli *et al.*, 2008)

These mesoporous silica are highly ordered, large specific surface area, hexagonal array and uniform mesoporous channel (Chen *et al.*, 2004, Tatsumi *et al.*, 1999). Especially for MCM-41 and MCM-48, the pore size can be controlled and widely used as adsorbent, catalyst and support (Tatsumi *et al.*, 1999). MCM-41 is in hexagonal packed rod-shaped micelle structure, whereas MCM-48 is in cubic and MCM-50 is in lamellar form (Vartuli *et al.*, 2008) which is depicted in Fig. 2. Later in 1995, the research focus was concentrated on mesoporous molecular sieves like HMS (Tanev *et al.*, 1995) and MSU (Bagshaw *et al.*, 1995). In 1998, a prominent research which produces hexagonal array of pores namely as Santa Barbara Amorphous no 15 (SBA-15) with larger pore size from 4.6-30 nm was a research gambit in mesoporous material development (Zhao *et al.*, 1998b). Not only because of its larger pores, but also thermal, mechanical and chemical resistance properties that makes it a preferable choice to other types of catalysts.

Purely siliceous SBA-15: Typical synthesis of SBA-15 requires triblock copolymer, typically non-ionic triblock copolymer (Zhao *et al.*, 1998b) as structure directing agent and Tetramethyl Orthosilicate (TMOS) (Zhao *et al.*, 2000), Tetraethyl Orthosilicate (TEOS) (Zhao *et al.*, 1998a) or Tetrapropyl Orthosilicate (TPOS) (Zhao *et al.*, 1998b) as silica source.

According to Zhao *et al.* (2000) the formation of ordered hexagonal SBA-15 with uniform pores up to 30 nm was synthesized using amphiphilic triblock copolymer in strong acidic media i.e., pH ~1. If pH is more than the isoelectric of silica i.e., at pH 2-6, no precipitation or formation of silica gel would occur. Disordered or amorphous silica would likely to be happened at neutral pH of 7 (Zhao *et al.*, 1998b). Nevertheless, Cui *et al.* (2005) have proved to synthesize SBA-15 at pH 2-5, which is above isoelectric point of silica. They suggested that the prehydrolyzed of TEOS at pH < 3 would interact with template agent to form a mesophase under weak acidic condition (Cui *et al.*, 2005).

The most recent study is the synthesis of highly siliceous SBA-15 from low silica inorganic precursor with the presence of impurities of industrial waste product which typically consist of metal oxide containing 42 wt% SiO₂. The method used in this study was claimed to be cost effective for bulk production of mesoporous silica since it used industrial waste as silica precursor and no pre-purification of precursor nor material washing steps were applied (Puputti *et al.*, 2009).

Template removal is one of the crucial aspects in ordered mesoporous silica synthesis in which this procedure could modify the final properties of desired porous structure. The usual method of removing template is calcination. According to Zhao *et al.* (1998a) the calcination of mesoporous structure SBA-15 at 500°C would produce final properties of porous structure with interlattice d spacing of 74.5-320 angstroms between the (100) planes, pore volume fraction up to 0.85 and silica wall thickness of 31-64 angstroms (Zhao *et al.*, 1998a). In preference to studying the final properties of porous structure after calcination, other researchers focused on the calcination behavior during the process of template removal. Kleitz *et al.* (2003) studied the in situ XRD pattern, intensities reflections and d spacing values of SBA-15 calcination up to 550°C and cooling to room temperature after 5 h (Kleitz *et al.*, 2003). Besides mesoporosity structure, SBA-15 was found to contain micropores which indicated the hierarchical template of material structure (Schmidt-Winkel *et al.*, 1998). These microporous structures are generally disordered and provide interconnectivity between ordered mesopores (Brady *et al.*, 2008).

Modifying SBA-15: Despite promising properties of SBA-15 in catalysis, biomolecule separation, etc, there is still a need to modify or functionalize SBA-15 i.e., to overcome its limitation of low acidity strength (Yue *et al.*, 2000), enhance and optimize its catalytic activity by supporting (Vizcaíno *et al.*, 2009) or

immobilizing (Li *et al.*, 2009) on other elements or complement other catalyst especially for thermal endurance (Grieken *et al.*, 2005), reusability (Liu *et al.*, 2009) and enzymatic activity (Takimoto *et al.*, 2008). Besides, SBA-15 is one of the best candidates to be modified and functionalized since it has controllable pore size, pore volume and high surface area (Liu *et al.*, 2008). Deposition of titanium in SBA-15 material render superior mechanical and chemical resistance (Liu *et al.*, 2008) while activation SBA-15 with different types of metal would develop and design large pore catalysts which allow high diffusion rates (Busuioc *et al.*, 2006). Recently, the attachment of organic functional group has caught attention for further development in which this could tune the hydrophilic-hydrophobic character of silica surface to give sorbent chemical selectivity for specific molecules or ions (Li *et al.*, 2008).

From available literature articles, modified and functionalized SBA-15 can be categorized into different types:

- Functionalization SBA-15 with sulfonic, aminopropyl, imidazole, triazole group (Grieken *et al.*, 2005, Li *et al.*, 2008)
- Enzyme immobilization onto SBA-15 i.e., *Porcine pancreatic* Lipase, Cytochrome-c (Li *et al.*, 2009, Washmon-Kriel *et al.*, 2000)
- Metal supported SBA-15 i.e., Pd-Zn, Co (Eswaramoorthi *et al.*, 2009, Prieto *et al.*, 2009)
- Different types of metal incorporation into SBA-15 framework i.e., Al, Ce, La, Ti, Mg, Ca (Calles *et al.*, 2009, Kim *et al.*, 2004, Vizcaíno *et al.*, 2009, Yue *et al.*, 2000)

Synthesis:

Methods: Various methods of synthesis have been employed, which includes direct synthesis, post synthetically impregnation and grafting, sol-gel as well as immobilization (Cui *et al.*, 2005, Grieken *et al.*, 2005, Li *et al.*, 2009, Calles *et al.*, 2009, Carrero *et al.*, 2007). Table 1 list down different types of modifying SBA-15 and syntheses. However, only direct synthesis and post grafting method will be discussed in this review.

Direct synthesis: Direct synthesis of modifying SBA-15 engaged the co-condensation of silica source i.e. TMOS, TEOS etc. with organotrialkoxysilane with presence of different templating agents. Apart from silane group, this method was then further explored and developed by co-condensing silica source with different groups of metal i.e. transition, alkaline earth, rare earth and poor metals.

Phenyl-functionalized-SBA-15 under acidic conditions was concertedly explored by Du *et al.* (2006). The phenyl-modified-SBA-15 was prepared

using direct synthesis method by co-condensation of different molar ratios of tetraethylorthosilicate (TEOS) and phenyltrimethoxysilane (PTMS). It was worthful to note that even at high molar ratio of TEOS: PTMS, the desirable hexagonal structure, large surface area and pore volume were still preserved besides its thermally stable and highly hydrophobic properties (Du *et al.*, 2006).

A study of Co-SBA-15 was investigated under different pH adjustment using sodium hydroxide, in which under optimum pH of 3, high surface area and pore volume of Co-SBA-15 were demonstrated (Lou *et al.*, 2008). In other work of transition metal incorporation, the effect high loading zirconium in the direct synthesis of Zr-SBA-15 was probed into its catalyst property as well as catalytic activity. The study reported that high ratio of Zr/Si established a high order mesostructure of Zr-SBA-15 and additional sulfation process increased its catalytic activity (Fuxiang *et al.*, 2007).

From the recent studies presented here, they are consistent with the argument reported by Zhao *et al.* (1998a) that direct synthesis proposes a uniform dispersion of functional groups on material surface and structure which preserve its surface properties (Zhao *et al.*, 1998a).

Post-grafting: Post-grafting was the first method used to modify mesoporous silica materials. Basically, this method involves reaction between organosilane with silanol group using solvent under reflux condition to form covalent attachment of functional groups on surface of material (Chong *et al.*, 2004).

It has been reported that post-grafting method has its downside aspects. Among disadvantages of this method includes the reductions of pore size and pore volume caused by the attachment of functional group on pore surface (Lim *et al.*, 1999), density limitation of reactive silanol group that would limit the loading of functional group on pore surface in which would further cause cross-linking between functional groups and silanol groups on surface (White and Tripp, 2000), difficulty in achieving uniformity of the functional group and tedious process which involves more than one step of preparation (Mercier and Pinnavaia, 1999).

Nevertheless, Ma *et al.* (2010) has employed post-grafting method in incorporating aluminum into SBA-15 to observe the effect towards structural, textural and acidity of the catalyst. They discovered that, in comparison with direct synthesis method, the acidity and catalytic activity of Al-SBA-15 synthesized by post-grafting method has shown to be higher due to

Table 1: Different types and synthesis of modifying SBA-15

Modifying SBA-15	Methods of synthesis	Properties	Remark
AP-SBA-15 (aminopropyl-SBA-15) (Li <i>et al.</i> , 2008)	One-step post grafting	$S_{BET} m^{-2} g^{-1} = 524$ $VP cm^{-3} g^{-1} = 0.60$ $Dp nm^{-1} = 6.5$ $d_{(100)}/ = 92.8$	After functionalization, XRD patterns show the hexagonal structure still remains intact. However, the $d_{(100)}$ spacing increased as shown in (100) shifting reflection to lower 2 values. The slight decrease in the reflection peak intensity of the SBA-15 indicated the grafting happened inside the pore channels.
Imi-SBA-15 (Imidazole SBA-15) (Li <i>et al.</i> , 2008)	Two-step post grafting	$S_{BET} m^{-2} g^{-1} = 362$ $VP cm^{-3} g^{-1} = 0.57$ $Dp nm^{-1} = 5.6$ $d_{(100)}/ = 87.3$	
Tri-SBA-15 (Triazole SBA-15) (Li <i>et al.</i> , 2008)	Two-step post grafting	$S_{BET} m^{-2} g^{-1} = 435$ $VP cm^{-3} g^{-1} = 0.65$ $Dp/nm^{-1} = 5.8$ $d_{(100)}/ = 90.1$	
Al-SBA-15 (Yue <i>et al.</i> , 2000)	Direct synthesis	$S_{BET} m^{-2} g^{-1} = 1004$ $VP cm^{-3} g^{-1} = 1.53$ $Dp nm^{-1} = 7.4$ $d_{(100)}/ = 108$	After various treatment i.e. acidic, basic, neutral and vapor medium, it could be concluded that Al-SBA-15 is more stable than pure SBA-15 in which the pore size, $d_{(100)}$ spacing, wall thickness still remain the same. However, specific surface area and pore volume decrease in basic medium treatment which indicated the disappearance of microporous phase.
Organically modified Ti-SBA-15 (Iglesias <i>et al.</i> , 2008)	Direct synthesis	$S_{BET} m^{-2} g^{-1} = 1004$ $VP cm^{-3} g^{-1} = 1.53$ $Dp nm^{-1} = 7.4$ $d_{(100)}/ = 108$	Organic modifications of Ti-SBA-15 give high dispersion of metal species and enhance the hydrophobic behavior. However, it displays poor structured mesophase. Catalytic activity in epoxidation of 1-octene depends on the length of organic functionalities in which catalytic activity increases with larger organic functionalities.
Ti-SBA-15 (Busuioce <i>et al.</i> , 2006)	Sol-gel method	$S_{BET} m^{-2} g^{-1} = 534$ $VP cm^{-3} g^{-1} = 0.63$	Controlling the amount of titanium, the pH, temperature at different stages of deposition, the characteristics, sorption capacity and catalytic activity can be tuned.
20%Ti-SBA-15 (Kim <i>et al.</i> , 2004)	Post-grafting	$S_{BH} m^{-2} g^{-1} = 566.4$ $VP cm^{-3} g^{-1} = 0.85$ $Dp nm^{-1} = 6.07$	Higher incorporation of titanium would decrease the specific surface area and pore volume. However, the catalytic activity increase with the increment of titanium loading but H_2O_2 selectivity decreased.
Co-SBA-15 (Can <i>et al.</i> , 2006)	Direct synthesis	$S_{BET} m^{-2} g^{-1} = 747.5$ $VP cm^{-3} g^{-1} = 0.70$ $Dp nm^{-1} = 4.68$	Surface area of SBA-15 decrease with the addition of 40 wt% Co. High loading of Co to SBA-15 as metal oxides lead to disappearance of long range order SBA-15 which indicates chemical reaction between host SBA-15 and guest metal oxides.
Pb-SBA-15 (Can <i>et al.</i> , 2006)	Direct synthesis	$S_{BET} m^{-2} g^{-1} = 648.9$ $VP cm^{-3} g^{-1} = 0.72$ $Dp nm^{-1} = 4.43$	No XRD peak characteristic observed for 5, 10, 15wt% Pb loading suggest Pb is finely dispersed on the surface of the sample or incorporated in the pore wall. XRD peak for 20 wt% Pb into SBA-15 indicated the presence of crystallites of metal oxide on the surface.

Table 2: Application of SBA-15 in biorefinery production

SBA-15 types	Application	Reaction condition	Conversion	Yield/selectivity
Cu-Ni/SBA-15 supported catalysts (Carrero <i>et al.</i> , 2007)	Production of hydrogen from bioethanol	Effect of reaction temperature was studied ranging from 400-650°C	At 600°C, conversion of ethanol ~100 mol%, water~38.6 mol%	At 600°C, hydrogen selectivity 85.3 mol%
SBA-15 (Badamali <i>et al.</i> , 2008)	Production of acetovanillone from monomer lignin, apocynol	Effect of reaction temperature in microwave reactor from 5-30 min	Double the amount of catalyst, substrate could achieve highest 47.8%	Double the amounts of catalyst, however, decrease the product selectivity
RuB/Sn-SBA-15 (Luo <i>et al.</i> , 2007)	Production of 1,2-propanediol from hydrogenation of ethyl lactate	Temperature at 149.85°C, H_2 pressure at 5.5 MPa, reaction time up to 10 h	Increasing the Sn doping amount, increase the substrate conversion to 68.4%	Increasing the Sn doping amount, increase the product selectivity to 98.9%
Al-SBA-15 (Ooi and Bhatia, 2007)	Production of gasoline from waste used palm oil	Reaction temperature at 449.85°C, feed rate of waste used palm oil $2.5 h^{-1}$ at atmospheric pressure	Substrate conversion of 70-80% with post-synthesis catalyst preparation	Achieve higher yield ~40% with post-synthesis catalyst preparation
1.Cu-Ni/Mg- SBA-15 2.Cu-Ni/Ca- SBA-15 (Vizcaino <i>et al.</i> , 2009)	Production of hydrogen from steam reforming ethanol	Reaction temperature at 600 °C Reaction time for 3 h	Ethanol conversion is as high as 100%	H_2 selectivity as high as 83% with Cu-Ni/Mg- SBA-15 H_2 selectivity as high as 85% with Cu-Ni/Ca- SBA-15
K-SBA-15 (Abdullah <i>et al.</i> , 2009)	Production of biodiesel from palm oil transesterification	Optimum reaction temperature at 70°C, reaction time of 5 h, 3.91 wt% catalyst, 11.6 mol mol ⁻¹ methanol: Oil	87% conversion at optimum reaction condition	Biodiesel yield 93% at optimum reaction condition
Ti-Ru-SBA-15 (Liu <i>et al.</i> , 2009)	Production of alcohol from allylation-isomerization of a. 1-phenyl-3-buten-1-ol b. benzaldehyde	Reaction temperature 100°C, reaction time 10 min	Conversion of 1-phenyl-3-buten-1-ol 96.3% Conversion of benzaldehyde 98.8%	Selectivity of 4-phenyl-but-3-en-2-ol 97.4% from 1-phenyl-3-buten-1-ol Selectivity of 4-phenyl-but-3-en-2-ol 95.5% from bezaldehyde

Table 2: continuous

SBA-15 (Cao <i>et al.</i> , 2009)	in aqueous media Production of oils from wood biomass and tire	Liquid yield from co-pyrolysis from at 500°C Density and viscosity measurement at 30°C	Liquid yield increase 46.4% reduction of oil density as high as 3.67%. Reduction of oil viscosity as high as 39.34%	Not reported
SO ₃ H-Pr-SBA-15 (Miao and Shanks, 2009)	Production of oil from esterification of acetic acid and methanol	Reaction temperature 70°C, reaction time 25 h	Conversion of acetic acid ~80%	Not reported

formation of Lewis and Brønsted acid sites (Ma *et al.*, 2010). In previous work by Zeng *et al.* (2005) the activity of Al-SBA-15 was proved to be affected by hydrolysis ratio and aluminum concentration which could be correlated to various ratio of Si/Al (Zeng *et al.*, 2005). This was substantiated by research work of the post-grafting in the synthesis of Al-SBA-15 with various ratio of Si/Al which could affect the catalytic activity and stability of the catalyst as well as exhibited better conversion and selectivity (Wu *et al.*, 2006).

The effect on structure and psychochemical properties: Particular interest in synthesizing SBA-15 is also focused on the effect of structure, physical and psychochemical properties of SBA-15.

The initiative to improve the adsorption characteristics of hexagonal has been successfully shown by Colilla *et al.* (2007) by enlarging the surface area of hexagonally ordered SBA-15 (Colilla *et al.*, 2007). The addition of weak acid H₃PO₄ together with strong acid hydrochloric in varied composition contributed to the increment of surface area, mesopores and micropore volume of SBA-15, which markedly characterized by N₂ adsorption, Brunauer-Emmett-Teller and Small Angle X-ray Diffraction.

The immobilization of *Porcine pancreatic* lipase on rod-like SBA-15 was investigated to have technical understanding on its adsorption and catalytic activity (Li *et al.*, 2009). The concerted investigations of the effect of pH medium and thermal stability were studied to find the optimum conditions of this biocatalyst activity. It comes to comprehension that the immobilized *Porcine pancreatic* lipase on rod-like SBA-15 has maximum activity in pH medium of 8, but decreases at the pH medium of 9. This could be suggested by the shifting of protons partitioning between bulk phase and enzyme microenvironment in optimum medium of pH value dependent on the immobilization method, the structure and the charge of the mesoporous carrier.

Incorporation of titanium into SBA-15 with different methods of synthesis, different solvents application and varied amount of titanium deposited

have lead to another new research finding of mesoporous material. Das *et al.* (2010) has successfully synthesized highly ordered 2-D hexagonal titanium incorporated into SBA-15 using non-ionic surfactant pluronic and co-solvent cyclohexane with small amount of titanium deposited (Das *et al.*, 2010). This direct synthesis method has exhibited significant increment surface area of 924 m²g⁻¹, compare to that of pure SBA-15 with 611 m²g⁻¹. However, this is in contrast to the findings from Kim *et al.* (2004) who found that the post-synthesis of Ti-SBA-15 has lead to the decrease in surface area compared to pure SBA-15 (Kim *et al.*, 2004).

Application in Biorefinery: SBA-15 has been reported to be used widely in biofuel and value-added chemical feedstock from biomass. In the investigations of oil characteristics produced from biomass and tire, SBA-15 has shown to highly reduce the oil density by 3.67% and oil viscosity by 39.4%, significantly better than that of MCM-41 and HZSM-5 (Cao *et al.*, 2009). A study involved different methods of deposition of Al into SBA-15 framework by direct synthesis and post synthesis in the production of biofuel from waste-used palm oil indicated comparable catalytic behavior, but regenerated post-synthesis Al-SBA-15 catalyst gave better catalytic activity and fuel yield due to better thermal stability (Ooi and Bhatia, 2007). Other study which also investigated different methods of Cu-Ni supported on SBA-15 reported that the catalyst prepared by incipient wetness impregnation showed better selectivity and conversion than that of direct synthesis method in the production of hydrogen from steam reforming bioethanol (Carrero *et al.*, 2007).

Table 2 summarizes some of the applications and catalytic activity of SBA-15 in biorefinery production.

CONCLUSION

The significant properties of SBA-15 and its modification are remarkably relevant towards the application of biorefinery production. It is important to design modifying SBA-15 with different organic,

silane, silanol, sulfonic and metal functional groups by improving its structural, textural and physicochemical properties for better shape selectivity and catalytic activity with different means of syntheses and methods. The remarkable research works presented in this review would definitely assist future research work development of mesoporous SBA-15 as novel catalyst in biorefinery application.

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