CHAPTER II
LITERATURE REVIEW

2.1 High Internal-phase Emulsion (HIPEs)

A high internal-phase emulsion (HIPEs) polymerization process to manufacture microcellular, polymeric foam system was patented by Unilever in 1982 (Barby *et al.*, 1982). This patent discloses a polymerization process that occurs in a water-in-oil emulsion in which the dispersed phase occupies more than 74% of the volume. The continuous organic phase, which generally constitutes less than 26% of the final volume, can contain monomers (styrene), crosslinking comonomers (divinyl benzene) and organic soluble surfactant (sorbitan monooleate) (Elmes *et al.*, 1988). A polyHIPE is a microporous material produced by the polymerization of the monomers in the continuous phase of a HIPE. Microporous foams of very high void fractions (porosities of up to 97%) can be made through polyHIPE synthesis. The dispersed aqueous, containing a water-soluble initiator (potassium persulfate) and stabilizer (calcium chloride) (Walsch *et al.*, 1996). Subsequent removal of the aqueous produces a highly porous material, as shown in Figure 2.1. The foams are open-cell; therefore the large spherical cavities in the material are term cells. The circular hole connecting adjacent cells are referred to as windows. In addition, feature of the morphology such as cell size, interconnecting hole size and porosity can be efficiently controlled.
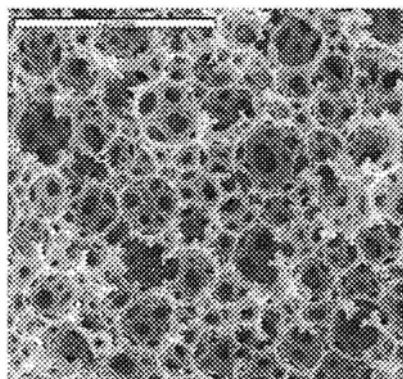

Figure 2.1 SEM of PolyHIPE. (Neil R. Cameron, 2005)

2.1.1 Factor Effective Properties of PolyHIPE

Characteristics of the obtained polyHIPEs could be affected by several factors such as addition of porogenic solvent and mixed surfactants to the monomer phase.

2.1.1.1 Porogenic Solvent

Porogen is inert diluents or non-polymerisable solvent such as toluene, chlorobenzene, 2-chloroethylbenzene, and 1-chloro-3-phynyl-propane. The type of porogen added to the continuous phase of polyHIPEs result in the formation of pores within the polymer phase (Barbetta *et al.*, 2004), as shown in Figure 2.2. The walls of the resulting polyHIPE are similar to morphology of permanently porous polymer beads. These may be micro-, meso-, or macropores depend on nature of the porogen.
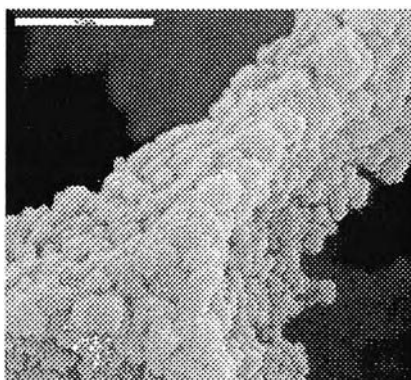

Figure 2.2 SEM of polyHIPE prepared with porogens. (Barbetta *et al.*, 2000)

The nature of the porogen has a strong influence on the surface area, and this is strongly related to the solvent type. Network, or solvent with better solvents for the growing, give rise to higher surface areas (Cameron *et al.*, 1996).

If a good swelling solvent is selected phase separation of the polymer gel phase will be delayed until late in the polymerization. This will produce a large number of small microparticles, which remain discrete until complete conversion is occured. Since the residual monomer is low, this will result in a material of high surface area. A less efficient swelling solvent, however, causes precipitation of polymer microparticles at an earlier stage when monomer levels are higher. This

residual monomer will locate in the polymer gel phase and cause "filling in" of the gaps between microparticles as it polymerizes. The result is a lower surface area material (Rabelo *et al.*, 1994).

In 2000, Barbetta *et* al. prepared highly porous open-cell polyDVB foams in the presence of various porogenic solvent, either as single components or mixtures, containing toluene (T), chlobenzene (CB), 2-chloroethylbenzene (CEB), and 1-chloro-3-phynyl-propane (CPP). The nature of the solvent has a profound influence on the foam morphology on both a large and small scale. From SEM, CB was found to reduce the foam cell size (high surface area) compared to T, whereas CEB and CPP seemed to destroy the characteristic PolyHIPE cellular morphology, However from the morphology described above, this material was mechanically very weak and was not likely to be usable in any practical situation. This situation can be remedied by employing mixed porogens. The surface areas of the resulting materials were not predictable in a simple fashion from the values of foams produced from their individual components.

2.1.1.2 *Addition of mixed surfactants to the monomer phase*

The effectiveness of a mixture of an anionic, or a cationic, surfactant with an amphiphilic compound for emulsion stabilization has been known for a long time. The interfacial film made by this mixture of surfactants shows an increased ability to withstand the pressure of droplet contacts (to prevent coalescence) and to act as a barrier to the passage of the dispersed phase into the continuous phase (to limit Ostwald ripening) (Tadros *et al.*, 1983).

In 2004, Barbetta *et al.* changed the surfactant employed from sorbitan monooleate (SPAN80) to a 3-component mixture of cetyltrimethylammonium bromide (CTAB), dodecylbenzenesulfonic acid sodium salt (DDBSS) and sorbitan monolaurate (SPAN20) and the result produced some further insights. With this surfactant mixture, surface area values were much higher in almost every case than with SPAN80 (for CB: 689 compared to $346\,\mathrm{m^2\,g^{-1}}$). The improvements were due to the mixtures of ionic and non-ionic surfactants are known to form a more robust interfacial film around each emulsion droplet, leading to enhanced emulsion stability.

In 2006, Sevil *et al.* successfully synthesized polyHIPE by using divinylbenzene and styrene as polymerisable continuous phase, aqueous phase containing potassium persulphate and calcium chloride dihydrate, a mixture of emulsifiers (SPAN20, CTAB and DDBSS) and toluene as a porogen. PolyHIPE samples were found to be porous and open-cell microstructures with the surface area of 370-430 m^2 g^{-1}.

2.2 Application of PolyHIPE

PolyHIPE can be used for many applications, especially as adsorption and filtration medias.

In 1996, Walsh *et al.* illustrated the effect that two properties of the emultion production process, water to monomer ratio and mixing time, can have on the resultant polyHIPE. It is shown that for an open fibrous type structure the emulsion must have high water content (95%), and that the emulsion must be mixed for a reasonable length of time, in this case of the order of one hour. Such foams have been shown to be very efficient at removing fine particulates from gas flows, with all atmospheric aerosol particles greater than 1 μm diameter being collected.

In 2002, Katsoyiannis *et al.* modified of polymeric materials (polystyrene and polyHIPE) by coating their surface with iron hydroxides in order to remove inorganic arsenic anions from contaminated water sources, among the examined materials, polyHIPE was found to be more effective in the removal of arsenic, because they were capable in holding much greater amounts of iron hydroxides, due to their porous structure. This enabled the adsorbing agents to penetrate into the interior of the material, which in combination with the surface coating provided a higher surface area available for adsorption.

2.3 Clay Minerals

Clay minerals are hydrous aluminium phyllosilicates, consists of sheets of silica tetrahedral and alumina octahedral which are held together by only weak inter atomic forces between the layers. Depending on the composition of the tetrahedral

and octahedral sheets, the layer will have no charge, or will have a net negative charge. If the layers are charged, these charge are balanced by interlayer cations such as Na^+ or K^+. In ease the interlayer can also contain water. The crystal structure is formed from a stack of layers interspaced with the interlayers. Clay minerals can be divided into four different groups and these four different groups are kaolite, smectite, illite, and chlorite. Among these, the one that is found to be useful in the field of gas adsorption or gas retention is a group of expandable clay known as smectite clay.

Smectite clay is a group of clay minerals. The smectites are 2:1 layer phyllosilicate constituted of the octahedral sheet containing Al or Mg ions between two tetrahedral silica sheets. There are two different series of smectites: dioctahedral and trioctahedral, according to whether the total number of ions in six-coordination per half-unit-cell layer lies close to 2 or 3, respectively. Montmorillonite, which is the main constitute of bentonites, is a mainly species of smectite clay, as shown in Figure 2.3. These layers organize themselves is a parallel fashion to form stacks with a regular gap between them, called interlayer or gallery. (Manias *et al.*, 2001)
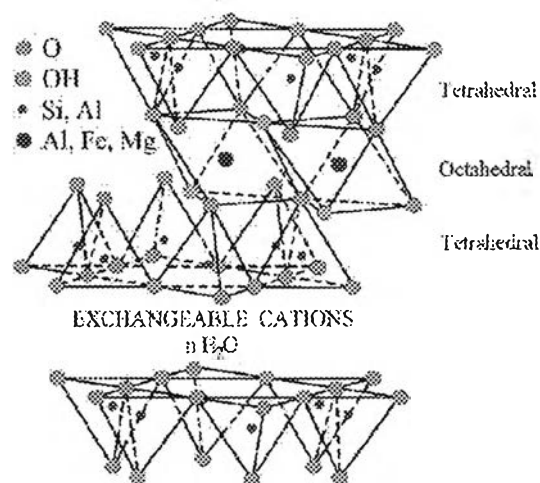

Figure 2.3 Stucture of montmorillonite. (Bailey *et al.*, 1980)

The smectites can retain gases but the presence of impurities such as quartz, feldspar, cristobalite, etc. in samples are unfavorable because the adsorption of these minerals is usually small (Volzone *et al.*, 1999; Melnitchenko *et al.*, 2000; Venaruzzo *et al.*, 2002).

Bentonite is clay generated frequently from the alteration of volcanic ash, consisting predominantly of smectite minerals, usually montmorillonite. The presence of these minerals can impact the industrial value of a deposit, reducing or increasing its value depending on the application. Bentonite presents strong colloidal properties and its volume increases several times when coming into contact with water. The special properties of bentonite (hydration, swelling, water absorption, viscosity, and thixotropy) make it a valuable material for a wide range of uses and applications.

In 2000, Volzone *et al.* demonstrated that bentonite rich in trioctahedral smectite is a better solid adsorbent than bentonite rich in dioctahedral smectite. Generally, the natural clays have low retention capacity for N_2, O_2, CO and CH_4 gases (0.05–0.08 mmol of gas per gram of clay) and a higher capacity for CO_2, C_2H_2 and SO_2 (0.150–0.636 mmol of gas per gram of clay). Actually, it is possible to mention that the natural smectite as solid adsorbent is better than natural illite and kaolinite (Volzone *et al.*, 2006).

Many of industrial used of smectite clays materials are related to adsorptive capacity which may be increased with acid treatment.

Acid treatment of clay minerals is chemical treatment of the clays to modify structural, textural and/or acidic properties, which influence the adsorption capacity. Changes in internal and external surface area, porosity, pore volume, chemical composition, charge density, contribute to the adsorption properties. Acid activated clay minerals (by using mainly acid HCl or H_2SO_4 solutions) (Mills *et al.*, 1950) are used as adsorbents and in catalysis because acidic and structural properties are favourable for such applications.

In 1998, Volzone and Ortiga have analysed the retention of CH_4, CO_2, CO, O_2, N_2 and C_2H_2 gases by acid-treated smectites and found that in all cases the acid treatments improved the gas retention with respect to the starting smectites, and the highest adsorption values were found for CO_2 and C_2H_2 gases.

In 2007, Volzone *et al.* treated bentonitic clay minerals with hydrochloric acid at boiling temperature originated an adsorbent with considerable capacities for the adsorption of CO_2, SO_2 gases found that the SO_2 adsorption (up to 1.231 mmol/g) by prepared acid materials were superior to the values of the CO_2 (up to 0.586 mmol/g) and CO (up to 0.119 mmol/g) adsorptions. These effects occur from acid

remove the interlayer cation such as Ca^{2+}, Na^+ and K^+, as well as octahedral cations of the smectite clays in the following order: $Mg^{2+}>Fe^{2+/3+}>Al^{3+}>Ti^{2+}$ result in increasing surface area due to increase porosity caused mainly by leaching octahedral layer cations of the clay.

In 2008, Pakeyangkoon *et al.* studied the effect of acid-treated clay to CO_2 gas adsorption of polyHIPE by incorporating the acid-treated clay into the monomer phase of the high internal phase emulsion, preparing single surfactant (SPAN80) found that CO_2 gas adsorption capacity increased when acid-treated clay was added.

2.4 Gasification Process

Gasification is a process that converts carbonaceous materials, such as coal, petroleum, or biomass, into carbon monoxide, carbon dioxide, and hydrogen by reacting the raw material at temperatures above 700°C when the carbonaceous materials are allowed to react with a gasification agent such as oxygen, air, or steam.

Air is one of the main basic elements of life. Air pollution implies the presence of harmful substances in the air (nitrogen oxides, particulate matter, sulphur dioxide, hydrocarbons, carbon monoxide, ozone, etc.). These substances needless to say caused bad serious effects on our health. Adsorption processes have become useful tools to remove pollutants by using mainly carbon (Kapoor *et al.*, 1989), zeolites (Jun *et al.*, 2002) and modified silica materials (Huang *et al.*, 2003)

In 2001, Zou Yong *et al.* studied the adsorption capacity of carbon dioxide on high surface area carbon-based adsorbents before and after chemical modification at 28°C and 300°C, found that the high adsorption capacity adsorbents for carbon dioxide at high temperature have been developed by introducing MgO and S-CaO-MgO on carbon-based adsorbents. Their adsorption capacities for carbon dioxide were 0.28 and 0.22 mmol/g at 300°C, 1 Bar, respectively.

In 2002, Jun *et al.* showed the zeolite adsorbents used for the gas adsorption processes. Especially, as the ratio of SiO_2/Al_2O_3 increases, the adsorbed amount of moisture is reduced while the adsorbed amounts of strong adsorbates like acid gases are little reduced. As a result, the selective adsorption of acid gases coexisting together with moisture becomes possible. It is known that the adsorbing performance

of zeolite is remarkably deteriorated because Al in the network of Si-O-Al constituting the crystal structure reacts with acid gases absorbed on zeolite and it is released from the crystal lattice.

In 2005, Dabek studied influence of method and conditions of spent Pd/Activated Carbons catalyst regeneration on its catalytic activity. It has been stated that supercritical fluid extraction (CO_2) followed by heating in hydrogen atmosphere is an effective method of the catalyst regeneration. The results of FTIR and XPS investigations indicate that regeneration of a spent Pd/Activated Carbons catalyst, irrespective of the reaction in which it has been used, should be based on the complete removal of by-products and cleaning the catalyst surface as well as on restoring the original form of the palladium.