

CHAPTER II

LITERATURE REVIEW

2.1 Preparation of Activated Carbon

Hsisheng Teng, Jui-An Ho, Yung-Fu Hsu, and Chien-To Hsieh (1996) prepared activated carbon from three Australian bituminous coals by using physical activation, which consists of carbonization followed by activation in CO₂. Experimental results reveal that the oxygen content of the coal has a great influence on the behavior during preparation and on the properties of the products. The coal with a higher O/C atomic ratio has a lower peak temperature for volatile evolution during carbonization and is able to produce a char with a higher surface area. The reactivity in CO₂, the surface area, and the pore volume of the resulting activated carbon are all increasing functions of the O/C ratio of the coal precursors. The gaseous environment in carbonization has little effect on the development of the surface areas and pore volumes of the resulting chars and activated carbons. For the same coal precursor, the average pore diameter of the activated carbon increases as the temperature for activation is increased in the range of 800-900 °C.

B.Serrano-Talavera, M.J. Munoz-Guillena, A. Linares-Solano, and C. Salinas-Martinez de lecea (1997) submitted Spanish anthracite into a two-stage activation process to explore its use as an activated carbon precursor and effect of preoxidation treatment on the resulting activated carbons. Several oxidation

treatments, with two oxidizing agents (air and nitric acid), have been studied. The results showed that activated carbon prepared from preoxidized chars, using CO_2 or steam, present much larger porous development than the activated carbon coming from the original coal. Because preoxidation treatments performed in air and HNO_3 increase the oxygen content of the sample in the following order: air 4h < air 8h < 4M HNO_3 << 15M HNO_3 . This oxygen content affects the porosity of the resulting activated carbon: the higher the oxygen contents the higher the char porosity. The porosity of the char has been found to be the main parameter for the activation process. Because the porosity development of the resulting activated carbon is directly related to the porosity of the starting char.

J. Sun, T.A. Brady, M.J. Rood, and C.M. Lehmann (1997) produced activated carbon for natural gas storage from scrap tires and Illinois coals by physical activation with steam or CO_2 and by chemical activation with KOH , H_3PO_4 , or ZnCl_2 . V_m/V_s values of tire-derived carbons were lower than those of coal-derived carbon because of their lower bulk densities. Compared with coal carbons, tire carbons had a higher percentage of mesopores and macropores [9].

N. Yoshizawa, Y. Yamada, T. Furuta, M. Shiraishi, S. Kojima, H. Tamai, and H. Yasuda (1997) attempted to prepare mesoporous activated carbon by steam activation of a mixture of coal and metal acetylacetonate at 900°C . The results showed that the porosity of activated carbon was influenced more by the type of acetylacetonate than by the rank of the coal. The activated carbon obtained from

TiO(acac)₂ had high mesoporosity even at an early stage of activation as evaluated by the BET and BJH analysis. They believed that the formation of mesoporosity in the activated carbon was closely related to the migration of TiO₂ from the carbon matrix [17].

Hsisheng Teng and Tien-Sheng Yeh (1998) prepared activated carbon by chemical activation from two Australian bituminous coals. The preparation process consisted of zinc chloride impregnation followed by carbonization in nitrogen. Experimental results reveal that an acid-washing process following the carbonization with ZnCl₂ is necessary for preparing high-porosity carbons. Surface area, pore volume, and average pore diameter of the resulting carbons increase with the carbonization temperature to a maximum at 500 °C and then begin to decrease. The maximum values of surface area and pore volume are larger for the carbon prepared from the coal with a lower O/C ratio, while earlier findings from physical activation with CO₂ have shown an opposite trend. An increase in particle size of coal precursor leads to a reduction in porosity of the resulting carbons. The duration of the carbonization period affects the porosity of the resulting carbons, and the influence varies with the activation temperature.

Daulan C. Lyubchick SB, Rouzard JN, Beguin F. (1998) produced activated carbon from La Mure (France) anthracite by HClO₄ chemical modification prior to physical gasification with CO₂. From the results, the main effect of the chemical pretreatment is to reduce the time of physical activation. This

reduction can be attributed to the creation of numerous channels in the anthracite macro texture during chemical pretreatment. The accessibility of the inner surface of the anthracite to CO_2 was increased, and was responsible for deep gasification of the anthracite. Finally, physical activation after chemical pretreatment led mainly to a microporous carbon with a significant amount of mesoporosity.

S. Nagano, H. Tamon, T. Adzumi, K. Nakagawa and T. Suzuki (1999) carbonized refuse derived fuel (RDF) produced from municipal solid wastes by partial combustion, and activated the carbonized RDF (cRDF) with steam. Since the molecular sizes of dioxins determined by abinitio MO (molecular orbital) calculation were relatively large, the mesopores of activated carbons were necessary for adsorption of dioxins. They found that the activated carbon that was treated by HNO_3 prior to the steam activation had more mesopore volumes than the commercial activated carbon and should be effective for adsorption of dioxins.

H. Tamon, K. Nakagawa, T. Suzuki, and S. Nagano (1999) proposed a novel pre-treatment method of steam activation to develop mesoporosity of activated carbons prepared from plastic button wastes and PET wastes. The results showed that impurities contained in button waste contributed to developing mesopores. When each waste was mixed with calcium salt and underwater carbonization, pretreatment with nitric acid, and activation by steam, the obtained activated carbons had higher mesoporosity than the commercial activated carbon.

H. Tamai, T. Yoshida, M. Sasaki, and H. Yasuda (1999) investigated the adsorption of acid dyes, direct dyes, and basic dyes on a highly mesoporous activated carbon fiber in terms of size of dye molecules, and pore size and surface charge of the activated carbon fiber. They showed that the adsorption of dyes on activated carbon fiber can vary greatly by changing the pore size and surface charge of activated carbon fiber.

D. Lozano-Castello, M. A. Lillo-Rodenas, Carzorla-Amoros, A. Linares-Solano (2001) prepared activated carbon from anthracite by activation with KOH. They analyzed the effect of different preparation variables on the final porous texture, such as KOH/anthracite ratio, heating rate, carbonization temperature and time, and nitrogen flow rate. The results showed that the nitrogen flow rate has a very important effect on porosity development. They found that an increase in nitrogen flow rate provided a increase in the micropore volume and BET surface area of obtained activated carbon. Among all parameters studied, the main factor affecting the final porous texture of the activated carbon is the KOH/anthracite ratio. The higher the KOH/anthracite ratio, the wider the micropore size distribution. The prepared activated carbon from anthracite in a single stage pyrolysis process is micropores activated carbon.

M.A. Lillo-Rodenas, D. Lozano-Castello, D. Cazorla-Amoros, A. Linares-Solano (2001) analyzed the development of porosity of anthracite by chemical activation with NaOH. They studied experimental variables in preparation

method: activating agent/coal ratio, drying process, method of mixing of the activating agent and coal, nitrogen flow rate during pyrolysis and mineral matter content of coal. The results obtained show the importance of the activating agent to coal ratio and the flow of gas during carbonization on the development of porosity. In addition, it shows that chemical activation with NaOH is successfully used to develop microporous activated carbon. Comparing chemical activation using an impregnation method and physical mixing they concluded that physical mixing, which is a very easy preparation method, renders the best results. Although impregnation produces a higher development of porosity, activated carbons with high micropore volumes can be synthesized through a much simpler method.

Yong Zou and Bu-Xing Han (2001) prepared activated carbon from Chinese coals by chemical activation technology with potassium hydroxide. Activated carbon with BET N₂ surface area of the order of 2400 m²/g, substantial microporosity and total pore volume of over 1.40 cm³/g, and methylene blue adsorption capacity of over 440 mg/g. was obtained.

2.2 Supercritical water and Hydrothermal Treatment

F. Salvador and C. Sanchez Jimenez (1995) investigated a new procedure for regeneration activated carbon based on thermal desorption with liquid water under subcritical conditions (300°C and 120 atm) was proposed. The method was assayed with three types of activated carbons exhausted with phenols (phenol and 4-nitrophenol), textile dyes (Sirius red C.I.: 29080 and orange II C.I.: 15510) and

pesticides (carbofuran and atrazine). In all case, total recovery of the adsorption capacity was achieved, even after seven regenerations. The mechanism and factors involved in regeneration were investigated using the TOD technique in liquid phase. The differences and advantages of this procedure as compared with others, such as thermal regeneration or regeneration with supercritical CO₂ are discussed.

F. Salvador and C. Sanchez Jimenez (1999) conducted the regeneration of three commercial activated carbons by thermal desorption with water at 320°C and 150atm. In the absence of oxygen, was investigated. The efficiency of this procedure was evaluated by measuring the rate and the amount of substance retained in successive cycles of adsorption-regeneration. The efficiency of the treatment was found to be very high. The study was conducted with the adsorption of two compounds differing greatly in their molecular sizes: phenol and an azo dye (direct red 79). In all three carbons a slight increase in the adsorptive power was observed with respect to the original carbons; this is attributed to the cleaning or opening of closed pores. The carbons exhausted with phenol showed the greatest difficulty in regenerating because part of the phenol may be chemically adsorbed. The effect of the treatment on the textural and chemical characteristics of the original carbons was also investigated using N₂ adsorption isotherm, mercury porosimetry, pycnometry, scanning electron microscopy and acid-base titration. The alterations found were not very significant, except for a slight increase in the true density, total pore volume and the acidity of the treated carbons.

J. Rivera-Utrilla, M.A. Ferro-Garcia, I. Bautista-Toledo, C. Sanchez-Jimenez, F. Salvador, M.D. Merchán (2003) studied the regeneration of three activated carbons exhausted with *ortho*-chlorophenol. The regeneration process was carried out using liquid water at 623 K and 150 atm in the absence of oxygen. The efficiency of this procedure was analyzed by determining the rate and amount of *ortho*-chlorophenol adsorbed in successive adsorption-regeneration cycles. The present procedure showed a much greater efficiency than that reported for chemical and/or thermal regeneration. Effects of this regeneration on the adsorption kinetics, adsorption capacity and textural characteristics of the carbon were investigated. The increase in adsorption capacity of the regenerated carbon compared with that of that of the original carbon seems mainly due to the opening of porosity during the regeneration treatment. [BB]

Udo Armbruster, Andreas Martin, Andre Krepel (2001) studied the potential of sub- and supercritical water as reaction medium for the partial oxidation of propane to oxygen-functionalised hydrocarbons (oxygenates) in temperature range 633 – 693 K and pressure from 16.7 – 18 MPa in a batch and continuous runs with synthetic air as oxidant. In addition, experiments with catalysts (Carulite 300, MnO₂, Co₂O₃, MnO₂-Co₂O₃, MoO₃, all supported on γ -alumina) were also studied to provide information about behavior of oxidic materials at hydrothermal conditions. The influence of reaction parameters like temperature, pressure, density, residence time and feed composition on conversion and selectivities was examined. Transition of reaction mixture from sub- to supercritical region shows significant

influence on propane and oxygen conversion rates, due to homogenization of reaction mixture and improved mass transfer. Influence of catalyst materials is comparatively small. Total sum of oxygenates selectivities reached 15% at 90% propane conversion and methanol was the mainly formed oxygenate.

Jeffrey T. Henrikson, Phillip E. Savage (2003) conducted supercritical water oxidation experiments in a tubular flow reactor at 420-465°C and 141-241 bar. Phenol was the organic reactant. Both pure water and a helium (1/3 by mol)-water mixture served as reaction media. Adding helium to the reaction medium permitted variation of the water concentration from the system pressure independently. By decoupling the water concentration from the system pressure, it was shown that the rate of phenol disappearance during supercritical water oxidation is influenced by the water concentration and not the system pressure. The experiments consistently revealed that adding helium, and thereby decreasing the water concentration at the fixed system pressure, increase the phenol conversion. In addition, experiments showed that lowering the water concentration using pure water as the solvent also increased the phenol conversion. The results suggest that dilution with helium or others inert gases maybe a new way to control supercritical water oxidation reaction rates.

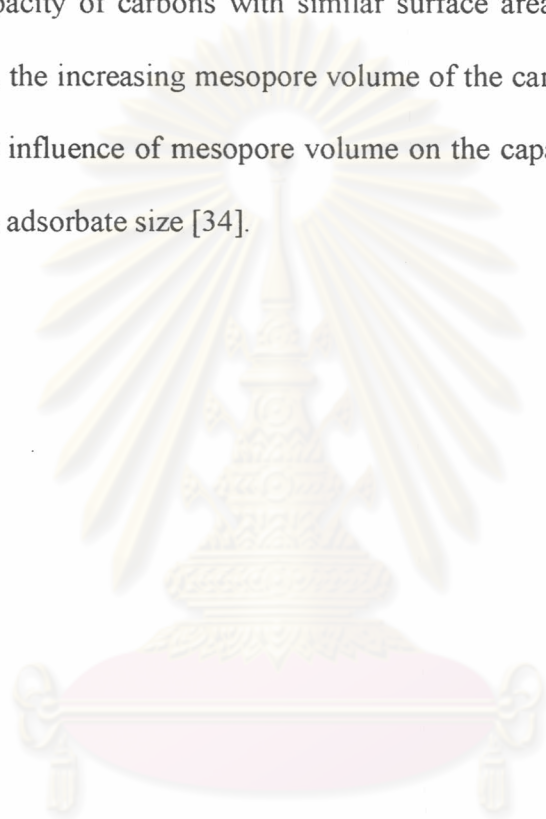
2.3 Adsorption of an organic dye

H. Tamon, T. Saito, M. Kishimura, M. Okazaki, and R. Toei (1990) applied ethanol regeneration to spent activated carbon that adsorbed an organic compound in aqueous solutions. High regeneration efficiency was achieved except for aromatic compounds substituted by electron-donating groups such as $-\text{NH}_2$, $-\text{OH}$, and $-\text{OCH}_3$. They also studied the solvent regeneration of carbon which adsorbed phenol using fixed-bed and found that the adsorption capacity of phenol on the regenerated carbon fell to 80% of that on the virgin carbon after five regeneration cycles [27].

S. H. Lin (1993) investigated the effectiveness of powered activated carbon (PAC) on the removal of chemical oxygen demand (COD) and a disperse dye, Red 60. The result revealed that the COD removal efficiency increased with decreasing particle mesh size. It was found that the multilayer BET isotherm fit the adsorption data better than the monolayer Freundlich and Langmuir isotherms [28].

M. Sankar, G. Sekaran, S. Sadulla, and T. Ramasami (1999) studied the removal of Direct Red 31, Acid Black 1, and Acid Green 16 using Rice Bran-based Activated Carbon (RBAC). They reported that the molecular weight of the dye chemicals, the mass of RBAC and the diameter of RBAC particle had positive effects on the rate of adsorption, in contrast, the initial concentration of dye chemicals, pH of the dye solution, and temperature of adsorption showed a negative impact on adsorption. It was concluded that the adsorption phenomenon is a physical process, so that regeneration of the adsorbent becomes easier [32].

C. Hsieh and H. Teng (2000) conducted the liquid-phase adsorption of phenol, iodine and tannic acid on commercial grade granular activated carbons and fabric activated carbon. On the basis of the adsorption isotherms and the analysis using the Langmuir and the Dubinin-Radushkevich models; they elucidated that the adsorption capacity of carbons with similar surface areas and micropore volumes increased with the increasing mesopore volume of the carbons. Furthermore, it was found that the influence of mesopore volume on the capacity was enhanced by the increase in the adsorbate size [34].



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