

PREPARATION OF ACTIVE CARBON FROM COKE BY CHEMICAL ACTIVATION

FF Prinsloo and SGE de Jager

SASTECH R&D, PO Box 1, Sasolburg 9570, Rep. of South Africa

Introduction

The chemical and physical activation of SASOL cokes, produced from waxy oil (WO) and medium temperature pitch (MTP), are currently under investigation in our laboratories. Chemical activation is of particular interest because large surface area products can be obtained utilizing this method. In this paper we report on the results of activation with KOH and NaOH. Results obtained on the development of microporosity in activated carbons produced from MTP coke, preoxidized with HNO₃ and O₂, are also presented.

Experimental

Coke precursors (uncalcined) produced from waxy oil and medium temperature pitch (0.8 to 3 mm) were activated between 0.5 and 9 base:coke ratio, 600 - 800°C heat treatment temperature (HTT) and 1.5 and 12 h heat treatment time (HTt). All activation and cooling cycles were carried out under a constant flow of nitrogen. The method of activation and product recovery is described elsewhere¹. The activated samples were ground to -45µm and dried at 100°C under a nitrogen atmosphere for subsequent analysis. In all the cases the products were isolated in powder form. Coke samples were oxidized in an autoclave under a constant flow of O₂ (T = 170°C; p = 42 bar; t = 4 h) or HNO₃ ([HNO₃] = 1 N; T = 100°C; t = 24 h). The humin fractions (NaOH insoluble) and the humic acids (NaOH soluble) were removed according to a literature procedure². In order to identify conditions for well developed porosity the iodine numbers of the products were determined. In addition BET surface areas were obtained from the adsorption of N₂ at -196°C using a Micrometrics, ASAP 2000.

Results and discussion

Representative iodine numbers and BET surface areas are summarized as a function of the activation time for the chemical activation of uncalcined WO - and MTP coke in Table 1. This data confirms that the [KOH], HTT and HTt have a significant influence on the total porosity. The best developed porosity is observed for uncalcined

MTP coke and this precursor was used in further activation experiments.

Table 1 Representative iodine numbers, BET-surface areas and micropore volumes of activated cokes.

KOH: coke	HTT (°C)	Htt (h)	carbon conversion (%)	I ₂ number	BET-surface area (m ² g ⁻¹)	Micro-pore-volume (cm ³ g ⁻¹)
activation of WO coke						
7	600	2	14	504		
7	700	2	28	1147	939	0.32
4	750	2	16	606		
5	750	2	15	825	506	0.21
7	750	2	61	1238	1158	0.41
9	750	2	60	1197	1096	0.40
activation of MTP coke						
5	750	1.5	22	1214	1208	0.30
3	750	4.0	84	828	378.5	0.08
5	750	4.0	71	1327	1070	0.26
7	750	4.0	75	1517	1510	0.18
5	750	8.0	71	1390	1140	0.259
5	750	12.0	80	1184	1089	0.229
5	800	1.5	58	1162	1073	0.274

Table 2. Influence of preoxidation on the iodine number of chemically activated MTP coke.

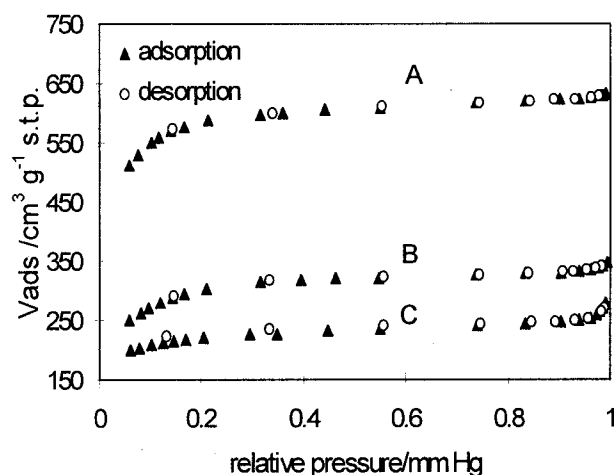
ratio	oxidation agent	yield (%)	I ₂ number
KOH:MTP = 3	no oxidation	84	828
KOH:MTP = 2	O ₂	68	1031
KOH:MTP = 3	O ₂	55	2020
KOH:MTP = 2	HNO ₃	64	1109
KOH:MTP = 3	HNO ₃	48	1248
NaOH:MTP = 3	no oxidation	92	400
NaOH:MTP = 2	O ₂	57	748
NaOH:MTP = 2	HNO ₃	66	982
NaOH:MTP = 3	HNO ₃	42	1251

A preliminary economic evaluation showed that the highest KOH:base ratio where the best adsorption capacity is observed would be uneconomical to implement. In an attempt to lower this ratio and to increase the product yield, the MTP coke was oxidized before the activation step. It has been shown that the

preoxidation of a carbon precursor plays an important role in the development of a highly microporous structure^{2,3}. NaOH was also evaluated as an activation agent because it is less costly than KOH. Representative results are summarized in Table 2. The iodine numbers in Table 2 confirm that the preoxidized activated MTP coke possesses a better developed porosity compared to the unoxidized samples.

Representative adsorption isotherms of N₂ by the activated cokes are shown in Figure 1.

Figure 1 Adsorption isotherm of N₂ by chemically activated MTP coke. A. preoxidized by oxygen; B. preoxidized by HNO₃; C. no preoxidation.



The isotherms are in correspondence with the type I in the BDDT classification and suggest that the activated products are highly microporous with low mesopore surface areas. The isotherms show a more rounded knee than that expected for activated carbons with a narrow micropore distribution, which suggests that the activated carbon contains narrow micropores (steep initial branch) as well as wider micropores. The isotherms show a slight increase in the volume of N₂ adsorbed with increase in the relative pressure between 0.2 and 0.8, which can be attributed to condensation of the gaseous nitrogen in the mesopores. The open loop hysteresis indicates that the equilibrium time allowed for desorption was too short. This phenomenon is generally observed in the case when emptying a pore filled with nitrogen occurs at a lower pressure than the filling of the pore due to constrictions in the pore, for example a narrow pore entrance. Typically these pores can be bottle-neck shaped.

The effect of KOH:coke ratio and preoxidation on the development of porosity is clear from Tables 1 and 2, i.e., an increase in iodine number is observed with an increase in KOH:coke ratio as well as preoxidation. To investigate this matter in more detail the Dubinin-Astakhov (DA) parameters such as limiting micropore volume, V₀, the surface characteristic energy, E₀, and the structural heterogeneity parameter, n, were calculated (Table 3) by a non-linear least square fit of the experimental data into the DA equation, and using 0.34 as the β factor. It is evident from the results in Table 3 that the values of E₀ decrease and the values of n and V₀ increase with increasing KOH:MTP coke and degree of preoxidation. This indicates that the microporosity becomes more uniform with an increase in the KOH:MTP coke and degree of preoxidation.

Table 3 Parameters of the DA equation for the nitrogen adsorption isotherms.

Sample	E ₀ (kJ mol ⁻¹)	V ₀ (cm ³ g ⁻¹)	n
KOH:MTP = 3	34.1	0.39	0.79
KOH:MTP = 5	19.3	0.64	0.99
KOH:MTP = 7	13.4	0.72	1.11
KOH:MTP = 3 (O ₂ oxidation)	11.7	0.96	2.17
KOH:MTP = 3 (HNO ₃ oxidation)	9.98	0.51	2.07

Conclusions

The results presented in this paper indicate that coke precursor, base:coke ratio, heat treatment temperature, heat treatment time and preoxidation are critical parameters for the production of high surface area activated cokes. Oxidation of carbon precursors eliminates aliphatic and disorganized carbon which results in a primary pore structure and which facilitates the activation process. Furthermore, preoxidation benefits the development of high microporosity at economic attainable base:coke ratios.

References

- Otowa, T., Tanibata, R. and Itoh, M., *Gas Separation & Purification*, 1993, 7, 241.
- Verheyen, V., Rathbone, R., Jagtoyen, M. and Derbyshire, F., *Carbon*, 1995, 33, 763.
- Parra, J.J., Pis, J.J., de Sousa, J.C., Pajares, J.A. and Bansal, R.C., *Carbon*, 1996, 34, 783.