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BOOK OF ABSTRACTS

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Cryogenic fixed-bed adsorption for H_2 recovery from natural gas grids

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In this work, a novel fixed-bed adsorption apparatus developed to carry out adsorption breakthrough curve experiments at cryogenic temperatures (between 195.15 and 273.15 K) and high pressures (up to 12 bar) was validated to screen candidate adsorbents for dynamic separation of H_2 from natural gas grids. To validate the apparatus, breakthrough curve experiments of CH_4 and H_2, and their mixtures on binder-free zeolite 13X were performed. The equilibrium data obtained were fitted with the viral, dual-site Langmuir, and Langmuir isotherm models. Moreover, the equilibrium data and the isosteric heat of adsorption were compared with the data available in the literature obtained by microcalorimetric, gravimetric, and volumetric methods. Additionally, binary experiments were performed and simulated by using Aspen Adsorption to evaluate the deviation of ideality due to the extreme experimental conditions.

Introduction

Green hydrogen produced from renewable energy can be a key to keeping global warming below 2°C in the coming 30 years. A recent forecast indicated an investment of $500 billion through 2030 to accelerate the green hydrogen deployment [1]. One of the challenges facing green hydrogen valorization is the cost associated with its transportation. A more economical way to transport the produced green hydrogen is to inject it into the natural gas grid. In this view, natural gas/hydrogen separation technology needs to be developed to provide hydrogen and natural gas with sufficient purity to be consumed. The present work seeks to study the dynamic separation of green hydrogen blended into natural gas grids in a range mixture of H_2/CH_4:20/80 vol. % at high pressures and low temperatures. In this way, we report here the validation of a novel fixed-bed adsorption apparatus that was developed to carry out adsorption breakthrough curve experiments at cryogenic temperatures.

Results and Conclusions

The pure adsorption experiments of CH_4 and H_2 on binder-free zeolite 13X were performed at three temperatures (195.15, 233.15, and 273.15 K) and pressures up to 12 bar. The maximum loading obtained for CH_4 and H_2 at 195.15 K and 12 bar was 6.95 and 2.08 mol kg^{-1}, respectively, which represents a selectivity of 3.34 in this condition. For data validation, the Virial isotherm model was fitted to the CH_4 equilibrium data. From that, the isosteric heat of adsorption at a zero coverage ($-\Delta H_{st}\,|_{n=0}$), was approximately 18.97 kJ mol^{-1}. This value is within the range of the

reported values in the literature: 18.80 [2], 17.6 [3], 19.1 [4], 19.2 [5], and 25.7 kJ mol^{-1} [6]. Additionally, the isosteric heat of adsorption as a function of the coverage is shown in Fig. 1a. It can be seen that the overall behavior of the isosteric heat is similar to the ones predicted by Llno-Restrepo [5], Maurin et al. [4], and Moreira et al. [6]. The analysis of isosteric heat of adsorption pointed out that the data obtained from the novel apparatus is thermodynamic consistent and agrees with the literature. As the range of temperature and pressure explored in this work is extreme, there is a need to evaluate the deviation of ideality. For this, a simulation of binary breakthrough curves was performed by considering two equations of the state, namely the ideal gas law and the Peng-Robinson through Aspen Adsorption. The experimental conditions were 195.15 K, 12 bar, and a mixture of H_2/CH_4 (20/80 vol. %). Fig. 1b shows the comparison between simulation using ideal gas law and the Peng Robinson models. As we can see, the results are practically the same which indicates that the ideal gas law is valid for this set of experiments. Additionally, the simulation results agree very well with the experimental data. In conclusion, the experimental unit developed to carry out adsorption breakthrough curve experiments at cryogenic temperatures provides consistent experimental data and will be used in future work to screen adsorbents targeting the dynamic separation of H_2 from natural gas grids.

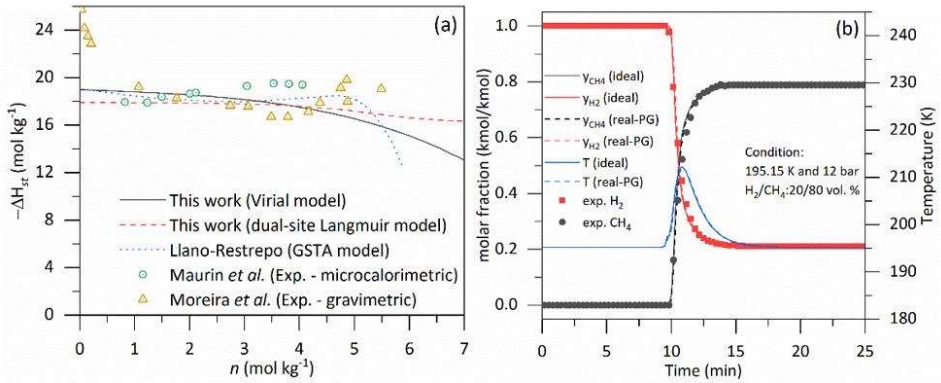

Figure 1 - (a) Isosteric heat of adsorption of CH_4 on binder-free zeolite 13X; (b) breakthrough curves for a mixture ratio of H_2/CH_4 (20/80 vol %) on binder-free zeolite 13X – deviation of ideality analysis.

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