Available Online at http://www.journalajst.com

ASIAN JOURNAL OF SCIENCE AND TECHNOLOGY

ISSN: 0976-3376

Asian Journal of Science and Technology
Vol. 08, Issue, 03, pp.4409-4412, March, 2017

RESEARCH ARTICLE

PREPARATION OF COPPER NANOPARTICLES AS STARTING MATERIALS FOR COPPER CLAY PRODUCTION

***Prodjosantoso, A.K., Utomo, M.P. and Padmaningrum, R.T.**

Chemistry Department, Yogyakarta State University, Yogyakarta, DIY 55281 Indonesia

ARTICLE INFO

Article History:
Received 06th December, 2016
Received in revised form
24th January, 2017
Accepted 17th February, 2017
Published online 31st March, 2017

Key words:

Copper nanoparticle,
Copper clay, XRD, TEM.

ABSTRACT

Copper nanoparticle and copper clay were prepared and investigated. The nanoparticle was prepared by reducing copper ion using iron as reduction agent. XRD, TEM and SEM methods were used to characterize the samples. Copper nanoparticle could be prepared, and copper clay could be produced and be used as raw material inbrass handicrafts.

INTRODUCTION

Over the years, the demand for copper and brass handicrafts were increasing. In general, brass handicrafts from Indonesia use brass metal plate or sheet with a thickness of less than 0.5 mm as starting material. Craft-making process takes a relatively long; starting from design to manufacture finishing. On the other hand, brass handicraft workmanship work through the process of metal melting followed by casting process or printing, and carving. Although the process is relatively simple, but this is monotonous, time consuming and wasting a lot of energy. This would require a relatively large production costs that can ultimately lead reducing amount of benefits of the employers. The metal craft businesses have made various efforts to improve the quantity and quality of its products, such as alloying copper with other metals. The incorporating aluminum into copper metal has been conducted. (Benedeti, *et al.*, 1995) Another effort is the use of metal raw materials in the form of particles of nanometer in size. These particles have a lower melting point than that of the metal in the form of pellets or sheets. (Yeshchenko, *et al.*, 2007) To be easily applied in the production of handicrafts, the metal can be combined with the aggregator material (eg, polyethylene glycol = PEG) into metal clay. (Ali and Lamprecht, 2013) Copper nanoparticles can be prepared by oxidation-reduction reaction.

****Corresponding author: Prodjosantoso, A.K.,***
Chemistry Department, Yogyakarta State University, Yogyakarta, DIY 55281 Indonesia.

In general, the oxidation-reduction reaction takes place based on the Volta series of the relative electrode potential cell compare to the hydrogen electrode. The more reactive metal (easier to remove an electron) and a reducing agent which is getting stronger (more prone elements oxidation). Cu precipitate can be obtained by reducing the Cu^{2+} ions using a more reactive metal.(Zhang, Yang, Ding, Lan, and Guo, 2010) In the reaction between $CuSO_4$ and Al metals,the salt $Al_2(SO_4)_3$ and Cu precipitate will occur.

$$2Al(s) + 3CuSO_4(aq) \rightarrow Al_2(SO_4)_3\ (aq) + 3Cu\ (s)$$

In this reaction the Al metal will oxidize into Al^{3+}, whereas Cu^{2+} will experience a reduction to Cu. In this study, the copper involved in an oxidation-reduction reaction.The expected final results from such reactions are nanoparticles of copper (copper nanoparticles). The oxidation-reduction reactions are as follows:

a. Dissolution of Cu with HNO_3

$$3Cu\ (s) + 8HNO_3\ (aq) \rightarrow 3Cu\ (NO_3)_2\ (aq) + 2NO\ (g) + 4H_2O\ (aq)$$

In this case the Cu oxidizes becomes Cu^{2+}.

b. Cu metal deposition with the help of Fe

$$Cu(NO_3)_2(aq) + Fe\ (s) \rightarrow Fe(NO_3)_2\ (aq) + Cu\ (s)$$

In this case Cu^{2+} ions reduce into Cu.

Copper resulted of the reduction of Cu 2+ ions are expected to have a size of nanometer scale. Copper nanoparticles have a high conductivity and can be used as a catalyst in various chemical reactions, such as the synthesis of methanol and glycol (Graciani, *et al.*, 2014; Twigg and Spencer, 2003; Kasatkin, *et al.*, 2007). Clay is a material that is naturally composed of fine-grained mineral which will harden when dried or heated.(Guggenheim, *et al.*, 1995; Velde and Meunier, 2008) Copper clay can be defined as a material composed of copper particles with a size which is very soft and aggregate material (eg. PEG) so has physical properties that resemble clay loam and harden when dried or heated (Akhrif, *et al.*, 2014). The copper clay behaves similarly to clay upon heating. When heated the copper clay will harden and forming aggregate materials. The PEG is burnt and the copper nanoparticles undergo aggregation. Aggregate copper has properties like the result of the cooling of the molten metal of copper. The copper aggregate is formed at a relatively lower temperature than the melting point of copper in the form of pellets. This will give us an advantage if copper clay used as raw material in the manufacture of metal craft, such as coins and other household appliances. This research studies the preparation of copper metal in the size scale of nanometers are expected to have a lower melting point than copper metal in the form of pellets or sheets. The metal will be aggregated with PEG to produce copper clay.

Experiment

MATERIALS

The copper wire(Sigma-Aldrich, ≥99.9%), iron powder(Sigma-Aldrich, ≥99.99%), HNO_3(Sigma-Aldrich, ≥90%), poly(ethylene glycol) 1000(Sigma-Aldrich), were used as received without any further purification.

Instruments

The samples were measured and characterized using powder X-ray diffractometer (XRD) RigakuMultiflex, transmission electron microscope (TEM) JEOL JEM-1400, and scanning electron microscope (SEM) JEOL JSM T-300.

Procedures

A total of 5 grams of copper wire were dissolved in 20 ml of 8M nitric acid.To the copper solution 1 gram of Fe was added with thoroughly stirring until copper precipitate exists. The copper precipitate were filtered and washed with chloroform, and then dried in an oven at 60 °C. The dry solid were measured by using powder XRD and TEM. Another dry sample were mixed with 5% w/w PEG 1000, grinded and then meltedin the furnace at 250 °C for 4 hours. After cooling at room temperature, the melt were characterized by using XRD and SEM.

RESULTS AND DISCUSSION

Copper nanoparticle

This work was conducted to prepare copper clay with the method of oxidation-reduction reactions and to understand the character of the copper nanoparticles and heated copper clay. Thecrystallinity and the phases of copper nanoparticles were studied using powder XRD.Figure 1.represents powder X-ray diffractogram of copper nanoparticle. The X-ray diffractogram indicates the presence of two main crystalline phases. The first and majority crystalline phase is Cu (d = 2.0823 Å, 1.8051 Å and 1.2767 Å) (JCPDScard no. 04–0836), andthe second phase is a compound of Cu_2O (d = 2.4609 Å and 1.5086 Å) (JCPDScard no. 05-0667)*et al.*, 2010; Pike, *et al.*, 2006). The size of copper nanoparticle crystallite could be determined using the Scherrerequation *et al.*, 2012). The Scherrer equation, in X-ray diffraction, is a formula that relates the size of sub-micrometre particles, or crystallites, in a solid to the broadening of a peak in a diffraction pattern.

The Scherrer equation can be written as:

$$\tau = \frac{K\lambda}{B\cos\theta}$$

Whereτ is the mean size of the crystallite, which may be smaller or equal to the grain size;K is a dimensionless shape factor, which has a typical value of about 0.9, but varies with the actual shape ofthe crystallite; λ is the X-ray wavelength; β is the line broadening at half themaximumintensity(FWHM), after subtracting the instrumental line broadening, in radians; and θ is the Bragg angle (in degrees). The crystallite of cooper is about 15 nm, which could be categorized as nanoparticle (Auffan*et al.*, 2009).

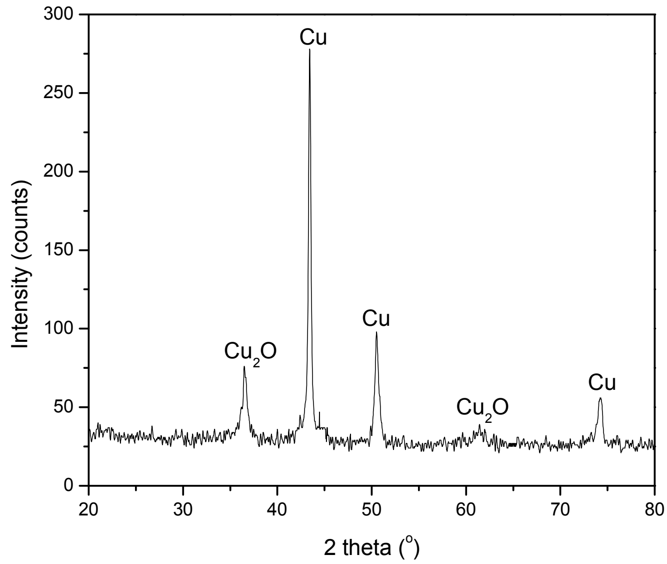

Figure 1. Powder XRD diffractogram of Cu nanoparticle

Transmission electron microscopy (TEM) was used to study the shape and size of the particles. Particles with a size of a few nanometers can be clearly observed using a TEM.(Muneesawang and Sirisathitkul, 2015) Figure 2 is a TEM micrograph of copper nanoparticle sample. The particle was irregular in shape with a size is between 20 nm and 50 nm. The size of the nanoparticles is heterogeneous due to the reduction reaction of copper with iron filings happen relatively quickly.

Copper clay

Copper clay was prepared by mixing copper nanoparticle with 5% w/w PEG 1000. The heating of copper clay at 250 ºC decomposed PEG and left an aggregate of copper.

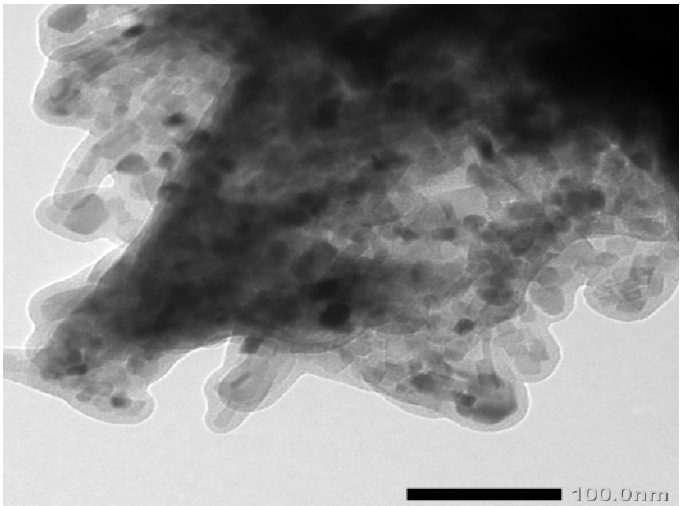

Figure 2. TEM micrograph of copper nanoparticle

Powder XRD (Figure 3) indicated some crystalline copper phases, such as Cu (d = 2.0386 Å and 1.8084 Å), Cu_2O (d = 2.4558 Å, 2.1318 Å and 1.5047 Å) and CuO (d = 2.5158 Å and 2.3235 Å) (JCPDS card no. 45-0937). The formation of $Cu^{II}O$ isdue to the oxidation of Cu^{o} and or $Cu_2{}^{I}O$ in air. The aggregate of Cu with a trace of CuO and Cu_2O is chemically reasonable material inbrass handicrafts.

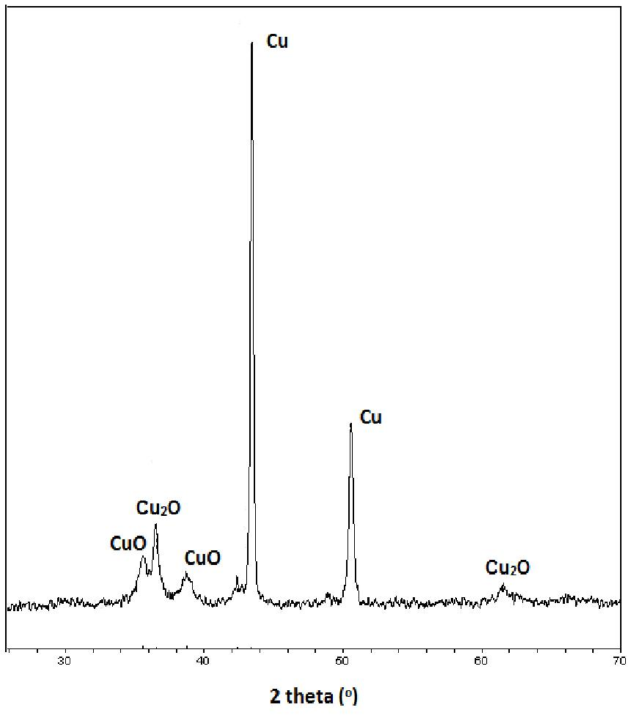

Figure 3. Powder XRD diffractogram of heat treated copper clay

Heat treated copper clay was characterized by using scanning electron microscopy (SEM), to determine the surface morphology and diameter of the nanoparticles. SEM micrograph shows the surface of the porous solid (Figure 4). The pores of the crystals caused by the evaporation of the polyethylene glycol (PEG) when copper clay is heated at a temperature of 250 °C for 4 hours. Upon heating, the copper nanoparticles melted and produced an aggregate with relatively very large size. At 1000x magnification, the surface of molten copper looks to be rough, and heterogeneous in terms of size and shape.

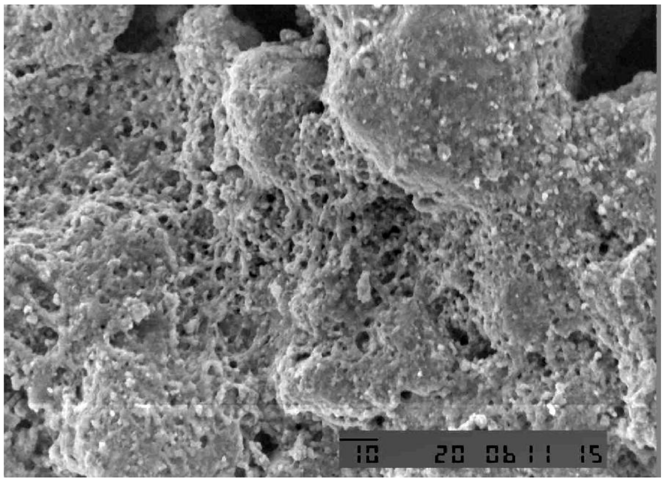

Figure 4. SEM image of heat treated copper clay at 250 ºC (1000x)

Conclusion

Copper nanoparticles can be prepared by the oxidation-reduction methods. The secondary phase of Cu_2O exists in copper nanoparticles. The nature of crystalline copper nanoparticles has a size of between 20 nm and 50 nm. In the other hand, heating copper clay produce s crystalline phases consisting of Cu, CuO and Cu_2O. However, the copper clay is suggested to be used in brass handicrafts.

REFERENCES

Akhrif, I., Jai, M. El, Mesrar, L., Elkhalfi, A., and Touache, A. 2014. Physical Characterization and Elaboration Discussion of a Clay-PEG 6000 Composite with Natural Clay Matrix. *Journal Engineering - Scientific Research*, *6*(June), 338–354.

Ali, M. E., and Lamprecht, A. 2013. Polyethylene glycol as an alternative polymer solvent for nanoparticle preparation. *International Journal of Pharmaceutics*.

Auffan, M., Rose, J., Bottero, J.-Y., Lowry, G. V, Jolivet, J.-P., and Wiesner, M. R. 2009. Towards a definition of inorganic nanoparticles from an environmental, health and safety perspective. *Nature Nanotechnology*, *4*(10), 634–41.

Benedeti, A. V., Sumodjo, P. T. A., Nobe, K., Cabot, P. L., and Proud, W. G. 1995. Electrochemical studies of copper, copper-aluminium and copper-aluminium-silver alloys: Impedance results in 0.5M NaCl. *Electrochimica Acta*, *40*(16), 2657–2668.

Graciani, J., Mudiyanselage, K., Xu, F., Baber, A. E., Evans, J., Senanayake, S. D., Stacchiola, D. J., Liu, P.J., Hrbek, Fernandez Sanz, J. and Rodriguez, J. A. 2014. Highly active copper-ceria and copper-ceria-titania catalysts for methanol synthesis from CO(2. *Science*, *345*(6196), 546–550.

Guggenheim, S., Martin, R. T., Alietti, A., Drits, V. A., Formoso, M. L. L., Galán, E., Köster, H. M., Morgan, D. J., Paquet, H., Watanabe, T., Bain, D. C., Ferrell, R. E., Bish, D. L., Fanning, D. S., Guggenheim, S. , Kodama, H., andWicks, F. J. 1995. Definition of clay and clay mineral: Joint report of the AIPEA nomenclature and CMS nomenclature committees. *Clays and Clay Minerals*.

Hung, L. L., Tsung, C. K., Huang, W., and Yang, P. 2010. Room-temperature formation of hollow Cu2O nanoparticles. *Advanced Materials*, *22*(17), 1910–1914.

Kasatkin, I., Kurr, P., Kniep, B., Trunschke, A., and Schlögl, R. 2007. Role of lattice strain and defects in copper particles on the activity of Cu/ZnO/Al2O3 catalysts for methanol synthesis. *Angewandte Chemie - International Edition*, *46*(38), 7324–7327.

Monshi, A., Foroughi, M. R., and Monshi, M. R. 2012. Modified Scherrer equation to estimate more accurately nano-crystallite size using XRD. *World J. Nano Sci. Eng.*, *2*(3), 154.

Muneesawang, P., and Sirisathitkul, C. 2015. Size Measurement of Nanoparticle Assembly Using Multilevel Segmented TEM Images. *Journal of Nanomaterials*, *2015*, 1–8.

Pike, J., Chan, S. W., Zhang, F., Wang, X., and Hanson, J. 2006. Formation of stable Cu2O from reduction of CuO nanoparticles. *Applied Catalysis A: General*, *303*(2), 273–277.

Twigg, M. V, and Spencer, M. S. 2003. Deactivation of copper metal catalysts for methanol decomposition, methanol steam reforming and methanol synthesis. *Topics in Catalysis*, *22*(3–4), 191–203.

Velde, B., and Meunier, A. 2008. Fundamentals of clay mineral crystal structure and physicochemical properties. In *The Origin of Clay Minerals in Soils and Weathered Rocks* (pp. 3–73.

Yeshchenko, O. A., Dmitruk, I. M., Alexeenko, A. A., and Dmytruk, A. M. 2007. Size-dependent melting of spherical copper nanoparticles embedded in a silica matrix. *Physical Review B - Condensed Matter and Materials Physics*, *75*(8.

Zhang, Q., Yang, Z., Ding, B., Lan, X., and Guo, Y. 2010. Preparation of copper nanoparticles by chemical reduction method using potassium borohydride. *Transactions of Nonferrous Metals Society of China*, *20*(50834003), s240–s244.

****