

Nanophase Iron Clusters Produced by CO₂ Laser Multiphoton-Decomposition of Fe(CO)₅: Their Generation and Characterization

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We have produced *nanophase* iron clusters inside a gas cell by decomposing iron pentacarbonyls from the mixture of ~20 Torr Fe(CO)₅/~3 Torr SF₆ with a pulsed CO₂ laser. The product displayed a black tint. Its composition was identified to be mostly iron from an inductively coupled plasma (ICP) atomic emission spectrum. The X-ray diffraction (XRD) pattern indicates a body-centered cubic structure for the cluster. A transmission electron micrograph proves that their diameter ranges between 50 and 70 Å and their average diameter is 60 Å.

Introduction

Through both theories and experiments a great deal of effort to study clusters and cluster ions has been made.^{1,2-5} In the last two decades we have literally seen so many struggles dealing with clusters. Although many research reports exist regarding small ($n < 10$, n : cluster size) and large clusters ($10 < n < 100$), only a few exist for clusters with n of greater than 100, especially for $n > 1000$ (the so called *nanophase*), which is close to the condensed matter.¹

Regarding metal clusters, there also exist numerous experimental and theoretical investigations focusing their attention on a variety of issues.^{2,3} Experimental studies were more or less dependent upon the production methods of metal clusters. Two familiar techniques, the oven beam⁴ and laser ablation methods⁵ possess a range of cluster sizes ranging from one to several hundreds, as evidenced from their mass spectrometry.

On the other hand, metal carbonyls⁶ as well as organometallics⁷ have been known to decompose through multiphoton processes with IR, visible, or UV photons to make metal particles. These particles formed thin films when deposited on a substrate.⁷ Shock tube⁸ and laser induced dielectric breakdown methods⁹ have also produced metal particles. Many studies on Fe(CO)₅ also exist, which include the bond energy measurements,¹⁰ electron affinity measurements,¹¹ catalytic activity studies,¹² and photofragmentation dynamics studies.¹³

Here, in our laboratory we have investigated generation, structure, and size of *nanophase* iron clusters. We have produced *nanophase* metal clusters in the gas cell by decomposing SF₆ photosensitized iron pentacarbonyls (Fe(CO)₅) with a pulsed CO₂ laser through a multiphoton process. We investigated their structure with XRD and their size with TEM.

Experimental: Generation of Nanophase Iron Clusters

We have produced *nanophase* iron clusters in the gas cell by shining a pulsed CO₂ laser beam to a gas mixture of 20 Torr Fe(CO)₅ and 3 Torr SF₆. A CW mode of a CO₂ laser provided the same results. A scheme of the experimental setup is presented in Figure 1. The CO₂ laser was operated

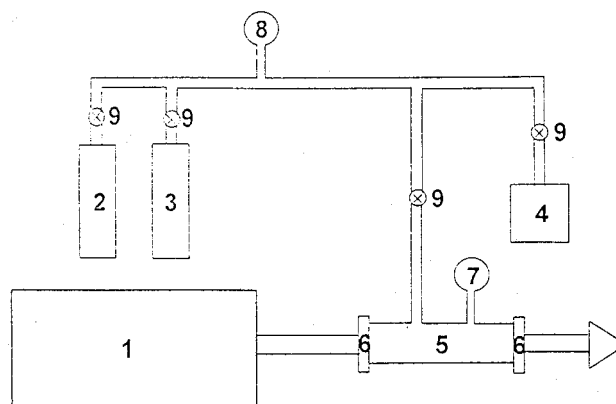


Figure 1. Schematic diagram of the experimental setup. 1: pulsed CO₂ laser, 2: SF₆, 3: Fe(CO)₅, 4: rotary pump, 5: gas cell, 6: KBr window, 7: thermocouple gauge, 8: pressure gauge (0 Torr-100 psig), 9: valve.

in a pulsed mode with a repetition rate of 1 Hz and the frequency was fixed at 10.6 μm. Its usual output power was ~10 watts when operated in the CW mode. The gas cell was made of a straight-through glass pipe with an internal volume of 300 cm³. The KBr windows were glued to the gas cell with epoxy. The cell was aligned to the laser beam axis so that the laser beam did not hit the wall when it passed through the cell. The gas mixture was composed of 20 Torr Fe(CO)₅ and 3 Torr SF₆. Here, SF₆ was a photosensitizer which absorbed IR photons and transferred its energy to Fe(CO)₅ through collisions. We initially pumped out the gas cell with a mechanical pump down to 10 mTorr and filled gases into the cell. We introduced a pulsed CO₂ laser beam into the gas cell and carefully observed the formation of iron particles. We could identify black particles formed inside the gas cell in ten minutes after shining the CO₂ laser. The place where the metal clusters were formed seemed to be dependent on the Fe(CO)₅ pressure. That is, we immediately observed a gas phase formation of metal clusters inside the wall of the gas cell after several shots of laser when the pressure of Fe(CO)₅ was above 30 Torr. When its pressure was below 20 Torr, metal clusters were formed slowly and steadily on the wall of the cell.

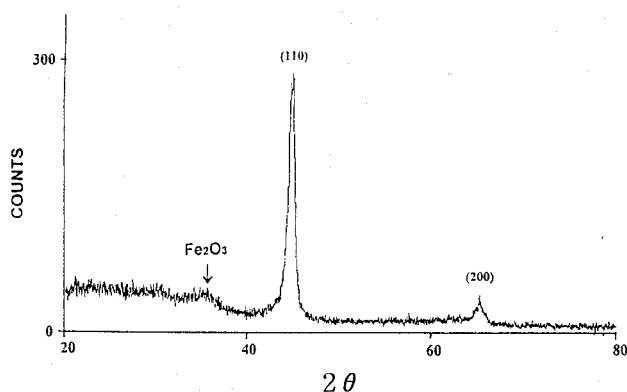


Figure 2. An X-ray diffraction pattern of *nanophase* iron clusters. The first small broad peak results from the iron oxide, Fe_2O_3 . The second and third peaks are from the body centered-cubic *nanophase* iron clusters. Their Miller indices are denoted in the figure.

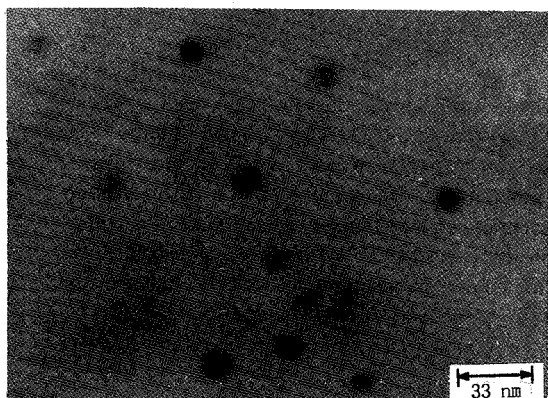


Figure 3. A transmission electron micrograph of *nanophase* iron clusters. A magnification used is 3×10^5 . The black spot represents "one" *nanophase* iron cluster. The cluster diameter is in the range of 50–70 Å and in average 60 Å (≈ 6 nm). This picture was obtained by dispersing the sample clusters with methanol.

Results and Discussion

In order to confirm that the particles produced in the gas cell were iron, we collected black particles and analysed their contents with an inductively coupled plasma (ICP) atomic emission spectrometer.¹⁴ It showed that more than 90% of the sample was metal iron. The remaining component was mostly oxygen as iron oxide which was confirmed from the X-ray diffraction pattern.

We took an X-ray diffraction pattern with XRD¹⁴ in order to investigate the structure of *nanophase* iron clusters. We found that they were body-centered cubic, which is a stable structure of iron at room temperature. An X-ray diffraction pattern of iron clusters is presented in Figure 2. The first broad peak is iron oxide, Fe_2O_3 . The remaining two peaks are from the body-centered cubic iron clusters. They are assigned as (110) and (200), respectively.

We took a transmission electron micrograph¹⁴ in order to determine the size (or diameter) of the *nanophase* metal clusters. A transmission electron micrograph is presented in

Figure 3. The size distribution is in the range of 50–70 Å with an average size of 60 Å (≈ 6 nm). With a packing fraction of 0.68 for the body centered cubic¹⁵ and an atomic radius of an iron atom of 1.24 Å,¹⁶ and assuming a spherical shape of the clusters, we estimated $\sim 10,000$ iron atoms composing one *nanophase* iron cluster with a diameter of 60 Å.

Other feasible metals from metal carbonyls which can be also produced using this method are Ru, Os, V, Cr, Mo, W, Co, Ni, and so on.¹⁷ It is extremely difficult to produce *nanophase* metal clusters with ordinary metal sources such as the oven or laser ablation.

Conclusion

We have produced *nanophase* iron clusters in the gas cell by decomposing SF_6 photosensitized metal carbonyls with a pulsed CO_2 laser via multiphoton process. In addition we have investigated their structure with XRD and their size with TEM. The cluster size produced in this work is in fact already close to the bulk metal. Their XRD pattern indicates that they possess a body-centered cubic structure. Their TEM picture shows that their diameters are in the range between 50 and 70 Å with an average size of 60 Å (≈ 6 nm).

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Synthesis and Characterization of Schiff Base-Cu(II) Complexes Derived from 2-Hydroxy-1-Naphthaldehyde and Aliphatic Diamines

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Tetradentate Schiff base ligands derived from 2-hydroxy-1-naphthaldehyde and aliphatic diamine have been synthesized. Cu(II) complexes of Schiff base ligands have been synthesized from the free ligands and copper acetate. The mole ratio of ligand to copper was identified to be 1:1 by the result of elemental analysis and Cu(II) complexes were in a four-coordinated configuration. The electrochemical redox process of Cu(II) complexes in a DMF solution has been investigated by cyclic voltammetry, chronoamperometry, differential pulse voltammetry, and controlled potential coulometry. The redox process of Cu(II) complexes is one electron transfer process in quasi-reversible and diffusion-controlled reaction. The electrochemical redox potentials and the kinetic parameters of Cu(II) complexes are affected by the chelate ring of Schiff base ligands.

Introduction

The control and understanding of the reactions of transition metal complexes with dioxygen is relevant to oxygen transport in biological systems, oxygenase enzymes, and homogeneous oxygenation catalysts.¹⁻⁴ Complexes of Schiff base ligands have been studied for their dioxygen uptake⁵ and oxidative catalysis.⁶ Also complexes of transition metal (II) involving derivatives of salicylaldehyde and aliphatic amines have gotten considerable attention because of their similarity to the biological dioxygen carriers, as well as their potential as catalysts for the insertion of oxygen into organic substrates.⁷⁻¹² Especially, Co(II) and Cu(II) complexes employing tetradentate Schiff base 2N2O donor ligands which coordinate through donor atoms have been studied as oxygen-carriers.^{13,14} Although the preparation, structure, spectral characterization, and the coordination chemistry of Schiff base complexes have been studied extensively,¹⁵⁻²⁰ yet little is reported on the electrochemical studies.

In this study, we synthesized several Cu(II) complexes of tetradentate Schiff bases derived from the condensation of 2-hydroxy-1-naphthaldehyde with aliphatic diamines. The ligands and their Cu(II) complexes were characterized by elemental analysis, IR, ¹H NMR, ¹³C NMR, UV-vis spectra, molar conductance, and thermogravimetric analysis. The electrochemical redox process of the ligands and their Cu(II) complexes in N,N-dimethylformamide (DMF) solutions was

investigated by cyclic voltammetry, chronoamperometry, differential pulse voltammetry, controlled potential coulometry. In this paper, syntheses and the electrochemical behavior of the Cu(II) complexes are reported.

Experimental

Materials. Ethanol, sodium hydroxide, copper(II) acetate monohydrate, 2-hydroxy-1-naphthaldehyde, ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, and 1,5-diaminopentane were obtained from Aldrich Chemical Co. and used without further purification. DMF was dried by a standard procedure²¹ before use. TEAP was recrystallized twice from distilled water and dried at 70 °C *in vacuo*.

Preparation of ligands. A typical procedure for the synthesis of tetradentate Schiff base is as follows. A solution of 0.1 mole diamine in 50 mL ethanol was slowly added to a solution of 0.2 mole 2-hydroxy-1-naphthaldehyde in 50 mL ethanol under nitrogen atmosphere. After stirring reaction mixture for 2 hrs, the precipitate was collected by filtration. The products were recrystallized from ethanol and dried under reduced pressure at 60 °C.

1,2-bis(naphthylideneimino)ethane; H₂NAPET. 97 % yield; mp 215-217 °C; Anal. Calcd for C₂₄H₂₀N₂O₂: C, 78.24; H, 5.47; N, 7.60; Found: C, 78.13; H, 5.55; N, 7.73; IR (KBr pellet, cm⁻¹): 3420 (O-H), 3057 (ArC-H), 2932 (C-H), 1642 (C=N), 1541 (C=C), 1452 (C=C), 1254 (C-O); UV-vis (DMF,