CHAPTER II
LITERATURE REVIEW

2.1 ZSM-5

ZSM-5, Zeolite Sieve of Molecular porosity – 5, (structure type MFI – mordenite framework inverted), a member of the pentasil family of zeolite, was first introduced by Argauer and Landolt (1972). ZSM-5 has been used in various applications especially as a catalyst in organic syntheses, oil refining, environmental management, and petrochemical industry (Yogo *et al.*, 1993; Hollander *et al.*, 2002; Perez-Ramirez *et al.*, 2003; Borges *et al.*, 2007; Feng *et al.*, 2009; Serrano *et al.*, 2010).

2.1.1 Structure and Properties

ZSM-5, is a microporous (average pore diameter of 0.50-0.54 nm.), aluminosilicate material, having crystal size in a micrometer range (~5-15 μ m) and the chemical formula of $Na_nAl_nSi_{96-n}O_{192}\cdot16H_2O$ (0<n<27). The structure of ZSM-5 is formed by pentasil units linked together by oxygen bridge, showing the characteristic IR-absorption band at 550 cm^{-1} (dyad five-member ring) (Coudurier *et al.*, 1982; Fan *et al.*, 1995). The unit cell of ZSM-5 contains 96 Si (or Al) sites and 192 O sites. The number of cationic counter-species, generally, Na^+, was depended on the ratio of Si/Al. The XRD diffractrogram of ZSM-5 was shown at 2 theta of ~7°, ~8°, and ~23° which ~23° contribute to {501} crystalline plane of ZSM-5.
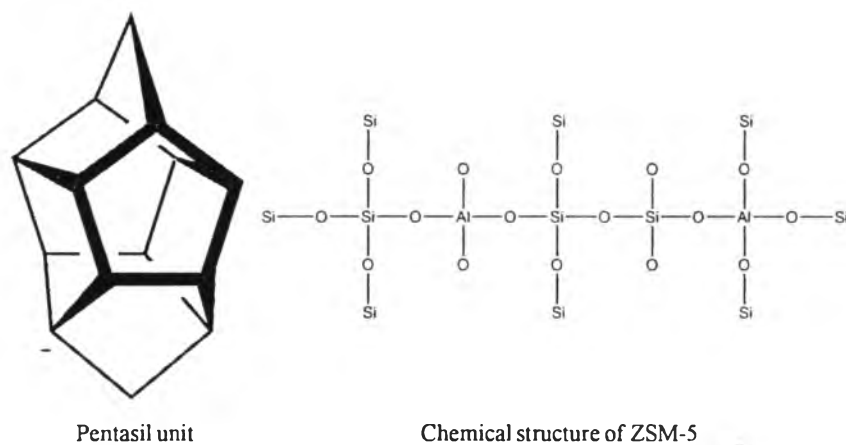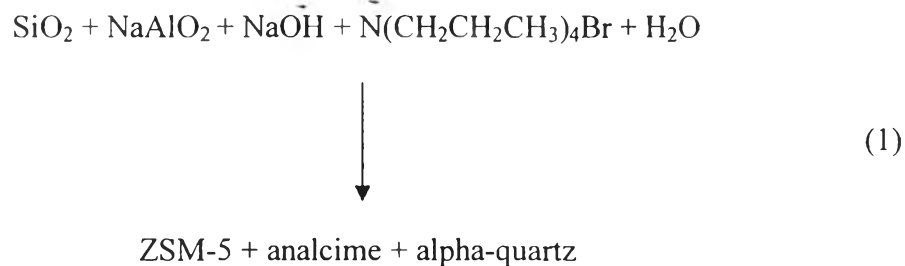
Pentasil unit   Chemical structure of ZSM-5

Figure 2.1 Structure of ZSM-5. (Yu *et al.*, 2007; DMacks, 2011)

ZSM-5 posses many outstanding properties such as size-selectivity, surface acidity, well-ordered pore network (3D network), high thermal stability (up to 1,000 °C) (Yu *et al.*, 2007), and cation-exchange capability which can be used in various applications.

2.1.2 Synthesis of ZSM-5 via Microwave Irradiation

Generally, ZSM-5 was synthesized by conventional-hydrothermal autoclave technique at high temperature and pressure using organic compounds as a directing agent, which took long reaction time (Li *et al.*, 2007; Zhu *et al.*, 2010) via a common chemical reaction as followed (Lermer *et al.*, 1985):

$$SiO_2 + NaAlO_2 + NaOH + N(CH_2CH_2CH_3)_4Br + H_2O$$

$$\downarrow \tag{1}$$

$$ZSM\text{-}5 + analcime + alpha\text{-}quartz$$

Microwave irradiation is of interest for the synthesis of ZSM-5. The wavelength of microwave was 1 mm. - 1 m. with the frequency ranging from 300 GHz to 300 MHz. By using microwave irradiation, heat was homogeneously-rapidly

generated by vibration of material molecules, instead of heat transfer from the external source occurred in the conventional-hydrothermal autoclave technique.

Therefore, microwave irradiation was alternatively used instead of conventional-hydrothermal autoclave technique to reduce the reaction time. By using microwave irradiation, Katsuki *et al.* (2005) and Anuwattana *et al.* (2008) found that the rate of ZSM-5 formation was faster than that of conventional-hydrothermal synthesis about 3-4 times and 4 times, at 150 °C, using carbonized rice husk and cupola slag as a silica source, respectively. Furthermore, in 2003, a homogeneous orthorhombic MFI zeolite has been successfully synthesized using silatrane, a novel organosilicate material, as a Si source via sol-gel process at 150 °C microwave temperature for 20 h by Phiriyawirut *et al.* (2003) who found that the formation rate of MFI depended on OH^- concentration, Na^+ concentration, and organic template concentration. Moreover, Jin *et al.* (2007) found that titanium-incorporated ZSM-5 zeolite could be synthesized within 1 h of synthesis time by microwave irradiation. Additionally, the different macroscopic morphologies of ZSM-5 were achieved by using disiloxane for spherical crystal (Ishii *et al.*,2011) and triethylenetetramine for rectangular sheet conglomeration crystal (Wei *et al.*, 2009), as directing agents.

2.1.3 Mesoporous ZSM-5

According to IUPAC classification, porous materials are classified into 3 types which are microporous material with the pore diameter of less than 2 nm, mesoporous materials with the pore diameter ranging from 2 nm to 50 nm, and macroporous materials with pore diameter of lager than 50 nm. ZSM-5 basically belongs to microporous material which could influence the catalytic performance for synthesis of large molecules due to a limitation of mass transfer (Perez-Ramirez *et al.*, 2003; Donk *et al.*, 2001). Mesoporous ZSM-5 was introduced to overcome these limitations. Carbon xerogels (Tao *et al.*, 2003, 2004, 2005, 2006) and carbon nanotubes (Schmidt *et al.*, 2001) were used as templates to produce mesoporous ZSM with the mesopore diameter of 9-25 nm and 12-30 nm, respectively. By using polymeric materials (Wang and Pinnavaia, 2006; Fujiwara *et al.*, 2011) and

surfactant (Choi *et al.*, 2006; Na *et al.*, 2011), non-ordered and ordered mesoporous ZSM-5 were successfully synthesized, respectively.

2.1.4 Nanosized ZSM-5

Generally, nanosized ZSM-5 was produced by using nanoporous hard template as confined space to control the sizes of ZSM-5 crystal. The sizes of ZSM-5 crystal will be identical with the pore of its own nanoporous hard template, as shown in Table 2.1 Nanosized ZSM-5 showed almost the properties as same as those of micronsized ZSM-5 except the pore structure properties and crystal sizes. Nanosized ZSM-5 showed mesoporous properties and higher surface area compared to those of micronsized ZSM-5 (Thubsuang *et al.*, 2012; Song *et al.*, 2004). Generally, nanosized ZSM-5 was produced by using carbon hard template as space confinement to control the size of the crystal (Madsen and Jacobsen, 1999; Tang *et al.*, 2006; Huang *et al.*, 2009). However, nanosized ZSM-5 can also be synthesized without the need of hard template as well. Therefore, the properties of nanosized ZSM-5 synthesized via diferent methods were different, as shown in Table 2.1.

Using this ZSM-5 nanocatalyst, Serrano *et al.* (2010) studied the epoxidation rearrangement reactions and found that nanocrystalline ZSM-5 with the crystal size in the range of 20-50 nm showed higher epoxide conversion than that of microcrystalline ZSM-5 with the crystal size of 5 μm.

Table 2.1 Characteristics of ZSM-5 derived by various methods

Sample	Temperature (°C)	Synthesis Time (h)	Synthesis method	Hard template	S_{BET} (m²/g)	V_{micro} (cm³/g)	V_{meso} (cm³/g)	V_{total} (cm³/g)	Crystal size (nm)
E4 (Petushkov *et al.*, 2011)	140	24	Autoclave	No	-	0.104	0.43	0.534	26[a]
NZ (Na *et al.*, 2011)	170	48	Autoclave	No	461.1	0.1321	0.0493	0.3855	-
n-ZSM-5 (Serrano *et al.*, 2010)	170	120	Autoclave	No	384	-	-	0.24	20-50[b]
CA1-ZSM-5 (Tao *et al.*, 2005)	150	96	Autoclave	RF-based carbon	385	0.15	0.2	0.35	-
Nanosized ZSM-5 (Tang *et al.*, 2006)	170	96-120	Autoclave	Carbon nanotubes	-	-	-	-	39[c]
SZ (Madsen and Jacobsen, 1999)	180	48	Autoclave	Carbon black	412.4	-	-	0.58	8-30[b]

Notes: S_{BET}: BET surface area; V_{micro}: micropore volume; V_{meso}: mesopore volume; V_{total}: total pore volume; a: The crystal size was calculated from method of Song *et al.*, (2004); b: The crystal size was obtained from TEM image; c: The crystal size was calculated by Scherrer equation

2.2 Polybenzoxazine

Polybenzoxaxine (PBZ), a new type of additional-cure phenolic system, is the new class of phenolic type resin which posed many exceptional properties than those of traditional phenolic resin such as ring-opening polymerization without added initiators or catalyst, no release of volatiles during polymerization, near-zero volumetric change upon polymerization, and low water adsorption.

2.2.1 Synthesis of Polybenzoxazine

Polybenzoxzazine can be synthesized via a solvent method proposed by Ishida (1996) through the Mannich condensation reaction of phenol, formaldehyde, and amine, having water as by-product. Figure 2.2 shows the synthesis reaction of polybenzoxazine.
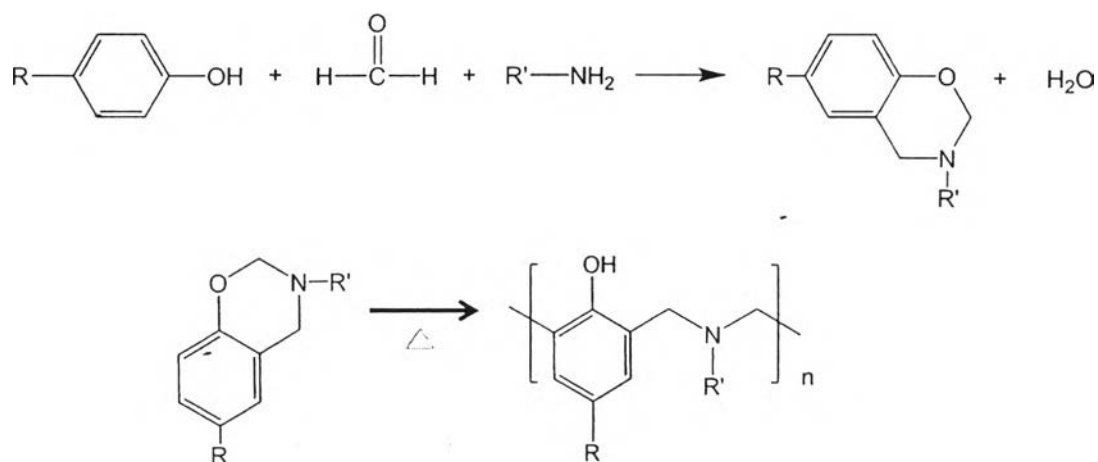

Figure 2.2 Synthesis reaction of polybenzoxazine.

Reflux method, a conventional solvent method, was used to synthesize polybenzoxazine. However, this method took the longer time to complete the process about 5 h (Takeichi *et al.*, 2005). In 2010, the facile quasi-solventless method was proposed to prepare polybenzoxazine within 1 h (Katanyoota *et al.*, 2010; Chaisuwan *et l.*, 2010). Polymerization of benzoxazine monomer/prepolymer can be carried out by the ring-opening reaction via heat treatment without added initiators/catalyst. The

mechanism of ring-opening polymerization of benzoxazine was also proposed by Macko and Ishida (2001a, b) that the oxazine ring will be opened through ionizing oxygen and nitrogen atoms, by heat treatment. Moreover, Wang and Ishida (2000) proposed the mechanism of ring-opening polymerization of polybenzoxazine via cationic catalysts.

2.2.2 Properties of Polybenzoxazine

Polybenzoxazine prepared from polymerization of difunctional benzoxazine monomers: B-a (bisphenol-A, aniline) and B-m (bisphenol-A, methyl amine), exhibit high Tg (~150-180 °C) and tensile moduli than those of both phenolic and epoxy resin (Ghosh et al., 2007; Ishida and Allen, 1996). Especially, PB-a showed high storage modulus in the glassy plateau about 2.2 GPa. Although polybenzoxazine showed low crosslink density around $1.1x10^{-3}$ mol/cm^3 comparing to that of cross-linked epoxy resin, polybenzoxazine still showed higher Tg than that of epoxy resin which can be ascribed in terms of intra and intermolecular hydrogen bonding in polybenzoxazine network (Ghosh et al., 2007; Kim and Ishida, 2002).

Furthermore, Ishida et al. found that the polymerization temperature of polybenzoxazine prepared from 44O-a benzoxazine monomers [44O-a stand for 6,6-bis(2,3-dihydro-3-phenyl-4H-1,3-benzoxazinyl)ketone] is always lower than its Tg, providing the good advantage for processibility (Russell et al., 1998; Shen and Ishida, 1999).

Polybenzoxazine also exhibited lower near-zero volumetric shrinkage after polymerization compared to that of epoxy resin. Water adsorption of 1.3-1.9% by weight was found in polybenzoxazine, which were lower than those of phenolic and epoxy resin (Ghosh et al., 2007; Wirasate et al., 1998). This property can be explained in term of hydrogen bonding that intra and intermolecular hydrogen bonding in polybenzoxazine network can prevent the hydroxyl group in polybenzoxazine to interact with water species (Ghosh et al., 2007; Bellenger et al., 1989). The dielectric constant of polybenzoxazine derived from aniline was lower than that of epoxide and traditional phenolic resin around 3.6, 3.7-4, and 4.8-5, respectively, resulting in lower electrical capacitance than that of epoxide and traditional phenolic resin (Ghosh et al., 2007; Ishida and Allen, 1996).

2.3 Porous Carbon Derived via the Sol-Gel Process

Porous carbon derived via the sol-gel process, is of particular interest in the current project due to their unique physical structure and flexibility of modification, resulting in many exceptional properties such as high surface area, light weight, high porosity, thermal stability, etc.

2.3.1 Types of Porous Carbon Derived via the Sol-Gel Process

Porous carbon derived via the sol-gel process, can be classified into 3 types depending on drying process used: carbon aerogels for supercritical drying process used, carbon cryogels for cryogenic drying process used, and carbon xerogels for evaporation drying process used (Job *et al.*, 2005). Drying methods play an important role on reservation of porosity in carbon gels (Job *et al.*, 2005). The most popular sol-gel derived porous carbon after carbonization were performed by the condensation reaction between resorcinol (R) and formaldehyde (F), having water as by-product, which was first introduced by Pekala (1989) in the end of 1980s. The synthesis of RF-based carbon aerogels via sol-gel process needed around 2 weeks to complete process. Furthermore, harsh catalyst and supercritical drying were required to promote polymerization and remove solvent without pore collapse due to the capillary force.

2.3.1.1 Carbon Aerogels

Carbon aerogels were the most popular ones, since their porous structure was preserved without the pore collapse by using supercritical CO_2 drying process. At the supercritical condition, CO_2 will be in a liquid state to carry the solvent out of the matrix, generating the pore after drying. However, supercritical drying is still an expensively drying method. Not only does it require multi-step procedures, but also yields low production rate, resulting in considerable amount of time and energy consumption. By using supercritical CO_2 drying, RF-based carbon aerogels show high surface area of 1270 m^2/g with the total pore volume of ~1.2 cc/g, especially, mesopore volume of 0.744 cc/g (Tamon *et al.*, 1997). In 2008, Baumann *et al.* found that acetic-catalyzed carbon aerogel activated by CO_2 showed the large surface areas exceeding 3000 m^2/g with total pore volume of 1.88 cc/g.

Moreover, Hanzawa *et al.* (2002) found that the absence of microporosity and 50 % of mesoporosity loss were found by heat treatment up to 2,000 °C and 2,800 °C, respectively. Interestingly, although porous carbon can be graphitized at temperature of 2,600 °C, the mesoporosity was still maintained, by adding block copolymer (F127) and strong hydrochloric acid during the synthesis step (Wang *et al.*, 2008).

2.3.1.2 Carbon Cryogels

Carbon cryogels can be produced by cryogenic drying process and then sublimation of freezing solvent. Carbon cryogels normally showed the huge channels (micrometer scale) due to the growth of freezing solvent and the small pores could not be maintained throughout the process as well (Job *et al.*, 2005). To avoid the structure collapse and the volume change of solvent to some extent by freezing, *t*-butanol with low degree of volume change was used in the solvent exchange step prior to cryogenic drying (Tamon *et al.*, 1999). Furthermore, acetone was also used to avoid the structure collapse instead of *t*-butanol in the solvent exchange step prior to cryogenic drying process (Arbizzani *et al.*, 2007). To improve the properties of carbon cryogels, modification of surface chemistry was employed by using ammonia borane. After modification, the carbon cryogels showed higher surface area (621 m^2/g) and mesopore volume (1.57 cc/g) compared to those of unmodified carbon cryogels (Sepehri *et al.*, 2009). However, the surface area and mesopore volume of carbon cryogels were still lower than those of carbon aerogels (Tamon *et al.*, 1999).

2.3.1.3 Carbon Xerogels

To reduce the cost of drying process, the less expensive evaporation process was employed. Generally, carbon xerogels exhibit the lowest surface area and pore volume compared to those of carbon cryo- and xerogels at the same condition due to high surface tension at the interface between solvent and pore wall, leading to high capillary force and structure collapse (Job *et al.*, 2005). To improve the textural properties of carbon xerogels derived from styrene-divinylbenzene copolymer, phosphoric acid activation was performed. The phosphoric-treated organic xerogels was carbonized in air for 30 minutes at temperature of 900 °C in which the surface area up to1,216 m^2/g and mesopore

volume of 0.55 cc/g were achieved (Puziy *et al.*, 2003). Base on low cost precursors, phenol and formaldehyde were used to prepare carbon xerogels using *n*-propanol as a solvent. The resulting carbon xerogels showed the porosity up to 88% with specifica surface area of 572 m^2/g and mesopore volume of 0.69 cc/g (Scherdel and Reichenauer, 2009). Furthermore, concerning about time consumption, microwave irradiation-assisted synthesis routes were performed to overcome this problem. Microwave irradiation was used to dry (Zubizarreta *et al.*, 2008) and synthesize (Calvo *et al.*, 2011) organic xerogels within the short preparation time of 30 minutes and 5 h, respectively. By using microwave irradiation, the properties of carbon xerogels were controlled as same as those of other drying method (Zubizarreta *et al.*, 2008). Furthermore, Microwave irradiation-assisted route also provided mesoporous carbon xerogels in the wider range of initial pH (4.5-6.5) compared to those of conventional synthesis route (5.8-6.5) (Calvo *et al.*, 2011). Table 2.2 shows the characteristics of porous carbon derived from different starting materials and preparation methods.

Characteristics of porous carbon derived from various starting materials and preparation methods

Starting material	Preparation time (day)	Catalyst	Drying method	S_{BET} (m²/g)	V_{meso} (cm³/g)	V_{micro} (cm³/g)	APD (nm)	Reference
) Formaldehyde(F)-based								
/=0.250, R/C=25	>11	Na₂CO₃	Freezing	881	0.550	0.220	2.50	Tamon et al. (1999)
/=0.11, R/C=500	>12	Na₂CO₃	Supercritical CO₂	1,270	0.744	0.407	-	Tamon et al. (1997)
6.5-7.4, Conc.=5 %wt	~14	Na₂CO₃	Supercritical CO₂	700	-	-	-	Pekala (1991)
6.5, Conc.=40 %wt	~14	Na₂CO₃	Ambient	~539	-	-	2.00-5.00	Hwang and Hyun (2004)
=250, Conc.=40 %wt	>2	Na₂CO₃	Ambient	683	-	-	4.10	Lee et al. (2010)
) Furfural(F)-based								
=25, R/S=0.1	~9	(HMTA)	Ambient	550	0.060	0.23	-	Wu et al. (2004)
Formaldehyde(F)-based								
m/W=0.1, Cm/NaOH=40	-	NaOH	Ambient	285	0.200	0.070	38.00	Zhu et al. (2006)
Furfural(F)-based		acid chlorides						
	>7		Supercritical CO₂	512	-	-	-	Pekala et al. (1995)
zine-based								
c.=35-45 %wt	~9	No	Ambient	311-368	0.210-0.270	0.130	3.70-5.40	Katanyoota et al. (2010)
c.=10 %wt	~9	No	Ambient	369	0.524	0.120	7.62	-
=20-40 %wt	~7	No	Ambient	384-391	0.050-0.060	0.15-0.17	2.20	Lorjai et al. (2009)

surface area; V_{micro}: micropore volume; V_{meso}: mesopore volume; APD: average pore diameter; Conc: Concentra

2.4 Porous Carbon Derived by Using Template

Generally, the creation of pore structure of porous carbon, especially meso- and macro- pore, is naturally depended on the phase separation mechanism of the matrix in the solvent during the sol-gel process (Pekala, 1989; Pekala and Schaefer, 1993; Bock et al., 1997; Wang et al., 2008) while microporosity of carbon gel could be easily managed by many activation processes (Hanzawa et al., 2002, 1996; Puziy et al., 2002; Wang et al., 2008). However, nowadays, many new routes to generate meso-macroporosity of carbon gels have been reported for example: surfactant-templated method (Matos et al., 2006; Liu et al., 2007), emulsion method (Lee and Oh, 2002; Wu et al., 2006), and hard-templated method (Gorka and Jaroniec, 2011; Baumann and Satcher Jr., 2004), etc.

2.4.1 Porous Carbon Derived by Using Surfactant as Soft Template

In 2002, Lee and Oh produce RF-based porous carbon with tunable pore size by using cethyltrimethylammonium bromide (CTAB) as cationic surfactant. They found that carbon nanospheres with particle diameter of about 15-2000 nm were obtained in which the sizes of clusters were controlled by monomer/surfactant concentration. Moreover, a wide range of pore diameters, in the range of 3.9 to more than 60 nm, were also CTAB surfactant. Afterward, in 2005, Nishiyama et al. found that microporous carbon derived from resorcinol-formaldehyde (RF) can be produced by using CTAB as well. Nishiyama et al. (2005) also founded that the formation of composites between polymer (RF) and cationic surfactant (CTAB) can be themselves taken placed by electrostatic force between positive charges of cationic surfactant and negative charges of RF polymer. Furthermore, the pore structure created by degradation of surfactant was the important key for the gasification of RF polymer at elevated temperature, especially, at high temperature. Three types of surfacatnts- including cationic (cethyltrimethylammonium bromide, CTAB), anionic (lauryl sulphate, sodium dodecilsulphate), and non-ionic (polyethyleneglycolnonylphenyl-ether) surfactant-on porous properties of porous carbon were studied by Matos et al. (2006). They found that non-ionic surfactant had no any effects on morphology and pore size distribution

of porous carbon whereas cationic and anionic surfactant had a significant role on pore size distribution of porous carbon. However, by using inverse emulsion technique, carbon microspheres with particle sized of 2-50 μm can be produced by using non-ionic surfactant (SPAN80) (Yamamoto *et al.*, 2002; Wang *et al.*, 2011). Those carbon microspheres also showed mesoporous properties. Anyway, non-ionic surfactant such as sorbitan monooleate and Pluronic F127 were used as soft template to generate porous carbon with high surface area and ordered uniform of mesopore, by self-assemble of non-ionic surfactant and polymer prior to carbonization process (Liu *et al.*, 2007; Zhai *et al.*, 2011).

2.4.2 Porous Carbon Derived by Using Silica as Hard Template

In 1999, Han and Hyeon produced porous carbon with high surface area by using silica nanoparticles as hard template. They founded that the specific surface area and mesopore volume were 1224-1238 m^2/g and 1.6-4.7 cc/g, respectively. However, pore size distribution of the as-synthesized porous carbon was shifted to monolithic pore diameter (Han and Hyeon, 1999a) which was larger than an average particle size of silica nanoparticles. The agglomeration of silica nanoparticles was responsible for this phenomenon. To prevent the agglomeration of silica nanoparticles, cetyltrimethylammonium bromide (CTAB) was used to stabilize silica as individual particles (Han and Hyeon, 1999b). After silica nanoparticles stabilized by CTAB, the as-synthesized porous carbon showed the narrow pore size distribution comparing to those of porous carbon synthesized by using silica nanoparticles without CTAB stabilization. Silica nanoparticles were used to produce carbon with uniform spherical mesopores by Jaroniec *et al.* (2008). Uniformity of mesopores in their carbon structure enabled the accessibility of inorganic nanoparticles into carbon structure (Jaroniec *et al.*, 2008). Another form of silica like mesoporous silica was also used to produce mesoporous carbon. After infiltration of carbon precursor into mesoporous silica and carbonization, the structure of mesoporous silica was duplicated into structure of as-synthesized mesoporous carbon (Karandikar *et al.*, 2007). Fine pores with diameter of 2 nm can also be created by using TEOS (tetraethyl orthosilicate) as silica source. After TEOS was hydrolyzed

by water, very small silica particles (SiO$_2$) was generated and then acted as hard template in the process of carbon preparation. The fine pores in carbon structure will be created after dissolution of small silica particles (Gorka and Jaroniec, 2011).

2.5 Points of Study

◆To study the effects of preparation conditions on cluster formation and microstructure of polybenzoxazine-based carbon xerogel by varying concentrations of solid contents, drying processes, and types of solvents

◆To synthesize ZSM-5 nanoparticles via microwave irradiation by using polybenzoxazine-based carbon xerogels as a template confinement to control the size of ZSM-5 crystal

◆To study the effects of cationic and non-ionic surfactant on microstructure of polybenzoxazine-based carbon xerogel

◆To synthesize ordered microstructure of polybenzoxazine-based carbon xerogel via silica hard template
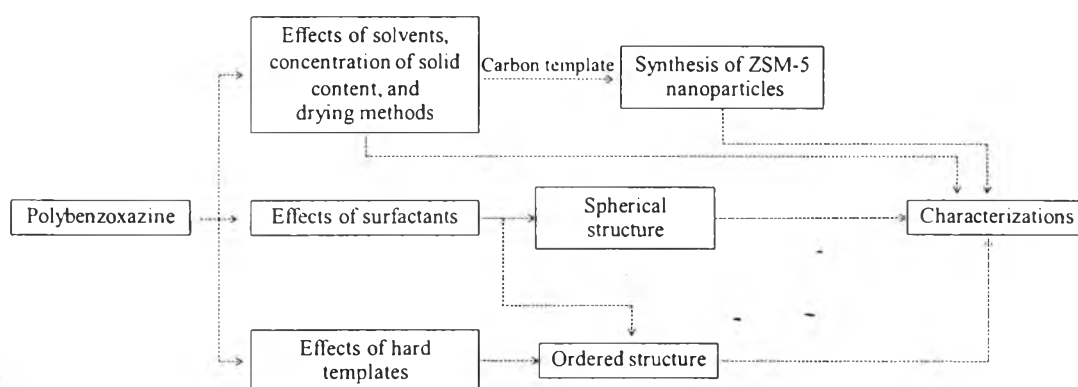
Scheme 2.1 Scope of research works.