BINARY ADSORPTION OF HYDROCARBONS AND CO_2 IN A SERIES OF CHEMICALLY ACTIVATED CARBONS

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Introduction

Activated carbon has been found to be a good candidate for storage of natural gas (NG). Although the low density of adsorbed gas in this material is still one of the drawback for the storage purposes, there are vast research activities in recent years to increase the adsorption density by modifying the structure of carbonaceous materials. NG consists mainly methane (85-95%) with minor amount of ethane, and higher-order hydrocarbons, nitrogen, carbon dioxide and sulfur compounds. These heavily adsorbing compounds are considered as impurities and they affect the adsorption of methane. Therefore, studying the impact of these components on the methane storage is very important. Also, the knowledge of interaction and competition of different gases in adsorption processes is necessary for design purposes.

The objective of this study was to investigate the multicomponent adsorption equilibria in a series of activated carbons with different pore structures prepared by KOH activation of Macadamia nutshell. Four different models have been used to predict the multicomponent adsorption equilibria using single-component isotherm information. The results have also been compared with the commercial Ajax and Nuxit activated carbons.

Experimental

The measurements of single and binary adsorption isotherms were conducted by volumetric technique. Binary experiments were performed at constant pressure of 500 torr and temperature of 30°C for the mixtures of CH_4-C_2H_6, CH_4-C_3H_8 and CH_4-CO_2 in four different activated carbons. These adsorbents were a commercial activated carbon (tradename: Ajax) and three home-made ACs derived from activation of nutshell with 25, 100, and 500% (wt%) KOH to nutshell ratio, respectively. The binary adsorption data for Nuxit AC was taken from the literature [1]. The preparation technique and physical properties of nutshell activated carbons are detailed elsewhere [2]. The following nomenclature is used to describe the nutshell carbons: NSK25, NSK100 and NSK500. In binary experiments the gas mixtures were dosed and circulated for 7 hours on a pre-cleaned to ensure that true equilibrium is achieved. At the end of the experiment a small part of the mixture in the gas phase was diluted up to 10 times in volume with helium and sent to the mass spectrometer for quantitative analysis.

Results and Discussion

A comprehensive investigation of the effect of preparation methods and structural parameters on adsorption behaviour of activated carbons have been carried out [2, 3, 4]. In the present study the binary adsorption of methane with ethane, propane, and CO_2 are performed on three carbons in a series of KOH-chemically nutshell activated carbon. The experimental results showed [2] that most of the pores of these activated carbons fall in the range of micropore. The binary adsorption equilibria of these carbons as well as two commercial ACs are predicted using four different models. These models are: IAST, Heterogeneous extended Langmuir equation with Micropore Size Distribution (MPSD) or with Energy Distribution (ED), and the extension of a new adsorption isotherm for heterogeneous adsorbent based on the Isosteric Heat as a Function of Loading (IHFL) which has recently been proposed by Do and Do [5].

In the first model the FastIAST algorithm proposed by O'Brien and Myers [6] was used for calculations. In the MPSD model, the distribution of slit-shaped micropores is treated as the intrinsic feature of the carbon structure and the sole source of energetic heterogeneity. The size exclusion effect is accounted for in the calculation of binary adsorption equilibria [7]. The ED model utilizes the energy distribution derived from the MPSD model and the energy matching between different species in this model takes the traditional cumulative energy matching approach.

Fig. 1 shows example of the experimental data (symbols) of the methane-ethane system in some of the activated carbons studied in the present investigation.

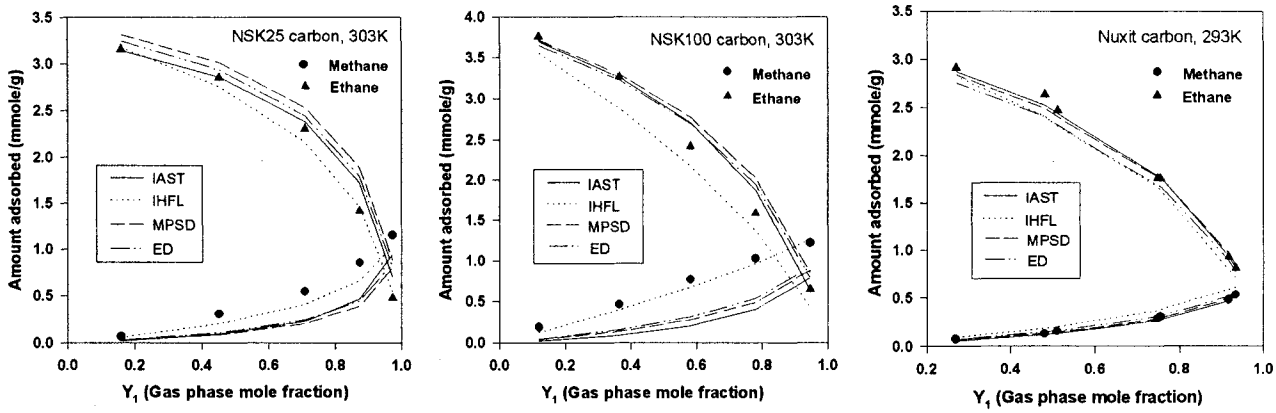

Figure 1. Amount adsorbed on different ACs for $CH_4(1)+C_2H_6(2)$ mixtures at 303 K and 66.7 kPa for NSK carbons and 293 K and 100 kPa for Nuxit.

The predictions of different models are also shown in the figure (lines). As seen in the figure the adsorption of methane in NSK carbons are about twice (even at higher temp.) of that of Nuxit in per mass basis at high concentration of this species. This is because of the large volume of the micropores developed under the effects of KOH during the carbonization process. The prediction of different models in the figure shows that all the models underpredict the adsorption behaviour of light component (CH_4) in NSK carbons but the quality of fitting is much better in the case of IHFL model. For ethane adsorption all the models, except IHFL, slightly overpredict the amount adsorbed of this component and for Nuxit carbon all the models show very good fitting to the experimental data. The reason for higher adsorption of methane in NSK carbons to those predicted by different models seems to be due to the large amount of functional groups on the carbon surfaces. A considerable number of surface functional groups were found in KOH activated carbon compared to the physically activated carbon in the investigation of Otowa et al. [8].

The IHFL model which takes into account the heterogeneity of carbons is seen to predict the adsorption of both species better than the other models. On the other hand, as it is known that the degree of goodness of fitting the pure component data can significantly affect the multicomponent model predictions. This has been seen for the other three models where the pure component data well not fitted by the single component adsorption isotherm equation in the whole range of pressure and temperatures. In the case of IAST the predictions can be slightly improved by the conventional algorithm using the Toth adsorption equation. It is interesting to mention that NSK100 and NSK500 carbons showed some nonideality behaviours for some the mixtures.

Conclusions

Binary adsorptions of methane with heavy compounds are studied in a series of chemically activated carbons with different pore structures. Two commercial ACs are also studied for comparison purposes. The experimental data have been fitted with four different multicomponent adsorption models. While all the models work reasonably well for the commercial ACs, only the IHFL model which takes into account the heterogeneity of carbons through the adsorbate-adsorbent interactions can predict the experimental data of NSK carbons with a reasonable accuracy.

References

1. Valenzuela, D.P. and Myers, A.L., *in Adsorption Equilibrium Data Handbook*, Prentice Hall, New Jersey, 1989.
2. Ahmadpour, A. and Do, D.D., submitted for *Carbon*.
3. Nguyen, C., Ahmadpour, A. and Do, D.D., *Adsorption Sci. Tech.*, 1995, 12, 247.
4. Ahmadpour, A. and Do, D.D., *Carbon*, 1996, 34, 471.
5. Do, D.D. and Do, H.D., *Chem. Eng. Sci.*, 1997, 52, 297.
6. O'Brien, J.A. and Myers, A.L, *Ind. Eng. Chem. Process Des. Dev.* 1985, 24, 1188.
7. Hu, X. and Do, D.D., *in Fundamental of Adsorption*, 1996, 385.
   Otowa, T., Nojima, Y.and Itoh, M., *in Fundamentals of Adsorption*, edited by LeVan, M.D., Kluwer Academic Publishers, Boston, 1996, 709.