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journal homepage: www.elsevier.com/locate/seppurAdsorption equilibria and kinetics of CO₂, CO, and N₂ on carbon molecular sieveYongha Park^{a,b}, Dong-Kyu Moon^a, Dooyong Park^a, Masoud Mofarahi^{a,c}, Chang-Ha Lee^{a,b,*}^a Department of Chemical and Biomolecular Engineering, Yonsei University, Seoul, Republic of Korea^b Next-Generation Converged Energy Material Research Center, Seoul, Republic of Korea^c Department of Chemical Engineering, Faculty of Petroleum, Gas and Petrochemical Engineering, Persian Gulf University, Bushehr, Iran

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ABSTRACT

Adsorption equilibria and kinetics of CO₂, CO, and N₂ on carbon molecular sieves (CMSs) were measured by a gravimetric method at temperatures of 298, 308, and 318 K and pressures up to 10 bar. The validity of the experimental isotherms and kinetics was confirmed by comparing with experimental results from an additional volumetric method. Experimental adsorption isotherms were well correlated with a temperature-dependent Sips model and the results were compared with the Langmuir and Sips models. The order of the adsorbed amounts and isosteric heats of adsorption were CO₂ > CO ≥ N₂ and their heats of adsorption changed from vertical interactions to lateral interactions with an increase in loading amount. The adsorbed amounts and heats of adsorption were lower for the CMSs than those of activated carbon, which has higher surface area and pore size. The microporous diffusional time constants (D_{μ}/r^2) of CO and N₂ could be obtained from an isothermal kinetic model, while a non-isothermal kinetic model was required for CO₂ due to its higher heat of adsorption and adsorption rate. In addition, the variation in D_{μ}/r^2 with surface coverage were well correlated by the Darken relation combined with Sips isotherm model, and a steep variation was observed from a surface coverage of 0.2 in all the components. The adsorption rate was highly affected by the electrical properties of the adsorbate rather than kinetic diameters. The order of adsorption rate was CO₂ >> CO > N₂, while the order of the activation energies in the Arrhenius equation was opposite. The validity of obtained equilibria and kinetics results was confirmed by comparing the experimental breakthrough curves and dynamic simulation results in a CMS bed.

1. Introduction

Hydrogen is widely used in many important applications in the chemical industry, such as in petroleum refineries and methanol and ammonia production [1,2]. Additionally, hydrogen is considered one of the most important energy sources for the future. The main applications of H₂ for energy generation are the combustion of H₂ and fuel cells for power generation and transportation [3,4]. Various effluent gases, such as the gases in coke ovens, blast furnaces, catalytic reforming, synthesis, and the water gas shift reaction, consist of a combination of CO₂, CO, N₂, and H₂ after pretreatment processes like particle removal, sour gas removal, sulfur removal/recovery, and/or drying [5,6]. Therefore, effective separation processes are required to produce H₂ from mixtures.

One of the representative reactions to produce H₂ is the water gas shift reaction (WGSR), especially because feeds contain H₂ and CO simultaneously [3]. Effluent gases from the WGSR are produced under pressurized conditions with high concentrations of CO₂ and H₂. Even though most of the CO can be converted to CO₂ in the WGSR [7], CO removal from the

product is critical for applications requiring high purity H₂ [8].

Adsorption technologies have been widely applied for gas separation in various industries. Due to their inherently low energy consumption, pressure (vacuum) swing adsorption (P(V)SA) processes are continuously being developed for methane separation, CO₂ capture, olefin-paraffin separation, and H₂ purification [9–11]. The development of PSA processes was widely studied for H₂ recovery from various feeds primarily containing CO₂, CO and N₂ [4,12,13]. The operating pressure of a PSA process highly depends on effluent gas pressure because compression of H₂-containing gas requires high energy consumption and has an explosive gas safety issue. Generally, H₂ PSA processes for coke oven gas and melting incinerator gas [8,13,14] are generally operated at less than 10 bar while those for water gas shift reactor, steam reformer, and refinery off-gas [2,15,16] are typically designed at less than 20 bar. Recently, the PSA process was reported to produce the ultrapure hydrogen from high pressure (35 bar) syngas of an integrated gasification combined cycle (IGCC) plant because the effluent gas is produced at 30–35 bar after sour gas removal and CO₂ capture [4,10,12]. Therefore,

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