Reconstruction of the Wet Chemical Synthesis Process: The Case of Fe₅C₂ Nanoparticles

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ABSTRACT: Wet chemical synthesis (WCS), especially under high temperatures, is one of the most frequently used strategies for nanostructured material construction, which has been used extensively in medical-, energy-, and environment-related applications. Although knowledge about the WCS process has been accumulated in the past two decades, the high temperature used in the process and multiphase nature of intermediates and products are key factors preventing the processes from rationalization. In this paper, by using multilevel in situ cells, we developed a strategy to monitor the reaction details of WCS processed in the solid, liquid, and gas phase simultaneously. This protocol has proven successful to reconstruct the WCS process of Fe₅C₂ nanoparticles (NPs) and unravel the complicated chemistry in the synthesis process.

INTRODUCTION

In a conventional high-temperature wet chemical synthesis (HWCS) process, metal precursors are dispersed in proper solvents (such as oleic acid and amine), with the existence of surfactants. The mixture is then heated for reaction to obtain the targeted nanomaterials. The complicated interactions between solvents, precursors, and products make it extremely difficult to rationalize the synthetic chemistry of HWCS process. In previous reports, the formation mechanisms of nanostructured materials synthesized by the HWCS method are mostly derived from indirect electron microscopy and ex-situ XRD observation, or from control experiments under different reaction conditions. Although these efforts help to understand the synthesis process and sketch out a strategy to prepare new nanomaterials, the off-line methods often provide incomplete or even misleading information. Therefore, the wet chemical synthesis is by far still an art than science. Applying online observation based on time-resolved spectroscopy, scattering and diffraction methods is highly desirable to solve this problem. However, the microreactors also suffered from laminar flow and poor fluidity. In HWCS using viscous organic medium, the disadvantages are magnified. In addition, it still requires a large effort to design microreactors that could work under inert atmosphere and fit to do the basic operations, such as degassing and hot injection.

Hägg iron carbide (Fe₅C₂), particular its nanosized form, is very important in various energy-related processes. Conventional strategies of carburization via either solid—solid or solid—gas reactions have difficulties in controlling the size and phase. However, HWCS method provides a facile and practical way to address the problems. In our previous work, we reported the controlled synthesis of Fe₅C₂ nanoparticles (NP) using the HWCS process for the first time. In the work, we proposed that the formation of well-crystallized Fe NPs is the key for the synthesis process. But as the understanding was based on the XRD and TEM characterization of limited number of off-line products, the description of the synthetic chemistry is possibly not accurate enough. Using these Fe₅C₂ NPs as an example, we demonstrate here the reconstruction of the HWCS process using in situ observation methods. Multiple real-time characterization methods were employed to address...
the reaction details happening in the solid, liquid, and gas phases (Scheme 1). This sophisticated system allows us to disclose the structural evolution and the accurate synthetic mechanism of Fe₅C₂ NPs for the first time. It can be adopted as a general protocol for the in situ investigation of wet chemical synthesis of various nanomaterials

## EXPERIMENTAL SECTION

### Typical Synthetic Process of Fe₅C₂ NPs

Octadecylamine (30 g) and CTAB (0.226 g) were mixed in a four-neck flask, stirred, and degassed under N₂ flow. The mixture was then heated to 120 °C, followed with the addition of Fe(CO)₅ (1 mL, 7.2 mmol) by injection under a N₂ blanket. The mixture was heated to 180 °C at 10 K/min and kept at this temperature for 30 min. A color change from orange to black was observed during the process. Subsequently, the mixture was further heated to 350 °C at 10 K/min and kept at that temperature for 10 min before it was cooled to room temperature. The product was filtered, washed with ethanol and hexane, and collected for further characterization.

**Operando XRD and Real-Time Mass Spectroscopy.** The time-resolved operando XRD data of the synthesis process of Fe₅C₂ NPs were collected at the BL14W beamline of SSRF using QXAFS mode, with the same operando setup. The XANES spectrum collection started 1 min after Fe(CO)₅ injection. Each shot took 30 s for collection and every 5 shots were merged into one spectrum to improve the quality of spectrum. Fe foil, FeO, and Fe₅C₂ NPs (synthesized and sealed under Ar protection) were employed as standards. All spectra were processed using Athena software inside IFEFFIT package. Due to the interference of bubbles generated at around 180 and 280 °C, the quality of QXAFS spectra was insufficient for further structural refinement. To solve this problem, we quenched the reaction using ice bath at those temperatures under parallel conditions to the operando measurements and did the XAFS measurements in the air-proof XAFS cell.

**Operando Transmission Infrared (IR) Spectroscopy.** The time-resolved operando transmission IR spectroscopy was done using an instrumental setup similar to the operando XRD and XAFS setup on a Bruker Tensor 27 IR spectrometer. Instead of a Teflon tube cell, a home-designed IR liquid cell with CaF₂ windows was utilized for spectrum collection. The thickness of liquid film was tuned with Pb foil to gain appropriate transmittance. The time resolution of operando measurement is set as 16 s/spectrum.

**GC–MS of the Liquid Phase.** The chemical composition of liquid phase at each temperature interval was analyzed using an Agilent 7890A-5975C GC–MS analysis system. Samples were collected and quenched under parallel conditions to the operando experiments. Appropriate amount of n-eicosane was added in the liquid phase as chemical inert inner-standard to improve the quality of spectrum. Fe foil, FeO, and Fe₅C₂ NPs collection and every 5 shots were merged into one spectrum to normalize the GC signals.

**Transmission Electron Microscopy (TEM).** TEM was carried out on an FEI Tecnai T20 microscope. High-resolution transmission electron microscopy (HRTEM) was carried out on an FEI Tecnai F30 microscope.

**Calculation Methods.** All spin-polarized density functional theory (DFT) calculations were performed by using projector augmented wave (PAW) potentials and the Perdew–Burke–Ernzerhof (PBE) functional implemented in the Vienna ab initio simulation package (VASP) code. The energy cutoff for the plane wave basis set was 400 eV. The structure optimizations were deemed converged when the forces on each atom were below 0.02 eV/Å. The optimized lattice constant for Fe with body center cubic (BCC) structure is 2.833 Å. Fe (310) surface consisted of B₅ site was considered in our calculations. This surface was simulated by using ten atom layers slab models and p(2×2) unit cell were applied. Neighboring slabs are separated by a vacuum of 15 Å to avoid the interactions between them. We used Monkhorst–Pack mesh k-points of 5×5×1 here. The top five layers of the slabs and the adsorbates were fully relaxed, and dipole correction was adopted.

The improved force reversed method was used to determine the transition states (TS) and the force tolerance of 0.02 eV/Å was used. And some of the TS are verified by climbing-image nudged elastic band (CI-NEB) methods. We have adopted the separate adsorption of the species involved as the initial and final states for the elementary reactions in this article.

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**Scheme 1. Schematic Illustration of Home-Made Circulate Apparatus for Operando High-Temperature Wet Chemical Synthesis Investigation**

[Diagram of the apparatus showing different components and processes involved in the reaction.]
RESULTS AND DISCUSSION

Infrared spectroscopy (IR) is an ideal tool to study carbonyl and adsorbed CO over the metal catalyst. We first used in situ IR to track the structure evolution at the early stage of the synthesis. After injection of Fe(CO)$_5$ into the solvent, typical C=O vibration bands at 2021, 1999, and 1962 cm$^{-1}$ appeared. At 180 °C, with the reaction going on, the intensity of these bands decreased rapidly (Figure 1a), suggesting the fast thermal decomposition of Fe(CO)$_5$. Meanwhile, a new broad band appeared at 1931 cm$^{-1}$, indicating the increase of π-back-bonding from Fe central atom to CO ligands. This signal is most likely attributed to the coordination between $\text{NH}_2$ (electron donor) of octadecylamine and the Fe carbonyl complexes. New signals at 1946 and 1756 cm$^{-1}$ appeared when the system was kept at 180 °C for around 30 min. These two bands are from the stretch vibration of CO adsorbed at the on-top and 3-fold sites of metallic iron. Although the appearance of CO adsorbed at 3-fold sites suggests the formation of iron clusters, we did not observe any iron species on the operando synchrotron XRD profile during this period of time (Figure 1c), which indicates that the size of generated iron species was still under the detection limit of XRD technique (around 2 nm). Significantly, the first two operando XANES spectra collected at 180 °C (right after injection of Fe(CO)$_5$ and before temperature ramping) show a relatively low absorption edge energy and low “white-line” intensity (Figure 1e), which suggests that the iron species are near metallic. Meanwhile, the corresponding Fe K-edge EXAFS spectra (Figure 1f and Table S1) show the existence of Fe–Fe coordination (coordination number, $N_{\text{Fe}-\text{Fe}} = 6.9$ at 2.75 Å; $N_{\text{Fe}-\text{Fe}} = 0.7$ at 2.53 Å) in addition to the Fe–C coordination from the adsorbed CO. This is another evidence for the formation of multinuclear metallic iron clusters upon the decomposition of Fe(CO)$_5$. During this period, online mass spectroscopy (MS) (Figure 2a) has detected the release of CO, whereas the octadecylamine solvent was almost intact at this temperature (see GC–MS in Figure 2d).

After 240 °C, all the IR bands disappeared, indicating the full conversion of precursors (Figure 1b). In the liquid phase (Figure 2d), nothing but the original solvent was detected before the temperature reached 215 °C. At this temperature, the reflections of cubic FeO (Fm3m space group, JCPDS No. 89–0690) at 28.8°, 33.4°, and 47.9° suddenly appeared (Figure 1c), indicating the formation of FeO NPs over 5 nm (see also the TEM images in Figure S2). The intensity of the FeO NPs increased with temperature elevation and reached a maximum at about 270 °C, which was associated with the size growth of FeO crystal (to about 20 nm). We attribute the formation of FeO intermediates to the oxidative nucleation/growth process under limited O chemical potential (the solution was degassed before reaction). It is worthwhile to note that Fe oxide particles would become final products if the oxygen removal is not executed.

The Fe K-edge EXAFS results highly support the oxidative nucleation hypothesis (Figure 1e,f and Table S1). At the very early stage of the reaction, i.e., 30 min reaction at 180 °C (Table S1, entry 2), the bonding of oxygen on Fe could already be observed ($N_{\text{Fe}-\text{O}} = 3.8$). Meanwhile, the existence of partially oxidized Fe(II) was resolved at 190 °C as the typical feature of FeO (7134 eV) appeared in XANES (Figure 1e), indicating that the oxidation of iron occurred gradually with the thermal decomposition of iron carbonyl precursor and formation of iron clusters (Figure 1e). By comparison with standard FeO pattern and Fe foil, the linear combination fit (LCF) result of the XANES spectrum suggests the system is composed by 63% of Fe(II) and 37% of metallic iron at 190 °C.

With a further increase of reaction temperature above 270 °C, however, the XRD signals of FeO particles dropped dramatically and finally disappeared at around 300 °C. Meanwhile, the
Reflections of $\chi$-Fe$_5$C$_2$ in the range 36–38° gradually appeared at 310–320 °C and grew stronger in intensity until 350 °C (JCPDS No. 36-1248), which is also confirmed by corresponding XANES spectra (Figure 2a). Although the XRD results indicate the conversion process at this stage is simple, it is still hard to understand the chemistry behind this phase evolution as iron carbide is normally regarded as a metallic crystal with interstitial carbon atoms. To understand this process, one needs to find out (1) how the oxygen was deprived of from FeO crystals, (2) what is the source of carbon in iron carbide, and (3) what the sequence of the process is. Analysis of the products from the gas phase as well as the liquid phase provides important clues for these issues.

The GC–MS chromatogram of the liquid phase proved that the initial state at 180 °C is mainly the solvent C$_{18}$H$_{37}$NH$_2$ (retention time = 9.9 min, Figure 2d). The cation of C$_{18}$H$_{37}$N(CH$_3$)$_3$ appeared at 8.5 min, which was associated with the addition of CTAB. The chemical composition of the liquid phase remained stable until 270 °C, when C$_{17}$H$_{35}$CN (retention time = 10.2 min), the dehydrogenation product of C$_{18}$H$_{37}$NH$_2$, appeared. The peak of C$_{18}$H$_{37}$NH$_2$ disappeared at 330 °C, indicating the complete conversion of C$_{18}$H$_{37}$NH$_2$ into C$_{17}$H$_{35}$CN. Meanwhile, a series of peaks of C$_{16}$–C$_{18}$ olefin and paraffin products appeared at 320 °C with the intensity increased with higher temperatures. Those alkane and alkene products were generated via the C–N and C–C cleavage of C$_{18}$H$_{37}$NH$_2$ or C$_{17}$H$_{35}$CN at relatively high temperatures (evidence of corresponding fragments have been track by online MS). As pure C$_{18}$H$_{37}$NH$_2$ has good thermal stability, it can be concluded that the dehydrogenation and C–C cleavage reactions are actually catalyzed by the iron species in the system. When correlating the GC–MS results with the structural evolution, we found that the C$_{18}$H$_{37}$NH$_2$ dehydro-

Figure 2. Online MS and GC–MS of the gas phase. Major products (a), main intermediates (b), and generation of light hydrocarbon compounds (c). GC–MS profiles of liquid phase at different reaction temperatures (d).
The combined in situ characterization sketched a vivid picture of the complicated oxidation state change and structural evolution of iron species during the HWCS process. The overall evolution of NPs and solvent during the reaction is illustrated in Scheme 2. It demonstrates that the interplay between iron species and the organic solvent plays a vital role, as the generated nanostructures catalyze the transformation of organic solvent in situ. It is worth noting that it is equally or even more important to understand the role of organic solvent in the synthetic process because the organic media provides the hydrogenation agent as well as carbon source for Fe₅C₂, which serves as the driven force for the phase transformation of the materials. Third, the synthetic temperature, as a necessary factor that triggers the mentioned reactions, directly determines the crystal phase of products. Changing the ramping rate may prolong or shorten certain chemical transformation stages and further influence the structure of final particles. On the basis of our understandings gained from the Fe₅C₂ system, we have managed to extend the synthetic protocol to other transition metal carbide nanostructures such as MoC and Co₂C NPs (Figure S7).

### CONCLUSION

In summary, we utilized a multilevel online cell to monitor the synthetic details happened in solid, liquid, and gas phases using multiple operando characterization methods. Utilizing this setup, we managed to reconstruct the formation mechanism of Fe₅C₂ NPs by the combination of operando IR, XRD, XAS, and MS methods for the first time. The operando observation discloses that FeO is an important intermediate phase in Fe₅C₂ NPs synthesis, which was not observed by previous off-line attempt. It is expected that this strategy can be used as a general protocol for mechanism study of the wet chemical synthesis processes.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.7b00198.

Photos of homemade in situ flow system, TEM and HRTEM of iron, cobalt, and molybdenum carbide materials, transition state geometries, potential energy diagrams, XRD patterns, EXAFS fitting results of Fe K edge spectra (PDF).

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## REFERENCES


