Understanding Pore Formation and Structural Deformation in Carbon Spheres During KOH Activation
(Memahami Pembentukan Liang dan Penyahbentukan Struktur Sfera Karbon Semasa Pengaktifan KOH)

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ABSTRACT

Carbon spheres (CSs) were synthesized from sucrose by hydrothermal reaction. The synthesized materials were further activated with potassium hydroxide (KOH) at different concentrations. The effects of KOH concentration on the surface area and morphology were investigated. The route for pore formation and structural deformation in carbon spheres during activation has been proposed and discussed based on micrographs and porosity trends. It was suggested that the pore formation and structural deformation phenomena were due to the intercalating power of energized K^+ into the carbon. This work provides an insight of the pore formation in carbon spheres for the development of adsorbents as well as for the understanding of the structural deformation of such materials at higher KOH concentrations.

Keywords: Carbon spheres; hydrothermal reaction; KOH activation; morphology; surface area

ABSTRAK

Sfera karbon (CSs) telah disintesis daripada sukrosa dengan tindak balas hidroterma. Bahan yang telah disintesis telah diaktifkan dengan kalium hidroksida (KOH) pada kepekatan berbeza. Kesan kepekatan KOH terhadap luas permukaan dan morfologi telah dikaji. Laluan bagi pembentukan liang dan penyahbentukan struktur sfera karbon semasa pengaktifan telah dicadang dan dibincangkan berdasarkan mikrograf dan tren keliangan. Dicadangkan iaitu fenomena pembentukan liang dan penyahbentukan struktur tersebut adalah disebabkan oleh kuasa tujahan $K+$ yang bertenaga ke dalam karbon. Kerja ini memberikan penerangan tentang pembentukan liang di dalam sfera karbon bagi pembangunan bahan penjerap dan juga pemahaman tentang penyahbentukan struktur bahan berkenaan pada kepekatan KOH yang tinggi.

Kata kunci: Luas permukaan; morfologi; pengaktifan KOH; sfera karbon; tindak balas hidroterma

INTRODUCTION

Carbon spheres (CSs) are spherical form of carbon having either semi-crystalline or crystalline structure with solid, hollow or core shell morphology. The spherical carbons include carbon blacks, carbon onions and carbon microbeads (Deshmukh et al. 2010). Many findings have been published in the literature related to the synthesis and activation of carbon spheres (Deshmukh et al. 2010; Li et al. 2011). These techniques include shock compression technique (Niwase et al. 2002), high temperature pyrolysis, chemical vapour deposition (Qian et al. 2004), hydrothermal treatment (Sevilla & Fuertes 2009; Wang et al. 2001), arc discharge (Qiao et al. 2006) and thermal plasma processes (Okuno et al. 2004) have been in practice for the synthesis of carbon spheres. Among these methods, hydrothermal approach is the simplest in terms of operation due to its mild reaction condition requirements (Hu et al. 2008).

Activated form of carbon spheres was found to possess properties like high specific areas, uniformity, high thermal stability and excellent conductivities which make them useful as catalyst support, adsorbents and super capacitors. They are also used in hydrogen storage (Li et al. 2011; Wang et al. 2001) and drug delivery. A frequently applied method to obtain carbons with high surface area and narrow micropore distribution is through chemical activation usually using alkaline hydroxides as activating agents due to their ability to activate carbon generated from many kinds of carbonaceous precursors like coals, chars and fibres (Lillo-Rodenas et al. 2003; Lozano-Castello et al. 2001).

Pores are formed in CSs when they are activated with KOH, but activation carried out at high KOH concentration may result in structural distortion of the CSs. There are basically two approaches in the activation process of carbon spheres using alkali-metal hydroxides and each depends on the physical state of the activating agent (solid or liquid). Mechanism of pore formation by physical mixing of solid activating agent like KOH pellet with carbon via grinding (solid-solid reaction) has been proposed to have occurred through reduction of KOH to K-metal and oxidation of carbon to carbonate (Raymundo-Pinero et al. 2005). However, no explanation is reported on the routes leading to the structural deformation of the sphere shape during the process especially when the activating agent is in liquid form (solid-liquid reaction). Apart from pure carbon, pore formation mechanism in other inorganic material (magnesium carbonate Upsalite) has also been reported by Frykstrand et al. (2014).

This work described for the first time the phenomenon of structural deformation of CSs during KOH activation specifically when the activating agent is in liquid form (aqueous solution). The routes for the pore formation and structural deformation were proposed based on the intercalation ability of the potassium ion into the material.

MATERIALS AND METHODS

Carbon spheres used in this study were hydrothermally synthesized from sucrose (Sigma-Aldrich, 99.5%; EMD Chemicals, ACS grade). Other reagents: absolute ethanol (99.9% Scharlab S.L, Spain), potassium hydroxide pellets (Darmstadt, Germany) were of analytical grade and used without further purification. Deionized water used was prepared in a Milli-Di Millipore machine (SAS 67120 Molshem, France).

SYNTHESIS OF ACTIVATED CARBON SPHERES

Fifty mL of 0.8 mol/L sucrose solution was prepared for the hydrothermal synthesis of CSs. A detail of the experimental procedure was described elsewhere (Li et al. 2011). The prepared solutions were further activated at different KOH concentrations (0.1, 1.5, 2.0, 2.5 and 2.75 mol/L) through pyrolysis. In each case, 0.15 g of CSs was mixed with 2.0 mL of the prepared KOH aqueous solution in a combustion boat and continued as reported by Li et al. (2011). The pyrolysis was carried out at 450°C for 1 h.

CHARACTERIZATION

The morphology and size of the CSs were determined on a JEOL JSM-6390LV scanning electron microscope (SEM). The Brunauer-Emmett-Teller (BET) surface area of each sample was measured using N_2 adsorption-desorption isotherms after degassing at 110°C using metrometrics ASAP 2010 surface area analyser (Georgia, USA).

RESULTS AND DISCUSSION

EFFECT OF KOH CONCENTRATION ON THE SURFACE AREA OF ACTIVATED CARBON

An increase in KOH concentration improves the number of pores formed during chemical activation which leads to an increase in the surface area. Table 1 provides the textural properties of CSs before and after activation. It can also be deduced from the table that apart from ACS-2.0 with pore size of 1.72 nm, the materials developed are mesoporous in nature (pore size between 2 and 50 nm).

However, all the N_2 adsorption-desorption isotherms (Figures 1(a)-1(d)) correspond to type I isotherm where high uptakes are observed at relatively low pressures due to the narrow pore width and high adsorption potential. Type I sorption isotherm is usually obtained on microporous materials (Lowell et al. 2004). These two pieces of information confirmed that with the exception of ACS-2.0 which is almost purely microporous, all the other activated carbon spheres consisted of micropore/mesopore structures.

Other evidences to support the existence of micropore structure in the activated carbon spheres is firstly the exhibition of open loop hysteresis in all the sorption isotherms (Figures 1(a)-1(d)) which looks more of H4 hysteresis and secondly a positive Y-intercept in their t-plots. The H4 hysteresis is often associated with narrow-slit pores including pores in the micropore region (Lowell et al. 2004) and a positve Y-intercept in t-plot is an indication of the presence of micropore volume/area in the sample.

Table 1 has clearly indicates very small BET surface area (7.8832 m²/g) and a negative value of micropore area (-0.6149 m²/g) against non-activated carbon spheres (CS-0.00). The small BET surface area may be attributed to the limited number of pores present in the sample since it has not been chemically activated. Furthermore, the negative value of the micropore area revealed that there is no micropore volume/area in the sample and therefore all the limited pores present were within the mesopore region. This assertion can be supported by observing a closed loop isotherm plot (Figure 1(e)) which is usually found in mesoporous materials and secondly the fact that a negative Y-intercept was noticed in the t-plot.

ENVISAGED ROUTE OF PORE FORMATION DURING KOH ACTIVATION OF CARBON SPHERES

SEM images coupled with porosity trend of KOH activated carbon spheres at different concentrations were used to investigate the route of pore formation and structural deformation during chemical activation. In this study, a

TABLE 1. Textural properties of CSs before and after activation at different KOH concentrations

Sample	BET surface area (m²/g)	Micropore area (m²/g)	Total pore volume (cm³/g)	Pore size (Å)
CS-0.00	7.88	-0.61	0.009	44.89
ACS-0.10	151.89	121.61	0.078	20.41
ACS-1.50	165.43	135.13	0.091	22.05
ACS-2.00	308.10	258.36	0.133	17.21
ACS-2.75	552.33	444.17	0.303	21.96

ACS = Activated carbon spheres and the attached values indicate KOH concentrations in mol/L.
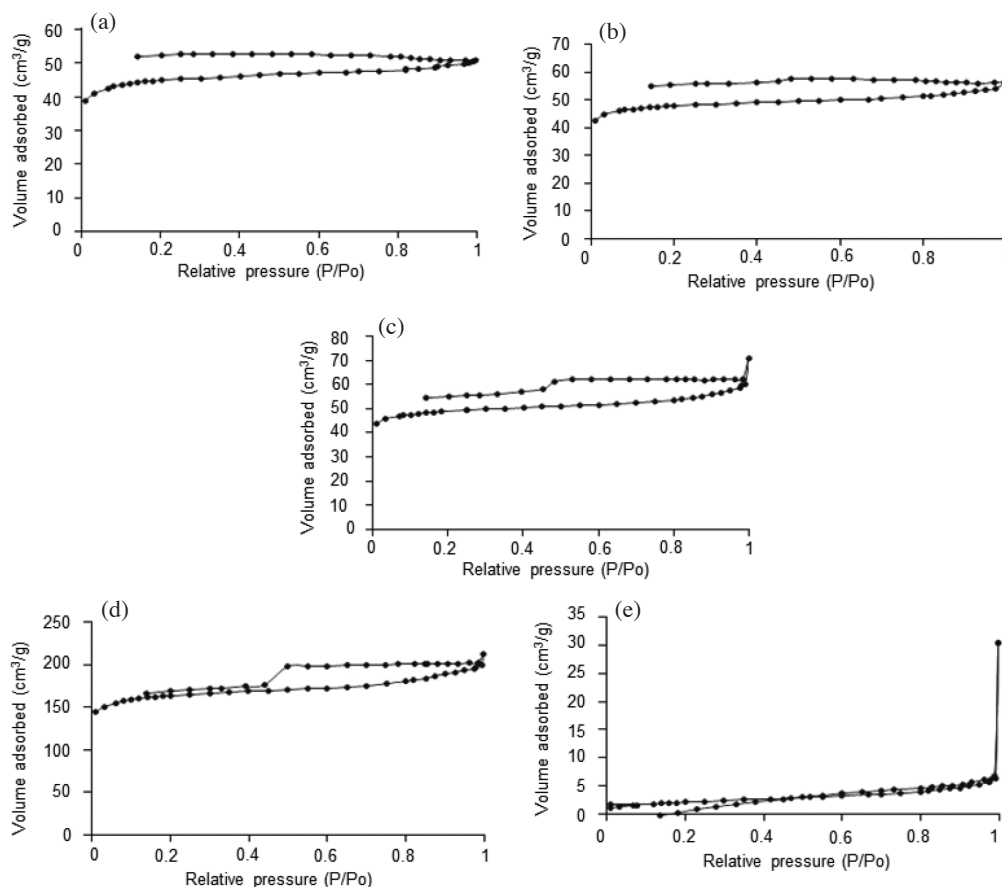While CS-0.00 = non-activated carbon spheres

FIGURE 1. N$_2$ adsorption-desorption isotherms for ACS-0.10 (a), ACS-1.50
(b), ACS-2.0 (c), ACS-2.75 (d) and CS-0.0 (e)

solid-liquid activation reaction using KOH aqueous solution and carbon spheres is considered.

The first step is dissociation of KOH in water according to the equation.

$$KOH_{(s)} \longrightarrow K^+_{(aq)} + OH^-_{(aq)}. \qquad (1)$$

Alkali metal ions are known to possess an intercalating power into different materials (Inagaki & Tanaike 2001). In aqueous solution, potassium ions (K$^+$) are randomly spread and free to move. During chemical activation, these ions are heated and become energized (*K$^+$) which then considerably intercalate into the carbon spheres to form the pores as demonstrated in Figure 2.

EFFECT OF KOH CONCENTRATION ON THE MORPHOLOGY OF CARBON SPHERES

SEM micrographs have shown that structural deformation on the CSs depends on the KOH concentration as observed in Figure 3(a)-3(e).

At 0.1M KOH (Figure 3(a)), the morphology virtually remains unchanged. The stability of structure observed was possibly as a result of very few energized K$^+$ at low KOH concentration which might have been used up in forming the pores.

However, at concentrations of 1.5 and 2.0 mol/L KOH, slight deformations were noticed on the morphology of the CSs (Figure 3(b) and 3(c)). The slight structural deformation observed at this concentration is associated to the presence of more energized potassium ions (*K$^+$) than in the previous case (Figure 3(a)). In this case, the few excess *K$^+$ probably rub the CSs at their surfaces thereby causing the defect. At relatively higher concentration of 2.5M KOH (Figure 3(d)), the surfaces become rough which could be due to higher number of excess *K$^+$ that consequently scrape and remove some parts of the CSs at the surface. When the concentration was increased above 2.5M KOH, the structure was found to collapse entirely (Figure 3(e)) and the foreseen route of such structural collapse is envisaged in section 3.4.

PROPOSED ROUTE OF STRUCTURAL COLLAPSE OF CSS AT HIGHER KOH CONCENTRATION

At higher KOH concentration (2.75 M and above), the number of potassium ions becomes large and therefore, there is high probability that more than one energized potassium ion (*K$^+$) can penetrate the CSs through the same point. Each penetrating *K$^+$ advances the depth of the pore further which consequently results into the creation of through pores (Pores that open channel at one
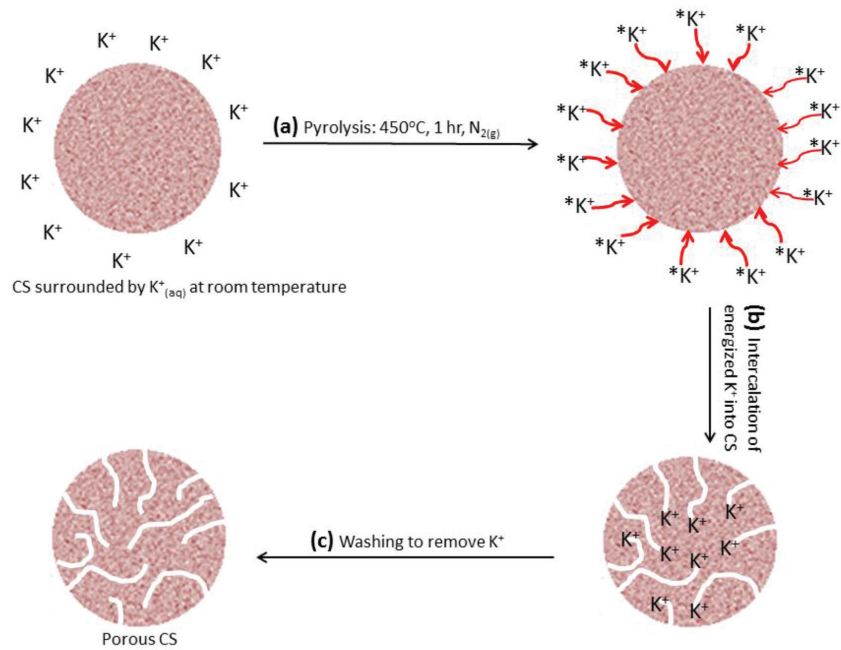
FIGURE 2. Illustration of pore formation processes at lower KOH concentrations (<2.0M): Carbon sphere surrounded by free K⁺ in aqueous solution (a), penetration of energized potassium ion, *K⁺ into the CS (b), removal of the ions to produce porous CS (c)
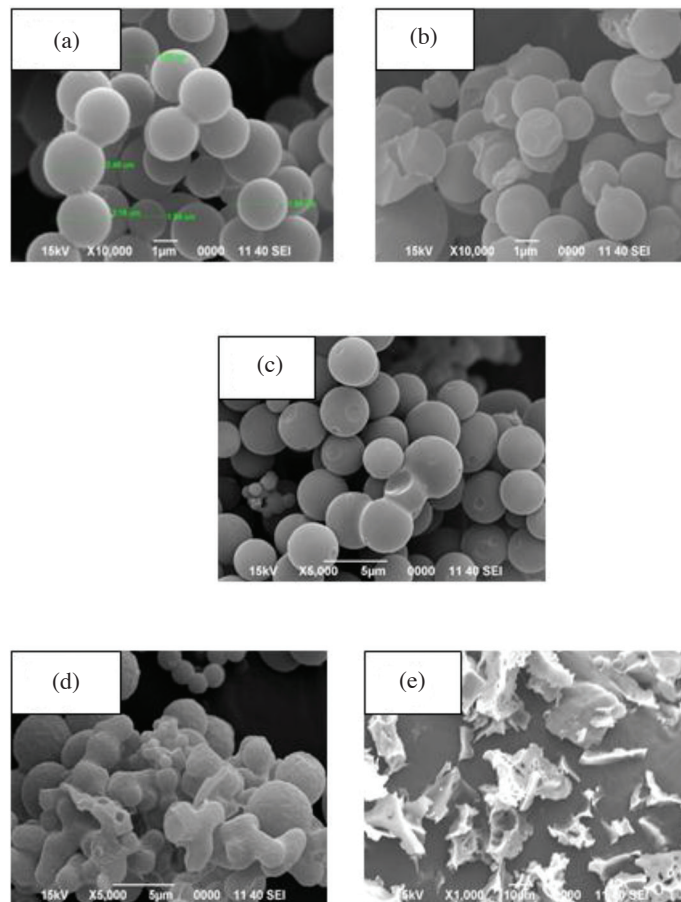

FIGURE 3. Micrographs of ACSs at 0.1M (a), 1.5M (b), 2.0 M (c), 2.5 M KOH (d) and 2.75 M KOH (e)
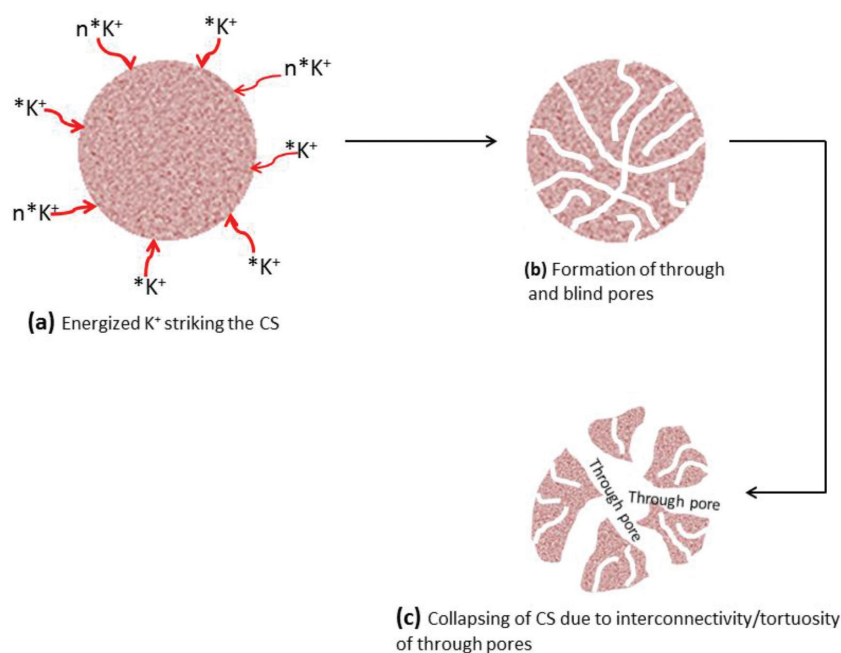
FIGURE 4. Pore formation and structural collapse of CSs at higher KOH concentrations (above 2.5M): Penetration/intercalation of *K⁺ into the CS (a); Formation of through and blind pores (b); Distortion of the sphere structure by the interconnecting through pores (c)

location, extend into particle and re-emerge at different location). Due to the interconnectivity/tortuosity properties of through pores, development of large number of such pores can distort to a greater extent, the binding forces holding a unit structure of carbon sphere and this could be the possible cause of the total collapse of the spherical structure. The phenomenon is demonstrated in Figure 4.

CONCLUSION

This study demonstrated that the surface area and structure of activated carbon spheres depend on the KOH concentration during activation. Optimum activation was achieved at ≤ 2.0 mol/L KOH producing micro- and or mesoporous CSs (1.7 - 4.5 nm pore size) with retained morphologies and appreciable BET surface areas. Pore formation and structural deformation were observed due to the intercalation of energized K⁺ into the carbon and interconnectivity of through pores. This work established a deeper understanding of pore formation as well as structural deformation of carbon spheres during KOH activation.

REFERENCES

Deshmukh, A.A., Mhlanga, S.D. & Coville, N.J. 2010. Carbon spheres. *Material Science and Engineering Reports* 70: 1-28.

Frykstrand, S., Forsgren, J., Mihranyan, A. & Strømme, M. 2014. On the pore forming mechanism of Upsalite, a micro- and mesoporous magnesium carbonate. *Microporous and Mesoporous Materials* 190: 99-104.

Hu, B., Yu, S., Wang, K., Liu, L. & Xu, X. 2008. Functional carbonaceous materials from hydrothermal carbonization of biomass: An effective chemical process. *Dalton Transactions* 40: 5414-5423.

Inagaki, M. & Tanaike, O. 2001. Determining factors for the intercalation into carbon materials from organic solutions. *Carbon* 39: 1083-1090.

Li, M., Li, W. & Liu, S. 2011. Hydrothermal synthesis, characterization, and KOH activation of carbon spheres from glucose. *Carbohydrate Research* 346: 999-1004.

Lillo-Ro´Denas, M.A., Cazorla-Amoro´S, D. & Linares-Solano, A. 2003. Understanding chemical reactions between carbons and NaOH and KOH: An insight into the chemical activation mechanism. *Carbon* 41: 267-275.

Lowell, S., Shields, J.E., Thomas, M.A. & Thommes, M. 2004. *Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density.* 4th ed. Dordrecht: Springer Publishers.

Lozano-Castello, D., Lillo-Ródenas, M.A., Cazorla-Amorós, D. & Linares-Solano, A. 2001. Preparation of activated carbons from Spanish anthracite I. Activation by KOH. *Carbon* 39: 741-749.

Niwase, K., Homae, T., Nakamura, K.G. & Kondo, K. 2002. Generation of giant carbon hollow spheres from C60 fullerene by shock-compression. *Chemical Physics Letters* 362: 47-50.

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Okuno, H., Grivei, E., Fabry, F., Grunberger, T.M., Gonzalez-Aguilar, J., Palnichenko, A., Fulcheri, L., Probst, N. & Charlier, J.C. 2004. Synthesis of carbon nanotubes and nano-necklaces by thermal plasma process. *Carbon* 42: 2543-2549.

Qian, H., Han, F., Zhang, B., Guo, Y., Yue, J. & Peng, B. 2004. Non-catalytic CVD preparation of carbon spheres with a specific size. *Carbon* 42: 761-766.

Qiao, W.M., Song, Y., Lim, S.Y., Hong, S.H., Yoon, S.H., Mochida, I. & Imaoka, T. 2006. Carbon nanospheres produced in an arc-discharge process. *Carbon* 44: 187-190.

Raymundo-Piñero, E., Azaïs, P., Cacciaguerra, T., Cazorla-Amorós, D., Linares-Solano, A. & Béguin, F. 2005. KOH and NaOH activation mechanisms of multiwalled carbon nanotubes with different structural organisation. *Carbon* 43: 786-795.

Sevilla, M. & Fuertes, A.B. 2009. Chemical and structural properties of carbonaceous products obtained by hydrothermal carbonizaon of saccharides. *Chemistry A European Journal* 15(16): 4195-4203.

Wang, Q., Li, H., Chen, L. & Huang, X. 2001. Monodispersed hard carbon spherules with uniform nanopores. *Carbon* 39: 2211-2214.

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