

EFFECTS OF ACID TREATMENT ON THE PORE AND SURFACE STRUCTURAL EVOLUTION DURING CARBONIZATION OF COAL-BASED MATERIAL

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Introduction

Acid treatment prior to carbonization is an effective chemical activation technique to tailor the pore structure and surface chemistry of activated carbons. This work aims to study the effects of nitric acid treatment on the evolution of pore and surface properties of carbonized chars from a coal reject material (high-ash coal). Acid concentration, reaction time and temperature are the main factors investigated. Pore and surface parameters are microporosity, adsorption energy, nitrogen retention, surface alumina-silica as well as functional groups.

Experimental

Acid treatment was carried out by refluxing 10 g of coal sample in 100 ml of nitric acid. All oxidized samples were then carbonized for 1.5 h at 600°C.

N₂ isotherms of all chars were obtained using a automated surface area and porosimeter (NOVA 1200, Quantachrome). XPS (PHI-560, Perkin Elmer) was used to determine surface nitrogen concentration on the char particles. Phenol adsorption capacities of the chars were determined by batch experiment using a Varian DMS90 UV Spectrophotometer at 269nm.

Samples are labeled as follows: treatment temperature °C (acid concentration, M) treatment time, hr.

Results and Discussion

The N₂ adsorption isotherms for three typical chars pre-treated under various conditions are shown in Figure 1. All isotherms manifest characteristics of Type I isotherms, and have hysteresis extending to low pressures. The adsorption capacity as reflected by the plateau height increases with acidic concentration but decreases under the condition: 100(15.5)23. However, the size of the hysteresis is found to decrease with increasing acid concentration. This clearly indicates that the accessibility to the micropores is enhanced by acid treatment. However, severe oxidation has caused the reduction in microporosity due to acid retention and functional groups formation as a result of carbon matrix oxidation.

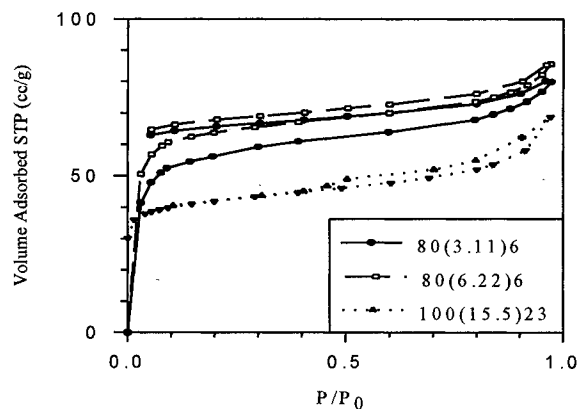


Figure 1. N₂ adsorption isotherms of chars pre-treated under various acidic conditions

DR energy of adsorption (E_0), determined from the DR plots of the chars, characterizes the interaction between the N₂ and the adsorbents (higher values corresponding to narrower pores¹).

Table 1. Acid treatment on Adsorption energy, surface functional groups in coal and char samples

Sample	E_0 (kJ/mol)	-COOH(R)/ Aromatics	C-O groups/ Amorphous
0(0)0	5.6	N/A	0.855
80(3.1)6	6.2	0	0.755
80(6.2)6	7.5	0	0.678
80(9.3)6	9.3	0.033	0.762
80(12.4)6	10.8	0.067	0.396
80(15.5)6	13.0	0.064	0.397
80(6.2)2	7.3	0.027	0.753
80(6.2)23	15.4	0.031	0.555
60(6.2)6	8.5	N/A	0.907
100(6.2)6	8.3	N/A	1.369

Table 1 shows the DR energy generally increases with the severity of acid oxidation. In a recent work², we examined the C¹³ NMR spectra of the acid-treated coals and Raman spectra of the carbonized chars. The ratio of -COOH (R) functional groups to the aromatics is seen to increase with acid oxidation but decreases at prolonged treatment. The opposite trend is observed from Table 1,

for the C-O groups in the chars. This suggests that with acid oxidation, more metastable functional groups are formed thus leading to more micropore creation during carbonization. However, at prolonged time of oxidation, the amount of stable C-O groups increased so that more of these groups remained in the chars causing significant narrowing of the micropores.

The effect of the DR energy (E_0) on phenol adsorption capacity (X_p) is shown in Figure 2. As E_0 values increase, phenol adsorption capacities of the derived adsorbents increase to a maximum after which X_p values decrease significantly. This is because that as E_0 increases accessible micropore area thus adsorption capacity increases. However, if the DR energy is higher than the characteristic energy of ca. 14 KJ/mol, micropores are too narrow to allow the passage of phenol molecules. This is the case where chars were pre-treated for longer periods of time in severe acid conditions.

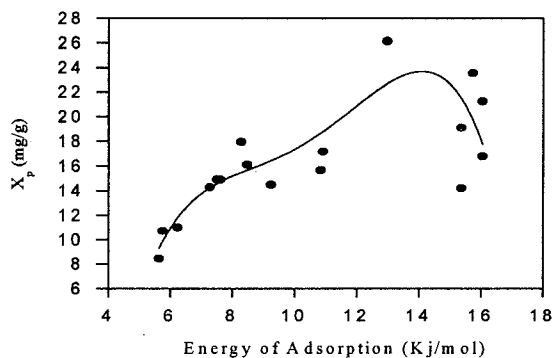


Figure 2. Variation of X_p with the DR energy of adsorption of various carbons

A plot of N concentration versus E_0 (Figure 3) shows that E_0 correlates well with the surface nitrogen concentration. This explains the narrowing of micropores because micropores are also likely to be blocked at the pore entrance by the nitrogen containing compounds formed by HNO_3 oxidation and its retention.

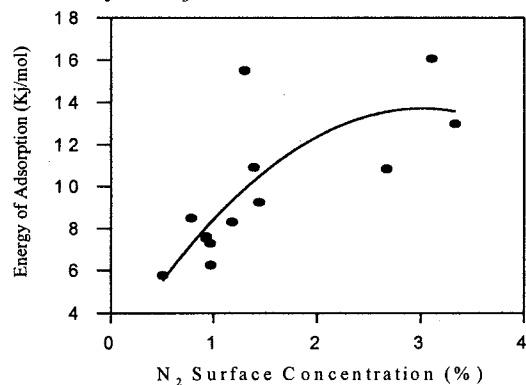


Figure 3. Correlation between the DR energy (E_0) and surface nitrogen concentration of various carbons

Carbonization of the acid-treated coals in a TGA revealed two temperatures at which the maximum rate of weight loss occurs. One is at 550°C, and another at a lower temperature. Since carbon dioxide and water begin to evolve at 200-300°C, the main components of the weight loss at lower temperatures are suggested to be mainly carbon dioxide and water³.

Figure 4 shows that the E_0 values of the chars depend on the temperature at which CO_2 and water were released. It is seen that those chars having higher temperatures for CO_2 and water release possess higher E_0 . This means that the stable surface C-O functional groups formed during the acid treatment resulted in the narrowing of accessible micropores thus enhancing the phenol adsorption, as seen in Figure 2.

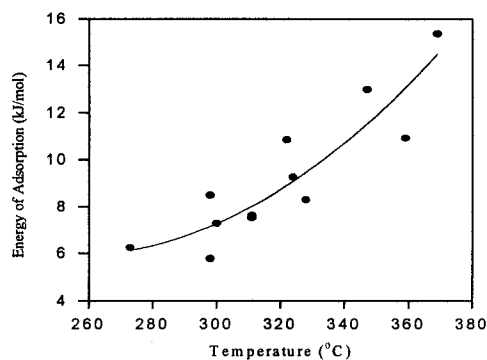


Figure 4. DR energy vs. characteristic temperature for maximum evolution CO_2 and H_2O

Conclusions

In this work, it is shown that pore structures and adsorption characteristics of the coal-derived carbons are strongly dependent on the pre-oxidation conditions. An increase in the severity of acidic oxidation significantly enhanced microporosity. Acid oxidation over prolonged time resulted in chars with narrower micropores. Surface nitrogen due to acid retention and C-O functional groups resulted from carbon oxidation are thought to play an important role in narrowing the micropores and increasing the DR energy of adsorption. Other aspects of the acid treatment such as ash removal (as surface Al + Si) and details of functional groups are also studied and will be presented at the conference.

References

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