Computational Investigation on CO₂ Adsorption in Titanium Carbide-Derived Carbons with Residual Titanium

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Abstract

We develop a new approach for modeling titanium carbide derived-carbon (TiC-CDC) systems with residual titanium by the generation of modified atomistic structures based on a silicon carbide derived-carbon (SiC-CDC) model and the application of weighted combinations of these structures. In our approach, the original SiC-CDC structure is modified by (i) removing carbon, (ii) adding carbon and (iii) adding titanium. The new atomic scale carbide-derived carbon (CDC) structures are investigated using classical molecular dynamics simulations, and their pure CO₂ adsorption isotherms are calculated using grand canonical Monte Carlo simulations. The system of TiC-CDC with residual titanium is modeled as weighted combinations of pure carbon CDC structures, CDC structures with titanium and a TiC crystalline structure. Our modeling is able to produce both

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structural properties and adsorption isotherms in accordance with experimental data. The fraction of different models in the systems successfully reflects the structural differences in various experimental TiC-CDC samples. The modeling also suggests that in partially etched TiC-CDC systems, the titanium that may be accessible to CO₂ gas at the transitional interface may provide significant interaction sites for CO₂ and may lead to more efficient overall gas adsorption.

1. Introduction

Carbide-derived carbons (CDCs) form a family of porous carbon materials derived from carbide precursors that are transformed into pure carbon via physical or chemical processes. They range from extremely disordered to highly ordered structures. The carbon structure that results from removal of the metal or metalloid atoms from the carbide depends on the synthesis method, applied temperature, pressure, and choice of carbide precursors.^[1] Most studies of CDCs to date focused on fully etched samples for tribological coatings,^[2] gas storage,^[3] catalyst supports^[4] and electrical energy applications.^[5] Fully etched CDCs were also investigated for gas adsorption applications^[6,7].

Metal impregnated carbons were widely investigated for gas adsorption, and the results indicated that the presence of metal sites in these carbons resulted in stronger adsorbate-adsorbent interactions.^[8,9] Examples of this observation include the study of hydrogen storage in carbon-based nanostructures with transition-metals^[10,11] and in graphene with adsorbed metal atoms.^[12,13] An incomplete etching of carbide precursors in experiments leads to CDCs with residual metal within the material that may provide potentially strong interaction sites. Iron carbide derived-carbon with residual iron nanoparticles has been experimentally investigated^[14] and these nanoparticles were found to interact strongly with adsorbed ammonia^[15]. However, it is still unclear where the residual metal resides within most CDC structures and how they interact with adsorbed gases. A focused investigation of the effect of CDC structures with residual metal is thus warranted.

In parallel with experimental studies, atomistic modeling and theoretical characterization of porous structures have undergone recent significant advances. Theoretical investigations were able to provide vital insights into the topology and morphology of carbon structures at microscopic scales that are usually unavailable directly from experiments.^[16] Atomistic simulation methods are powerful tools in investigating the structural and thermodynamic properties of porous materials. These methods are capable of generating morphologically realistic models for partially crystalline and amorphous carbons and can be used to study their microporous structures. Building atomistic models of porous carbons such as CDCs is complex, but attempts have been made to model fully etched CDCs using hybrid reverse Monte Carlo (HRMC)^[16] and quenched molecular dynamics (QMD)^[17]. These models are able to capture structural properties of CDCs with no residual metal. However, to our knowledge no previous studies report the modeling of CDCs with residual metal due to the complexity of these systems. In this paper we report a new approach for modeling CDCs with

residual metal, with a focus on TiC-derived carbons (TiC-CDC) with residual titanium.

An experimental investigation of TiC-CDC was carried out by Dutzer et al.^[18]. In these experiments, TiC-CDC samples with different residual titanium loadings were prepared by chlorination of titanium carbide using three types of reactors, a horizontal-bed reactor, a packed-bed reactor, and a fluidized-bed reactor, characterized by the way which the chlorine gas contacted the carbide precursor. In each case, the amount of residual titanium was controlled by varying the etching time, and the pore volumes and surface areas of resulting samples were analyzed. Comparisons with the results from these experiments are used below to validate and interpret our models of TiC-CDCs.

In this study, a SiC-CDC model generated by HRMC^[16] was used as the original structural model. For the modeling of TiC-CDC structures, we modified this original model and generated new structures in three ways: (i) removing certain carbon atoms from the original structure, (ii) adding extra carbons to the original structure, and (iii) adding Ti atoms or small Ti clusters to the original structure. All these structures were relaxed using classical molecular dynamics (MD) simulations; dangling bonds associated with carbon atoms in the structures were removed during MD simulations. A newly developed Ti-C charge optimized many-body (COMB3) potential was used to obtain the atomic forces in all the MD simulations.^[19] This potential has been shown to accurately describe the interactions between Ti and graphene^{*}. It also reproduced polarization and changes in the charge carried by the atoms as their bonding environment changes.^[19]

The resulting structures obtained from the MD simulations were used as the candidate structural models for further study. In particular, structural information such as accessible surface areas, total pore volumes and residual metal loadings of these structures was determined. Grand Canonical Monte Carlo (GCMC) simulations were then applied to generate the CO₂ adsorption isotherms of these structures. By fitting calculated and experimental structural properties, a weighted combination approach was applied to structural properties and adsorption isotherms of candidate models to effectively model CDCs with various residual titanium loadings. Using this approach, adsorption behaviors were predicted from our structures and compared to corresponding experimental adsorption isotherms. Those combinations, which produced both structural properties and adsorption isotherms in agreement with experimental results, provide important insights into the way in which

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residual titanium within the CDCs influences structural composition and gas adsorption.

2. Experimental Method

The full details for the design of experimental reactors can be found elsewhere^[18]. The experimental carbon dioxide (Airgas, Bone Dry Grade) isotherms used in this work were measured using a lab-built volumetric system. Approximately 30 mg of sample were outgassed under dynamic vacuum at 150°C for approximately 16 h. Adsorption isotherms were measured at 25°C for pressures ranging from 0 to approximately 5.0 bar. CO₂ adsorption loadings were determined by measuring and converting the pressure drop in the sample cell to moles using the Peng-Robinson equation of state.

3. Computational Details

3.1 Classical Molecular Dynamics Simulations

As discussed in Section 1, classical MD simulations were employed to investigate atomistic models in this work. All MD simulations were carried out using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), an open source MD code made available by Sandia National Laboratory.^[20] The structures modeled in these simulations consisted of TiC, pure carbon CDCs, and CDCs with residual titanium, containing 2000-4000 atoms each. A newly developed COMB3 potential for Ti-C systems^[19] was used to determine the energies and forces on the atoms in the MD simulations. The COMB3 potential is a variable charge, reactive interatomic empirical potential where the total energy of the system is expressed as a sum of electrostatic energy (U^{es}), charge dependent short-range interactions (U^{short}), van der Waals interactions (U^{vdW}), and correction terms (U^{corr}) as shown in Eq. (1). Here $\{q\}$ and $\{r\}$ refer to the charge and coordinates of the atoms in the system, respectively. More details of the COMB3 potential and the parameters for the Ti-C system can be found elsewhere.^[19,21]

$$U^{total}[\{q\}, \{r\}] = U^{es}[\{q\}, \{r\}] + U^{short}[\{q\}, \{r\}] + U^{vdW}[\{r\}] + U^{corr}[\{r\}] \quad (1)$$

The COMB3 potential is able to capture carbon-titanium interactions in bulk TiC and where Ti atoms and clusters are interacting with sp²- and sp³-hybridized carbon structures.^[19] This potential has also been shown to accurately describe the interactions between Ti and graphene*. Importantly, the potential is able to reproduce polarization and changes in the charge carried by the atoms as their

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bonding environment changes.^[19]

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3.2 Modified Structures of CDC Systems

All the structures considered in this work were built from a CDC atomistic model generated by HRMC simulations for SiC-derived carbons, the full details of which could be found elsewhere.^[16] This model used a 4 nm cubic supercell containing 3052 carbon atoms. This original structure was modified to generate three types of new structures. The first type, denoted *type-1* models, were created by generating pores of various diameters through the removal of atoms at different locations. Typically 100-500 carbon atoms were removed from the original model. The second type of structures, denoted as *type-2* models, were generated by adding clusters of carbon to the pores of the original model. Typically 1-12 clusters containing 50-500 new carbon atoms were added to the original structure. Although sp^2 -hybridized carbons were found to be dominant in experimental CDCs samples, there was still a small population of sp^3 -hybridized carbon. Thus several carbon clusters were derived from a diamond-like carbon (DLC) structure and added to the original SiC-CDC structural model in order to tune the overall percentage of sp^3 -hybridized carbons within a small range. The third type of structures, denoted as *type-3* models, were generated by adding various amounts of titanium atoms or small Ti clusters to the pores of original structure. The total number of added titanium atoms ranged from 10 to 1500. In particular, we considered Ti_7 , Ti_{13} , and Ti_{15} , the sizes and shapes of which were taken from magic clusters investigated with DFT calculations.^[22,23] In addition to these modified CDC structures, we also considered a rocksalt structure of crystalline TiC during our modeling since titanium carbide was the precursor used in the experiments and some TiC was found to remain in several experimental CDC samples^[18]. This TiC model was built in an approximately 3.9 nm cubic supercell containing 2916 carbon and 2916 titanium atoms, which is similar to the supercell dimensions of the original CDC models. Full details for generation of these models are given in supplementary materials.

All structures were allowed to evolve in MD simulations after the manual removal of under coordinated carbon atoms with dangling bonds. A cutoff of 2.0 Å was used to calculate the neighbor list of carbon atoms, and carbon atoms without a neighbor in this size range were considered to have a dangling bond. A Nosé-Hoover barostat and a Langevin thermostat were applied to control the pressure and temperature of systems, respectively, and the pressure and temperature within the simulations were set to 0 Pa and 300 K, respectively. The timestep used in simulations was 0.2 fs and the simulations ran for 100 ps or until the energies of the systems fluctuated slightly about a constant

value. Accessible surface areas, pore volumes and pore size distributions of the final, relaxed structures were calculated using the algorithm of Sarkisov and Harrison (Poreblazer)^[24].

3.3 Grand Canonical Monte Carlo Simulations

The GCMC simulations were employed to calculate the adsorption isotherms of pure CO₂ gas of all candidate structures. Due to the relatively large size of these structures, only a 1×1×1 unit cell was considered in the simulation box and periodic boundary conditions (PBC) were considered in all directions. At least 10 million trials were used in the GCMC simulations. Among these trials, the first half was used for system equilibration and the second half was used to calculate average properties. The temperature in all GCMC simulations was 298 K. Four types of moves with equal probability were included: insertion, deletion, translation and rotation of gas molecules. The charges of individual atoms in the CDC models were taken from the final structures of the MD simulations. In addition, CO₂ was modeled as a linear molecule with charges on each atom, and these molecules were kept rigid during the GCMC simulations. All pair-wise interactions in the GCMC simulations were described with Lennard-Jones (LJ) dispersion and repulsion terms, and the LJ force field parameters and charges are provided in Table 1. Lorentz-Berthelot (LB) mixing rules were employed to calculate the adsorbate/adsorbate and adsorbate/adsorbent parameters. All GCMC simulations were carried out using the Multipurpose Simulation Code^[25].

Table 1. LJ and charge parameters used in the GCMC simulations

Component	Site	$\sigma(\text{nm})$	$\varepsilon/k_b(\text{K})$	$q(\text{e})$	Angle($^\circ$)	Bond length(nm)	Ref.
CO ₂	C	0.280	27.0	+0.7	180	0.1162	26
	O	0.305	79.0	-0.35			
TiC-CDC	Ti	0.2830	8.555				27
	C (sp ³)	0.34	43.0				28
	C (sp ² , sp)	0.34	28.0				29

4. Results

4.1 Modified CDC Atomistic Models

The original CDC structure used in this work was developed for SiC-CDC systems and reproduced structural properties of pure carbon SiC-CDC.^[16] This model was used in this work due to the absence of validated TiC-CDC atomic-scale models, the difficulty associated with generating new disordered porous carbon models, and the fact that modification of a similar structure is a time-efficient approach to producing TiC-CDC structures. It has been established that etching different carbide precursors results in CDCs with diverse pore structures, so TiC-CDC will not necessarily have the same structure as SiC-CDC. However, the pore structures of TiC-CDCs and SiC-CDCs have been found to be similar in experimentally characterized samples^[30,31] and given the nanometer-scale size of the atomistic structural models considered in this work, the porous nature of TiC-CDCs should be captured using structures similar to this SiC-CDC model. The SiC-CDC model was therefore used as a starting point to generate additional porous carbon structural models for TiC-CDC materials. Specifically, the densities, total pore volumes and accessible surface areas of the structures were controlled by adding or removing carbon atoms. While the resulting structural models may not be exact reproductions of the structures of TiC-CDC, we expect that they should do a good job of capturing the porous character of TiC-CDC. The addition of titanium atoms and clusters not only affected the structural properties of CDCs in a similar manner, it also controlled the titanium loading of the structural models. Calculated pore volumes and surface areas of different models are illustrated in Fig. 1, and snapshots of representative models and clusters used in this work are provided in Fig. 2.

Figure 1: Calculated accessible surface area, total pore volume and density for different types of

modified models.

Figure 2: Snapshots of models and clusters used in this work. (a) The original SiC-CDC model; (b) a *type-1* model; (c) a *type-2* model; (d) a *type-3* model; (e) a carbon cluster; (f) a Ti₇ cluster; (g) a Ti₁₃ cluster; and (h) a Ti₁₅ cluster. Carbon-carbon bonds are black, titanium atoms and titanium-titanium bonds are red, and carbon-titanium bonds are hidden for clarity.

During the relaxation of *type-3* models (CDC structures with titanium) in the MD simulations, the Ti atoms and clusters that were initially added to the pores of the original CDC structure moved through pores or to the walls of pores to form new Ti-C bonds. These new Ti-C bonds were stable

during the time scale of our simulations. Some Ti atoms also formed small agglomerates of pure titanium. In some instances, these agglomerates connected otherwise unconnected carbon walls but this was not predicted to change the local porous character of the CDC structures, as illustrated in Fig. 3a. However, some of these Ti atoms or groups did dramatically alter the local structure so that the amount of sp^2 -hybridized carbon was reduced, as shown in Fig. 3b. Such titanium agglomerations in some instances pulled neighboring carbon atoms around them, resulting in the shrinkage of local structures and an overall reduction of porosity. The resulting structures were locally more similar to the carbide form than to a porous carbon network.

Figure 3: Examples of local CDC structures with titanium where the addition of Ti atoms (a) did not alter the local CDC structure and (b) did alter the local CDC structure. Carbon atoms and carbon-carbon bonds are black, titanium atoms and titanium-titanium bonds are red, and carbon-titanium bonds are half-red/half black.

4.2 Comparison of Single Structural Models and Experimental TiC-CDC Samples

In the experiments carried out by Dutzer et al.^[18], three reactor designs were considered. Chlorine gas contacted the TiC precursors in different ways in these reactors, resulting in differing structures of TiC-CDC with residual titanium. In the horizontal-bed reactor, chlorine gas flowed over the TiC and produced samples containing mainly two layers: completely etched TiC-CDC and unreacted TiC. In the packed-bed reactor, chlorine flowed through the carbide precursor and created channels. This resulted in uneven etching so that TiC particles along the channels were the first to become fully etched. In the fluidized-bed reactor, the TiC precursor particles were dispersed based on the density

in the chlorine gas flow. Partially etched samples from this reactor were mainly comprised of core-shell particles, with unreacted TiC cores and fully etched TiC-CDC shells.

In all these reactors, titanium was removed from the system as the chlorine gas etched the TiC precursor until only carbon was left that formed the porous CDC. Since this etching reaction was rapid, the unreacted regions in samples that were untouched by the chlorine gas remained in the form of titanium carbide. Due to the complexity of these systems, it is reasonable to conclude that single atomic-scale structural models would not be able to represent the entire system of a partially etched TiC-CDC sample. Both *type-1* and *type-2* models have diverse surface areas due to the addition and removal of carbon, but they have no titanium in the structures. Thus they are limited to the study of pure carbon CDC structures. In the case of *type-3* models, although they describe systems of CDCs with titanium, their surface areas and pore volumes do not necessarily match these properties within the experimental samples, especially as their porosity decreases with increasing residual titanium loadings. The surface areas of *type-3* models and experimental samples are shown in Fig. 4 as an example.

Figure 4: Comparison of surface area between *type-3* structural models and experimental samples from the indicated reactors.

Hence we assume that a system of TiC-CDC with residual titanium has mainly three regions: a fully etched CDC region, an unreacted TiC region, and an interfacial region between them. These

regions can be represented by the various atomistic structural models discussed above. In this work, the *type-1* and *type-2* models (pure carbon CDC structures without titanium) were used to model the fully etched regions since such regions were found to be pure carbon in experimental observation. The TiC model was used to represent the unreacted titanium carbide regions in the experimental samples. Due to the difficulty of distinguishing the transitional interface from the fully etched regions and unreacted regions without damage in the experiments, it was difficult to experimentally characterize the structures of the interfacial regions. The interfacial region connected a disordered, pure carbon region with a titanium carbide crystalline region, thus this region should both contain titanium species and be structurally disordered. Therefore, the *type-3* models (CDC structures with titanium) were used to model the interfacial regions. Given the large length scale of experimental samples relative to the nanometer scale of our simulation models, the boundaries among these different structural models were neglected.

4.3 Weighted Combinations of GCMC Results

A weighted combination approach was applied to the structures in order to effectively model TiC-CDC systems with different residual titanium loadings. Although including more computational models may allow more precise fitting to experimental data, it also brings unnecessary complexity if too many structures are involved. Thus, we used the TiC model for modeling unreacted carbide regions. We also chose two structures from either the *type-1* or the *type-2* models to represent the fully etched regions in order to maintain structural diversity, and one *type-3* model for the interfacial regions due to their structural similarity. Therefore, for a certain amount of residual titanium, the TiC-CDC system was modeled as a weighted combination of two of *type-1* or *type-2* models, one *type-3* models and the TiC model. Each structural model was part of a database, and we tested every possible combination of these models.

Calculated structural properties of models, including total pore volumes, accessible surface areas and residual metal loadings, were used to fit the weightings in each combination by comparing their combined values to experimental results. The combined values were calculated using Eqs. (2)-(4). Taking into account error and broader searches for solutions, we estimated the target surface area (SA) and pore volume (PV) to have a 10% error range. Each combination of models led to one set of

weightings from these equations. If all weightings were above zero, they were used to calculate the weighted combined CO₂ adsorption using Eq. (5). This adsorption result was then compared to experimental data for the samples with corresponding structural properties to those of the combination of structural models.

$$SA = \frac{S_1 \cdot w_1 + S_2 \cdot w_2 + S_3 \cdot w_3 + S_M \cdot M}{w_1 + w_2 + w_3 + M} \quad (2)$$

$$PV = \frac{P_1 \cdot w_1 + P_2 \cdot w_2 + P_3 \cdot w_3 + P_M \cdot M}{w_1 + w_2 + w_3 + M} \quad (3)$$

$$RM = \frac{R_1 \cdot w_1 + R_2 \cdot w_2 + R_3 \cdot w_3 + R_M \cdot M}{w_1 + w_2 + w_3 + M} \times 100\% \quad (4)$$

$$Adsorption = \frac{A_1 \cdot w_1 + A_2 \cdot w_2 + A_3 \cdot w_3 + A_M \cdot M}{w_1 + w_2 + w_3 + M} \quad (5)$$

In Equations (2)-(5), SA , PV and RM are the surface area (m²/g), pore volume (cc/g) and residual metal percentage (wt%) from experiments. w_1 , w_2 , w_3 and M are the weightings (g) corresponding to the two *type-1* or *type-2* models, *type-3* model and the TiC model, respectively. M is fixed as 1 among them. S_1 , S_2 , S_3 and S_M are the calculated accessible surface areas (m²/g) of the corresponding models. P_1 , P_2 , P_3 and P_M are the free pore volumes (cc/g) of the corresponding models. R_1 , R_2 , R_3 and R_M are the residual metal loadings (wt%) of the corresponding models. A_1 , A_2 , A_3 and A_M are the adsorption (mmol/g) of the corresponding models.

As a result of this approach, certain combinations of models were found to be able to successfully produce both consistent structural properties and CO₂ adsorption isotherms that matched experimental data well. The comparisons of adsorption isotherms, surface areas and pore volumes between experiments and modeling are illustrated in Fig. 5. Although three experimental reactors produced partially etched samples with slightly different structural properties and adsorption isotherms, this approach captured the overall behaviors of samples from all three reactors. The simulated adsorption isotherms match experimental results better at higher residual titanium loadings than for residual titanium below 10 wt%. These combinations of models can thus be used as

representative structures for TiC-CDC systems with different amounts of residual titanium.

Figure 5: Comparison of CO₂ adsorption, surface area and pore volume between combined systems of models and experiments. (a) Horizontal-bed reactor; (b) Packed-bed reactor; (c) Fluidized-bed reactor. (c) Surface areas in the three reactors. (d) Pore volumes in the three reactors. Numbers on the right side in the adsorption isotherm figures indicate residual titanium loadings (wt%).

Due to differences in the etching process, the partially etched samples from the three experimental reactors had dissimilar structures.^[18] In the modeling, this diversity was reflected in the fractions of different types of structural models used in each combination. Since these models represent their own regions as discussed above, their fractions within the weighted combinations replicated the relative amount of their regions in the experimental systems. In particular, the fraction of TiC corresponded to the amount of remaining carbide precursor in the samples. The total fraction of *type-1* and *type-2* models corresponded to the amount of fully etched CDC in the sample as they were all pure carbon structures, and the fraction of *type-3* model corresponded to the amount of interfacial region between fully etched and unreacted regions. These fractions in each system were determined after normalizing by the molar mass of the atoms in the models and the results for all three reactors are illustrated in Fig. 6. The weightings of models in the three reactors were distributed differently as the residual titanium loadings decreased in the corresponding experimental samples. Such differences reflect the way in which these experimental samples were etched and the resulting compositions of the samples from the different reactors.

Figure 6: Comparison of the fractions of different structural models in the samples produced by the three reactors. (a) Fraction of TiC model; (b) total fraction of *type-1* and *type-2* models; (c) fraction of *type-3* models.

Fig. 6a shows the fractions of TiC models, which represents the amount of carbide precursor in experimental samples. The fraction of carbide precursor in the fluidized-bed reactor dropped rapidly as the residual titanium loading started to decrease, whereas the horizontal-bed reactor lost carbide precursor slowly. For a specific residual titanium loading, the fluidized-bed reactor had the lowest fractions of TiC model in the system while the horizontal-bed reactor had the highest amount. These results are in agreement with experiments^[18] that showed that TiC particles in the fluidized-bed

reactor were dispersed in the chlorine gas flow so that the contact between gas and carbide precursor was maximized. This accelerated the etching of the precursor, and TiC was rapidly removed from the system. In contrast, the flow-over horizontal-bed reactor must overcome chlorine diffusion limitations to remove the titanium located farthest away from the gas flow, so that more TiC precursor remained unreacted without the contact of chlorine gas. The flow-through packed-bed reactor created channels to improve the contact between chlorine gas and precursor but only TiC located near the channels were removed without significant gas diffusion limitation; thus its fraction data was between the results of the other two reactors.

The amount of fully etched regions in the samples were represented by the total fractions of *type-1* and *type-2* models as shown in Fig. 6b. In accordance with results of TiC models in Fig. 6a, the highly efficient etching of the TiC precursor in the fluidized-bed reactor resulted in a large amount of fully etched TiC-CDC most rapidly among the three reactors and the horizontal-bed reactor produced fully etched TiC-CDC in the slowest way due to gas diffusion limitations.

Fig. 6c illustrates the fractions of *type-3* models, which indicates the amount of interfacial regions between unreacted TiC and fully etched TiC-CDC in the systems. It was demonstrated in the experiments that the transition from unreacted TiC to fully etched TiC-CDC was rapid^[18]; thus the amount of interface should be low in the partially etched experimental samples. Comparing the fractions in Figs. 6a, 7b and 7c, our models consistently predicted that the fractional amounts of interfacial regions were below 0.35 in all systems and either the TiC precursors or fully etched TiC-CDC particles were predominant in experimental samples. The fractions in the fluidized-bed reactor were higher than those in the other two reactors at high residual titanium loadings. This is in agreement with experimental results that the fluidized-bed reactor produced core-shell particles, with unreacted TiC cores and fully etched TiC-CDC shells, whereas the other two reactors produced uneven etching of particles.^[18] Such core-shell structures are known to maximize the interface between the core and shell.^[32]

In each plot from Fig. 6, when residual titanium loading was small, corresponding to almost fully etched experimental samples, the three reactors have similar results for fractions of atomistic structural models. This finding indicates that, although the etching of samples proceeded in different ways in the three reactors, the fully etched TiC-CDC structures shared similar structures on a

nanometer scale. Ideally, the fully etched TiC-CDCs were pure carbon structures, so the fractions of models with titanium in the system should be near 0% residual titanium loading. In fact, under these loading conditions, the fractions of the TiC model in Fig. 6a were below 0.05, but the fractions of *type-3* models in Fig. 6c were around 0.25-0.3. One possible reason for the non-negligible amount of *type-3* models (CDCs with titanium) is that the TiC precursors were depleted first and the interfacial titanium became the main source of residual titanium. Thus the *type-3* models, which were initially modeling the interfaces, now represent independent regions in the systems. As discussed above, in Fig. 5 the simulated adsorption isotherms match experimental data at low residual titanium loadings less well than at higher metal loadings. This might also indicate that this approach could be less accurate when metal content is low in the systems so that it overestimates the amount of interface at low residual titanium loadings.

Fig. 5 shows that the CO₂ adsorption decreased with increasing residual titanium loadings because of the decline in the surface areas and pore volumes of the structures. This reduction in the porosity of the structures is consistent with the fractions of weightings in Fig. 6. When the titanium loadings became larger, the amount of TiC-CDC decreased while the amount of TiC increased. Since these two regions were predominant in the system, the addition of titanium was mainly the increment of titanium in carbide form. As crystalline TiC is dense without inner pores and its titanium is mostly inaccessible to gas molecules, such addition of titanium would not improve gas adsorption.

The experimental CO₂ adsorption isotherms shown in Fig. 5 reveal overall adsorption within the experimental samples. These results do not reveal the contribution of each part of the sample to the overall adsorption loadings. The simulated adsorption isotherms indicate that the experimental adsorption isotherms in Fig. 5 may be deconstructed into the individual compositions to reveal the adsorption loadings contributed by each part of the system. As only fully etched TiC-CDC and the interfacial region could possibly contribute to the CO₂ adsorption, the contributions of *type-3* models (representing the interfacial region) to the adsorption isotherms at different experimental pressures are illustrated in Fig. 7. The CO₂ gas adsorption in a partially etched TiC-CDC system is shown to be mainly derived from the fully etched TiC-CDC region. Although the calculated contributions of interfacial regions may be exaggerated due to the overestimation of the amounts of *type-3* models, the interfacial region still contributed to the gas adsorption as a result of the existence of porosity and

the accessibility of titanium in its structure. For each residual metal loading, the contribution of interfacial region to CO₂ adsorption increased as the pressures of adsorption decreased in experimental samples from the three reactors. This may also suggest in the partially etched TiC-CDC systems, titanium played more important roles for CO₂ gas adsorption under low pressures.

Figure 7: The contribution of *type-3* models to the overall adsorption isotherms of systems at different pressures in the three reactors. (a) Horizontal-bed reactor; (b) Packed-bed reactor; (c) Fluidized-bed reactor.

As a result of the small amount of interfacial region in the samples revealed by Fig. 6, these regions contribute a small portion to the overall adsorption loadings. However, when comparing the

adsorption loadings of different types of models per unit surface area as illustrated in Fig. 8, the simulation results reveal that the interfacial region (*type-3* models) has higher adsorption loadings than the fully etched region (*type-1* and *type-2* models) has per unit surface area. This indicates that the interfacial region is more efficient for the CO₂ gas adsorption than the fully etched CDC region. The possible explanation for this may be that the titanium in the interfacial region is accessible to CO₂ molecules so that it provides additional interacting sites for these molecules at the surface, even if the titanium reduces the overall surface area and the porosity of CDC material. The interfacial regions are thus predicted to behave in manner that is similar to metal-impregnated carbon materials for acid gas uptake.

Figure 8: Comparison of CO₂ adsorption isotherms per unit surface area among the different types of models used in the simulations.

5. Conclusions

We used a SiC-CDC atomistic structure generated by HRMC simulation as the original model of TiC-CDC and constructed several new structures. In particular, the original SiC-CDC model was modified in three ways: (i) removing C atoms, (ii) adding C atoms, and (iii) adding Ti atoms or clusters. These structures were then examined and relaxed using classical MD simulations with a newly developed Ti-C COMB3 potential. Textural properties such as accessible surface areas and total pore volumes were calculated for these structures, and the adsorption isotherms of pure CO₂

were investigated using GCMC simulations.

The predictions of the simulations were compared to experimental data of TiC-CDC with residual titanium that were derived from samples produced by three reactors: a flow-over horizontal-bed reactor, a flow-through packed-bed reactor and a fluidized-bed reactor. A weighted combination of atomic-scale structural models was used for modeling TiC-CDC systems with different residual titanium loadings. For a certain residual titanium loading in TiC-CDCs, the system was modeled as a weighted combination of two CDC models without titanium, one CDC model with titanium and a bulk TiC model. Corresponding to experimental samples, the TiC model was used to model unreacted TiC precursors, the pure carbon CDC models were used to model fully etched regions, and the CDC models with titanium atoms or clusters were proposed in this work to represent interfacial regions between the unreacted and fully etched regions in the systems. The pore volumes, surface areas and residual titanium loadings of computational models were employed to fit the weightings of each model in every combination of models by comparing their calculated combined results to corresponding experimental data. Using these weightings of models, the combined CO₂ adsorption isotherms from simulations were compared to experimental data. Certain combinations were able to produce both structural properties and adsorption isotherms in agreement with corresponding experimental results. The simulation results matched experimental data more accurately as the residual titanium loadings increased in the systems. Furthermore, the fractions of weightings of models were also found to be consistent with different samples produced by three experimental reactors. The low fractions of weightings for interfacial regions also indicated a rapid transition between fully etched TiC-CDCs and unreacted TiC precursors, which is in accordance with experimental results that there was no large transitional phase. However, these transitional regions still contribute a small portion to the CO₂ adsorption of samples and such contributions were higher at low pressures of gas adsorption. This suggests that in partially etched TiC-CDC systems, the titanium that is possibly accessible by CO₂ gas at the interface may provide interaction sites at low CO₂ pressures. Due to the presence of the titanium, the interfacial regions are also found to be more efficient for gas adsorption than fully etched CDCs. These predictions by the simulations are difficult to observe directly in the experiments and the comparison of the simulations and experimental data is a powerful approach to extracting these insights.

Thus this work proposed a new approach for modeling of TiC-CDCs with residual titanium based on weighting the results of different models. The agreement between this approach and experimental results provides insights on the compositions of such CDC systems with various residual metal loadings. It also indicates the applicability of this approach to the study of structural modeling and gas adsorption in other residual metal-based porous structures.

Acknowledgements

This work was supported by UNCAGE-ME, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award #DE-SC0012577. A.F.F. acknowledges grants #2013/10036-2 and #2016/00023-9 from São Paulo Research Foundation (FAPESP) and additional support from the Brazilian Agency CNPq.

References

- [1] V. Presser, M. Heon, Y. Gogotsi, Carbide-Derived Carbons - From Porous Networks to Nanotubes and Graphene, *Adv. Funct. Mater.* 2011; 21:810–833.
- [2] B. Carroll, Y. Gogotsi, A. Kovalchenko, A. Erdemir, M.J. McNallan, Effect of humidity on the tribological properties of carbide-derived carbon (CDC) films on silicon carbide, *Tribol. Lett.* 2003; 15(1):51-55
- [3] M. Oschatz, E. Kockrick, M. Rose, L. Borchardt, N. Klein, I. Senkovska et al., A cubic ordered, mesoporous carbide-derived carbon for gas and energy storage applications, *Carbon* 2010; 48(14):3987-3992
- [4] A. Schlange, A.R. Dos Santos, B. Hasse, B.J.M. Etzold, U. Kunz, T. Turek, Titanium carbide-derived carbon as a novel support for platinum catalysts in direct methanol fuel cell application, *J. Power Sources* 2012; 199:22-28
- [5] P.C. Gao, W.Y. Tsai, B. Daffos, P.L. Taberna, C.R. Pérez, Y. Gogotsi et al., Graphene-like carbide derived carbon for high-power supercapacitors, *Nano Energy* 2015; 12:197-206
- [6] G. Yushin, R. Dash, J. Jagiello, J.E. Fischer, Y. Gogotsi, Carbide-Derived Carbons: Effect of Pore Size on Hydrogen Uptake and Heat of Adsorption. *Adv. Funct. Mater.* 2006; 16:2288–2293
- [7] A. Silvestre-Albero, S. Rico-Francés, F. Rodríguez-Reinoso, A.M. Kern, M. Klumpp, B.J.M. Etzold et al, High selectivity of TiC-CDC for CO₂/N₂ separation, *Carbon* 2013; 59:221-228
- [8] M.P. Cal, B.W. Strickler, A.A. Lizzio, High temperature hydrogen sulfide adsorption on activated carbon: I. Effects of gas composition and metal addition, *Carbon* 2000; 38(13):1757-1765
- [9] K. Sakanishi, Z. Wu, A. Matsumura, I. Saito, T. Hanaoka, T. Minowa et al., Simultaneous removal of H₂S and COS using activated carbons and their supported catalysts, *Catal. Today* 2005; 104(1):94-100
- [10] E. Durgun, S. Ciraci, T. Yildirim, Functionalization of carbon-based nanostructures with light transition-metal atoms for hydrogen storage, *Phys. Rev. B* 2008; 77:085405
- [11] S.A. Shevlin, Z.X. Guo. Density functional theory simulations of complex hydride and carbon-based hydrogen storage materials, *Chem. Soc. Rev.* 2009; 38:211-225
- [12] C. Ataca, E. Aktürk, S. Ciraci, H. Ustunel, High-capacity hydrogen storage by metallized graphene, *Appl. Phys. Lett.* 2008; 93:043123

- [13] Z.M. Ao, F.M. Peeters, High-capacity hydrogen storage in Al-adsorbed graphene, *Phys. Rev. B* 2010; 81:205406
- [14] M.C. Mangarella, J.L. Ewbank, M.R. Dutzer, F.M. Alamgir, K.S. Walton. Synthesis of Embedded Iron Nanoparticles in Fe₃C-Derived Carbons, *Carbon* 2014; 79:74-84
- [15] M.C. Mangarella, K. S. Walton, Tailored Fe₃C-Derived Carbons with Embedded Fe Nanoparticles for Ammonia Adsorption, *Carbon* 2015; 95:208-219
- [16] A.H. Farmahini, G. Opletal, S.K. Bhatia, Structural Modelling of Silicon Carbide-Derived Nanoporous Carbon by Hybrid Reverse Monte Carlo Simulation, *J. Phys. Chem. C* 2013; 117:14081–14094
- [17] J.C. Palmer, A. Llobet, S.-H. Yeon, J.E. Fischer, Y. Shi, Y. Gogotsi et al., Modeling the structural evolution of carbide-derived carbons using quenched molecular dynamics, *Carbon* 2010; 48(4):1116-1123
- [18] M.R. Dutzer, M.C. Mangarella, J.A. Schott, S. Dai, K.S. Walton, The Effects of Reactor Design on Residual Metal in Titanium Carbide-Derived Carbon, *Carbon*, In review.
- [19] T. Liang, M. Ashton, K. Choudhary, D. Zhang, A.F. Fonseca, B. Revard et al., Properties of Ti/TiC Interfaces from Molecular Dynamics Simulations, *J. Phys. Chem. C* 2016; 120:12530-12538
- [20] S. Plimpton, Fast Parallel Algorithms for Short-Range Molecular Dynamics, *J. Comput. Phys.* 1995; 117(1):1-19
- [21] T. Liang, T.R. Shan, Y.T. Cheng, B.D. Devine, M. Noordhoek, Y. Li et al., Classical atomistic simulations of surfaces and heterogeneous interfaces with the charge-optimized many body (COMB) potentials, *Mater. Sci. Eng. R Rep.* 2013; 74(9):255-279
- [22] M. Castro, S.R. Liu, H.J. Zhai, L.S. Wang, Structural and electronic properties of small titanium clusters: A density functional theory and anion photoelectron spectroscopy study, *J. Chem. Phys.* 2003; 118:2116
- [23] M. Salazar-Villanueva, P.H. Hernández Tejeda, U. Pal, J.F. Rivas-Silva, J.I. Rodríguez Mora, and J.A. Ascencio, Stable Ti_n (n= 2-15) Clusters and Their Geometries: DFT Calculations, *J. Phys. Chem. A* 2006; 110:10274-10278
- [24] L. Sarkisov, A. Harrison, Computational structure characterization tools in application to

ordered and disordered porous materials, *Mol. Simul.* 2011; 37:1248-1257

- [25] A. Gupta, S. Chempath, M.J. Sanborn, L.A. Clark, R.Q. Snurr, Object-oriented Programming Paradigms for Molecular Modeling, *Mol. Simul.* 2003; 29(1):29-46
- [26] J.J. Potoff, J.I. Siepmann, Vapor–liquid equilibria of mixtures containing alkanes, carbon dioxide, and nitrogen, *AIChE J.* 2001; 47:1676–1682
- [27] A.K. Rappe, C.J. Casewit, K.S. Colwell, W.A. GoddardIII, W.M. Skiff, UFF, a full periodic table force field for molecular mechanics and molecular dynamics simulations, *J. Am. Chem. Soc.* 1992; 114(25):10024–10035
- [28] Z. Nickmand, S.F. Aghamiri, M.R.T. Khozanie, H. Sabzyan, A Monte Carlo Simulation of the Adsorption of CO₂ and SO₂ Gases in Pure and Functionalized Single Walled Carbon Nanotubes, *Sep. Sci. Technol.* 2014; 49(4):499-505
- [29] A.I. Skoulidas, D.S. Sholl, J. K. Johnson, Adsorption and diffusion of carbon dioxide and nitrogen through single-walled carbon nanotube membranes, *J. Chem. Phys.* 2006; 124:054708
- [30] M. Kormann, H. Gerhard, N. Popovska, Comparative study of carbide-derived carbons obtained from biomorphic TiC and SiC structures, *Carbon* 2009, 47(1), 242-250
- [31] Y. Gogotsi, C. Portet, S. Osswald, J.M. Simmons, T. Yildirim, G. Laudisio et al., Importance of pore size in high-pressure hydrogen storage by porous carbons, *Int. J. Hydrogen* 2009, 34(15), 6314-6319
- [32] T. Mitsudome, Y. Mikami, M. Matoba, T. Mizugaki, K. Jitsukawa and K. Kaneda, Design of a silver–cerium dioxide core–shell nanocomposite catalyst for chemoselective reduction reactions, *Angew. Chem. Int. Ed.* 2012; 51:136 –139