



CHAPTER II

LITERATURE REVIEW

2.1 SBA-15 Mesoporous Silica

Wongkasemjit and coworkers (1999–2009) reported a convenient and inexpensive way to synthesize silatrane complexes from widely available and inexpensive silica (SiO_2) and triethanolamine (TEA) via the “Oxide One Pot synthesis (OOPS)” process to be used as a silicon precursor for synthesizing mesoporous materials. The synthesized silatrane complexes are hydrolytically stable in air for several weeks. Besides, they have been effectively and successfully used to synthesize mesoporous siliceous materials via sol-gel method, such as SBA-1, Fe-SBA-1, and Ti-SBA-1 cubic mesoporous silica (Tanglumleart, *et al.*, 2007), MCM-41 and Fe-MCM-41 hexagonal mesoporous silica (Thanabodeekij *et al.*, 2006; Thitsartarn, *et al.*, 2007)

To synthesize SBA-15, many researchers have been successfully synthesized under conventional hydrothermal condition using tetramethyl orthosilicate (TMOS), or tetraethyl orthosilicate (TEOS) as silicon sources, triblock copolymer P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) as a structure-directing agent, and HCl or H_3PO_4 as acid source. The obtaining products were calcined at about 500 °C to remove the template to obtain highly ordered hexagonal mesoporous structure. Zhao *et al.* (1998) used TEOS and P123 as a silicon source and a template, respectively, at various temperatures (35 ° to 80 °C) in an acidic media (In some cases, 1,3,5-trimethylbenzene (TMB) was also used as an organic swelling agent) to obtain highly ordered, two-dimensional hexagonal (space group $p6mm$) silica-block copolymer mesophases. After calcination at 500 °C, they obtained porous structures with large inter-lattice d spacing in a range of 74–320 Å with pore size from 46 to 300 Å, pore volume fraction up to 0.85, and silica wall thickness of 31–64 Å.

Samran *et al.* (2008) have discovered a novel room temperature route for synthesizing SBA-15, using a moisture-stable silatrane as a silica precursor and triblock copolymer (P123) as a structure-directing agent under acidic condition. After stirring at room temperature for 24 h without any thermal assistance, they found that

the obtained SBA-15 had properties that could be comparable with the SBA-15 obtained from thermal-assisted synthesis route (as shown in the table below).

Table 2.1 The properties of SBA-15 as a function of synthetic route

Synthesis*		Surface Area (m ² /g)	Channel Volume (cm ³ /g)	Channel Diameter (Å)			d ₍₁₀₎ /d ₍₃₀₎
		BET	BET	BET	TEM	SAXS	SAXS
Route 1	Without hydrothermal treatment	486	0.6	50	~45	60-63	3
	With hydrothermal treatment via microwave assisted method at 100 °C for 2 h.	572	0.8	55	~45	63-67	2.8
Route 2	With hydrothermal treatment via microwave assisted method at 120 °C for 1 h.	613	0.8	54	~45	63-67	2.8

2.2 Metal Incorporated SBA-15

2.2.1 Fe-SBA-15

Li *et al.* (2005) reported that Fe-SBA-15 could be successfully synthesized using a simple direct hydrothermal method under weak acid condition in the presence of fluoride, using TMOS and iron nitrate (Fe(NO₃)₃·9H₂O) as silicon and iron precursors, triblock copolymer surfactant EO₂₀PO₇₀EO₂₀ as a template. They found that when the pH value of the solution was lower than 2.0, the highly isolated framework iron species (4-coordinated Fe³⁺) were obtained. Besides, under neutral condition, adding more iron precursor could improve the order of the mesostructure because of the effect of protons generated from the hydrolysis of Fe precursors. Moreover, different iron species were produced by changing the pH value of the solution, and, for all of the calcined samples, the iron ions exhibited tetrahedral coordination in the silica framework with Fe/Si molar ratio below 0.0022 at pH 1.5.

2.2.2 Ti-SBA-15

For titanium-substituted SBA-15, Zhang *et al.* (2001) successfully prepared Ti-SBA-15 using TMOS and titanium isopropoxide as silicon and titanium sources, respectively. Since the hydrolysis of titanium alkoxide is fairly instantaneous, whereas the hydrolysis of silicon precursor much slower, certain amount of fluoride ($F/Si = 0.03-0.05$) was added to accelerate the hydrolysis of TMOS; and pH value was adjusted to below 1.0 to obtain high quality of Ti-SBA-15.

Chen *et al.* (2004) successfully synthesized Ti-SBA-15 under acidity and hydrothermal conditions using titanium trichloride ($TiCl_3$) and TEOS as titanium and silicon sources, respectively. They pre-mixed H_2O_2 with a certain amount of $TiCl_3$ before adding into the gel-solution to improve the ordered structure of the Ti-SBA-15. At the maximum Si/Ti ratios, only the samples prepared in the presence of H_2O_2 could maintain their ordered structure. In addition, the products synthesized by adding H_2O_2 tended to have higher surface area, bigger pore size and larger pore volume than those synthesized without adding H_2O_2 .

To synthesize Ti-containing porous materials, Wongkasemjit and coworkers (2002–2006) successfully prepared titanium glycolate using inexpensive and widely available titanium oxide (TiO_2) and ethylene glycol as starting materials via the OOPS process. The resulting moisture stable titanium glycolate could be effectively used to synthesize many types of materials, such as high surface area anatase TiO_2 (Phonthammachai *et al.*, 2003), sillenite ($Bi_{12}TiO_{20}$) (Thanabodeekit *et al.*, 2005), titanium loaded TS-1 zeolite (Phonthammachai *et al.*, 2006), and highly ordered mesoporous Ti-SBA-1 (Tanglumert *et al.*, 2008).

2.2.3 Mo-SBA-15

Melero *et al.* (2007) have reported the preparation of molybdenum-containing SBA-15 using co-condensation technique under acidic condition using non-ionic surfactant as a template, TEOS and ammonium molybdate tetrahydrate $[(NH_4)_6[Mo_7O_{24}] \cdot 4H_2O]$ as silica and molybdenum sources, respectively. They prehydrolyzed molybdenum precursor for at least 3 h to depolymerize heptamolybdate species to form monomeric soluble molybdenum(VI) species before adding silica and molybdenum precursors into the template solution. After stirring at 40 °C for 20 h the mixture was aged at 100 °C for 24 h and further calcined. The

resultant product from this method showed good mesoscopic ordering, narrow pore size distribution and high dispersion of molybdenum species.

Wongkasemjit *et al.* (2009) have been successful to use molybdenum glycolate to prepare Mo-SBA-1 in dilute acidic condition at room temperature using silatrane as a silica source and C₁₆TMAB as a template. The mesoporous Mo-SBA-1 obtained from this method maintained a well-order mesostructure and high surface area. The amount of molybdenum that could be incorporated into the SBA-1 framework was quite high (upto 5 %mol) without any extraframe work.