

H₂ /CO SEPARATION BY OXIDIZED AND REDUCED MOLECULAR SIEVE CARBON FIBERS

Berveno V.P.*, Bryukhovetskaya L.V., Naimushina T.M., Petrov I.Y., Lyrshchikov S.Y.

Institute of Solid State Chemistry & Mechanochemistry, SB RAS, Kemerovo Division

18 Sovetsky Avenue, Kemerovo 650099, Russia,

E-mail: carbnanof@kemnet.ru

Introduction

Carbon molecular sieves are used as adsorbents for syngas (H₂/CO mixtures) separation and hydrogen cleaning. They have a number substantial advantages over traditional zeolite-containing materials since they are highly hydrophobic and easily regenerated at even ambient temperatures. More advantages can be attained in the case of adsorbents prepared on the base of molecular sieve carbon fibers (MSCFs) in view of much better kinetics of adsorption/desorption processes occurred on the surfaces of carbon fibrous materials. In the present work relationships between structural and surface characteristics of coal tar pitch-based MSCFs (both oxidized in air and reduced in hydrogen) and their efficiencies in H₂/CO mixtures separation have been investigated using quantum-chemical computations analysis of the texture MSCF nanofragments and experimental measurements by the gas adsorption chromatography.

Results and Discussion

Carbon fibers (CF) used in this work were prepared from isotropic coal tar pitch with softening points ~ 220-240°C. Nanostructured carbon fibers (diameter of 15-20 μm) with spatially disordered arrangement of textural blocks were melt spun from pitch, followed by thermal oxidative cross-linking of arene associates (by heating in air up to 300-350°C) and then carbonization/activation

of infusible products by their heating up to 500-800°C in the presence of water steam. Structural characterization of arene associates (estimation of L_a, L_c, number of layers, molecular pore sizes) in the MSCFs was carried out with X-ray diffraction measurements in both small and wide angle ranges (SAXS and WAXS). The separation efficiencies of MSCFs for H₂/CO mixtures were determined chromatographically at

30 °C (using 0.5 m-length columns) by comparison of H₂ and CO specific retention volumes.

According to X-ray data, elementary fragments of MSCs having pore sizes of ~ 0.3 nm consist of three-layer sandwich-like graphene associates with the following sizes: L_c – 0.8-1.2 nm, L_a – from 0.5 to several nanometers. Molecular pore volume is determined as interspace volume between outer layers of MSCF textural blocks (Fig.).

An analysis of changes in conformations of MSCF elementary textural fragments has been performed for graphite-like model structures of CF samples using a PM-3 method as a molecular orbital calculation package. Distances between lateral H-atoms located at the edges of the outer graphene layers of arene associates have been evaluated from calculated MSCF model structures. These distances determine both sizes of molecular pore entries in the elementary textural fragments and selectivity's for gas mixtures separation exhibited by molecular sieve adsorbents.

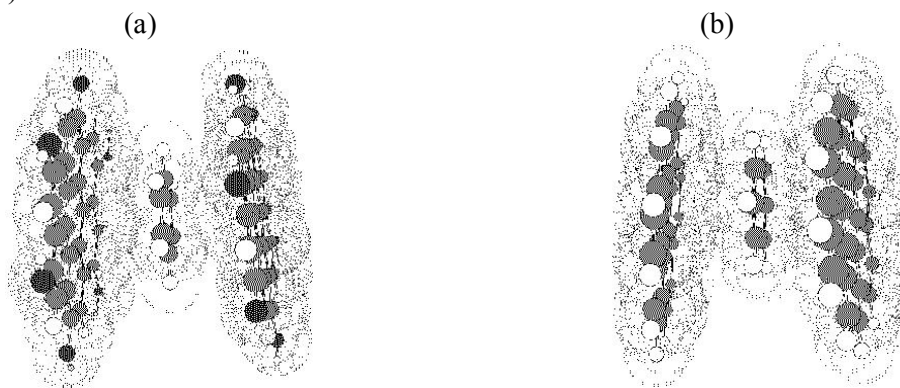


Fig. Models of elementary fragments of oxidized (a) and reduced (b) MSCFs activated at 500°C.

During activation heating of MSCFs from 500 to 800°C, the thickness of elementary textural fragments (according to XRD results) is not practically changed, i.e., three associated arenes are remained in these carbon structures in the course of oxidative treatment. However, a linear molecular size (L_a) tends to rise from 0.5 nm for MSCFs with activation temperature (T_a) of ~ 500°C to 3-4 nm for MSCFs with T_a ~ 800°C.

For MSCFs activated at 500°C, a three-layer coronene associate (a seven-ring molecule) was accepted as a model elementary textural fragment of MSCFs (L_a ~ 0.5 nm and L_c ~ 1.1 nm). It has been established that a positive charge at H-atoms of a middle coronene layer is less than that located at H-atoms of two outer coronenes. On the other hand, an electron density at the C-atoms of middle coronene is higher than at the C-atoms in the outer coronene layers. It may be supposed that the increased electron density at the edge C-atoms of the associate middle layer, providing its increased reactivity compared to outer layers, is the main reason for its preferential burning during oxidative activation of MSCFs. Then this procedure was repeated for the above associate with constant numbers of aromatic rings in the outer layers but decreased numbers of these rings in the middle layer. For the associate from outer coronenes and a benzene molecule between them, electron density distributions at the edge C- and H-atoms in the outer layers are similar to the above mentioned associates, but at the C-atoms of the inner (benzene) layer an electron density is substantially higher than that at the C-atoms in the outer arene layers. Hence, with decreasing a size of the inner arene, its reactivity should increase faster, compared to reactivities of outer arene layers.

Thus, it may be supposed that at the burn-off levels of ~ 30-35%, a middle layer of the arene associate burns out completely. Depending on the bond strength of outer arenes with other associates, as well as on their capability to form three-dimensional carbon matrix, two different scenarios of the development of carbon texture can be realized: 1) a slit-shaped pore may disappear and 2) it may remain. The first case is characteristic for low-temperature carbon materials with relatively labile and weak bonds between elementary textural fragments; during their oxidative activation, pores are easily removed, pore volumes decrease and adsorbent densities tend to increase. This explains an experimentally found decrease in the volume of oxygen-available pores in low-temperature carbon fiber activated up to more than 30% burn-off: at

the burn-off levels < 30% available pore volume increases but at the burn-offs > 30% it decreases.

During oxidative activation of carbon adsorbents with nanofragments, strongly cross-linked into a three-dimensional matrix, pores do not vanish. At the high values of burn-off, outer arene layers of three-layer associates begin to burn. An electron density at the edge C- and H-atoms of single arene molecules and two-layer arene associates is higher than in three-layer arene associates. Thus, in the course of oxidative activation of such nanostructured MSCFs fragments, slit-shaped pores with sizes multiple to 0.3 nm (about 0.6 nm) are formed. Maximal pore volumes may attain 0.3-0.35 cm³/g. But at the burn-offs > 35%, arenes located between molecular pores start to burn out, and pores with critical sizes of ~0.6 – 1.2 nm are formed.

With increasing linear molecular sizes of nanotextured fragments of MSCFs, a slit size between outer arenes in the associate is several times enhanced. Correspondingly, it may be expected that selectivity of gaseous mixtures separation would also increase. Indeed, with increasing activation temperature of MSCFs from 500 to 800°C, experimentally measured separation coefficients of H₂/CO mixtures tend to rise from 10-15 to 35-45.

Quantum-chemical calculations have also shown that hydroxyl-groups (OH-groups) of oxidized arenes in the MSCF elementary textural fragments partially cover outer molecular pore entries and hinder the mobility of larger gas molecules to be separated from the smaller ones. However, during the treatment of MSCFs with H₂ at elevated temperatures (400-500°C), OH-groups are eliminated, and sizes of molecular pore entries are continuously enlarged. Therefore, H₂ and CO specific retention volumes for the reduced MSCFs are on average by 20% as much as for the oxidized ones. Syngas separation efficiency coefficients (ratios of CO and H₂ specific retention volumes $K_s = V_{CO}/V_{H_2}$) for oxidized MSCFs are of ~ 50, while for reduced MSCFs they are about 30rs. The sizes of molecular pore entries (slits) can be controlled by functionalization (with oxygen-containing species) of terminal C-atoms in the outer arenes of MSCFs textural fragments.

Conclusions

The increased electron density at the edge carbon atoms of the middle layer of three-layer arene associates is the main reason for its preferential burning during oxidative activation of MSCFs. At the burn-off levels of ~ 30-35%, a middle layer of the arene associate burns out completely. The sizes of molecular pore entries (slits) can be controlled by functionalization of terminal carbon atoms in the outer arenes of MSCF textural fragments.

* Separation coefficients were determined as ratios of CO and H₂ specific retention volumes: $K_s = V_{CO}/V_{H_2}$.