Copper Nanoparticle Catalysed Aerobic Oxidation of α-pinene

Masruri1* and K K Pamungkas1,2

1Chemistry department, Faculty of Mathematics and Natural Sciences, Brawijaya University, Jl. Veteran 65145 Malang, Indonesia
2Faculty of Mathematics and Natural Sciences, Gifu University, Japan

*Corresponding Author: masruri@ub.ac.id

Abstract. A green aerobic-oxidation of alpha-pinene using air and catalyzed by copper nanoparticle (CuNP) was studied. The study involved preparation and characterization of copper nanoparticle with three different calcination temperatures (300, 500 and 800°C). Nanoparticle characterization was conducted using FTIR spectrophotometry and SEM-EDX analysis. Evaluation of the catalytic activity was done using direct air-bubbled to the alpha-pinene with and without catalyst. It was found that oxidized alpha-pinene was formed as the major product.

1. Introduction

Derivation of naturally abundant chemicals sources is key steps for broadening the further applications. Including transformation of alpha-pinene from turpentine oil, into other derivatives products. For examples conversion into pinene oxide, pinene diol, pinene diamine, carveol, borneol, verbenon, pinonaldehyde [1, 2], pinonic acid [1–3] etc. All these products are important intermediate for chemicals synthesis, agrochemicals, pharmaceuticals, catalysis and ligands in asymmetric synthesis.

The alpha-pinene structure consists of a single carbon-carbon double bond (C=C). Oxidation can break the π–bond down into two new σ–bond and forms the product. The general methods such as dihydroxylation [4], epoxidation [5, 6], and aminohydroxylation [7, 8] reaction catalyzed by osmium tetroxide or other rare earth and precious metals [4, 9–13]. The isolated product are 1,2-diol, epoxide and 1,2-amino-hydroxyl of pinene, respectively. Other oxidation method involves not only the π–bond breaking but also the σ–bond of alpha-pinene. The cleavage affords pinonaldehyde and pinonic acid [1]. Catalyst reported for the reaction such as potassium permanganate [1, 14], palladium [15], rhodium [16], ruthenium [4, 17, 18], gold [10–13, 19]. All these strategies remain as issues regarding the availability, cost the precious metals catalyst, and toxicities issues. Development of aerobic oxidation by using air contain oxygen about 30% become a green alternative for oxidation reaction. However, the strategy requires catalyst to promote interaction between the reagents. Recently, nanoparticle copper has been reported for catalyzed aerobic oxidation of alcohols [20, 21]. The corresponding aldehyde was produced in moderate to excellent yield. Aliphatic and aromatics substrate were applied, and also oxidation of propargylic alcohols [20]. Addition of co-reagent 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) as an electron transfer mediator improve the selectivity and product yield. Other report implement an immobilized of copper nanoparticle in an aminopropyl-group functionalized of pore glass [21]. Similar oxidation result is produced in moderate yield.
This paper reports a copper nanoparticle as catalyst for an aerobic oxidizing of alpha-pinene. The procedure involved preparation and characterization of copper nanoparticle. Some oxidation products are formed with hydroxyl, carbonyl, and carboxyl-functionality on pinene structure.

2. Materials and Method

2.1. Chemicals
Sample of alpha-pinene is isolated and purified from turpentine oils [22] produced by local manufacturer. Meanwhile chemicals were used directly as supplied by manufacturer, namely copper sulfate (Merck), copper chloride (Merck), ethanol (Smart Lab), n-hexane (smart Lab), ethyl acetate (Smart Lab), and pre-coated TLC (Merck).

2.2. Synthesis of copper nanoparticle
A 100 mL of solution of copper sulfate pentahydrate (5.00 g, 26.93 mmol) was mixed with 100 mL solution of urea (1.80 g, 29.97 mmol). The mixture was stirred for 5 h at 80°C or until the mixture color changed from green to brown dark. The gel produced was concentrated by heating in the oven for 2 hours at 130 °C and washed with ethanol 4 x10 mL. The product was divided into 3 separated equally, and each part was calcinated for 2 hours in different temperature, namely 300, 500, and 800°C.

2.3. FTIR analysis
The FTIR analysis was conducted in Shimadzu FTIR using sodium chloride plate and polystyrene used as a standard to baseline. Data recorded as wavenumber (cm⁻¹) to transmittance (%).

2.4. SEM-EDAX analysis
The surface morphology of nanoparticle was analysed using scanning electron microscope (SEM) coupled with energy dispersive analysis X-ray (EDAX) and recorded in SEM FEI, typed Inspect-S50.

2.5. GCMS analysis
Mass spectra was recorded using GCMS spectrometer (Shimadzu GCMS, column Rtx-50 semi-polar, 30 m in length). The mass spectra were scanned as mass per charge (m/z). Alpha-pinene was used as internal standard (retention time in 20 min).

2.6. Aerobic oxidation of alpha-pinene
A stirred of 5.0 mL of alpha-pinene (32.6 mmol) was bubbled with air by using commercial aerator. Temperature was adjusted to 25-30 °C at room atmosphere. Progress of reaction was monitored on every 10 min by spotting in TLC. The presence of new spot or decreasing of alpha-pinene spot was monitored. After completion, the product was separated by extraction with ethyl acetate. This fraction was then evaporated under reduced pressure to isolate the product. Separate procedure was done using addition of copper nanoparticle (25 mg) as the catalyst and addition of hydrogen peroxide (7.5 mL, 30%) as co-oxidation reagent.

3. Result and Discussion

3.1. Synthesis and characterization copper nanoparticle
Copper nanoparticle has two band absorptions in 510 and 1100 cm⁻¹. Both are bands for stretching and bending vibration of Cu-O [2]. Identical and sharp results are detected for both bands (Fig 1), using sample with calcination at 800°C. However, other peaks are also detected for calcination product at 500 and 300 °C. Both products are masked by organic compound which are indicated by bands for hydroxyl-group (3600 cm⁻¹), carboxylate group (broad 3500-2500 cm⁻¹), and olefin group (1620 cm⁻¹).
The masking of copper nanoparticle by organic molecule is confirmed in SEM (Fig 2). Copper nanoparticle calcined at 500 cm\(^{-1}\) (Fig. 2a) is coated with cotton-like structure of organic molecule. For calcination at 800 cm\(^{-1}\) (Fig. 2b), the masking agent was burnt out completely. Thus, easier to measure each particles distance. The approximate particle size was about 30 and 180 nm. Meanwhile, the energy dispersive X-ray (EDAX) analysis (Fig 2 C-D) confirms that calcination at 800°C remove the carbon element to masking the copper nanoparticle, but for sample that calcined at 500°C, carbon and excessive oxygen element still remain.

**Fig 1.** FTIR spectra of copper nanoparticle with calcination at 300, 500, and 800°C.

**Fig 2.** SEM image of copper nanoparticle afforded from calcination at 500°C (A) and 800°C (B). The EDX spectra (C, D) and observed copper-oxygen ratio.

| Element | Calcination temperature of copper nanoparticle |
|---------|-----------------------------------------------|
|         | 500°C (C) | 800°C (D) |
|         | Wt% | At% | Wt% | At% |
| Cu      | 2.15 | 0.55 | 77.96 | 47.11 |
| O       | 97.96 | 99.45 | 22.04 | 52.89 |
3.2. Aerobic oxidation of alpha-pinene

Oxidation of alpha-pinene under air-bubbled condition gave oxide of alpha-pinene. The structure contains an epoxide, hydroxyl, carbonyl, nor carboxyl-functionality on the alpha-pinene skeleton. The FTIR spectra (Fig. 3) detect the presence of carboxyl (3500-2500 cm\(^{-1}\)) and carbonyl (about 1700 cm\(^{-1}\)) group for reaction using hydrogen peroxide and with or without the nanoparticle catalyst (CuNP). But, CuNP catalyst can eliminate the formation of oxidation product contains carbon-carbon double bond (C=C), which is detected in 1620 cm\(^{-1}\).

The product tabulation in each condition is summarized in Table 1. The targeted product is trans-2-caren-4-ol (A), verbenone (B), trans-3-caren-4-ol (C), alpha-pinen oxide (D), and carvone (E). Copper nanoparticle catalyses the epoxide formation after 12 and 24 h reaction. Addition of hydrogen peroxide as co-reagent increase the yield. However, other products are also formed.

![Fig 3. The FTIR spectra of the product from aerobic oxidation of alpha-pinene in given conditions](image)

**Table 1.** Tabulation of the oxidation product from alpha-pinene under reaction conditions.

| Reaction condition | air bubble (aeration) | Product identified |
|--------------------|----------------------|--------------------|
|                    |                       | A  | B  | C  | D   | E   |
| 1 CuNP             | 12 h                 | n.d. | n.d. | n.d. | 0.63 | n.d. |
| 2 CuNP             | 24 h                 | n.d. | n.d. | n.d. | 0.40 | n.d. |
| 3 CuNP, H\(_2\)O\(_2\) | 12 h                 | 11.78 | 6.49 | 5.06 | 1.58 | 1.12 |
| 4 No catalyst, H\(_2\)O\(_2\) | 12 h                 | n.d. | n.d. | n.d. | n.d. | n.d. |

Note: n.d. is not detected of oxidation product. The product percentage was calculated from chromatogram of GCMS. The major identified product structure was identified as the following structures.
Fig 4. Product chromatogram from aerobic oxidation of alpha-pinene after 24 h reaction catalyzed CuNP (A), and 12 h reaction catalysed by CuNP with addition of hydrogen peroxide (B).

4. Conclusion
Copper nanoparticle has been synthesized and can be applied as an aerobic-oxidation catalyst for alpha-pinene with addition of co-reagent hydrogen peroxide. Product selectivity still requires further study.

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