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Competitive adsorption of $CO_2/N_2/CH_4$ onto coal vitrinite macromolecular: Effects of electrostatic interactions and oxygen functionalities

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ABSTRACT

Here, the influences of oxygen functional groups (OFGs, −C═O, −C−O−C−, −C═O, and −COOH) and the effects of electrostatic on the binarily competitive adsorption of $CO_2/CH_4/N_2$ onto the coal vitrinite molecular model (CVMM) were systematically investigated through the giant canonical Monte Carlo (GCMC) and density functional theory including dispersion correction (DFT-D3) method. The absolute adsorption amounts of the origin CVMM (Ori-CVMM), carbonized CVMM (C-CVMM), and functionalized CVMMs follow the sequence of OH-CVMM > COOH-CVMM > Ori-CVMM > C2O-CVMM > CO-CVMM > C-CVMM for CO_2 and N_2 and OH-CVMM > CO-CVMM > C2O-CVMM > Ori-CVMM > C-CVMM > COOH-CVMM for CH_4. The increasing microporous heterogeneity and binding sites and affinity induced from the OFGs interact more favorably with CO_2 than CH_4 due to the stronger quadrupole moment and polarizability of CO_2, leaving a much more disadvantageous environment for CH_4 adsorption. The inclusion of the OFGs can significantly enhance the selectivity of CO_2 over CH_4 ($S_{CO2/CH4}$), following the sequence of COOH-CVMM > OH-CVMM > Ori-CVMM > C2O-CVMM > CO-CVMM > C-CVMM. The electrostatic interactions are advantageous to the adsorption for CO_2 and N_2 but disadvantageous for CH_4 adsorption. Both the electrostatic contributions (ECs) for $S_{CO2/CH4}$ and $S_{CH4/N2}$ decrease with the increasing pressure when pressure < 6 MPa and then keep stable during 6–10 MPa. The electrostatic interactions induced from the carbon skeleton framework are significantly weaker than the Ori-CVMM and the functionalized CVMMs and is insensitive to the pressure. The inclusion of OFGs enhances the accessible surface area and enlarges the microporous spaces and diameters, especially for the carboxylation and carboxylation functionalized CVMMs, creating a more favorable microporous surrounding for adsorption. The adsorption energy (ΔEs) of pure CO_2, CH_4, and N_2 are −31.69 to −67.61 kcal/mol, −29.43 to −46.83 kcal/mol, and −14.57 to −29.74 kcal/mol respectively, indicating that the CO_2 interacts with the CVMM surfaces more strongly than CH_4 and N_2.

1. Introduction

Anthropogenic greenhouse gas (GHG) emissions and their impact on the global climate represent one of the defining environmental issues facing modern society [1,2]. Of particular concern is the emission of CO_2, which is the largest contributor (responsible for about 64%) [3] to climate change effects [4–7]. Indeed, more than 30 billion tons of CO_2 are added to the atmosphere each year [7,8]. Therefore, CO_2 removal has been an urgent problem all over the world. Efficient methods to CO_2 capture, utilization, and sequestration (CCUS) have been of increasing interest [9–12]. Existing carbon capture technologies that adopt oxy-fuel combustion, pre-combustion, or post-combustion approaches are highly energy- intensive, leading to decreased power generation efficiency and increased costs [13]. In recent years, coal bed methane (CBM), as also known as coal seam gas (CSG), coal seam methane (CSM), and coal seam natural gas (CSNG), is becoming an available and effective clean energy source [1]. Enhanced coal bed methane (ECBM) recovery involving the injection of CO_2 into the deep coal seams to enhance methane desorption has been found to have dual advantages [5,6,14] of not only enhancing the safety and yields of the co-mining project and CBM but also effectively reducing greenhouse gas emissions by trapping CO_2 [4,15]. In addition, another alternative method to enhance the CBM recovery is to inject the N_2 into coal seams, which can efficiently reduce the partial pressure of CH_4 in the adsorption equilibrium conditions and ultimately promote the CH_4 desorption from the surfaces of the micro- and meso-pores in coal [16]. There exists

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competitive adsorption between CO_2 and CH_4 and N_2 and CH_4 during the CO_2-ECBM and N_2-ECBM engineering respectively [17–20].

Thus, the in-depth understanding of adsorption behavior of CH_4, CO_2, and N_2 in coals is essential to evaluate the viability of an ECBM recovery operation [1,8,21,22]. Pure gas adsorption data are required to estimate the gas capacity of the coal, while the information of competitive adsorption of these gases is a prerequisite to describe the dynamics in the coal seam [23–26]. Coal is a highly complex organic polymer [27,28] composed of various functional groups and a combination of aliphatic and aromatic compounds [29]. There exist distinct differences in adsorption affinities of CO_2, CH_4, and N_2 absorbing at different functional groups due to their various properties in polarities, basicity, and acidic [19,20,29]. Investigations on the competitive adsorption properties and the effects of the functional groups on adsorption selectivity of CO_2 and N_2 over CH_4 is of broad interest in CBM and CCS engineering. Molecular simulations for the microscopic adsorption mechanisms of small gaseous molecules on the stacked graphene sheets [30–35], a high-surface-area activated carbon [36,37], pristine mesoporous carbons, carbon nanotubes, and nanoporous models modified with hydrophilic carboxylic groups [38–40], as well as a realistic molecular model of coal has been widely prevalent in recent years [18–22,29,32,41–44]. The pore size distribution and the surface functionalization are the dominant factors determining the gas adsorption mechanism in coals [18,19,42,45,46]. By density functional theory (DFT) and grand canonical Monte Carlo (GCMC) simulation, Liu et al., investigated the adsorption affinity of CH_4, CO_2 and N_2 molecules onto the heterogeneous surface models of coal (HSMC, mimicked by Gr surfaces with different arrangements of C^*) and proposed that CO_2 preferentially adsorbs at importantly greater loadings than CH_4 and N_2, whereas CH_4 is more preferentially adsorbed than N_2 on HSMC [17]. Zhang et al., explored the CO_2−CH_4 competitive adsorption and induced coal swelling and discovered that CO_2/CH_4 adsorption selectivity decreases with increasing concentration of CO_2 based on an intermediate-rank bituminous coal building block of 191 atoms, $C_{100}H_{82}O_5N_2S_2$ and MC method [47]. Xiang et al., reported that CH_4 molecules displayed an aggregated distribution in the pores, whereas CO_2 molecules were cross arranged in pairs when competitively absorbing on Yanzhou coal model ($C_{222}H_{185}N_3O_{17}S_5$) [42]. Zhao et al., determined the selective adsorption of CO_2−CH_4 onto the Wiser model and proposed that the absolute adsorption amount of each species in the binary mixture decreases as temperature increases, but increases as its own bulk mole fraction increases [1]. Hu et al., evaluated the small-molecule (CO_2 and CH_4) gas sorption onto the Wiser model and proposed that sorption heat of CO_2 was larger than that of CH_4 (7.9 and 5.8 kcal/mol respectively), accounting for the fact that the CH_4 adsorbed in the coal seam could be replaced by CO_2 [22,33]. Lu et al., discussed the adsorption selectivity of CO_2 and N_2 over CH_4 onto the different adsorbent surfaces of the carbon nanoporous adsorbents under a wide range of temperature and pressure and the results show that foam structures have the highest adsorption capacity of all the pristine structures studied because of its special architecture [48]. Yu et al., investigated the competitive adsorption of $CH_4/CO_2/H_2O$ on low rank coal vitrinite ($C_{214}H_{180}O_{24}N_2$) and reported that that high temperature is not conducive to the vitrinite's adsorption for adsorbates and the adsorption capacity order is H_2O > CO_2 > CH_4 (263–363 K) in the one-component, binary, and ternary adsorbate systems [21,22]. Song et al., calculated the saturated adsorption capacity of CH_4, CO_2, and N_2 in low-rank coal and proposed that the adsorption of vitrinite reaches the saturation state after absorbing 17 CH_4, 22 CO_2 and 7 N_2 per vitrinite macromolecule respectively, indicating that the adsorption ability order manifests as [CO_2] > [CH_4] > [N_2]. Furthermore, the energy of non-covalent bond energy (E_{Non}s) were −200.32, −281.45, and −77.48 kcal/mol for vitrinite-CH_4, vitrinite-CO_2, and vitrinite-N_2 respectively [25].

Furthermore, as coal is a polymeric material with complicated heterogeneous structures, another crucial issue for the separation or purification of CBM in coals respects to the effect of the coal structure [21,22,25,49] due to a wide range of aliphatic hydrocarbons, polynuclear aromatic, microcrystalline graphite sheet and functional groups in the coal macromolecular structures [50,51]. Bastos et al., established the relationship between surface characteristics and methane adsorption capacity by adsorption isotherms and XPS, also indicating that hydrophobicity is a significant factor in determining the methane adsorption properties for the adsorbent, i.e., the coal samples with slightly more hydrophobic surfaces had superior methane adsorption properties as compared to less hydrophobic samples with more favorable [36]. Joubert et al., conducted the experiments of methane sorption in bituminous coals ranging from low-volatile to high-volatile B and the results indicated that capacities of high-oxygen coals undergo a much greater reduction when saturated with moisture than do low-oxygen coals [52]. Hao et al., investigated the effects of the surface oxygen groups on methane adsorption on coals and discovered that coal with a higher amount of oxygen surface groups, and consequently with a less hydrophobic character, had lower methane adsorption capacity utilizing the bituminous coal was modified with H_2O_2, $(NH_4)_2S_2O_8$ and HNO_3 [53]. Gensterblum et al., proposed that the oxygen-containing functional groups represent the primary sorption sites for which CO_2 or CH_4 compete with water molecules based on the conceptual molecular model and experimental evidences of competitive adsorption of H_2O, CO_2, and CH_4 on organic materials [54]. Based on the molecular dynamics (MD) and GCMC methods, Yu et al., established that the optimal adsorption location of oxygen function groups for CH_4 follows the order carbonyl (−C═O) > carboxyl (−COOH) > ether (−C−O−C−), while for CO_2 it manifests as −COOH > −C−O−C− ≈ −C═O based on the adsorption energy results [21,29]. Dang et al., reported that the basicity of the oxygen- and nitrogen-containing groups has a large influence on the CO_2 adsorption, while for the sulfur functional groups the determining factor is the polarity [19]. Using the GCMC method, Xiang et al., confirmed that the levels of the main RDF (radial distribution function) peaks, in descending order, were hydroxyl group (−OH) (1.70) > −C═O (1.50) > −COOH (1.33) for CO_2 and −COOH (1.87) > −OH (1.64) > −C═O (1.42) for CH_4 [42]. Fu and Yu proposed that the stability order of CH_4 absorbed onto coal vitrinite with CO_2 at the different functional groups manifests as aromatic > pyridine > pyrrole > carboxyl while that of the CO_2 absorbed onto coal vitrinite with CH_4 at the different functional groups manifests as [aromatic] > [−COOH] > [pyridine] > [pyrrole] based on the density functional theory including dispersion correction (DFT-D3) results [26]. Thus, as mentioned above, the functional groups act as primary (high energetic) sorption sites on coal heterogeneous surface for the small gaseous adsorbates. Although Liu et al. has proposed that the high density oxygen containing, pyridine, and thiophene functional groups are energetically favorable for CO_2 adsorption with the sequence of −C−O−C− > pyridine-N > −C═O > −OH > thiophene−S > −COOH, whereas they has less influence on CH_4 adsorption [19]. Liu et al., investigated the effects of oxygen-containing surface functionalities on the adsorption of mixtures including CO_2/CH_4, CO_2/N_2, and CO_2/H_2O and discovered that the oxygen-containing functionalized surfaces not only increase the total adsorption of CO_2, but also enhance the separation selectivity of a given gas mixture [55,56]. However, there are still many doubts about the effectiveness of the oxygen-containing functional groups for CO_2/CH_4 adsorption, as well as the internal mechanisms. Additionally, there exists significant challenge to distinguish the improvement effects coming from other heteroatoms N-, and S-containing functionalities.

Here, the effects and internal mechanisms of oxygen- (−C═O, −C−O−C−, −C═O, and −COOH) functional groups (OFGs) on the adsorption selectivity of CO_2 and N_2 over CH_4 were systematically investigated based on the modified highly heterogeneous coal vitrinite macromolecular model (CVMM) with plenty of side aliphatic chains and functional groups built in our previous work. The plane CVMM was first geometrically and energetically optimized through the molecular