Synthesis of Embedded Iron Nanoparticles in Fe₃C-Derived Carbons

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Carbide-derived carbons with embedded Fe nanoparticles are synthesized by partial chlorination of iron carbide at 600°C. Interestingly, the residual Fe studied by X-ray absorption near edge spectroscopy, scanning electron microscopy, and transmission electron microscopy show the extraction process does not follow a layer-by-layer extraction process, as proposed in the literature for the chlorination of other carbides. Instead, a large percentage of iron carbide converts to iron (II) and iron (III) chloride nanoparticles, which remain trapped within the resulting nanoporous carbon framework. Further reductive treatment can be used to produce dispersed Fe nanoparticles with an average particle diameter approaching 10nm.

1. Introduction

Porous carbons have long been attractive materials due to their low cost, tunable porosity, and superior chemical stability. Over the past few decades, carbon materials have garnered great attention as catalyst supports, sorbents, electrodes, etc. due to increased control over their pore structure through the use of nanocasting and other synthesis approaches.^[1-4] In addition, increasingly ordered carbon structures, such as SWNTs, graphene, fullerenes and nanodiamond, have been investigated due to great inherent tribological and conductive properties.^[4] A new class of highly tailorable nanoporous carbons, carbide-derived carbons (CDCs), has also recently been established.^[2, 5-9] These materials are produced through the selective extraction of a metal or heteroatom from a carbide precursor, commonly by halogenation. The resulting nanoporous carbon exhibits large specific surface areas and a high degree of microporosity. Many comprehensive studies have demonstrated that the pore size can be tuned with sub-angstrom precision by varying the chlorination temperature.^[2, 7, 9-12] Therefore, many CDC materials have been investigated for gas storage, filtration, catalysis, capacitance, and other applications.^[11, 13-17]

There has been growing interest to functionalize CDCs with metal nanoparticles.^[18-20] Many traditional methods focus on impregnation of the metal by wetting the adsorbent with a solution containing the metal precursor. However, this often results in limited control of metal particle size, pore blockage of the carbon support, and weak support-metal interactions, particularly within templated pore architectures that rely on interconnecting pores.^[21] As such, many new approaches have focused on in-situ approaches to limit pore blockage and maximize dispersion.^[20, 22] Still these approaches can require lengthy synthesis procedures, and have motivated this study to investigate the viability of the metal in the metal carbide as an active site. This requires a careful look into the extraction process of the metal atom from the metal carbide,

to fundamentally understand the species and dispersion of the metal if the chlorination reaction is halted before complete extraction. Studies within the literature for certain carbides, such as NbC and SiC, show largely layer-by-layer extraction of the carbide precursor, leading to an undesirable and poorly distributed core of metal carbide.^[23, 24] However, other metal carbides should be investigated as there is good evidence in the literature that they would undergo a different extraction mechanism than layer-by-layer extraction.

Iron carbide (Fe_3C) was chosen as the carbide precursor. Iron has also been shown to play an interesting role in CDC synthesis. The presence of minute quantities of iron has been shown to affect the nanostructure of the resulting CDC, producing nanodiamond, barrel-like carbon nanoparticles, and other structured carbon domains.^[25-28] Graphitic carbon nanospheres and amorphous carbon nanotubes are found in the chlorination of ferrocene, and some structures are seen to surround FeCl_2 nanoparticles.^[29, 30] Interestingly, FeCl_3 is the only expected product from the chlorination of ferrocene. It is hypothesized that these particles originate from retained FeCl_3 species that are reduced to FeCl_2 while they remain trapped in carbon nanostructures that prevent their sublimation. The retention of iron chloride nanoparticles upon the chlorination of Fe_3C would be highly attractive and a significant deviation from traditional layer-by-layer extraction. A previous investigation into the chlorination of Fe_3C demonstrated iron's role as a graphitization catalyst, producing high purity graphite at certain chlorination temperatures.^[31, 32] Previous thermodynamic simulations on the chlorination of Fe_3C have shown that chlorination at moderate temperatures could produce solid FeCl_2 products within a closed system.^[31] The presence of residual iron chloride species for certain chlorination temperatures was also noted by X-ray diffraction (XRD) in this study, and it was postulated that H_2 gas could be used to reduce

the iron chloride species to prepare Fe supported catalysts.^[32] However, the iron chloride species were removed by HCl washing, and no further characterization was reported.

In this work, Fe_3C is chlorinated for varying chlorination times and samples were characterized by many techniques to understand the evolution of Fe dispersion and speciation. The objective of this study is to fundamentally understand the dispersion and speciation of the residual Fe at various extents of the chlorination reaction, and gain insight into the extraction process of Fe from Fe_3C . The goal of this study is to demonstrate the ability to create and control retained metal nanoparticles in Fe_3C -derived carbons (Fe_3C -CDCs) to aid their use in catalytic and adsorptive applications. Iron is an ideal candidate for this study because of the pervasiveness of iron species as adsorptive sites in catalytic and filtration processes, as well as the availability and low-cost of iron carbide.^[33, 34] In addition, though Fe_3C has been chlorinated to form CDC materials previously in the literature, no porosity characterization for Fe_3C -derived carbons have currently been published to the best of the authors' knowledge, which is of principle interest for these applications.

2. Experimental Section

2.1. Materials

One gram of Fe_3C (F. J. Brodmann & Co. 99.5% purity -200/+275 mesh) was placed on a quartz boat and inserted into a quartz tube of ID 1", length 20" and into a horizontal tube furnace. Each sample was heated to 600°C at a ramp rate of 5°C min⁻¹ under Ar flow (Airgas 99.999%) at a rate of 100 ml min⁻¹ and at ambient pressure. After reaching 600°C, chlorine gas (Airgas 99.5%) flow was introduced into the reactor at a flow rate of 25 ml min⁻¹ for a predetermined chlorination time ranging from 0.25-3 hours. The Ar flow was maintained during

chlorination. Acidic gases present in the effluent stream (Cl_2 , HCl , iron chlorides) were neutralized with a concentrated NaOH scrubber solution downstream of the reactor.

After the chlorination time had elapsed the chlorine gas flow was turned off. Samples were maintained at 600°C for 30 minutes under Ar flow, and then cooled to room temperature. A second series of annealed Fe_3C -CDCs were prepared for each chlorination time. These samples were purged with Ar for 30 minutes at 600°C , after which the Ar flow was switched to 5% H_2 in Ar (99.999%) at a rate of 100 ml min^{-1} for 3 hours at 600°C to remove residual chlorine. Afterwards, these samples were cooled to room temperature under Ar flow.

Unannealed samples were subsequently labeled as Fe_3C -CDC-CT, where CT stands for chlorination time, such as 0.25h, 0.5h, 0.75h, 1.0h, and 1.5h. Annealed samples were labeled as Fe_3C -CDC-CT- H_2 to denote exposure to hydrogen. In addition, layer separation was noted for Fe_3C -CDC-0.25h and Fe_3C -CDC-0.5h samples. These samples were hand-sieved and separated into a top, black powdered layer, and a bottom, silver/brown particulate layer. These samples were further subdivided into Fe_3C -CDC-CT-top and Fe_3C -CDC-CT-bot to denote either the top or bottom layer, respectively. The Fe_3C -CDC prefix is dropped in subsequent figures and throughout the paper for brevity.

2.2. Methods

2.2.1. Powder X-ray Diffraction

PXRD (Powder X-ray Diffraction) patterns were collected using an X'Pert X-ray PANalytical diffractometer with a $\text{Cu K}\alpha$ X-ray source ($\lambda = 1.5418\text{ \AA}$). XRD spectrums were collected from a range of $4\text{--}90^\circ$ in two theta (2θ) with a step size of 0.02° . All samples were run at room temperature.

2.2.2. Nitrogen Adsorption Measurements

Nitrogen adsorption measurements were obtained on a Quadrasorb System from Quantachrome Instruments. Isotherms were collected at 77K using a sample of 30-50mg. Prior to each isotherm, samples were activated overnight at 423K under vacuum. Specific surface areas were calculated using the BET model under the pressure range 0.01-0.05 P/P_0 . Pore size distributions for all samples were obtained using the Quenched Solid Density Functional Theory (QSDFT) model built into version 5.11 QuadraWinTM software. An adsorption branch slit-pore/cylindrical pore model, nitrogen adsorbate, and carbon adsorbent were assumed for the DFT model parameters.

2.2.3. Thermogravimetric Analysis (TGA)

Thermogravimetric analyses of all samples were carried out on a NETZSCH STA 449 F1 Jupiter instrument. Approximately 10mg of sample were heated from 25-1500°C at a ramp rate of 5°C min⁻¹ and a flow rate of 20 ml min⁻¹ of air (Airgas 99.999%). Residual metal % was calculated by assuming total combustion of carbon, and conversion of Fe to Fe₂O₃.

2.2.4. X-ray Absorption Near Edge Structure (XANES)

Pre-edge and XANES Fe K-edge spectra were collected at beamline 12-BM-B at the Advanced Photon Source of Argonne National Laboratories (Chicago). A Si(111) double monochromator was used to select the beam energy for all measurements. The beam size was 800μm x 1000μm. Samples were pressed into wafers of 13mm diameter and fixed to a sample stage with adhesive tape. The beam was internally calibrated with a metallic Fe reference foil, which was also run in series with all samples to account and correct for the energy shift of the beam. The first inflection point of the Fe K-edge was set to 7111.08 eV. XANES data was collected in transmission mode via the use of ionization chambers, and a step size of 0.3 eV was used. Before each sample, an area scan of beam flux was taken to ensure no pinholes in the pressed wafer. Data was analyzed within Athena software.^[35]

2.2.5. Scanning electron microscopy (SEM)

SEM images were obtained using a LEO 1530 Thermally-Assisted Field Emission (TFE) Scanning Electron Microscope (SEM). All samples were deposited onto carbon tape and not sputter coated prior to scanning. Images were scanned at an accelerating voltage of 3-10kV, depending on the charging effects of the sample. Particle size distributions were obtained by measuring the diameter of 50-100 particles from multiple SEM images of each sample.

2.2.6. Transmission electron microscopy (TEM)

TEM images were obtained using a JEOL 100CX II transmission electron microscope (TEM) at an operating voltage of 100kV. Samples were suspended in a solution of methanol and deposited on a lacey carbon grid. High resolution (HRTEM) images were obtained using a FEI Tecnai F30 at an operating voltage of 300kV. Other HRTEM images were obtained using a Hitachi HT7700 TEM at an operating voltage of 120kV.

3. Results and Discussion

3.1 Structural properties and porosity characteristics of prepared Fe₃C-CDCs

Figure 1. Reaction Schematic and Summary

Figure 1 provides a reaction schematic for prepared Fe₃C-derived carbons. Iron was extracted by chlorine gas to form iron chloride compounds by the following reactions:

The adsorption properties were investigated by nitrogen physisorption. The isotherms at 77K can be seen in the Supporting Information in Figure S1, with porosity results summarized in Table 1. The Fe₃C precursor exhibits little specific surface area (20 m² g⁻¹) and pore volume (0.02 cc g⁻¹). Unannealed Fe₃C-CDCs prepared at chlorination times ≤ 0.5 hours formed two layers: a black, powdery top layer and a silver/brown clay bottom layer. The relative mass percentages of each layer are reported in Table S2. At chlorination times ≥ 0.75 hours, no layer separation was seen, and the Fe₃C-CDC visually resembled the black, powdery top layer at low chlorination times. All Fe₃C-CDCs annealed in H₂ formed one visually homogenous black powder layer irrespective of chlorination time.

The specific surface area and pore volume are strongly affected by the chlorination time and annealing treatment. The bottom layers (0.25h-bot, 0.5h-bot) have little (~50 m² g⁻¹) porosity while the top layers (0.25h-top, 0.5h-top), as well as 0.75h and 1.0h samples, have progressively increasing porosity and characteristic type IV isotherms according to the Brunauer classification.^[36-38] Annealed samples also exhibit type IV isotherms, seen in Figure S1, with a H2 type hysteresis that exhibits a sharp desorption branch and a gradual increase in the adsorption branch. This signifies the presence of cavitation effects, and the closure of the hysteresis around the relative pressure P/P₀ = 0.42 can be attributed to a sudden nucleation of nitrogen gas bubbles within the mesopores of annealed Fe₃C-CDC samples.^[39-41] To verify that the hysteresis was not caused by a chemisorption mechanism due to residual Fe, a sample with a

large amount of residual iron, 0.25h-H₂, was recorded twice in series. There was no significant change in specific surface area, signifying no irreversible chemisorption.

Table 1. Porosity and residual metal for prepared Fe₃C-CDCs

Sample Name	Chlorination Time (h)	Annealing Time (h)	Specific Surface Area (m ² g ⁻¹) ^a	Pore Volume (cc g ⁻¹) ^b	Residual Metal (%) ^c
Fe ₃ C	0	0	20	0.02	93
0.25h-top	0.25	0	96	0.18	-
0.25h-bot	0.25	0	53	0.14	-
0.25h-H ₂	0.25	3	147	0.13	77.3
0.5h-top	0.50	0	229	0.26	-
0.5h-bot	0.50	0	51	0.15	-
0.5h-H ₂	0.50	3	356	0.31	25.5
0.75h	0.75	0	339	0.34	-
0.75h-H ₂	0.75	3	667	0.53	8.4
1.0h	1.0	0	374	0.40	-
1.0h-H ₂	1.0	3	657	0.48	4.0
1.5h	1.5	0	353	0.38	-
1.5h-H ₂	1.5	3	683	0.54	2.7
3.0h-H ₂	3.0	3	-	-	0.8

a) Obtained by BET[36] Analysis at a Relative Pressure Range of 0.01-0.05 P/P₀ b) Obtained at P/P₀ = 0.99 c) Calculated by TGA Experiments

Annealed samples exhibit significantly higher surface areas, with a 97% increase in surface area comparatively between 0.75h and 0.75h-H₂. Hydrogen has been shown to be a far more effective annealing gas than Ar for Cl₂ removal from CDCs, and the drastic increase in porosity can be explained by a combination of the removal of physisorbed chlorine gas, bonded surface Cl species, and the conversion of FeCl_x species.^[42] There is a maximum surface area and pore volume obtained at chlorination times ≥ 0.75 hours (0.75h-H₂ – 667 m² g⁻¹, 0.53 cc g⁻¹). These values are low for CDC materials, but the reaction temperature in this study was not optimized to obtain maximum porosity. Also, the onset of significant graphitization, as seen in

the synthesis of other carbide-derived carbons, has been shown to severely reduce surface area and pore volume.^[12] The presence of well-ordered graphitic sheets seen in Fe₃C-CDCs can limit porosity as the d-spacing of graphite, 3.4Å, can hinder the accessibility of the nitrogen probe molecule.^[31]

The hysteresis loop for unannealed Fe₃C-CDCs at long chlorination times and annealed Fe₃C-CDCs corresponds to a broad (002) graphite reflection in the XRD spectrum as seen in Figure 2, indicating the formation of a significant amount of mesoporosity as the degree of graphitization increases. The formation of highly ordered graphitic sheets was also observed in SEM, which will be discussed in greater detail in Section 2.2.1. In addition to the (002) graphite reflection, the (004) graphite reflection can be seen at $2\theta = \sim 55^\circ$ for longer chlorination times. Other peaks were observed for annealed samples, present at $2\theta = \sim 45^\circ$, $\sim 65^\circ$, and $\sim 82^\circ$ corresponding to the (011), the (002), and the (112) reflection of α -Fe. Peaks are also seen in unannealed samples at >0.75 h present at $2\theta = \sim 32^\circ$, $\sim 35.5^\circ$, $\sim 48^\circ$ with d-spacings of 0.272, 0.244, and 0.178 nm respectively. Other studies have attributed similar peaks to more ordered carbon structures, such as nanodiamond, but confirmation of these structures was not obtained by TEM in this study.^[28] The possible attribution of these peaks to residual iron complexes was also studied. The disappearance of peaks from the commercial Fe₃C spectrum in Figure 2(b) after short chlorination times indicate the precursor is quickly converted to iron chloride products. In Figure 2(a), the intensity of the peak at $2\theta = \sim 45^\circ$ correlates very well with the percent of residual metal in annealed samples, supporting its attribution to reduced Fe in annealed samples and the (011) reflection of α -Fe. There were no definitive XRD peaks for Fe₂O₃, Fe₃O₄, FeCl₃, or FeCl₂ in both series of samples, therefore, more in-depth investigations on Fe speciation were conducted with XANES, discussed in **Section 2.2**.

Figure 2(a,b). XRD spectra of (a) annealed Fe_3C -CDCs and (b) unannealed Fe_3C -CDCs

For more insight into the pore structure, Quench Solid Density Functional Theory (QSDFT) calculations were carried out and pore size distributions for annealed samples are presented in Figure 3. The QSDFT model is a quantitative model designed for curved, non-homogenous surface geometries, and can be used to accurately describe CDC porosimetry.^[43] Due to the cavitation effect, the adsorption branch of the N_2 -isotherm was applied.^[44] A slit-pore and cylindrical pore model were used in the QSDFT model to account for the hysteresis and the degree of graphitization within the samples, which are both indicative of significant mesoporosity. In Figure 3(a), all pore size distribution plots have similar shapes, with a distinct micropore diameter of $9\text{\AA}$. The peak area increases with the total amount of N_2 adsorbed, and levels off near complete conversion at chlorination times $\geq 0.75\text{h}$. There is a broad development of mesopores with an average diameter of 4 nm seen at chlorination times $\geq 0.75\text{h}$. The increase in mesoporosity is consistent with the increase in graphite crystallinity seen in XRD, and is likely due to increased ordering at longer reaction times, as well as an increase in overall porosity. It is common for graphitized carbide-derived carbons to exhibit more mesoporosity.

In Figure 3(b), different porosity characteristics are seen for the top and bottom unannealed samples. Top layer CDCs are more closely aligned with annealed samples, and feature a microporous peak at 13 Å in diameter, as well as mesopores of around 3.4 nm in diameter. Bottom layer CDCs are more mesoporous, with most pores greater than 5 nm in diameter and a broad range of mesopores up to 20 nm in diameter. The 0.25h-bot sample has characteristics of both 0.25h-top and 0.5h-bot, suggesting it is a mixture of the layers, possibly due to poor layer separation. Further analysis was done to couple these porosity differences with the specific carbon and Fe nanostructures present in the top, bottom, and annealed series of samples.

Figure 3. Pore size distributions for (a) annealed Fe_3C -CDCs and (b) unannealed Fe_3C -CDCs

3.2. Nanostructures obtained from partial chlorination of Fe_3C

3.2.1. Nanostructures of Unannealed Fe_3C -CDCs

Representative SEM images of unannealed Fe_3C -CDCs are presented in Figure 4 and Figure 5. More SEM images are available in the Supporting Information in Figures S2-S14. Planar graphitic sheets were observed in all samples, consistent with XRD patterns in Figure 3(b). Depending on the chlorination time and layer, vastly different substructures were formed.

Figure 4. SEM Images of (a)(b) 0.5h-top, (c) 0.75h, (d) 1.0h

Top layers at chlorination times ≥ 0.5 h, as seen in Figure 4, are largely graphitic, disordered, and contain embedded FeCl_3 nanoparticles. The XANES spectra in Figure 6(a) and Figure 6(b) were used to confirm the oxidation state of the iron. There is a well-established separation of 1.4eV between the Fe^{2+} and Fe^{3+} oxidation states in the pre-edge region, as the position of the pre-edge centroid shifts towards higher energy with an increase in Fe oxidation state.^[41] The characteristic pre-edge region at ~ 7114 eV is indicative of an Fe(III) state, and the pre-edge feature matches very closely with the FeCl_3 standard.^[45] There is some discrepancy between the 0.25h-top spectra and the other CDCs, particularly in the white line region but also in the isosbestic point shared by the other CDCs at ~ 7127 eV. This is likely due to the presence of unreacted iron carbide at low chlorination times. Stoichiometrically, the minimum time

required for complete conversion is calculated to be between 45 minutes, assuming complete selectivity to FeCl_2 in Equation (2), and 67 minutes, assuming complete selectivity to FeCl_3 in Equation (1).

The presence of FeCl_3 is surprising, as its boiling point of 315°C is well below the 600°C chlorination temperature. It is hypothesized that after the surface reaction, FeCl_3 products agglomerate as they begin to diffuse through the resulting CDC, and catalyze the formation of carbon nanostructures before entering the bulk gas phase. As previously stated, the role of FeCl_3 as a graphitization catalyst has been seen in the formation of graphitic carbon nanospheres, amorphous carbon nanotubes, and well-ordered graphite where FeCl_3 is hypothesized to transport carbon and facilitate graphitization.^[29-31] In the chlorination of ferrocene, carbon nanostructures are thought to prevent FeCl_3 sublimation until it is reduced to FeCl_2 .

The decomposition of FeCl_3 occurs by either the vaporization of FeCl_3 or the dimer Fe_2Cl_6 . The dimer is reported to be the dominant species as high as 400°C .^[46,47] A thermodynamic study of the chlorination of Fe_3C by Gogotsi et al. have also shown significant amounts of Fe_2Cl_6 at equilibrium at 600°C .^[29] FeCl_3 and Fe_2Cl_6 have D_{3h} and D_{2h} symmetry, respectively and the size of Fe_2Cl_6 is 0.502 nm long by 0.379 nm wide, while FeCl_3 can be calculated to be 0.318 nm long from the equilibrium bond length of 0.2122 nm.^[48, 49] Given the size and shape of FeCl_3 and Fe_2Cl_6 , it is plausible that they are sterically prevented from escaping by graphitic carbon nanostructures. The diffusion of FeCl_3 decomposition species are hypothesized to be inherently slow and hindered by graphitic carbon nanostructures, as a sample chlorinated at 3 hours contained less than 1% residual Fe. A similar phenomenon has recently been observed for the chlorination of TiC nanopowders, where residual TiC is postulated to be preserved due to surrounding graphitic carbon nanostructures that prevent chlorine diffusion.^[50]

Later, in annealed samples, graphite layers are seen surrounding a reduced Fe particle, further supporting this theory.

Figure 5(a-d). TEM and SEM Images of 0.5h-bot

Different substructures were observed at lower chlorination times for each layer. The 0.25h-top sample shows the presence of small tubular structures approximately 200-400nm in length in Figure S2 and planar graphitic sheets can be seen in the 0.25h-bot sample, as well as Fe nanoparticles in Figure S4. Due to charging effects, however, we were unable to increase magnification for a closer look without adding excessive noise to the detector signal. At 0.5h chlorination time, there is a more pronounced difference between the top and bottom layers. In

Figure 5, 0.5h-bot sample SEM and TEM images are shown. Rod-like structures were observed in the 0.5h-bot sample, with diameters ranging from ~30-50nm and lengths up to 10 μ m. This was further investigated in TEM. It has been suggested that FeCl₃ can facilitate carbon dissolution, which is responsible for the creation of amorphous hollow carbon nanotubes upon the chlorination of ferrocene.^[24, 30] The contrast difference between the tubular structure and the tip in Figure 5(a) greatly supports FeCl₃ catalyzed carbon nanotube formation in the bottom sample. Figure 5(b) shows many joined structures with domains that have an observed lattice parameter of 7Å, on the order of a unit cell and much larger than the d-spacing of a graphitic carbon nanotube (3.4Å). It is heavily supported from the XANES spectra in Figure 6(b) that this sample contains predominantly FeCl₂, and these are suggested to be needle-like FeCl₂ structures. In Figure 6(b), samples have a pre-edge transition of ~7112.1eV, which is indicative of the Fe²⁺ oxidation state. In addition, both samples match the same double peak white line and post-edge features of the FeCl₂ standard spectrum.

Significant amounts of residual FeCl₂ in the bottom layer samples are unexpected, as a previous thermodynamic study of the chlorination of Fe₃C by Gogotsi et al. showed that only small amounts of FeCl₂ could be produced at low chlorine concentrations.^[29] It is possible that the formation of FeCl₂ in Fe₃C follows the same mechanism proposed for the chlorination of ferrocene.^[31, 33] FeCl₂ was not supported as an initial product for the chlorination of ferrocene, and is suggested to form via the reduction of FeCl₃.^[29, 30] Carbon nanostructures would consequently encapsulate the crystalline FeCl₂ to prevent oxidization by excess Cl₂. It is interesting that the bottom layer is no longer seen at longer chlorination times. The melting point and boiling point for FeCl₂ are 676°C and 1020°C, and FeCl₂ has a low vapor pressure at

600°C.^[46, 47] Intuitively, FeCl₂ could be further oxidized to FeCl₃, which slowly diffuses to the bulk phase.

Figure 6(a-c). Fe-K edge for (a) unannealed bottom layer Fe₃C-CDCs, (b) unannealed top layer Fe₃C-CDCs, and (c) annealed Fe₃C-CDCs

These results show marked differences for Fe₃C-CDCs compared to other CDCs in terms of both metal dispersion and speciation. Kinetic studies with SiC have suggested a layer-by-layer extraction of Si, while the extraction of Fe results in dispersed residual iron chloride domains.^[5, 32] Studies with WC, NbC, SiC, and TiC have observed that when the extraction process has not proceeded to completion, the residual metal is largely in unreacted carbide form. In Table 1 and Figure 6, it is shown that 0.5h-H₂ features 25.5% residual iron which is present as FeCl₂ and FeCl₃ in 0.5h-top and 0.5h-bot samples before reduced during annealing treatment.^[9, 11, 32, 33]

3.2.2 Nanostructures of Annealed Fe_3C -CDCs

Representative SEM and TEM images of annealed Fe_3C -CDCs are presented in Figure 7 and XANES spectrum for annealed samples are present in Figure 6(c). A high degree of graphitic ordering is seen in all annealed samples, consistent with the intense (002) reflection of graphite in the XRD spectrum in Figure 2(a). X-ray diffraction spectra for annealed samples show a steep (100) reflection for α -Fe at 45° , indicating H_2 annealing reacts with metal chlorides and removes chloride species. Dispersed within the observed planar graphitic crystals are Fe nanoparticles with diameters ranging from 5-100nm. Particle size distribution versus chlorination time was calculated for annealed samples, and the results are summarized in Figure 8. Mean particle size decreases with increasing chlorination time, and almost all particles are less than 10nm in diameter at chlorination times $\geq 0.75\text{h}$. This suggests that $>10\text{nm}$ Fe particles are mainly derived from reduced FeCl_2 species in the bottom layer, and upon annealing treatment they are partially or fully removed along with the disappearance of the carbon nanotubes. Upon chlorination times $\geq 0.75\text{h}$, after the disappearance of the bottom layer, only $<10\text{nm}$ particles are present. Low resolution TEM images in Figure 7(e) and high resolution TEM images in Figure 7(f) further suggest that these particles are embedded within the CDC framework. HRTEM shows that there are evident graphitic sheets that envelope the Fe nanoparticle, supporting the hypothesis that these graphitic nanostructures prevent the sublimation of iron chloride species during chlorination.

XANES spectra for the annealed Fe_3C -CDCs in Figure 6(c) also confirm metallic Fe is present in the annealed samples, and closely match the Fe reference foil spectrum. Therefore, iron chloride species present in unannealed samples are seen to be easily reduced to metallic Fe for catalytic applications. It is important to note that there is a significantly higher white line for

Fe_3C precursor compared to annealed Fe_3C -CDCs and the reference foil. This is likely due to mild surface oxidation on the Fe_3C precursor, which can result from a common passivation treatment at the end of Fe_3C synthesis that requires exposure to dilute O_2 to create a non-reactive surface on the freshly prepared carbide.^[24]

The successful reduction of FeCl_3 particles during the annealing treatment demonstrates that there is some selective accessibility between the bulk gas phase and the trapped iron chloride nanoparticles. For instance, during the annealing treatment, for the case of longer chlorination time samples which contain FeCl_3 nanoparticles, H_2 gas is able to diffuse into a trapped FeCl_3 particle, reduces the particle to metallic Fe, and HCl gas is able to diffuse back out to the bulk phase. We believe that the size and shape differences between H_2 and HCl and the iron chloride decomposition species explain this behavior. The kinetic diameters of H_2 and HCl are quite small, 0.289 nm and 0.442 nm, and the linear shape of these gases offers much less steric hinderance than molecules with D_{3h} and D_{2h} point groups.

Figure 7. SEM and TEM Images of (a) 0.25h-H₂, (b) 0.5h-H₂, (c) 0.75h-H₂, (d-f) 1.0h-H₂

Figure 8. Particle size distributions for Fe nanoparticles in annealed Fe₃C-CDCs

4. Conclusion

Fe₃C-CDCs were synthesized at 600°C at various chlorination times to study their porosity and residual metal characteristics. At low chlorination times, XANES analysis shows two distinct layers form with different FeCl_x oxidation states: A porous layer containing FeCl₃ forms on top of unannealed samples, and a significantly less porous layer containing FeCl₂ forms on the bottom of unannealed samples. Unique structures are formed for each layer – with notable carbon nanotubes of ~30-50nm diameters in the bottom layer. Annealed Fe₃C-CDCs form mainly planar graphitic sheets with embedded Fe particles.

The present study clearly shows that the chlorination of Fe₃C at 600°C does not follow a traditional layer-by-layer extraction of Fe from the carbide matrix. After the surface reaction of chlorine with iron carbide, a significant percentage of FeCl₂ and FeCl₃ products do not diffuse out of the resulting carbide-derived carbon, and are able to agglomerate and catalyze the

formation of graphitic carbon nanostructures. These graphitic carbon nanostructures prevent the diffusion of vaporized iron chloride species and their decomposition products, and allow iron chloride species to remain as supported nanoparticles. This is a marked difference from traditional layer-by-layer extraction, in which the chloride products would diffuse out of the carbide-derived carbon into the bulk gas phase.

There are many attractive features of these retained iron chloride species. These nanoparticles can subsequently be reduced in H_2 and approach an average Fe nanoparticle size of 10 nm. Fe_3C -CDCs can be synthesized with specific surface areas and pore volumes approaching $700\text{ m}^2\text{ g}^{-1}$ and $0.54\text{ cm}^3\text{ g}^{-1}$, and a high degree of microporosity, which renders them as good supports for catalytic and filtration applications. Theoretically, these materials can also be calcined to allow for Fe oxide sites and thus be further tailored for desired sorbate-sorbent interactions. These results provide a new strategy for a facile, one pot synthesis for supported Fe nanoparticles in CDC materials.

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