J. of Supercritical Fluids 90 (2014) 53–59

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Hydrothermal synthesis of metal nanoparticles using glycerol as a reducing agent

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ARTICLE INFO

Article history:
Received 25 July 2013
Received in revised form 26 February 2014
Accepted 27 February 2014
Available online 12 March 2014

Keywords:
Supercritical water
Glycerol
Metal particles
Metal oxide particles
Hydrothermal reduction

ABSTRACT

Metal and metal oxide nanoparticles were synthesized using supercritical water (SCW) as a reaction medium and glycerol as a reducing agent at 400 °C and 300 bar. X-ray diffraction (XRD) patterns confirmed that silver, copper and nickel nitrates were reduced to zero-valent metal nanoparticles. On the other hand, cobalt, iron and manganese nitrates were partially reduced into low-valent metal oxides. Scanning electron microscopy (SEM) images showed that the reduced metals and metal oxides were smaller than the metal oxides formed without glycerol. The difference in reduction behavior of elements is explained using their reduction potentials. Glycerol proved to be an effective reducing agent for hydrothermal applications.

1. Introduction

Synthesis methods of metal nanoparticles have been under research for decades since they are used in various fields of industry such as catalysis, ceramics, coatings, and magnetic materials. Commonly known solution methods for synthesizing metal nanoparticles are polyol process [1], micro-emulsion [2], chemical reduction [3], solvothermal [4,5], and inverse micelle [6]. Each method has its own advantages and disadvantages. The common disadvantages are the use of toxic reagents, requiring an inert atmosphere, and the need for organic waste treatment. As an alternative, hydrothermal crystallization of metal oxides was first introduced by Adschiri et al. [7] which heats up aqueous acidified metal salt solution to a supercritical state of 400 °C and 35 MPa. Despite the high temperature and pressure, the supercritical water (SCW) method allows rapid and simple synthesis of pure metal oxides which is an environmentally friendly process. Water is cheap, abundant, environmentally benign, and is a well-known oxidizing agent as well as a solvent. In spite of the water's strong oxidizing nature, there have been several attempts to synthesize metals using SCW with formic acid as a reducing agent. Sue et al. produced nickel fine particles [8], Ohara et al. and Seong et al. have successfully synthesized cobalt nanoparticles [9,10], and Arita et al. attempted to synthesize iron nanoparticles [11], all in the presence of SCW and formic acid.

Supercritical alcohol was also found to be a superb reductive medium. Kim et al. synthesized copper, nickel and silver using supercritical methanol at 400 °C without any reducing agents or stabilizers [4]. The supercritical alcohol was not only the reaction solvent but also a reducing agent. Supercritical methanol was also used for synthesizing cobalt nanoparticles [5] and magnetite nanoparticles [12]. Synthesis of metals or metal oxides using supercritical alcohols have the advantage of not using any reductants which allows simpler production process and product recovery.

In this paper, we examined the hydrothermal reduction of metals and metal oxides using SCW as a reaction medium and glycerol as a reducing agent. Silver, copper, nickel, cobalt, iron and manganese nitrates were tested for their reduction. Glycerol differs from other reductants in many ways; it is readily available, environmentally benign, odorless, safe upon skin contact, and does not require a glovebox for formulation. Reducing agents themselves become oxidized during reaction. Glycerol can be oxidized into many products such as glyceraldehyde, glyceric acid, dihydroxy acetone, and hydroxypyruvinic aldehyde [13]. Glycerol treated in SCW can also dehydrate to form acrolein. Therefore, various glycerol-derived chemicals can be made simultaneously.

2. Materials and methods

2.1. Materials

The metal precursors were nickel (II) nitrate (Hayashi Pure Chemical), copper (II) nitrate (Shinyo Pure Chemical),

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http://dx.doi.org/10.1016/j.supflu.2014.02.022
0896-8446/

silver (I) nitrate (Sigma–Aldrich), cobalt (II) nitrate (Junsei Chemical), iron (III) nitrate (Sigma–Aldrich) and manganese (II) nitrate (Kanto Chemical), which were all used as received. Glycerol was obtained from Sigma–Aldrich and water was deionized using Millipore Milli-Q Advantage A10 apparatus.

2.2. Experimental methods

The hydrothermal synthesis of metal nanoparticles was carried out in a stainless steel (SUS316) reactor with an inner volume of 23 ml. A thermostat-monitored salt bath system consisting of KNO_3, $NaNO_3$ and $Ca(NO_3)_2$ were used to heat up the reactor to the desired reaction temperature. For a typical synthesis, an appropriate amount of 0.1 M metal nitrate precursor solution was placed in the reactor so that the pressure would be 300 bar at 400 °C [14]. The reducing agent glycerol was added to the reactor according to the prescribed mole ratio of glycerol to metal precursor which was 5–15. The reactor loaded with metal salt solution and glycerol was tightly sealed and put into the salt bath for 10 min with constant shaking. After 10 min, the reaction inside the reactor was terminated by rapidly quenching the reactor in a cool water bath. The resulting powders were isolated and washed three times with water to remove organic residues. The washed powders were dried in a vacuum oven at 80 °C for 24 h.

2.3. Physical characterization

The hydrothermally synthesized nanoparticles were analyzed using X-ray diffraction (XRD; Rigaku D/Max-3C diffractometer with Cu Kα radiation) and scanning electron microscopy (SEM; Carl Zeiss Auriga). XRD patterns confirmed the phase and purity of the product nanoparticles, whether they were uncharged metals, reduced metal oxides or ordinary metal oxides. SEM images were taken to check the particle size and shape.

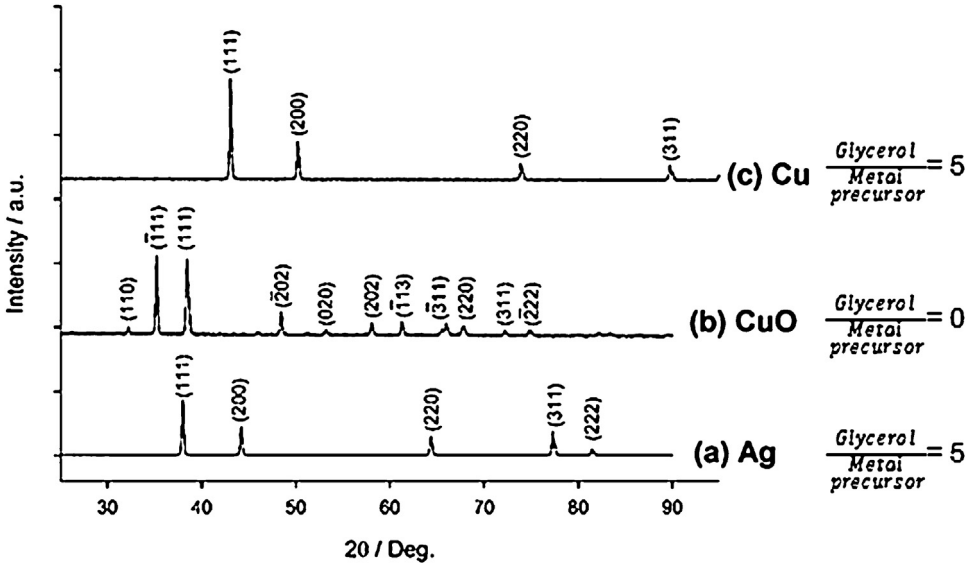

Fig. 1. XRD patterns of (a) Ag, (b) CuO, and (c) Cu synthesized using SCW at 400 °C. Mole ratio of glycerol to metal precursor was 5 for Ag and Cu synthesis.

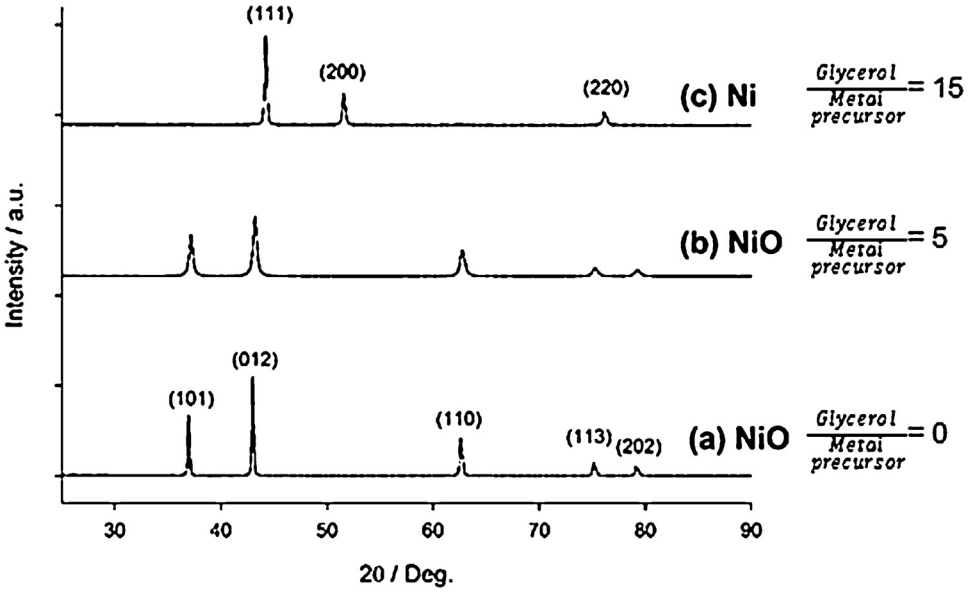

Fig. 2. XRD patterns of (a) NiO, (b) NiO and (c) Ni synthesized using SCW at 400 °C. Mole ratio of glycerol to metal precursor was (a) 0, (b) 5, and (c) 15.