CHAPTER I

INTRODCUTION

1.1 Background of the research

Since the significant finding of buckminsterfullerene (C_{60}) [1] and carbon nanotubes (CNTs) [2] considerable efforts have been made toward the synthesis of functional carbonaceous materials with diverse morphologies and structures, such as colloidal spheres [3], nanofibers [4], coin-like hollow carbons [5], macroflowers [6], and so on. Among the different morphologies of carbonaceous materials, carbon microspheres (CMSs) have attracted widespread interest, owing to their potential properties in adsorbents [7], catalyst supports [8], and anode material for lithium ion batteries [9] and templates for fabricating core-shell or hollow structures [10]. The CMS particles have been synthesized by many techniques, such as pressure carbonization [11], chemical vapor deposition [12], mixed-valence oxide-catalytic carbonization [13], and reduction of carbides with metal catalysis [5].

Carbohydrate materials, such as glucose, fructose and sucrose, were excellent carbon precursors for preparing CMSs. For example, Sun et al. synthesized the colloidal carbon spheres by a hydrothermal technique using glucose as carbon precursor [3]. A two-step route which was addressed by Wang et al. was used to prepare hard carbon spheres from sugar by a hydrothermal method [14]. Recently, hydrothermal under moderate condition was developed by Mi and co-workers for synthesizing CMSs with the aqueous glucose solution as starting materials [13]. However, as inexpensive and more available carbohydrates, native starch was rarely used as a carbon precursor to prepare CMSs because it is difficult to dissolve in water to form a clear solution. Moreover, native starch is difficult to be hydrolyzed during hydrothermal reaction. Consequently, obtained carbon microspheres were larger in size and difficult to be controlled particle size distribution.

1.2 Motivation of the research

Carbon microspheres (CMSs) are carbonaceous polymerized materials which mainly consist of carbon, oxygen and hydrogen in typical weight ratios O/C and H/C of 0.3 and 0.8, respectively [15]. Carbon microspheres (CMSs) are also reactive functional carbonaceous materials with spherical morphology [3]. In recent years, the discovery of new forms of carbon has greatly elucidated the important of the investigating carbonaceous materials. Since the discovery of fullerenes and carbon nanotubes, there have been noteworthy efforts toward the synthesis of functional carbon materials with diverse morphologies and structures to fit in each application, such as coin-like hollow carbons, macroflowers, colloidal spheres, nanofibers, etc. When it comes to the different forms of carbon materials, carbon microspheres (CMSs) have attracted a lot of interest from many scientists, due to their potential and practical applications in catalyst supports, anode material for lithium ion batteries, and templates for fabricating core-shell or hollow structures. For example carbon spheres are an excellent support for electrocatalyst and give better performance than carbon black [16]. For example there are several reasons why Pd/CMS performs better than Pd/C [17]. The first is the ability of carbon microspheres to stabilize the high dispersion of palladium particles [18]. The second is such structure permits liquid alcohol to diffuse into the catalyst layer easily and forms larger three-phase interface, resulting in the reduction of liquid sealing effect [8]. For anode materials, carbon with spherical morphology has been proved to be competent in using as anode material for Li-ion batteries owing to its high packing density, low surface-to-volume ratio and maximal structural stability, etc [15]. In addition, it is evident that the micropores within the carbon can supply extra capacity [19]. In the template application, well-dispersed colloidal carbon spheres were chosen as templates for fabricating Pt hollow capsules [20], highly sensitive WO_3 hollow-sphere gas sensors [21].

Although carbon microspheres have been prepared by various methods, hydrothermal method is an easy and low cost method to synthesize carbon microspheres. Carbohydrate materials, such as glucose, sucrose, and sugar, were excellent carbon precursors for synthesizing carbon microspheres. Firstly, Wang et al. used sugar to prepare CMSs with uniform nanopore for reversely lithium ion storage [20]. Sun and co-worker had prepared the carbon spheres from glucose under hydrothermal conditions at 160–180°C, which is higher than the normal glycosidation temperature and leads to aromatization and carbonization [18]. Although the narrow size distributions of the final products were obtained, the colloidal carbon nanospheres have diameters in the narrow range of 200 and 1500 nm [22]. Sucrose was used as a carbon precursor to prepare the Pt and Pd supported on carbon microspheres with 1.5 μm in diameter for methanol and ethanol electro-oxidation in alkaline media [23]. Nevertheless, an inexpensive and more available native starch was rarely used as a carbon precursor to synthesize carbon microspheres because it is difficult to dissolve in water to form a clear solution (native or crystalline starch). As with any other research, although carbon spheres were obtained from corn starch by a two-stage process, uniform spheres were difficult to obtain even though graphitized at very high temperature (2600°C), and the particle size, which ranged from 5 to 25 μm, could not be controlled [24]. Furthermore Zheng et al. reported the preparation of monodisperse CMSs by hydrothermal method using soluble starch as a carbon precursor, the narrow controllable range of size was obtained at high temperature (500-600°C) by varying starch concentration [25].

In this work, we have developed an easy and cost-effective method to prepare uniform carbon microspheres with wide range of particle size but narrow particle size distribution via a hydrothermal process under mild conditions (180, 220°C). Different classes of carbohydrates, i.e. native corn starch, modified starch (HI-CAP®100), amylopectin, amylose, and glucose were chosen as carbon precursors to investigate effects of initial concentration of starch, reaction time and temperature on carbon microspheres morphology and particle size controlling. The soluble modified starch (HI-CAP®100) was hydrolyzed of waxy maize starch and then derivatized to impart lipophilic properties with n-octenyl succinic anhydride. They can be immediately dissolved in water to form clear solution. Meanwhile, other carbohydrates or crystallized starch (native corn starch) could be hardly dissolved in water.

After hydrothermal process, the CMSs had been carbonized under nitrogen atmosphere. The carbonization process had highly developed microporosity of CMSs but had removed the reactive functional group (-OH,-COOH) on their surface [19]. The porous CMSs have highly microporosity and inert surface that can be used as adsorbents or gas storage materials. Without carbonization process, the CMSs have the reactive functional group on CMSs surface which can be immobilize target reactive agents on the surface without further surface modification. The uniform CMSs can be determine particle morphologies and particle size distributions by scanning electron microscopy (SEM) and laser diffraction method (Mastersizer 2000), respectively. Moreover, synthesis of carbon microspheres (CMSs) by a hydrothermal process of native starch has been systematically investigated in a batch reactor to obtain controlled particle size distributions and formation mechanisms of CMSs. To find reaction pathways of CMS formation and deeply understand the formation mechanisms, concentrations of intermediates formed during the hydrothermal carbonization were determined at different times for the determination of reaction kinetic parameters and reaction pathway. Furthermore, the main process in this method will be carried out in aqueous solution without involving any organic solvents or catalysts. This catalyst-free synthesis strategy will promote a better understanding of CMSs growth, and moreover, the as-synthesized CMSs may lead to many new potential applications. Particularly, in precisely applications need more precise size of carbon microspheres.

1.3 Aim and objectives

In this work, carbon microspheres were synthesized by hydrothermal process of different classes of carbohydrates (including native corn starch, HICAP®100, amylopectin, amylose, and glucose) in order to study effects of types of starch, initial concentration of starch, reaction time, reaction temperature on their yield rates and morphology. We addressed the operating conditions in hydrothermal process for controlling particle size and their morphology. Moreover, reaction pathways of carbon microspheres formation in hydrothermal process were also investigated. In addition, we also addressed reaction model for carbon microsphere formation by pseudo-first order reaction. In further study, after hydrothermal process, we carried out carbonization process of carbon microspheres in order to reveal their many particularly properties. Therefore, the objectives of this work were divided into four points as follows:

- To investigate operating conditions and factors for controlling particle size of carbon microspheres which were types of starch, initial concentration of starch, reaction temperature, and reaction time,
- To study effects of carbonization process on structure of carbon microspheres,
- To find a kinetic parameter of main reactions during hydrothermal process including rate constants (k_{ij}),
- To propose reaction pathways of carbon microspheres formation in hydrothermal process.

1.4 Scope of the research

1. Examine operating conditions for synthesis of carbon microspheres by varying the following parameters;

   1.1 Type of carbon precursor including native corn starch, modified starch (HI-CAP®100), amylopectin, amylose, and glucose,

   1.2 Initial concentration of carbon precursor from 1-20wt%

   1.3 Reaction time from 0-1440 min,

   1.4 Reaction temperature from 140, 180 and 220°C,

2. Investigate effects of carbonization process under nitrogen atmospheres which had conditions as follows;

   2.1 Nitrogen gas flowrate of 100 mL/min,

   2.2 Heating rate of 1°C/min,

   2.3 Target temperature of 600°C,

   2.4 Holding time of 3 hours,

3. Find rate constant (k_{ij}) of main reactions during hydrothermal process by pseudo-first order reaction assumption,

4. Propose reaction pathways from occurring and disappearing of intermediates such as glucose, fructose, 5-HMF, furfural and TOC compound,

   4.1 Liquid products were analyzed by HPLC and TOC technique to determine main occurred intermediates during hydrothermal process,

   4.2 Solid products were analyzed by elemental analyzer to determine their chemical transformation.