A MODEL FOR MICROPOROSITY DEVELOPMENT DURING CHAR ACTIVATION

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Introduction

Gas storage by adsorption on activated carbon is possible at relatively low pressures using activated carbons with a well developed microporosity, i.e., with pores whose radius, r_p, is less than $r_{limit} \cong 10$ Å. The generation of microporosity requires a uniform surface phenomenon, such as steady-state gasification in the limit of kinetic control or an alternating adsorption/desorption process that uniformly covers the surface with a reactant gas and then allows it to react with, and remove, the carbon from the walls of the pores. If one removed 5 Å from the walls of every pore, the volume of the 2 Å pore would grow by 1000%, while that of the 100 Å pore would grow by only 10%. Hence, the dominant increase in pore volume would occur in the microporosity. In this paper, a model is presented that describes pore growth in microporous carbons. The model has been used to relate the potential micropore volume to the characteristics of the starting material (initial char).

Theoretical Model

Consider a porous particle containing a continuous distribution of pore sizes from a microscale (r_{min}) of the order of Ångstroms to a macroscale (r_{max}) which is a significant fraction of the particle radius. The number of pores in size range dr_p in an arbitrary particle cross-section is denoted by $g(r_p)$ and is proportional to $1/r_p^3$ [1]. Due to the random orientation of the pores, the porosity is the $2\pi r_p^2$ moment of $g(r_p)$, and the internal surface area is the $4\pi r_p$ moment of $g(r_p)$. The expression for $g(r_p)$ was derived from statistical arguments [2] and has been validated through extensive comparison of the predicted pore-volume distributions with mercury-intrusion data [3].

When the pore growth is uniform in pore space, $r_p(t)$ is expressed as $r_p(t) = r_p(0) + \xi(t)$ where $\xi(t)$ represents the growth of the pore from time $t = 0$. If the $1/r_p^3$ distribution is valid at $t = 0$, $g(r_p,\xi)$ readily becomes

$$g(r_p,\xi) = \frac{\theta(0)}{2\pi\beta(r_p-\xi)^3}$$

where $\theta(0)$ is the value of the total open porosity at $t = 0$, and β is a constant characterizing the pore structure [1]. The radius of the smallest pore r_{min} is related to the internal surface area ($4\pi r_p$ moment of $g(r_p)$), the microporosity is defined as the open porosity ($2\pi r_p^2$ moment of $g(r_p)$) between r_{min} and r_{limit}, while the total open porosity is that between r_{min} and r_{max}. A relationship between microporosity θ_{micro} and total porosity θ during burnout is then defined parametrically in terms of the pore growth $\xi(t)$.

During the pore growth defined by $\xi(t)$, the exposure and subsequent growth of "blind porosity" is an important factor in generating microporosity. Assume that a "blind porosity," θ_B, which is initially present in the char sample is in no way connected to the initial open pore structure. Blind porosities of coals are typically 5 per cent. Furthermore, assume that θ_B is contained within pores of size $r_{min}(0)$ and are uniformly distributed in physical space. Blind pores are exposed continuously and experience growth from the time of birth. The evolution of open porosity via this mechanism is also described parametrically in $\xi(t)$.

Results and Discussion

The model described above has been exercised to determine the effect of the initial-char properties on the development of microporosity during burnoff. In Fig. 1, θ_{micro} versus total porosity θ is presented for an initial open porosity $\theta(0)$ of 10%, and initial blind porosities θ_B of 0%, 2.5%, 5% and 7.5%. The strong sensitivity of θ_{micro} to θ_B is evident, and blind porosities of the order of 5% are required to explain available data [4]. The numerical results demonstrate a clear maximum in the microporosity with burnoff. This is due to the expansion of the pore radius beyond the range of the microporosity (r_{limit}) due to both surface recession and pore combination. Fig. 2

illustrates the strong effect of the initial open porosity of the char precursor on char-microporosity development. Restricting the mesoporosity at the onset severely reduces further development of mesoporosity (and also macroporosity), and enhances the formation of the microporosity. Fig. 3 illustrates the strong dependence of the microporosity on the initial surface area of the precursor. It is shown that high initial surface area, at a given value of initial porosity, is associated with a large proportion of small pores (microporosity). This large surface area may be present initially, or it may emerge with the exposure of the blind porosity during burnout.

Conclusions

A model of porosity evolution was developed that includes pore growth due to char gasification reactions and the formation of new microporosity via opening of initially blind pores. Results of the modeling effort show that the microporosity can be maximized by choosing an initial char with minimum initial open porosity and significant initial blind porosity within angstrom-size pores. The model predictions are equally appropriate for steady-state gasification in the limit of kinetic control and for a transient char-activation process based on alternating adsorption-desorption cycles [5].

Acknowledgments

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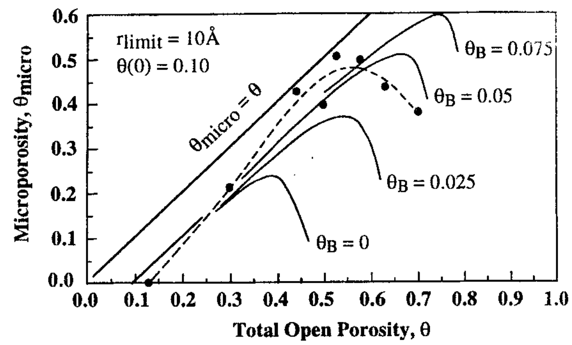

Figure 1. θ_{micro} vs. total open porosity (θ) and θ_B (experimental data from ref. [4]).

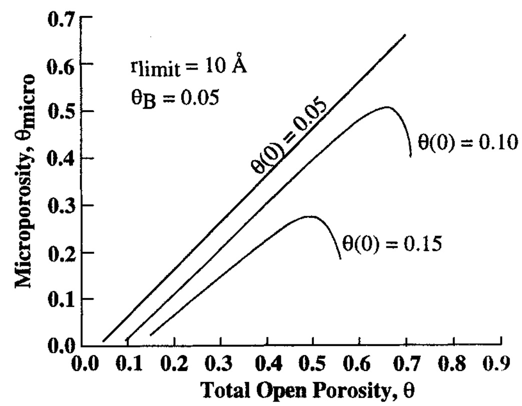

Figure 2. θ_{micro} vs. total open porosity (θ) and $\theta(0)$

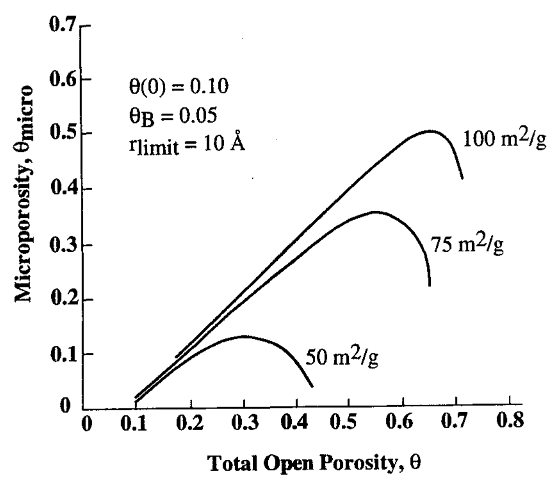

Figure 3. θ_{micro} vs. θ and initial surface area