REVIEWS

Architecting mesoporous AlSBA-15: An overview on the synthetic strategy

Parasuraman Selvam, Nunna V. Krishna AND Balasubramanian Viswanathan

National Centre for Catalysis Research, Department of Chemistry, Indian Institute of Technology-Madras, Chennai 600 036, India
selvam@iitm.ac.in

Abstract | The architecture of mesoporous solids has seen many innovations based on template mechanism. Among them, SBA-type materials has thicker walls, more silanol groups, large pore sizes and enormous pore volumes imparting them with high thermal and hydrothermal stability. Thus making them advantageous for a variety of applications, and hence generated a lot of interest. In this regard, this review examines the various aspects of synthesis and their influence on altering the properties SBA-type silica materials with respect to hetero-ion substitution in the framework structure. Further, this review also deals with critical evaluation in exploiting this class of materials, in particular SBA-15 matrix, for aluminum incorporation in the framework. Different synthesis methodologies have been described and it is hoped that this review will not only serve as a source of information but also can be expected to push the knowledge domain of mesoporous solids.

Keywords: Mesoporous materials; Silicates, Aluminosilicates, SBA-15.

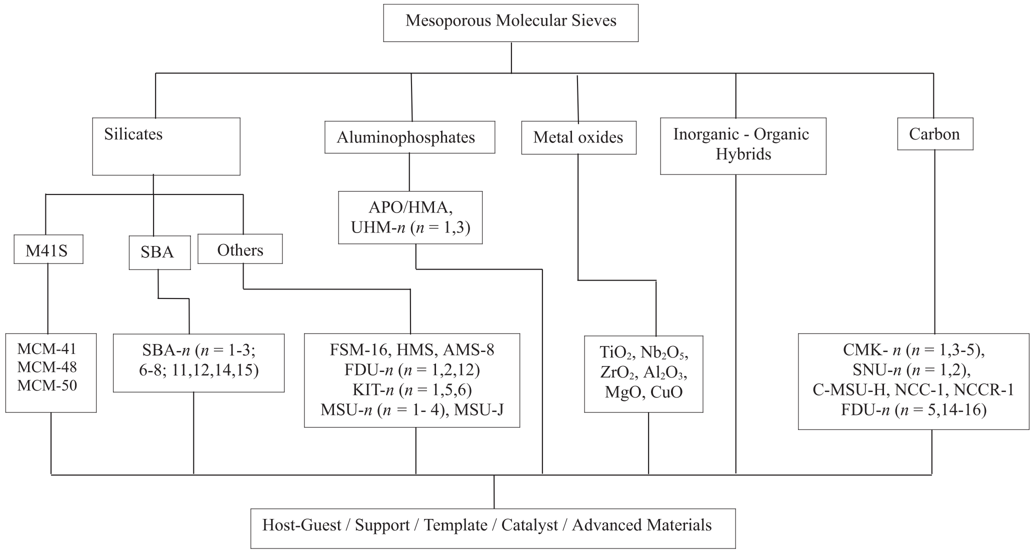
1. Introduction

In porous solids, the reactant molecules interact not only on the surface but also inside the pore walls of the materials. Due to this property of enhancement in reaction sites, they are of great importance. Porous solids are classified in to three groups basing on their pore sizes, microporous materials ($d < 2$ nm), mesoporous materials (2 nm $< d > 20$ nm) and macroporous materials ($d > 20$ nm).[1] In recent years, there is a great urge to use biomass and heavy petroleum fractions for energy conversion and production of chemicals. Since small pore sizes of microporous materials (zeolites) can be suitable only to molecules of limited size and causes diffusivity problems for large molecules wherein the mesoporous materials can very well be used for such purpose.[2] Table 1 summarizes the various mesoporous materials reported in literature.

In the early 1990s, mesoporous materials were synthesized using a series of self assembled surfactants as templates.[3,9,19] The interaction between the inorganic species and surfactants can be electrostatic, covalent, hydrogen bonding and co-ordination bond governed by the synthesis medium (acidic, basic or neutral). These produced uniform mesoporous materials with large pore sizes, large pore volume, high surface area and narrow pore size distribution. Various mesoporous materials and their classification are listed in Fig. 1. It is interesting to note that different choices of the inorganic precursor, organic template, reaction conditions, and synthetic pathway have resulted in a variety of novel mesostructured materials. Although a majority of the studies have focused on MCM-41, there has been continued interest in developing new mesophases. A number of reviews have appeared on various aspects of different mesoporous materials.[23]

Ordered mesoporous materials, due to its large pore volume, high surface area and presence of silanol groups lead to homogeneous dispersion of active species, e.g., enzymes, organic functional

Figure 1: Various mesoporous materials and their applications.



groups and organo metallic complexes, making it applicable as nanoreactors, adsorbents, sensors and fillers.[24–26] With these properties they can be generated with 3–10μm particles sizes in order to avoid pressure drop, with different morphologies and are stable in chromatographic conditions making it a suitable stationary phase for HPLC applications[27]. Furthermore, the larger pores allow adequate diffusion of bigger molecules favoring direct interaction with the active sites promoting conversion as well as decreasing secondary interactions to increase selectivity in catalytic reactions.[28] In addition, the mesoporous materials have sufficient mechanical strength, thermal and *p*H stability and are bio-compatible. By changing functional groups attached to silanol groups their absorption properties can be varied. All these properties make them suitable for drug release and in bio medical applications.[29] The various physico-chemical properties of some mesoporous silicates are tabulated in Table 1.

On the other hand, much larger pore size materials such as the SBA-family (SBA-11, SBA-12, SBA-15 and SBA-16) were synthesized in acidic medium using non-ionic surfactants having poly ethylene oxide (PEO) units.[4−10] The framework structures such as SBA-1, SBA-2 and SBA-3 were prepared employing cationic surfactants; they are mediated by $S^0H^+X^-I^+$ or by $S^+X^-I^+$ type mechanism, where S^0 is non-ionic surfactant; S^+ is cationic surfactant, X^- is anion and I^+ is silicate species. The templates can be removed easily from SBA materials without affecting the structure as X^- mediation decreases the interaction between silicate species and the template. SBA materials have thicker walls than their counterparts as their formation is mediated by electrostatic double layer hydrogen bonding; this confers them with high hydrothermal stability. SBA materials synthesized by non-ionic surfactant have higher degree of cross linking as each non-ionic surfactant molecule used as the template for the synthesis has a larger number of PEO units which can interact with neighboring units but whereas in the case of materials mediated by cationic surfactants, it will be one to one interaction with surfactant head group and inorganic species, this confers the former with good thermal stability and crystalline framework. Due to its crystalline framework, strong acidic and/or redox sites can be generated by isomorphous substitution of metal ions in the SBA matrix. For example, alkylation of hydroquinone with *t*-butanol is efficiently catalyzed by aluminium substituted SBA-15 (AlSBA-15) than the corresponding AlMCM-41.[30]

SBA-family of materials have large number of silanol groups than materials prepared in the basic conditions, e.g., M41S family, due to faster condensation of silanol groups in the latter case, making former more suitable for grafting functional groups. In addition, the functionalized SBA materials are much stronger than their counterparts.[31] Moreover, the SBA materials have larger pores which can be tuned by varying the conditions/procedures such as synthesis, temperature, additives and time. Furthermore, SBA materials have in-built microporosity and

Table 1: Physico-chemical characteristics of mesoporous silica.

Mesophase	Surfactant	Interaction	*p*H	Structural data				Pore size (nm)	Surface area (m^2/g)	Wall thickness (nm)
				Dimensionality	Crystal system	Space group	Lattice constant (nm)			
MCM-41[3]	$C_{16}H_{33}(CH_3)_3N^+$	S^+I^-	basic	2D	hexagonal	P6mm	a = 4.04	3.70	1041	0.34
MCM-48[3]	$C_{16}H_{33}(CH_3)_3N^+$	S^+I^-	basic		cubic	$Ia\bar{3}d$	a = 8.08	3.49	1010	0.86
SBA-1[4]	$C_{16}H_{33}(C_2H_5)_3N^+$	$S^+X^-I^+$	acidic		cubic	$pm\bar{3}n$	a = 7.60	2.10	1355	2.14
SBA-2[5]	C_{16-3-1}[a]	$S^+X^-I^+$	acidic	3D	hexagonal	$P6_3/mmc$	a = 5.40, c = 8.70	2.22	990	3.18
SBA-3[6]	$C_{16}H_{33}(CH_3)_3N^+$	$S^+X^-I^+$	acidic	2D	hexagonal	P6mm	a = 3.60	2.60	1430	1.00
SBA-6[7]	$18B_{4-3-1}$[a]	S^+I^-	basic		cubic	$Pm\bar{3}n$	a = 14.60	2.00	686	6.15
SBA-7[8]	C_{16-3-1}[a]	S^+I^-	basic	3D	hexagonal	P6mm	a = 4.60, c = 7.50	2.30	555	1.50
SBA-8[9]	R_{12}[b]	S^+I^-	basic	2D	rectangular	cmm	a = 7.49, b = 4.98	2.91	1022	2.07
SBA-11[10]	Brij 56; $C_{16}EO_{10}$	$S^0H^+X^-I^+$	acidic		cubic	$Pm\bar{3}m$	a = 10.64	2.50	1070	3.44
SBA-12[10]	Brij 76; $C_{18}EO_{10}$	$S^0H^+X^-I^+$	acidic	3D	hexagonal	$P6_3/mmc$	a = 5.40, c = 8.70	3.10	1150	2.30
SBA-14[10]	Brij 30; $C_{12}EO_4$	$S^0H^+X^-I^+$	acidic		cubic	$Pm\bar{3}n$	a = 4.47	2.20	670	0.30
SBA-15[10]	P123; $EO_{20}PO_{70}EO_{20}$	$S^0H^+X^-I^+$	acidic	2D	hexagonal	P6mm	a = 12.12	8.90	850	3.20
SBA-16[10]	F127; $EO_{106}PO_{70}EO_{106}$	$S^0H^+X^-I^+$	acidic		cubic	$Im\bar{3}m$	a = 17.60	5.40	740	9.84
KIT-1[11]	$C_{16}H_{33}(C_2H_5)_3N^+$	S^+I^-	basic	3D	hexagonal	disordered	a = 4.80	3.40	1000	0.70
KIT-5[12]	F127; $EO_{106}PO_{70}EO_{106}$	$S^0H^+X^-I^+$	acidic		cubic	$Fm\bar{3}m$	a = 19.00	9.30	715	1.53
KIT-6[13]	P123; $EO_{20}PO_{70}EO_{20}$	$S^0H^+X^-I^+$	acidic		cubic	$Ia\bar{3}d$	a = 22.90	8.20	800	3.31
FDU-1[14]	B50-6600;$EO_{39}BO_{47}EO_{39}$	$S^0H^+X^-I^+$	acidic		cubic	$Im\bar{3}m$	a = 20.70	9.00	650	8.90
FDU-2[15]	$C_{18-2-3-1}$[a]	S^+I^-	basic		cubic	$Fd\bar{3}m$	a = 12.00	3.02	964	8.98
FDU-12[16]	F127; $EO_{106}PO_{70}EO_{106}$	$S^0H^+X^-I^+$	acidic		cubic	$Fm\bar{3}m$	a = 25.30	10.00	712	4.42
Alumina[17]	P123; $EO_{20}PO_{70}EO_{20}$	$S^0H^+X^-I^+$	acidic	2D	hexagonal	P6mm	a = 9.58	6.70	410	2.88
HMA[c,18]	$C_{16}H_{33}(CH_3)_3N^+$	S^+I^-	basic	2D	hexagonal	P6mm	a = 3.20	1.80	980	1.40
MSU-1[19]	Tergitol; $C_{11-15}(EO)_{12}$	S^0I^0	neutral	3D	hexagonal	disordered	a = 4.73	3.10	1005	1.00
MSU-2[19]	TX-114; $C_8Ph(EO)_8$	S^0I^0	neutral	3D	hexagonal	disordered	a = 7.04	2.00	780	4.10
	TX-100; $C_8Ph(EO)_{10}$						a = 7.16	3.50	715	2.70
MSU-3[19]	P64L; $EO_{13}PO_{30}EO_{13}$	S^0I^0	neutral	3D	hexagonal	disordered	a = 7.04	5.80	1190	0.30
MSU-4[20]	Tween-20	S^0I^0	neutral	3D	hexagonal	disordered	a = 6.01	3.40	773	1.80
HMS[21]	$C_{12}H_{25}NH_2$	S^0I^0	neutral	3D	hexagonal	disordered	a = 4.55	2.80	1070	2.70
HMM[d,22]	$C_{18}H_{37}(CH_3)_3N^+$	S^+I^-	basic	2D[e]	hexagonal	P6mm	a = 5.70	3.10	750	2.60
				3D[f]	hexagonal	$P6_3/mmc$	a = 8.86, c = 5.54	2.70	1170	6.10

[a] Gemini surfactant; [b] Bolaform surfactant; [c] Hexagonal mesoporous aluminophosphate; [d] Hybrid mesoporous material; [e] silica: surfactant $= 1:0.57$; [f] silica: surfactant $= 1:0.12$.

it can very well be controlled by synthesis and aging temperature and time.[32] Such micropores connects the mesopores will give a better access for a reagent to active site and these can also be used as confined reactors avoiding blockages in mesopores without losing mesoporous volume and surface area. SBA-type materials can be synthesized in various morphologies as linear silicate oligomers are mainly generated in acidic medium. All these properties make SBA-family of materials more significant than many other ordered mesoporous materials like MCM-41and MCM-48.[23]

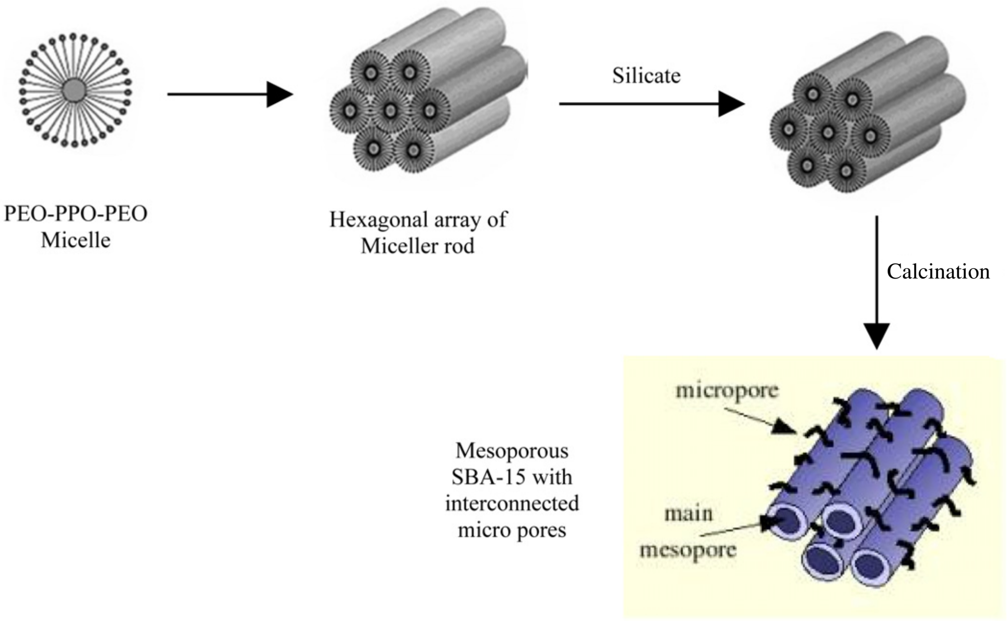
In recent years, environmental and economic considerations have raised strong interest to redesign commercially important processes such that usage of harmful substances and the toxic waste generation could be avoided. In this respect, there is no doubt that heterogeneous catalysis can play a key role in the development of environmentally benign processes in chemical industry as well as in the production of chemicals from biomass. For instance, substitution of liquid acid catalysts ($AlCl_3$, H_2SO_4 and BF_3) by solid acid catalysts could alleviate some of these problems elegantly. Furthermore, homogeneous catalysts are not selective and final isolation of the product necessitates aqueous quenching and neutralization steps to remove the acid, resulting in enormous quantities of hazardous waste. In addition, the cost of waste disposal often outweighs the value of the product. On the other hand, heterogeneous catalysts can offer several intrinsic advantages over their homogeneous counterparts, viz., ease of product separation and catalyst reuse; bifunctional phenomenon involving reactant activation/spillover between support and active phases; and process advantages through reactor operation in continuous flow versus batch configuration. Moreover, for the conversion of bulky substrates usage of zeolites is limited and hence aluminium-incorporated mesoporous materials will be attractive for such purpose. For example, isomorphous substitution of trivalent metal ions like Al^{3+}, Ga^{3+} and Fe^{3+} in siliceous matrix generate Bronsted acidity. Aluminium incorporation is most advantageous but it posses, in particular in SBA matrix, a challenge as aluminium is present as cationic species in acid medium making its condensation with silicate species is much harder. Other difficulties involved are easy dissociation of Al–O–Si bond under acidic hydrothermal conditions and the remarkable difference between the hydrolysis rates of silicon and aluminum alkoxides. Thus, in this review an attempt has been made to describe various strategies adopted for the aluminium incorporation in SBA materials with a special referene to SBA-15.

2. Formation of mesoporous framework

In general, mesoporous materials are formed by four different mechanisms, viz., liquid crystal templating (LCT),[33] co-operative self-assembly (CSA),[34] folded sheets (FS)[35] and Neutral templating (NT).[36] FS mechanism occurs only when layered ordered inorganic precursor, e.g., sodium kaenamite, is used whereas NT mechanism holds good in neutral synthesis medium. On the other hand, ordered mesoporous materials are mostly formed by CSA mechanism and/or by LCT pathway. Former occurs at low surfactant concentration while the latter at higher concentrations. SBA-15 is another kind of material which exhibits very good textural properties. It is formed using non-ionic triblock co-polymers, generally poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide); $EO_{20}PO_{70}EO_{20}$ (PEO-PPO-PEO; P123). Solubilization of non-ionic poly(alkylene oxide) block copolymers in aqueous media is due to the association of water molecules with the alkylene oxide moieties through hydrogen bonding enhanced by the acid media (usually HCl) where the hydronium ions associate with the alkylene oxygen atoms. The template formation and structure formation mechanism is similar to the M41S-series, i.e., MCM-41 and MCM-48 types. Like MCM-41, SBA-15 has one dimensional pore channels with two-dimensional hexagonal structure. However, unlike MCM-41, the SBA-15 matrix is bound by a number of micropores running across it. Furthermore, SBA-15 has larger pores than MCM-41 owing to the larger chain length of the polymer template used for the synthesis. In addition, it has thicker walls (*cf.* Table 1) and has a much greater mechanical and hydrothermal stability than MCM-41. Fig. 2 depicts a schematic representation of the formation mechanism of SBA-15 structure.[10]

SBA materials are obtained by sol-gel process involving hydrothermal treatment as per the procedure described below.[37] At first homogeneous solution of surfactant is obtained, to which silica precursors are added. Since the isoelectric point of silica is (pH) is 2 and hence highly acidic solution is used ($p\mathrm{H} < 2$) in order to get positively charged silica species. The mixture (surfactant solution, silica precursors and acid) is stirred at a particular temperature, which is determined by critical micelle temperature (CMT) and cloud point (CP) of the surfactant. The synthesis or gelation temperature should be such that it is above CMT and below CP of the surfactant. In synthesis, HCl is mainly used as acid catalyst as it takes less time to precipitate than other acids as precipitation time mainly depends on radius, charge and strength of anion of the acid.[10] Acid catalyst hydrolyzes silica precursors form oligomers which in turn aggregate around micelle through CSA. High concentration of acid leads to faster polymerization but highly concentrated acid (>4 M) is not preferred. Low concentration of acid catalyst favors slow condensation of silicate species leading to a highly ordered material. The final gel is subjected to hydrothermal treatment. The precipitate obtained is filtered and washed; actually washing is not necessary as volatile HCl can be removed with surfactant upon calcination. At this juncture, it is to be noted here that only tetraethyl orthosilicate (TEOS) or sodium meta silicates are used as silicate precursors for SBA synthesis while in the case of basic synthesis various silica sources can be used.[38] In alkaline medium synthesis cross-linking is reversible which is not possible in acidic medium synthesis. However, drying the sample helps further cross-linking of silanol groups. The surfactant/template was removed by calcination which also leads to pore shrinkage, lower surface area and low pore volume. This causes higher cross-linking and therefore high hydrothermal stability. Surfactant can also be removed by solvent

Figure 2: Mechanistic pathway for the formation of SBA-15.[10]



extraction using ethanol or tetrahydro furan; small amount of HCl is added to improve cross linking and to minimize effects on mesostructure. Supercritical fluids have better solubility than normal solvents, which makes extraction and recovery exceed 90%. Solvent extraction leads to presence of more silanol groups enhancing hydrophilic property. This method generates large pore sizes than calcined samples as in later case; more silanol groups condensation reduces the pore size. The surfactant removal by this method is not 100% efficient.[39] Linear silicate oligomers are main products of hydrolysis under acidic conditions favoring the formation of various morphologies whereas base catalysts leads to faster polymerization and condensation of silicate species making difficult to control morphology mainly yielding spherical particles only.

For example, mesoporous SBA-15 materials were synthesized using non-ionic surfactant, triblock poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide — $EO_{20}PO_{70}EO_{20}$), wherein the PEO units functions as head and alkyl chain and poly propylene oxide (PPO) units acts as core. Orderness of mesostructure can be improved on decrease of surfactant concentration as this allows slow assembly of silicate species with surfactant molecules. As micelle size increases pore size increases and wall thickness decreases. PEO units get dehydrated and become hydrophobic upon increase in synthesis temperature or by increasing time taken for hydrothermal treatment and hydrothermal treatment temperature, this leads to increase in pore size.[40] Pore size can also be increased by adding hydrophobic species which moves in to the hydrophobic core which leads to swelling of micelle.[41] SBA-15 materials templated by non-ionic surfactants will have microporosity, which originates from penetration of EO chains in silica walls, thus creating interwall porosity, connecting the different mesoporous cavities.[42] Microporosity is mainly controlled by synthesis temperature, aging temperature and time and by silica/surfactant ratio.

There are at least three synthesis routes for the derivation of silicate molecular sieves of various mesophases; the basic route (S^+I^-; M41S family), the acidic route ($S^+X^-I^+$; SBA family), and the neutral route (S^0I^0; HMS/MSU family). It is of interest to note that the acidic route-derived materials (e.g., SBA-*n*) have thicker pore walls and a framework charge (slightly positive) different (negatively charged) from the basic route-derived mesoporous materials (MCM-41 and MCM-48), due to the different precipitation conditions and charge balance requirements. Therefore, in the former case surfactant and counter ion species could be removed in ethanol under reflux while in the case of the latter, the surfactants could be washed out only with acidic alcohol under reflux condition. Another aspect of mesophase formation is the manner in which the surfactant tail groups pack in the material in terms of an effective surfactant packing parameter $g (g = V/a_0 l)$[43] where V is total volume of surfactant hydrophobic chains plus any organic moieties between chains, a_0 is the effective hydrophilic head group at aqueous micelle surface and l is the kinetic surfactant tail length. The expected mesophase sequence as a function of g value is: cubic (Pm$\bar{3}$n) and 3D hexagonal (P$6_3/mmc$) with $g < 1/3$; 2D hexagonal (P6 mm) with $1/3 < g < 1/2$; cubic (Ia$\bar{3}$d) with $1/2 < g < 2/3$; lamellar with $g = 1$. It is noteworthy here that as the g value increases, the curvature of the mesophase decreases and therefore the dimensionality. On the other hand, ionic radii of hydrated anions, cations and the inorganic salts affects g values of ionic surfactants. Further, the SBA materials are governed by $S^+X^-I^+$ mechanism and that X^- mediates it, the anions affect significantly the mesophase formation. That is, the anions transform mesostructure of larger curvature to smaller curvature as we move from NO_3^- to HSO_4^- of Hofmeister series as low hydrated anions bind strongly and closely to head groups of surfactants reducing electrostatic interaction between charged surfactant head groups resulting mesostructure of low curvature and *vice versa*.[44] Organic additives also have an effect on the g values of surfactants; small organic additives are mainly present near micelle-water interface while large molecules remain in the core. These organic additives are effective at low concentration as, at high concentration, surfactant molecules get dissolved in them and micelles get affected. In the case of non-ionic surfactants, V_H/V_L (hydrophilic/hydrophobic volume ratio) is mainly suggested to account for the formation of different mesophases.[45] Block copolymers with high V_H/V_L ratios favor mesophases with high curvatures whereas block copolymers with medium V_H/V_L favor mesophases with medium curvature. Radii and dehydration of PEO (salting affect) units by anions also has to be considered in order to assign which mesophase will be formed.[46] In a hydrothermal treatment, concentration and temperature of surfactant determines final mesostructure as predicted by phase diagram but generally it is not followed exactly as hydrophobic/hydrophilic properties of system changes constantly on silicate polymerization.

3. Preparation methods of AlSBA-15

Among the various metal-substituted mesoporous molecular sieves, aluminum incorporated mesoporous materials have great potentials in moderate acid-catalyzed reactions for large molecules. Therefore, much effort have been devoted to the incorporation of aluminum into SBA-15 by various synthetic strategy to create acidic sites and/or improve hydrothermal stability which include direct synthesis, post-treatment of SBA-15 with aluminum solutions, post-synthesis alumination in organic or aqueous solutions, etc. In addition, a two-step synthesis procedure of assembling pre-formed aluminosilicate precursors with Pluronic P123 template has been widely investigated to transform amorphous SBA-15 walls into crystalline aluminosilicates. In fact, the post-synthesis routes always led to lower-quality textural characteristics. Many other works such as those that use the '*p*H-adjusting' method, premixing of the liquid organic aluminium and silicon sources, employ a single silicon and aluminum source, semi-crystallization of the framework or use of zeolite matrix to modify the wall of SBA-15, and monitor the crystallization process of a zeolite structure on SBA-15 mesopore walls, etc., have been reported. Nevertheless, the direct synthesis of AlSBA-15 is difficult because, under strongly acidic conditions of preparation of siliceous SBA-15, free aluminum species such as Al^{3+} only exist in cationic form and thus cannot enter the framework of SBA-15 by conventional synthesis. That is, the easy dissociation of Al–O–Si bond under acidic hydrothermal condition and the remarkable difference between the hydrolysis rates of silicon and aluminum alkoxides makes it much more difficult. Furthermore, the resulting materials have many extra-framework/non-framework aluminum species. Hence, it remains a challenge to find a simple and easy single-step preparation method for the synthesis of AlSBA-15. Several approaches have been adopted to unravel some of these problems caused by the difference in reactivity toward hydrolysis and condensation of silicon and aluminum alkoxides.

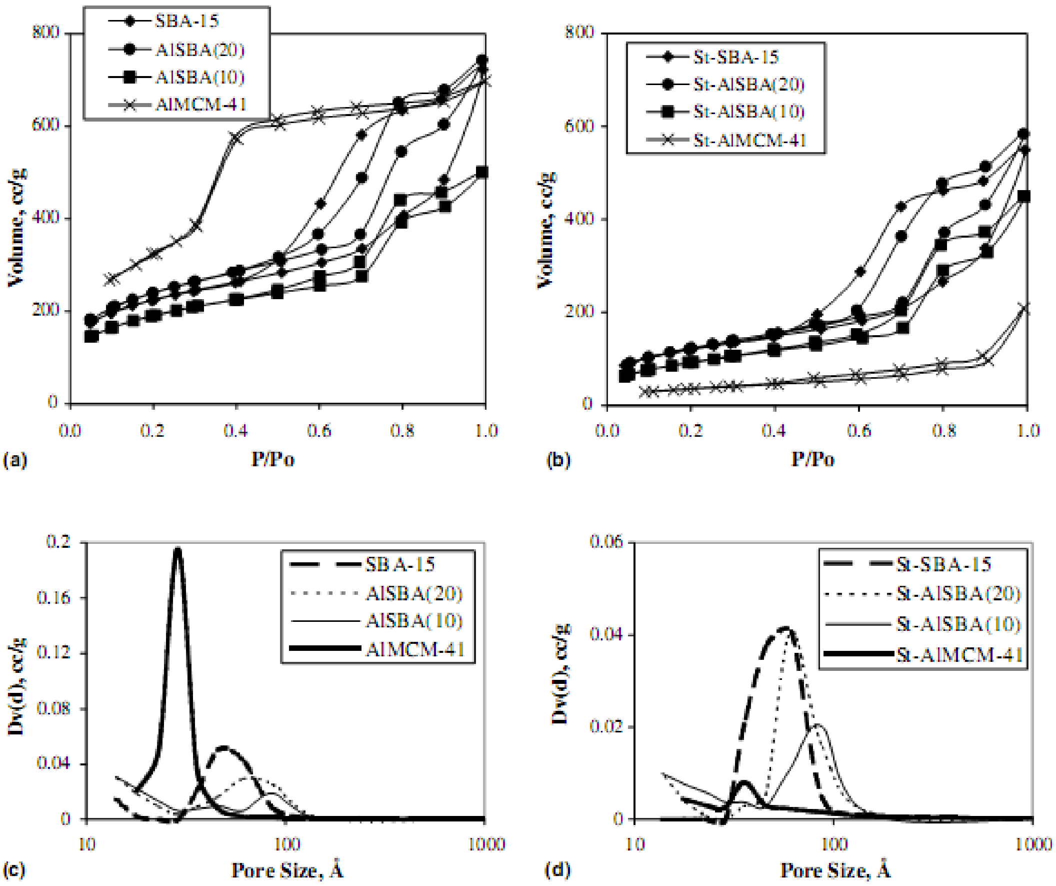
Table 2 summarized the textural and acidic properties of commonly used 2D hexagonal materials.[47–49] Among these materials, the aluminium incorporated SBA-15 matrix is considered one of the best candidates as it has several advantages, such as high crystallinity making it thermally stable and it imparts stronger activity upon metal incorporation; thicker walls making it more hydrothermally stable; larger pores making it useful for catalyzing bulky molecules. Table 3 present the results of various reaction catalyzed by AlSBA-15 and AlSBA-15 supported catalyst systems. For a comparion, other mesoporous systems suh as MCM-41 and HMS also included. It is clear from this table that AlSBA-15 shows much higher activity as compared to AlMCM-41 and AlHMS owing to its stronger acidity. In the case of supported systems, the stronger acidity of AlSBA-15 leads to higher dispersion of metallic species and therefore the activity. The high hydrothermal stability of

Table 2: Textural and acidic properties of mesoporous silicates and aluminosilicates.

	Si/Al (molar ratio)[a]	a_o (nm)	Pore size (nm)	Surface area (m²/g)	Wall thickness (nm)	Acid amount (mmol/g)
SBA-15	∞	13.33	9.41	632(281)[b]	4.22	—
H-AlSBA-15	10.2	13.82	9.09	773	4.74	0.70
MCM-41	∞	4.39	2.70	1143(106)[b]	1.69	—
H-AlMCM-41	14.1	4.50	2.80	857	2.70	0.96
HMS	∞	4.96	3.30	975(228)[b]	1.66	—
H-AlHMS	15.5	4.27	2.50	1138	1.77	0.95

[a] Si/Al ratio determined by ICP-AES; [b] Surface area after humid treatment at 100 °C for 16 h.

Figure 3: N_2 sorption isotherms and pore size distribution of SBA-15, AlSBA-15 and AlMCM-41 (a,c) before and (c,d) after steaming at 800°C.[59]



AlSBA-15 can very well be deduced from Fig. 3 wherein the N_2 sorption isotherms along with pore size distribution before and after steaming clearly elucidate that AlSBA-15 is more stable than the analogous AlMCM-41. Many synthesis methods were tried in order to incorporate more aluminum mainly in tetrahedral coordination (Isomorphous substitution or framework substitution) as it generates Bronsted acidity such that it can replace Zeolites. Some of those methods are listed below.

3.1. *Direct synthesis*

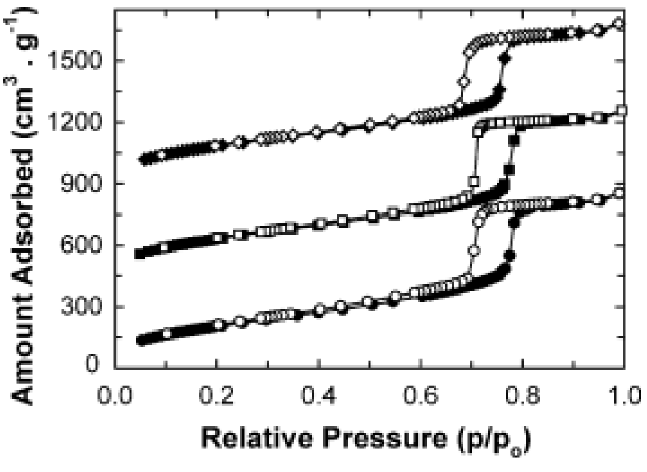
In this method, aluminum source is directly added to the final gel and then subjected to hydrothermal treatment. The product obtained was then filtered, washed, dried and calcined in order to obtain AlSBA-

Table 3: Catalytic properties of aluminosilicate mesoporous materials.

Reaction	Catalyst	Activity	Selectivity (%)
Cracking of cumene [50,48]		cumene[a]	Benzene
	H-AlSBA-15	<15.0	100.0
	H-AlHMS	2.3	100.0
	H-AlMCM-41	1.4	100.0
Alkylation of hydroquinone with *t*-butanol [51]		Hydroquinone[a]	2-*t*-butylhydroquinone
	H-AlSBA-15	64.5	80.5
	H-AlMCM-41	17.9	100.0
Benzylation of benzene[52]		Benzylchloride[a]	Diphenylmethane
	H-AlSBA-15	100.0	90.0
	H-AlMCM-41	20.0	80.0
Hydroamination of ethyl acrylate with aniline[53]		Ethyl acrylate[a]	Mono addition
	H-AlSBA-15	77.0	100.0
	H-AlMCM-41	82.0	100.0
Alkylation of phenol with *t*-butanol[49]		Phenol[a]	2,4-di-*t*-butyl Phenol
	H-AlSBA-15	75.2	31.3
	H-AlMCM-41	61.3	13.4
Hydrogenation of cyclohexene[54,55]		Cyclohexene[b]	Cyclohexane
	8%Mo/ SBA-15	25.0	100.0
	8%Mo/H-AlSBA-15	61.0	100.0
	10%Mo/HMS	36.3	100.0
	8%Mo/H-AlHMS	61.8	100.0
Hydrodesulfurization of dibenzothiophene[56,57]		Dibenzothiopene[a]	Cyclohexylbenzene
	1.5%Ni 6%Mo/SBA-15	30.0	18.0
	1.5%Ni 6%Mo/H-AlSBA-15	71.0	15.0
	3%Ni12%Mo/MCM-41	37.0	18.2
	3%Ni12%Mo/H-AlMCM-41	98.0	11.2

[a] Conversion (%); [b] Reaction rate (mol $h^{-1}g^{-1}$ catalyst $\times 10^{-3}$).

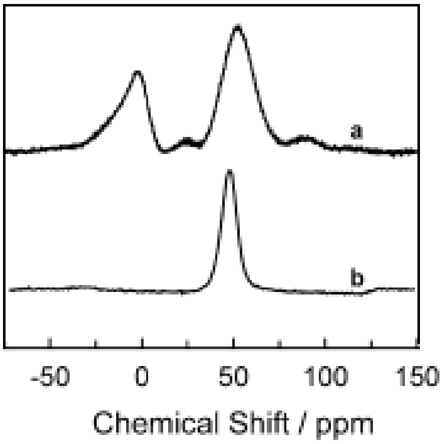
Figure 4: N_2 sorption isotherms of AlSBA-15(X) (X = Si/Al) prepared using direct method; (♦) 215, (■) 136 and (•) 45.[60]



15. However, owing to acidic synthesis medium, aluminum species will get solubilized and are present in cationic form making its condensation more difficult with silicon species. Therefore, aluminium alkoxides are only used exclusively as aluminum source since the aluminum salts (e.g., aluminum sulphate, aluminum nitrate, etc.) will decrease pH further which makes aluminum condensation much difficult.[58] Alternatively, the use of aluminum tri-tert-butoxide at pH 1.5 (just below the isoelectric point of silica; $p\text{H} = 2$) and as a consequence more aluminum incorporated in the framework structure of SBA-15.[59] On the other hand, the slow hydrolysis of aluminum tri-tert-butoxide (as the alkoxide group of aluminum becomes bulkier its hydrolysis becomes slower), the trivalent aluminum also condensed to polymeric species resulting in extraframework species. The use of aluminum isopropoxide,[60] however, reduced considerably the extraframwork aluminum. As shown in Fig. 4, the direct method gives well ordered materials with large surface area and pore volume but they have high Si/Al ratio than that in the synthesis gel due to high solubility of aluminum species as shown in Table 4. In addition, the structural ordering was also found to decrease upon higher loading of aluminum in the framework.

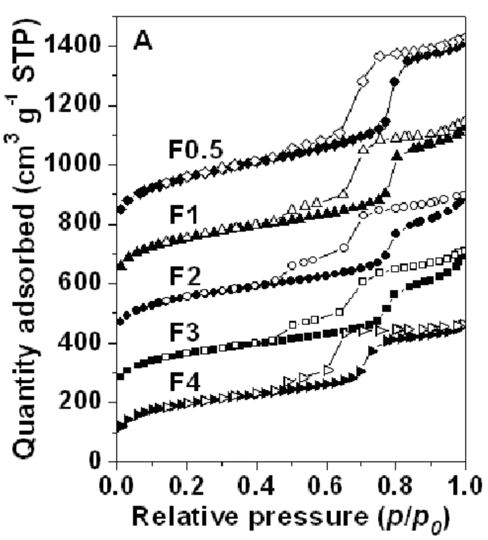
The variation of n_{H_2O}/n_{HCl} ratio (pH can be increased)[61]and reduction of surfactant

Figure 5: ^{27}Al MAS-NMR of AlSBA-15(X) (where X = Si/Al) prepared using by varying n_{HCl}/n_{H_2O} ratio method (a) AlSBA-15 (7) and (b) AlSBA-15 (45). [61]



concentration allows slow condensation of silicon species thereby generating ordered mesoporous material with higher loadings of aluminum in the framework can be synthesized as low as 7 (Si/Al molar ratio) ratio. However, the main disadvantages of this method are low incorporation of aluminum and the presence of extraframework/non-framework species at higher loadings of aluminium (Fig. 5). Likewise, aluminum nitrate is used as aluminum source in which acid is generated *in-situ* by hydrolysis.[62] By increasing aluminum nitrate, plugged hexagonal templated silica (PHTS) are formed which is nothing but SBA-15 with plugs as indicated by two step branched desorption as shown in Fig. 6. PHTS has extra microporous amorphous silica nanoparticles within mesopores and will have higher micropore volume and higher stability than regular SBA-15. As with the other preparation methods, the main disadvantages of this method are low amount of aluminium incorporation and the presence of extra-framework species in mesopores (*see* Table 4).

Figure 6: N_2 sorption isotherms of AlSBA-15 prepared without using mineral acid; shows two step branched desorption indicative of plugs (micropores).[65]



3.2. *Post-synthesis grafting*

Since lower Si/Al ratios cannot be achieved in direct synthesis, a post-synthesis grafting approach is used to achieve higher Si/Al ratios in AlSBA-15. In this method, dehydrated pre-formed (siliceous) SBA-15 is treated with (aqueous or organic) aluminum salt solution followed by calcination, as the presence of water decreases the amount of isolated silanol groups due to hydrogen between them and water.[63–65] Several aluminum sources, viz., aluminum chloride in ethanol, aluminum isopropoxide in dry hexane and sodium aluminate in water were employed, as grafting agents (*see* also Table 4).[63] All of them generated good structured materials but grafting with aluminum isopropoxide and sodium aluminate has reduced surface area and pore volume of AlSBA-15 (Fig. 7). Yet another aluminium source, tri-methyl aluminum in dry toluene, was also use to graft aluminum to siliceous SBA-15.[64] The structural ordering of the obtained material decreased after alumination as well as the surface area and pore volume due to the formation of extraframework species. Polymerization mainly occurs if the charge is more localized on aluminum. In order to avoid the usage of organic solvents, aqueous ammonium hexafluoroaluminate in alkaline conditions was used for grafting,[65] and that the obtained materials show well ordered 2D hexagonal structure but with a high Si/Al ratio and low textural properties owing to the dissolution of silica under alkaline conditions (*cf.* Table 4). Although, post-synthesis grafting method seems to be interesting but it requires stringent conditions, organic solvents and that the materials obtained have low surface area and low pore volume.

3.3. *Hydrolysis approach*

In this method,[66] the reaction mixture is maintained at *p*H = 1.5, just below *p*H = 2 where cationic silicate species is generated so that more aluminum can get incorporated in the matrix, and fluoride ion is added so as to match the hydrolysis and condensation rates of silicon alkoxides with that of aluminum alkoxides. The *p*H is then adjusted to 7 so

Figure 7: (A) N_2 sorption isotherms and (B) pore size distribution of (●) SBA-15 and (▲) AlSBA-15 prepared using post-synthesis.[62]

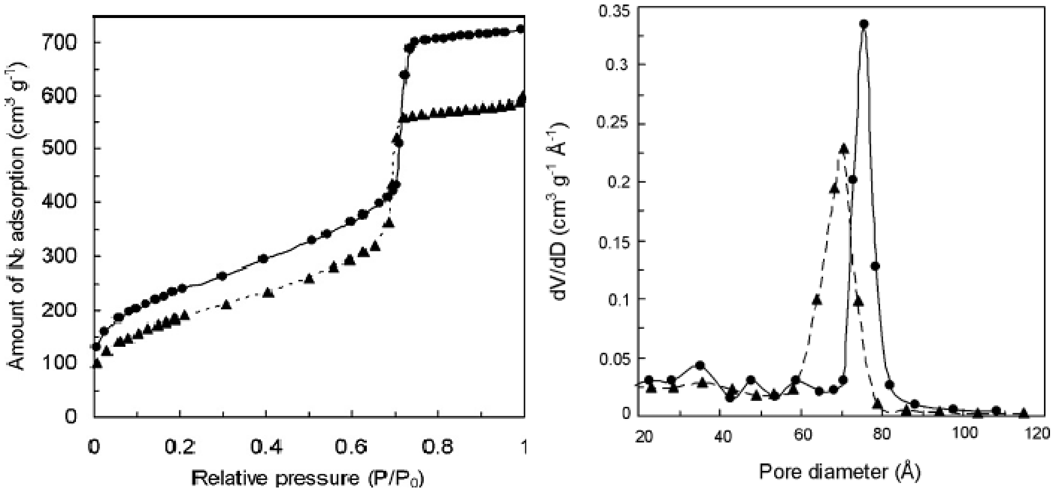


Table 4: Textural Properties of AlSBA-15 prepared by different methods.

Method	Aluminum source	Si/Al		Unit cell parameter (nm)	Pore size (nm)	Surface area (m^2/g)	Pore volume (cm^3/g)
		Gel	Product				
Direct synthesis	Al(O–i–Pr)$_3$[60]	7.0	45.0	11.30	9.70	930.0	1.40
		14.0	136.0	10.20	9.60	1025.0	1.40
		27.0	215.0	9.60	8.90	1035.0	1.30
	$Al(NO_3)_3 \cdot 9H_2O$[62]	2.0	63.4	11.60	9.20	863.0	1.05
		1.0	25.6	12.20	9.20	771.0	0.87
		0.5	18.7	11.60	9.20	697.0	0.77
Post-synthesis	$AlCl_3$[63]	30.0	30.7	10.40	5.80	802.0	1.09
		20.0	20.5	10.40	5.70	754.0	1.02
	Al(O–i–Pr)$_3$[63]	40.0	37.0	—	6.02	674.0	0.97
		20.0	17.0	—	5.91	619.0	0.93
	$NaAlO_2$(anhydrous)[63]	20.0	20.8	—	5.51	428.0	0.71
	$(NH_4)_3AlF_6$[65]	30.0	24.8	—	6.80	770.0	0.97
		15.0	12.5	—	6.50	725.0	0.87
Hydrolysis approach	Al(O–i–Pr)$_3$[66]						
	without fluoride	20.0	28.9	—	7.90	966.2	1.10
	with fluoride ($F^-/Si = 0.03$)	20.0	40.5	—	7.40	1023.9	1.28
	two-step method[a]	20.0	22.0	—	7.40	863.0	1.25
*p*H adjusting	$Al_2(SO_4)_3 \cdot 18H_2O$[67]	15.0	20.6	14.70	8.10	525.0	0.63
Zeolite precursor	ZSM-5[68]	25.0	40.0	13.39	8.00	967.0	—

[a] $F^-/Si = 0.03$ and $pH = 1.5$–7.

as to protect Si–O–Al linkage. The resultant mixture is then hydrothermally treated and the obtained product was filtered, washed, dried and calcined to get AlSBA-15. It is noteworthy here that the use of fluoride ions eliminates disorderness, as shown by N_2 sorption isotherms in Fig. 8, and also removes extraframework/non-framework aluminum species as depicted in ^{27}Al MAS-NMR spectra (Fig. 9). This is further confirmed by the increase in Bronsted acid sites as shown in Fig. 10. However, this method also has a shortcoming of the low incorporation of aluminium in the framework. Table 4 summarizes

Figure 8: N_2 sorption isotherms of AlSBA-15 prepared using hydrolysis approach (A) without fluoride and (B) with fluoride.[66]

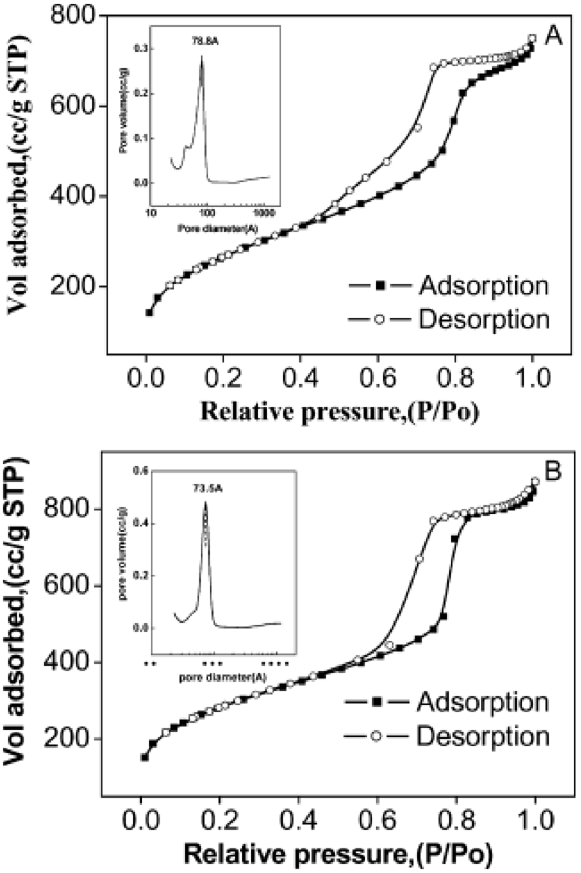
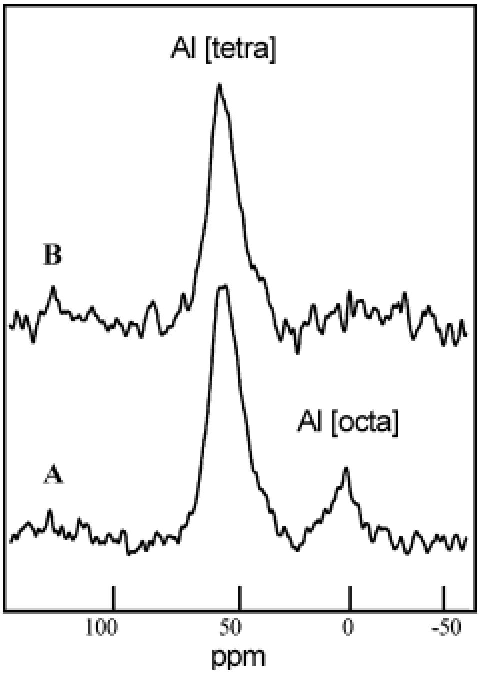


Figure 9: ^{27}Al MAS-NMR of AlSBA-15 prepared using hydrolysis approach (A) without fluoride and (B) with fluoride.[66]



the textural properties of AlSBA-15 synthesized with and without fluoride ion.

3.4. *pH adjusting method*

The *p*H adjusting method an effective and convenient method for the grafting of aluminium onto SBA-15 synthesized in strongly acidic media with high heteroatom content.[67] In this method, aluminum source is first added into the initial reaction mixture in strongly acidic media, just as in the case of direct-synthesis; when the mesostructure is basically formed, the *p*H value of the system is adjusted from a strong acid to neutral *p*H (= 7.5) followed by a hydrothermal treatment for another period of time, during which a large amount of heteroatoms can be introduced into the mesophase. The obtained materials is filtered, washed, dried and calcined in order to get AlSBA-15. At $p\text{H} < 1$, aluminum is mainly present as Al^{3+} which makes its condensation difficult with silanol groups (or silica species), therefore after hydrothermal treatment (once SBA-15 is formed), the *p*H is adjusted to 7.5 such that all aluminum species are converted to $Al(OH)_4^-$ species allowing them to condense with silanol groups and Si-O-Al linkage formed is further strengthened by hydrothermal treatment. The *p*H is adjusted to 7.5 as monomeric species of aluminum are generated in the *p*H range 7.2–7.8, thus makes the condensation easier. Using this procedure, nearly all aluminum species in the initial mixture can be grafted to the product exclusively in tetrahedral coordination up to Si/Al = 5 as shown in Fig. 11, which much greater than that achieved by post-synthesis grafting as usage of calcined product results in reduction of number of silanol groups available for grafting. The textural properties of the material prepared using this method is also listed in Table 4. The AlSBA-15 prepared by this method show highly ordered mesostructures with large surface areas and uniform mesopore size distribution (Fig. 12). Furthermore, various physic-chemical studies indicate that almost all the aluminium ions added into the initial reaction mixture can be introduced into the products, and moreover, the heteroions introduced by this route locate at mainly tetrahedrally coordinated sites.

3.5. *Zeolitic precursors*

Primary zeolitic structural units assembled with P-123 surfactant in acidic media generates

Figure 10: FT-IR spectra of AlSBA-15 prepared using hydrolysis approach (A) without fluoride and (B) with fluoride; increase in bronsted acidity (1547 cm^{-1}) to lewis acidity (1455 cm^{-1}) is seen when fluoride is used. [66]

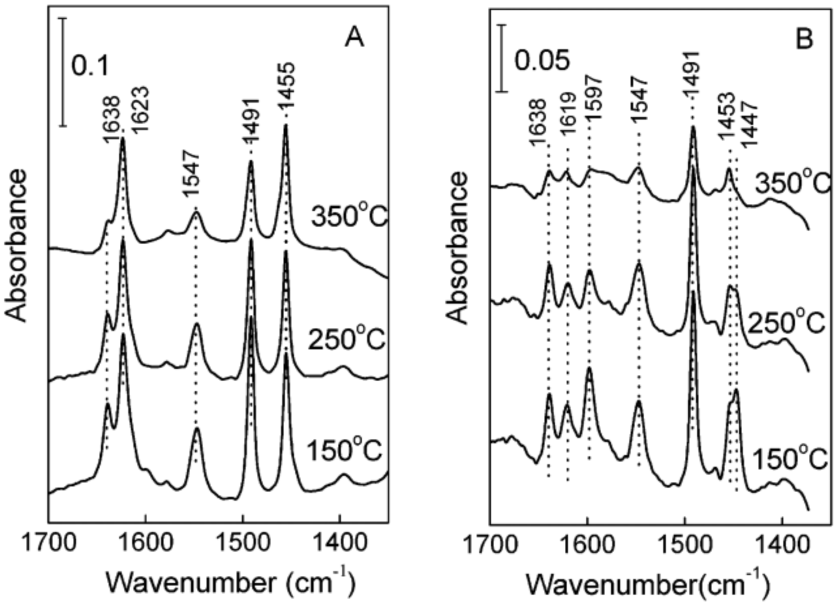
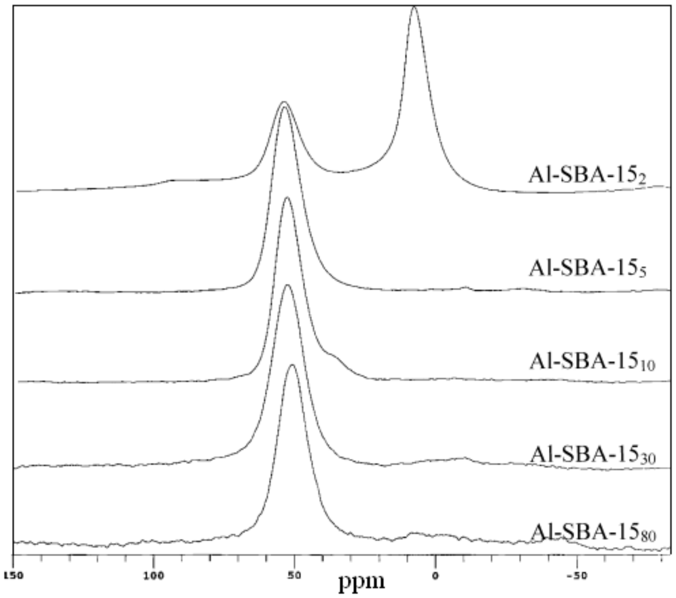


Figure 11: ^{27}Al MAS-NMR of as synthesized AlSBA-15$_x$ (where x = Si/Al) prepared using pH adjusting method.[67]



crystalline framework with aluminum in tetrahedral coordination with good surface area and pore volume. The textural properties of these zeolitic AlSBA-15 materials are tabulated in Table 4. However, the mesostructure is partially collapsed due to difference in density of amorphous (mesostructure) and crystalline (microstructure) states of the physical mixtures of the phases. This problem can be avoided by using carbon as filler which restrict the physical mixture formation.[68]

Figure 12: N_2 sorption isotherms of AlSBA-15(10) (Si/Al = 10) using pH adjusting method.[67]

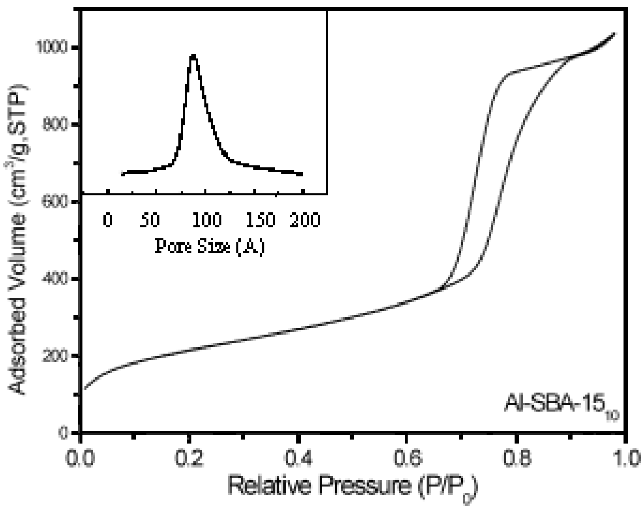
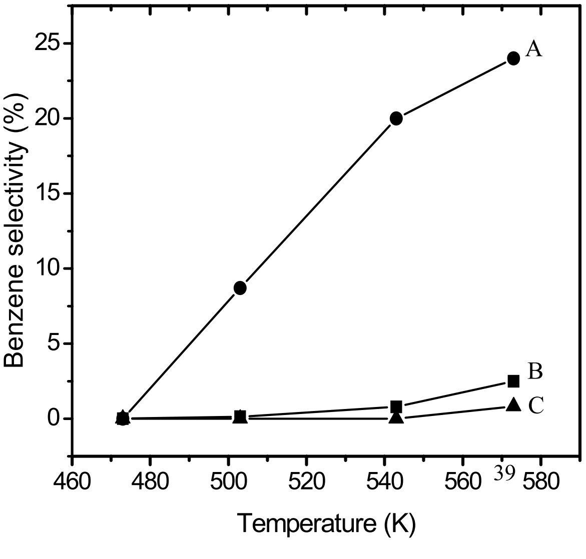


Figure 13: Catalytic activity of (A) H-ZSM-5, (B) ZMM-1 (AlSBA-15 prepared using zeolitic precursors) and (C) AlSBA-15 (post synthesis method) towards cumene cracking; shows ZMM-1 is more active than AlSBA-15 at lower temperatures due to crystalline walls.[69]



As compared to zeolites, aluminum incorporated mesoporous materials show low acidity and low hydrothermal stability due to its amorphous walls which can be improved by introducing zeolite structural units in to their walls thereby strong acidity can be imparted. The acidity of ZMM-1, AlSBA-15, and ZSM-5 were measured by cumene cracking, which is well known as a model reaction to confirm Brønsted acidity. Fig. 13 depicts the catalytic activities of these samples.[69] These results indicate that ZMM-1 contains the same type of Brønsted acid site as ZSM-5 from the activation energy viewpoint. The improved catalytic activity of ZMM-1 compared to Al–SBA–15 is caused by the zeolite primary and secondary building units which exist in the mesopore walls. Although, this method generates AlSBA-15 with crystalline framework and that aluminum is located in framework sructure,[69] they too have low amounts of aluminum incorporated combined with low structural ordering. On the

Table 5: Catalytic activity of AlSBA-15 materials with crystalline and amorphous walls.

Catalyst[a]	Conversion (%)	
	Cumene	1,3,5-Tri-isopropyl benzene
H-MAS-7(30)[b]	43.5	96.6
H-AlSBA-15(30)[c]	7.8	36.5
H-ZSM-5 (30)	94.4	1.7

[a] Si/Al ratio taken in gel is indicated in parenthesis. [b] Mesoporous aluminosilicates (MAS) prepared using zeolitic precursors. [c] Prepared using post-synthesis method.

other hand, these zeolitic AlSBA-15 materials show high conversion of bulky substrates than zeolites due to their large pore size as shown in Table 5. The mesoporous aluminosilicate (MAS-7) shows high catalytic activities for the cracking of both small (cumene) and bulky (1,3,5-triisopropylbenzene) molecules because it combines the advantages of both zeolites (strong acidity) and mesoporous materials (large pores).[70] In contrast, Al–SBA–15 samples prepared from both "post-synthesis" and "direct synthesis" present much lower catalytic activities than MAS-7. Though, the above said methods are available for aluminum incorporation in to SBA-15, each one has its own advantages and disadvantages. The *p*H adjustment method and two-step hydrolysis approach incorporates aluminum nearly complete amount but this will have serious impact on the mesostructure of the material.

4. Conclusion

In this review, we addressed the problems of the synthetic methodology adopted by various groups for the preparation of mesoposous AlSBA-15 as they possess desirable characteristics for exploiting them for a variety of catalytic applications. This article also examines the possible synthetic strategies to generate aluminum incorporated SBA-15 and evaluates the domain of the catalytic activity of these mesoporous solids. Among the above said methods, *p*H adjusting method and hydrolysis approach seems to produce good structured materials with nearly same amount of Si/Al ratio present in the material similar to that taken in gel. We can also obtain AlSBA-15 with high surface area and good pore volume but these methods generate AlSBA-15 with amorphous walls only.

Received 12 June 2010.

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Parasuraman Selvam is currently a Professor in the Department of Chemistry, Indian Institute of Technology Madras. Earlier, he was a Faculty in the Department of Chemistry, Indian Institute of Technology Bombay. His research interests are in the areas of solids (advanced materials including nanomaterials and nanoporous materials) and surfaces (heterogeneous catalysis including green chemical processes) with emphasis on applications relating to energy and environment. http://www.nccr.iitm.ac.in/staff/selvam.htm

Nunna V. Krishna is a Ph.D. student in the Department of Chemistry, Indian Institute of Technology Madras, working under the guidance of Professor P. Selvam. His main research interest is focused on the synthesis and characterization of mesoporous silicates/metallosilicates in particular the stabilization of trivalent aluminium in SBA family under acidic conditions.

Balasubramanian Viswanathan is a Professor and Head of National Centre for Catalysis Research, Indian Institute of Technology Madras is a renowned scientist and a distinguished teacher. His research contributions are enormous in the fields of heterogenous catalysis, materials science, computational chemistry, energy, nanotechnology and information science. http://www.nccr.iitm.ac.in/staff/bvis.htm