QUANTUM MODELING OF THE DIFFUSION OF GASES IN CARBON MOLECULAR SIEVES

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Introduction

The increasing number of applications based on gas mixture separation processes using the Pressure Swing Adsorption - PSA [1] technology, which use adsorbent materials working as molecular sieves, require a better knowledge about the gaseous diffusion process, aiming at optimization of manufacturing techniques of those molecular sieves.

In addition to the study of noble gases diffusion in Carbon Molecular Sieves - CMS of Walker [2], Rao and co-workers [3] developed a model based in empirical Lennard-Jones potential, applied to spherical and linear molecules. In this model, it was considered slit-shaped micropores formed by the volume between two walls composed by graphite basal planes. The authors showed that the gas diffusion analysis in a gas/CMS system is directly related to the separation between the two graphite basal planes and defined a very important parameter, the critical pore dimension - CPD. Below this pore dimension diffusion for a particular species becomes activated.

In this work, a new approach to the problem of gas diffusion into CMS micropore is presented. This approach is carried out using the Molecular Orbital Theory, which is based on Quantum Chemistry Formalism. The diffusion in CMS is studied for H_2, N_2, O_2, CO_2 and CO, because of the potential application of these materials in industry and also due to the results reported in the literature which can be used as means comparison with the present model.

Computational Method

The steps developed in this study are:

- building of the CMS cavity model assuming the hypothesis of a slit-shaped micropore. This micropore configuration is largely discussed in literature [4];
- passing of a gas molecule into the micropore along the central plane parallel to and equidistant of the graphite basal planes;
- quantum calculation of the formation enthalpy of the gas/CMS system. The calculations were carried out employing the Gamess/96 suite program [5], using the semiempirical Hamiltonian AM1. Our motivation for using this methodology comes from its success in the modeling of polymers [6];
- variation of the distance between the graphite basal planes ($2d$) and the calculation of formation enthalpy to the system being studied. The range of distances was chosen to include the values of the CPD discussed in the literature.

Results and Discussion

The validity of the proposed model to study the gaseous diffusion can be checked considering the case of N_2 diffusing in the central plane of a CMS micropore (Figure 1) composed by 2 basal planes with 14 condensed benzene rings each. It was observed that when the distance of separation between the graphite basal planes is large, approximately 0.6 nm, there is a relative small energetic barrier to penetration into micropore (E_1) and no barrier to internal diffusion (E_2). As the plane separation distance decreases in value, E_1 increases and the gas molecules tend to adsorb at deeper sites into the micropore.

To investigate the selective character of CMS to the several gases studied, the E_1 and E_2 barriers were analysed as functions of the distance between the graphite basal planes ($2d$). A computational simplification was introduced by using only 4 condensed benzene rings in each basal plane. The results explain the selective behaviour of the CMS.

For example, the faster diffusion of O_2 into the micropore compared to N_2 is associated to the lower barrier E_1 (Figure 2). This is consistent with the production process of N_2 gas from atmospheric air in the PSA adsorption step. Similarly, the H_2 production - also during the adsorption step - is explained by its lower values of E_1 and E_2 (Figures 2 and 3) barriers compared to the other gases. The very rapid CO_2 diffusion can also be explained by this model since for CO_2 a small barrier of admittance into the micropore is observed (Figure 3).

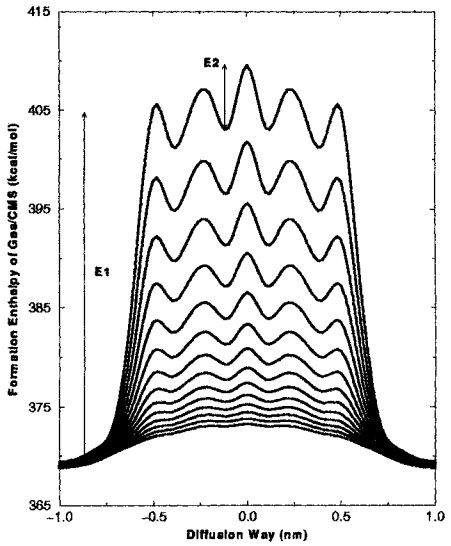

Figure 1 - Formation enthalpy of the N_2/CMS system. The calculations were carried out to *2d* varying in the range 0.48 nm in lower curve to 0.61 nm in the upper curve with a 0.01 nm increment.

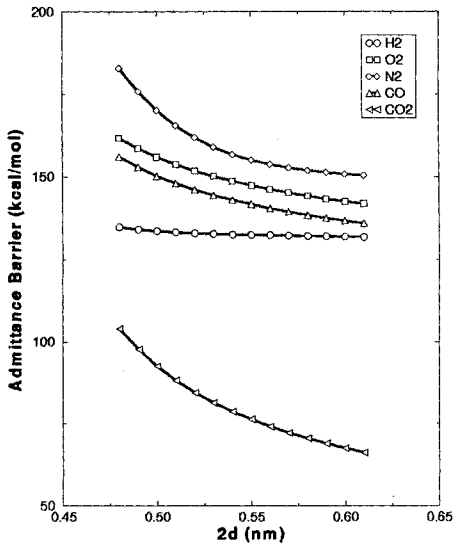

Figure 2 - Barrier to admittance versus 2d to several species.

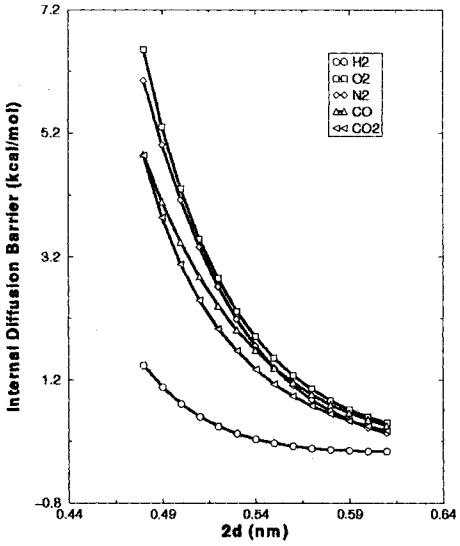

Figure 3 - Barrier to internal diffusion versus *2d* to several species.

Conclusion

This model yields a qualitative picture of the behaviour of CMS in agreement with experimental observations Further analysis with an extended *2d* range will be presented elsewhere. The subsequent introduction of the specific features of each element, as well as improvements in the micropore model as mentioned above, is likely to further substantiate the results shown in this work.

References

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