The effects of reactor design on the synthesis of titanium carbide-derived carbon

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ABSTRACT

Titanium carbide-derived carbon with residual metal is synthesized by partial chlorination at 500 °C. This partial metal removal in the carbide creates vacancies, about which the carbon reorganizes to form an amorphous, porous carbon structure. To understand the titanium removal process on a bulk scale, three reactor designs were tested: (1) a flow-over horizontal-bed reactor, (2) a vertical flow-through packed-bed reactor, and (3) a fluidized-bed reactor. These reactors were chosen to investigate how various Cl_2 flow patterns impact the etching uniformity on individual TiC-CDC particles. Both the horizontal- and packed-bed reactors lost approximately 10–15 wt% of the original Ti content in 0.5 h and lost more than 95 wt% of the Ti content at 3 h of etching; however, the fluidized-bed reactor lost approximately 85 wt% of the original Ti content in 0.5 h and reached a level of etching corresponding to more than 95 wt% at 1 h. Additionally, the horizontal- and packed-bed reactors were found to etch the TiC-CDC particles non-uniformly, while the fluidized-bed reactor produced samples with uniformly etched particles that followed the core-shell model of Ti extraction.

1. Introduction

Activated carbons are among the oldest and most widely used adsorbents in water purification (Otowa et al., 1997), gas purification (Carter et al., 2011), metal extraction (Johns et al., 1998), and multiple other applications (Matisová and Škrabáková, 1995). Typical synthesis methods include pyrolysis of precursors including wood, fruit pits, and shells to create a hierarchal pore structure. The resulting carbon structures can be chemically tuned through the addition of functional groups or by inserting metal nanoparticles to target specific compounds in post-carbonization treatment processes (Bandosz et al., 1996; Rychlicki and Terzyk, 1998). While these methods are beneficial for adsorption, newer carbon sources have been evaluated to target a narrow pore size distribution in the final porous carbon. A uniform pore size distribution enables more effective molecular sieving, which allows for selective adsorption based upon adsorbate size while other aspects of the carbon material introduce selective adsorption based upon chemical properties.

Carbide-derived carbons are a class of amorphous carbon materials defined by their narrow pore size distribution, which is created through the selective removal of the metal heteroatom from a crystalline carbide structure. This removal or etching process is typically done with chlorine gas at temperatures at or exceeding 400 °C; the chlorine reacts with the metal to form a metal chloride, which immediately enters the gas phase and is removed from the system. The remaining carbon then rearranges around these metal vacancies to form tunable pore sizes based upon the metal atom size, metal configuration within the carbide, and etching temperature (Presser et al., 2011a). In addition to a narrow pore size distribution, CDCs offer physical and chemical properties that make CDCs ideal for use in electronic (Chmiola et al., 2006; Portet et al., 2009), adsorption (Presser et al., 2011b), and reactive applications (Borchardt et al., 2012). For adsorption applications, the addition of metal nanoparticles is beneficial, as seen with other activated carbons, (Rezaee et al., 2014; Tsoncheva et al., 2014) to introduce active sorption sites for the selective adsorption of target molecules. These nanoparticles can be created in a CDC through a partial etching of the carbide precursor, (Mangarella et al., 2014) rather than a post-synthesis impregnation necessary for activated carbons. To control the residual metal loading, composition, and location, and in-depth understanding of the reaction mechanism is of utmost importance.

The reactor design can significantly impact how the metal is removed from the bulk carbide sample by affecting the flow of Cl_2 gas at high etching temperatures. Conventionally, CDCs are created in a

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horizontal flow-over tube reactor (Gogotsi et al., 2003). In this reactor design, chlorine must diffuse through the sample bed to react with the metal. If the reaction kinetics are faster than chlorine diffusion through the bed, layers form (Mangarella et al., 2014). A packed-bed reactor allows chlorine to flow through the sample, which should reduce the effects of chlorine diffusion through the bed. However, uneven etching could still occur through the bed, especially if channels form. A fluidized-bed reactor allows for mixing within the bed based upon differences in density and has not been studied widely in CDC literature (Glenk, 2012). The mixing of CDC particles during etching should negate any chlorine diffusion limitations through the bed and create uniformly etched CDC samples.

Titanium carbide is a well-studied CDC that is known to follow a core-shell model of Ti extraction, where Ti is removed first from the surface of the particle according to reaction described in Eq. (1) and then deeper to the particle's core (Becker et al., 2010)

$$TiC_{(s)} + 2Cl_{2(g)} \rightarrow TiCl_{4(g)} + C_{(s)}. \tag{1}$$

Depending upon the exact reaction conditions, including temperature and chlorine concentration, various products are formed. At higher Cl_2 concentrations (greater than 5:1 Cl_2:TiC), the products are dependent upon reaction temperature. Specifically, at temperatures below 400 °C, $TiCl_4$ and CCl_4 are equally thermodynamically favored, while at temperatures exceeding 600 °C, only $TiCl_4$ is thermodynamically preferred. However, these thermodynamic calculations were performed in a closed system, while the reactors tested herein are open systems. This allows for the preferential formation of $TiCl_4$ at lower temperatures (Presser et al., 2011a; Yushin et al., 2006). In addition, titanium metal (Hanson et al., 1982) and titanium dioxide (Liu et al., 2005) have shown promise for selectively adsorbing chemicals and is a widely used catalyst. Titanium chloride has not been shown to form metal nanoparticles in literature or act as a graphitization catalyst, which would affect the resulting carbon structure (Leis et al., 2002; Xu et al., 2013). For these reasons, TiC is a good candidate to understand fundamentally how metal removal on a bulk scale affects individual particle properties. By testing three reactor designs, insight can be gained into controlling the amount and location of residual metal.

2. Experimental methods

2.1. Materials

Titanium carbide-derived carbon (TiC-CDC) was synthesized using three different reactors depicted in Fig. S1: (1) a horizontal-bed reactor; (2) a packed-bed reactor; and (3) a fluidized-bed reactor. The samples were prepared under similar conditions for all reactors. The reactors were purged with Ar while being heated to 500 °C at a 5 °C min^{-1} ramp rate. The samples were etched at 500 °C with a mixture of 1:4 Cl_2:Ar (Airgas, 99.5% purity; Airgas, Ultra High Purity, respectively) ratio, and the reaction time was varied. The horizontal- and packed-bed reactor samples had etching times ranging from 0.50 to 2.00 h in 0.50 h increments with an additional sample etched at 3.00 h, while the fluidized-bed reactor samples had chlorination times ranging from 0.25 to 1.50 h in 0.25 h increments. After the reaction, the reactors were cooled under a pure Ar purge. A NaOH scrubber is placed at the outlet of each reactor to neutralize the acidic metal chlorides and unreacted Cl_2.

For samples prepared in the horizontal-bed reactor, 2 g of TiC (Sigma-Aldrich, 98% purity, −325 mesh) were placed into a quartz boat and inserted into a quartz tube (OD 1″, 20″ long) in a horizontal tube furnace. The previously described etching reaction was performed at a total flow rate of 200 mL min^{-1} and an Ar purge flow rate of 160 mL min^{-1}. For reaction times less than 3.00 h, two horizontal layers were formed in the sample: a black top layer and a silvery gray

bottom layer. These layers were mixed for bulk sample analysis for each reaction time. For layer characterization, an additional sample was chlorinated for 1.50 h, and the layers were manually separated. Samples are identified through their chlorination time, e.g. 1.50 h.

For the packed-bed reactor, TiC-CDC samples were created in a vertical tube furnace. 2 g of −325 mesh TiC were funneled into a quartz tube (OD 0.75″, 28″ long) containing a quartz frit (Technical Glass, porosity 1). The samples were prepared using the same reaction parameters as the horizontal-bed reactor. Due to the absence of any noticeable layering and system setup limitations, only bulk sample characterization was performed.

The fluidized-bed reactor is similar to the packed-bed reactor; however, Ar and Cl_2 flow rates and TiC particle size were increased to ensure bed fluidization. TiC (Inframat Advanced Materials, 99.7% purity, +100 −60 mesh) was sieved to have a narrower particle size distribution of +100 −80 mesh. The same quartz tube used in the packed-bed reactor was filled with two grams of TiC and then tube placed in the vertical tube furnace. The etching reactions were then performed at a total flow rate of 400 mL min^{-1}. The Ar purge was set to 400 mL min^{-1} while the reactor heated and to 320 mL min^{-1} as the reactor cooled.

2.2. Methods

2.2.1. Power X-ray diffraction (PXRD)

PXRD was used to analyze the crystal structure of the resulting TiC-CDC samples. A PANalytical X-ray diffractometer with a Cu Kα X-ray source (λ=1.54 Å) was used to obtain PXRD patterns. The samples were evaluated from 15° to 90° with a step size of 0.02°. All samples were run at room temperature without activation.

2.2.2. Nitrogen adsorption at 77 K

Nitrogen (Airgas, Ultra High Purity) adsorption experiments were performed at 77 K on a Quantachrome Quadrasorb EVO to determine the surface areas and pore size distributions. The surface areas and pore size distributions were calculated using the Braunauer, Emmett, and Teller (BET) theory using $0.005 < p/p_0 < 0.03$ and Quenched Solid Density Functional Theory (QSDFT) assuming slit-shaped pores are present between graphene sheets, respectively (Kleitz et al., 2010; Neimark et al., 2009). QSDFT is a modified DFT model that calculates pore size distribution for disordered carbons and takes into account the heterogeneity of the rough, disordered carbon surface (Gor et al., 2012). Prior to N_2 adsorption, approximately 25 mg of sample were outgassed under dynamic vacuum on a Quantachrome FloVac Degasser at 150 °C for approximately 16 h.

2.2.3. Carbon dioxide adsorption at 273 K

Carbon dioxide (Airgas, Bone Dry) adsorption isotherms for the fluidized-bed reactor samples were performed at 273 K on a Micromeritics 3Flex. Non-Linear Density Functional Theory (NLDFT) using $4E-06 < p/p_0 < 0.032$ and assuming slit-shaped pores calculated a pore size distribution. NLDFT is another modified DFT model that calculates pore size distribution based upon partial CO_2 adsorption isotherms. Prior to measurement, approximately 30 mg of sample were outgassed at 150 °C for 12 h under dynamic vacuum using Micromeritics Smart VacPrep System.

2.2.4. Thermogravimetric analysis (TGA)

Residual metal loading was calculated using thermogravimetric analysis (TGA) data, gathered on a TA Instruments TGA Q50. Approximately 30 mg of sample were placed in a platinum sample pan and allowed to equilibrate at 25 °C. Then the sample was heated at 5 °C min^{-1} under air flow (Airgas, Ultra Zero Grade) at 20 mL min^{-1} to a final temperature of 900 °C, which was maintained for 2 h for the samples created with the horizontal- and packed-bed reactors and for 4 h for the samples synthesized with the fluidized-bed reactor to ensure