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Thermal decomposition of copper (II) acetylacetonate in supercritical carbon dioxide: In situ observation via UV–vis spectroscopy

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ABSTRACT

The thermal decomposition of copper (II) acetylacetonate ($Cu(II)(acac)_2$) in supercritical carbon dioxide ($scCO_2$) was investigated via in situ UV–vis spectroscopy. Release of acetylacetone ligands from the central metal atom was observed as the initial step in the decomposition. The kinetics of the decomposition at 423–453 K and 15–25 MPa in $scCO_2$ were studied. The decomposition reaction generally followed the first-order kinetics. The reaction rate was slightly increased with an increase in the pressure, due to changes in the $scCO_2$ density. The activation energy of the decomposition was calculated as 60.3 $kJmol^{-1}$ at 15 MPa, 56.3 $kJmol^{-1}$ at 20 MPa and 52.4 $kJmol^{-1}$ at 25 MPa, which are lower values than those observed in air and in vacuum. The pressure dependence of the activation energy of the decomposition reaction was clarified quantitatively for the first time, and revealed the energy conservation benefit of using $scCO_2$ as a process solvent for a variety of metal/metal oxide deposition process of nanomaterials.

1. Introduction

The application of organometallic precursors in the fabrication of nanomaterials using supercritical carbon dioxide ($scCO_2$) is well-known [1–5]. Since $scCO_2$ can, due to its low viscosity and zero surface tension, penetrate very fine structures in the course of such processes, these $scCO_2$-based technologies are promising for designing nanoscale structures of metals and metal oxides. Deposited thin films metal or metal oxide nanoparticles are frequently employed for catalytic and microelectronic devices [5]. The use of supercritical fluid deposition (SCFD) assisted by hydrogen as a reducing agent [6,7] has become an active research field for the deposition of copper thin films on semiconductor devices with complex three-dimensional structures [8–10].

The final step in such depositions is the thermal decomposition or reduction of the organometallic compound into metal or metal oxide. Hence, the decomposition/reduction process of the metal complexes plays a very important role the fabrication of the nanostructured material. Research on the use of metal complexes in $scCO_2$ has shown that both thermal [11,12] and hydrogen [13] reduction of the metal complex in $scCO_2$ is observed at temperatures lower than their decomposition temperature under other conditions. However, reports on the kinetics of the reduction and decomposition of organic metal compounds in $scCO_2$ are scarce. Zong et al. reported the kinetics of the hydrogen reduction of (2,2,7-trimethyloctane-3,5-dionato) copper(II) in $scCO_2$ through the growth of the copper films formed [14]. Peng, et. al also reported reaction kinetics of the pyrolysis of aluminum acetylacetonate and gallium acetylacetonate through the growth rate of films, and reported that the activation energy for thermal decomposition of aluminum acetylacetonate in $scCO_2$ was lower than that of the vacuum-based thermal decomposition [15]. Such studies have provided qualitative evidence that reaction of metal complexes in $scCO_2$ results in faster reaction rates and lower activation energies than under other conditions. The effect of $scCO_2$ can be attributed qualitatively to the effect of solvation in $scCO_2$, which is documented for other chemical reactions in $scCO_2$ [16,17]. However, few quantitative studies on the effect of using $scCO_2$ as the solvent in organometallic decomposition/reduction reactions have been conducted.

We have studied the kinetics of the thermal decomposition of metal acetylacetonate in $scCO_2$ using in situ UV–vis spectroscopy. We consider this method to have advantages for the direct observation of the thermal decomposition in the $scCO_2$ medium, in that

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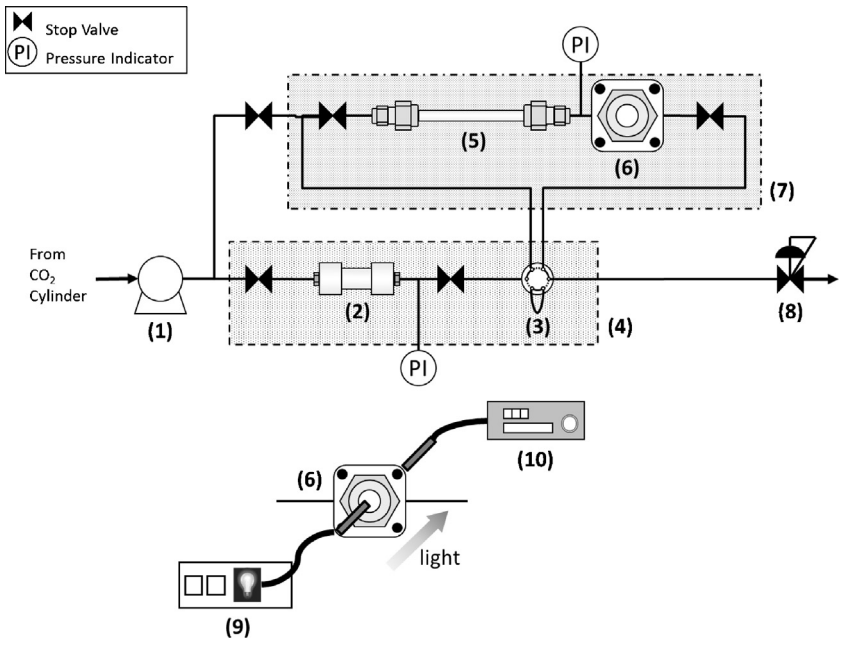

Fig. 1. Schematic diagram of equipment. (1) high pressure pump (JASCO SCF-Get), (2) sample column for Cu(II)(acac)$_2$, (3) 6 port valve for flow channel change, (4) constant temperature oven for saturation column, (5) buffer column (2.2 cm^3), (6) high-pressure optical cell (optical path 4 mm, inner volume 0.2 cm^3), (7) constant temperature oven for optical cell, (8) back pressure regulator, (9) UV-spot light source, with fiber optics attachment, (10) Photonic multi-channel analyzer with fiber optics attachment.

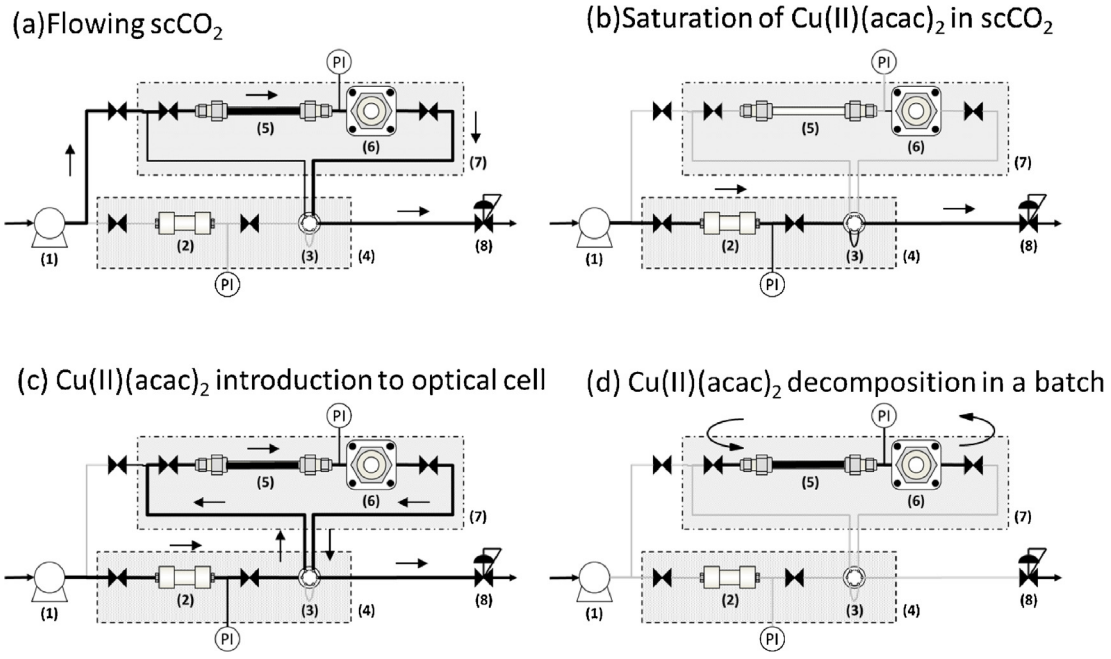

Fig. 2. Schematic diagrams of flow changes for each experimental procedure. (a) Flowing $scCO_2$ in the optical cell, (b) Saturation of Cu(II)(acac)$_2$ in $scCO_2$, (c) Cu(II)(acac)$_2$ introduction to optical cell, (d) Cu(II)(acac)$_2$ decomposition in a batch.

it is a bulk technique and does not rely on measurements at the surface of the reactants. A similar technique was reported in the study by Garriga et al. of the decomposition of copper (II) fluoroacetylacetonate in a $scCO_2$/alcohol mixture [18]. We have already conducted preliminary research on the decomposition of copper (II) acetylacetonate (Cu(II)(acac)$_2$) and Pd(II)(acac)$_2$ using fiber optical systems [19]. Here we report our integrated research results on the kinetics of the thermal decomposition of Cu(II)(acac)$_2$. We first quantitatively investigated the effects of temperature, pressure and the density of the CO_2 on the decomposition rate and the apparent activation energy quantitatively. The effects of $scCO_2$ on the decomposition of the Cu(II)(acac)$_2$ are discussed from the viewpoint of CO_2 molecular clustering around the organometallic molecules.

2. Experimental

2.1. Materials

Carbon dioxide (CO_2, 99.995%, Syowa Tansan Co. Ltd) was dried by flowing through dehydrated zeolite 5A column before use. Cu(II)(acac)$_2$ (Aldrich, >99.8%) was handled in an inert gas and was used without further purification.