

CATALYTIC ACTIVITY OF Cr₂O₃/SEPIOLITE IN THE OXIDATION OF BENZYL ALCOHOL

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Abstract. Cr₂O₃/sepiolite samples with different loadings have been synthesized from corresponding nitrate salts at constant pH conditions and characterized by several physical methods including X-ray diffraction, TEM, nitrogen physisorption, and TGA, etc. The as-prepared materials have large surface area, high distribution of Cr₂O₃ nanoxides on the nanofibrous sepiolite. The prepared solids were used as heterogeneous catalysts for the oxidation of benzyl alcohol with *t*-BuOOH. Chromium oxides were found to be active sites for the liquid oxidation of benzyl alcohol to aldehyde. The catalytic activity varied with reaction time and temperature. The appropriate temperature is about 60-70 °C with conversion of 40-60 % and benzaldehyde selectivity of 90 %.

Keywords: benzyl alcohol, sepiolite, fiber, benzaldehyde, Cr₂O₃.

Classification numbers: 2.5.1; 2.6.1; 2.10.1.

1. INTRODUCTION

The oxidation of alcoholic compounds to carbonyls was known as an important reaction in organic synthesis due to its oxidation products are widely applied in the synthesis of fine chemicals [1, 2]. Conventionally, large amounts of heavy transition metal salts, metal oxides, and peracids are used in the oxidation reaction of organic compounds. As a consequence, these methods always create a huge amount of heavy metal wastes that further violate with environmental regulations [2, 3]. This makes researchers seek alternative procedures using metal oxide catalysts and more benign stoichiometric oxidants. In general, the heterogeneous catalysts have been mainly prepared from the transition metals, but their structure stability, heterogeneity and recyclability are still major problems [1, 4-6]. More recently, group VIB transition metal ions become more attractive for the oxidation reactions since they often exhibit a very high selectivity to desired oxygenated products at milder reaction conditions [2, 5-7]. Among of the VIB metal oxides supported-catalysts, Cr-containing solids have been commonly used over the last 20 years. In practical, various oxidative reaction of organic compounds performed by reduction-oxidation Cr-molecular sieves [8], especially by chromium-exchanged zeolite [2,9]

have been currently investigated. In experimental, Cr-ZSM-5 prepared from HZSM-5 using the exchangeable method has been applied in the oxidation of benzyl alcohol with *t*-BuOOH [9]. Thus, the chromium is still great potential applicability in the development of oxidation reaction catalysts.

The present study is to deal with the distribution of Cr₂O₃ particles over sepiolite which was known as a fibrous clay mineral with peculiar surface properties [10]. Indeed, sepiolite is constructed of magnesium silicate fibers. A block is composed of an octahedral Mg-OH layer intercalating between two tetrahedrally structured SiO₄ planes. Each one of the Mg²⁺ cations at the edges of the octahedral sheets bound to two molecules of water [10, 11]. Therefore, Cr₂O₃ nanoxides dispersed on high surface area magnesium silicate are expected to exhibit an excellent catalytic activity in the liquid oxidation of aromatic alcohols.

2. EXPERIMENTAL METHODS

2.1. Catalyst preparation

Sepiolite obtained from Aldrich was used as the supporting materials. To prepare each sample, 4.0 grams of sepiolite were dispersed in 100 mL of aqueous chromium(III) nitrate (Sigma-Aldrich, 99 %) solution with a desired quantity of chromium(III) oxide. Afterwards, the solution was mixed with a given amount of sodium hydroxide solution under vigorous stirring. The suspension mixture kept stirring for 2 h in ambient condition prior to be filtered. The filtrate was removed while filter cake was washed via distilled water. The cake was then kept in an oven at 80 °C for 24 h prior to calcine at 410 °C for 2 h (samples subjected to TGA/DrTGA experiments were not calcined).

2.2. Catalyst characterization

Phase structure of the powdered specimens was investigated by X-ray diffraction (XRD) patterns on a D8 Advance-Bruker (CuK_α, λ = 0.1549 nm). DTA/TGA experiments were performed using a DTA/ DSC/TGA Labsys Evo S60/58988 (Setaram). Brunauer-Emmett-Teller (BET) surface area of the as-synthesized sample was analyzed on an Autochem II 2920 (USA). TEM micrographs of the solids were recorded on a Japan Jeol. Jem.1010 instrument.

2.3. Catalytic oxidation of benzyl alcohol

Oxidation reaction between benzyl alcohol and *t*-BuOOH solution was performed in a 100 mL three-necked glass flask equipped for an iced-water condenser. In brief, a mixture of benzyl alcohol (3 mL) and powdered catalyst (0.20 grams) was stirred in flask reactor and heated to the desired temperature. Afterwards, a determined volume of *t*-butyl hydrogen peroxide (70%, Sigma Aldrich) was introduced into the mixture. After a period of time, the flask reactor was cooled to room temperature. Then, the catalyst was removed from reaction mixture via centrifugation step. The obtained liquid phase was quantitatively determined by using a GC-MS (HP-6890 Plus) with a capillary column (5 %-phenyl)-methylpolysiloxane HP-5, 30 m × 0.32 μm × 1 μm and oven temperature programmed from 35 (5 min) to 210 °C (5 min) 5 °C/min. Injection: 0.2 μL.

3. RESULTS AND DISCUSSION

3.1. Characterization of the as-prepared catalysts

The catalyst phase and structure are investigated by XRD method. Figure 1 presents three XRD patterns of sepiolite and Cr_2O_3 loaded samples. As seen in Figure 1, a set of reflection signals at 2-theta of 7.30, 20.58, 23.78, 26.73, 35.06, 40.09° are corresponding to reflections of the magnesium silicate (Joint Committee on Powder Diffraction Standards: 01-075-1597) [10, 11]. The signal-to-noise of the sepiolite loading Cr_2O_3 sample is slightly higher as compared with that of the raw sepiolite, indicating a lower crystalline degree of the Cr-containing catalysts. This characteristic may possibly be related to the thermal treatment of the as-synthesized catalysts which usually lead to the removal of adsorbed water molecules and structural modification of the supporting material [10, 12]. In the XRD patterns of Cr_2O_3 /sepiolite, Figure 1 appears some weak reflection peaks at 2-theta of 24.78, 32.82 and 54.59° corresponding to the signals of Cr_2O_3 crystalline domains (Joint Committee on Powder Diffraction Standards: 00-038-1479) [13].

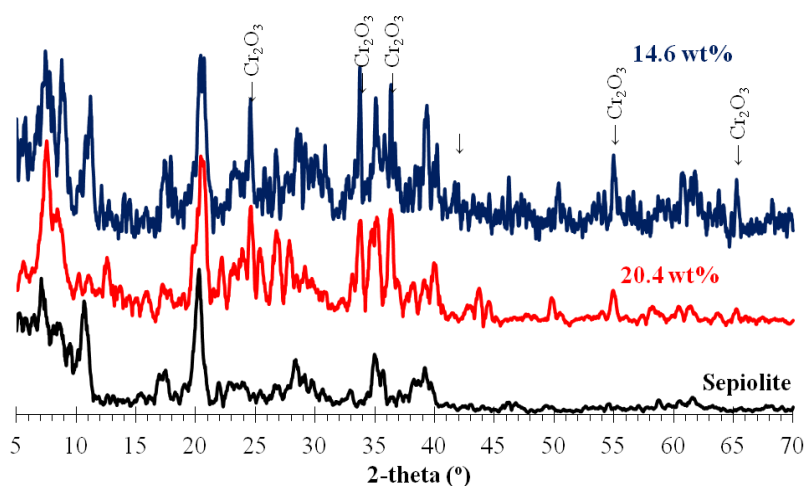


Figure 1. XRD patterns for Cr_2O_3 /sepiolite catalysts and sepiolite.

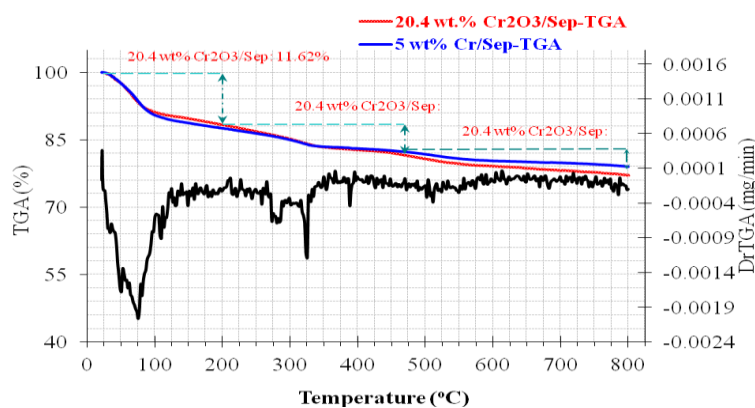


Figure 2. TGA and DrTGA curves of the as-synthesized Cr_2O_3 /sepiolite catalysts prior to calcination at 410 °C.

TGA/DrTGA patterns of two Cr₂O₃/sepiolite catalysts are shown in Figure 2. It is interesting to note that the DrTGA analysis reveals some endothermic processes. The first temperature signal is between room temperature and 200°C which is ascribed to the elimination of adsorbed and some zeolitic water. The weight loss in this range is about 11.62 and 12.40 % for 14.6 and 20.4 wt% Cr₂O₃/sepiolite catalyst, respectively; that is in good agreement with the literature reports [11, 14, 15]. The weight loss (5.31 - 6.84 %) in the second temperature range of 200-475 °C is essentially associated with the liberation of coordinated water and the dehydration of chromium hydroxides [12, 15]. In the third temperature range of 475-800 °C, the weight loss of 3.52-4.36 % is associated with the elimination of the last part of the coordinated water in the tunnels of sepiolite blocks, the dehydroxylation of sepiolite anhydride, and the reaction between chromium oxide and Mg-O-Si sepiolite [10, 15].

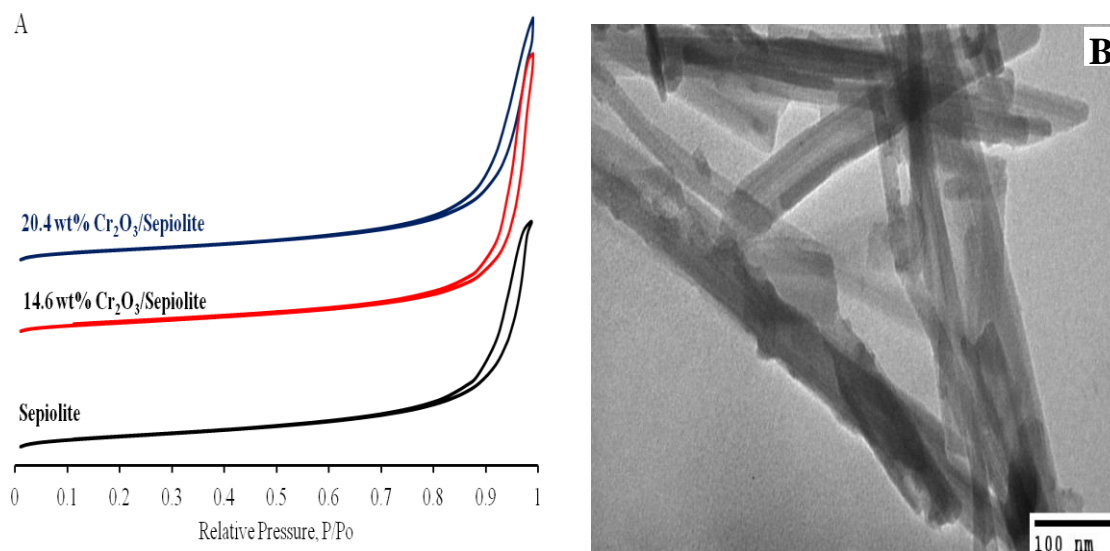


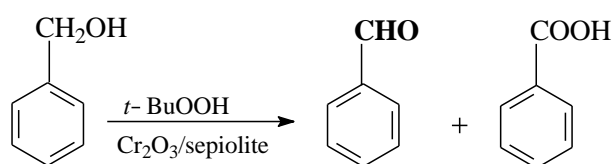
Figure 3. Nitrogen adsorption-desorption isotherms (A) and TEM image (B) of 20.4 wt% Cr₂O₃/sepiolite catalyst.

Figure 3A depicts nitrogen adsorption/desorption isothermal profiles while Fig. 3B shows a TEM image of 20.4 wt% Cr₂O₃/sepiolite. Firstly, the isothermal profiles of the two samples are slightly slanted towards the right in the relative pressure range of 0 - 0.85. Furthermore, a steep hysteresis loop appears in the relative pressure window of 0.85 – 1.0. These isotherms of the samples are likely in good agreement with the type II in the IUPAC classification, indicating that the existence of some micropores and slit-shaped open pores [10, 14]. Indeed, the H3 type-hysteresis was known as typical characteristics for formation of tubular pores in the solids. The specific surface area of such material is about 192 m²/g [11, 16]. Secondly, TEM image reveals that the 20.4 wt% Cr₂O₃/sepiolite is composed of nanofibers. Each fiber has a length of some microns and a diameter of 170-200 nm. The arrangement of these nanofibers makes the sample more porosity and better uniformity.

3.2. Catalytic studies

The oxidation reaction of benzyl alcohol was carried out at atmospheric pressure. For comparison, the first experimental reaction was done in the absence of catalyst, but no benzyl alcohol conversion was observed. A second experiment was performed on sepiolite support only

and about 1-2 % conversion of benzyl alcohol is monitored. When the catalyst has Cr₂O₃ component, the conversion of benzyl alcohol increases sharply from 2 to 23 % and the oxidation reaction is very selective for the formation of benzaldehyde although a small amount of benzoic acid byproduct is simultaneously produced as represented in Scheme 1 [5, 7, 17, 18]. Figure 4 shows a remarkably increased conversion of benzyl alcohol from 20 to 52% with increasing reaction time. It is worth noting that both Cr-containing samples present similar trends in conversion versus reaction time, confirming the systematic property of all catalysts. Among the two Cr-based samples, 20.4 wt% Cr₂O₃/sepiolite gives a better benzyl alcohol conversion than the other Cr-sample (Fig. 4A). In both the experimental series (Fig. 4), benzaldehyde selectivity is always a better value (88-95 %) as compared with the data reported in the literature [19-21]. This may suggest that Cr₂O₃ was highly dispersed on fibrous magnesium silicate and chromium oxide component is a key factor to ensure high selectivity to product. In addition, uniform channel-like pore geometry of the sepiolite material should promote diffusion processes of reactants and products during the reaction [5, 9, 19].



Scheme 1. Oxidation of benzyl alcohol to benzaldehyde and benzoic acid.

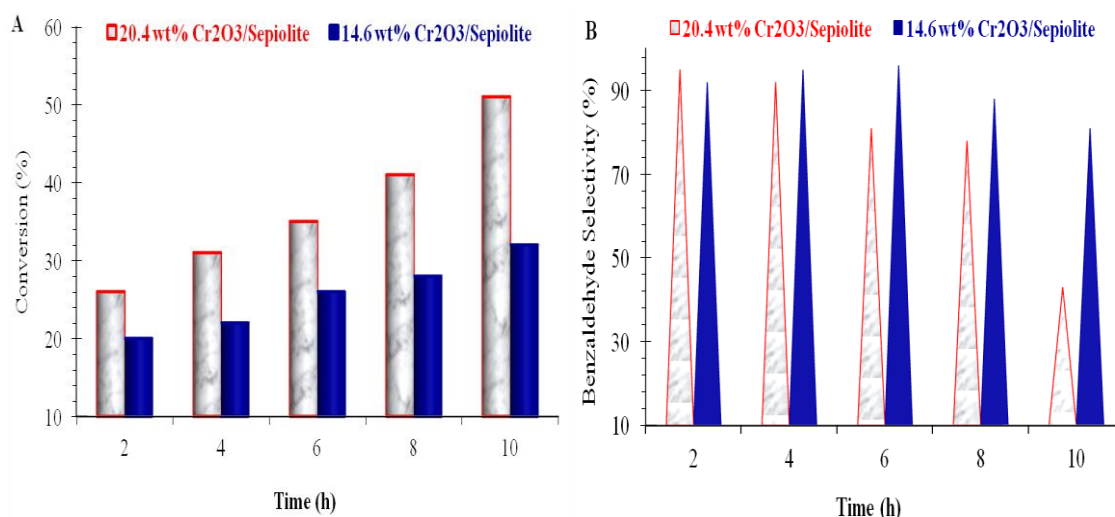


Figure 4. Relationship between conversion (A), product selectivity (B) and oxidation reaction time over Cr₂O₃/sepiolite catalysts (60 °C, C₆H₅CH₂OH/TBHB = 1/1.5).

The selectivity to benzaldehyde exhibits a minor decrease after 6 reaction hour-on-time possibly due to the production of an amount of benzoic acid in the product mixture. This is possibly explained by the overoxidation of benzaldehyde product to benzoic acid as kept for a long time in the bath reactor [1, 20]. Since an increased reaction time have negative effects on the product selectivity, changing in reaction temperature may raise remarkably substrate conversion. Figure 5 displays the relationship between catalytic activity and reaction

temperature. It is observed that the conversion increases linearly with increasing reaction temperature. However, a relative quantity of benzoic acid byproduct is formed at elevated temperatures. Figure 5 also reveals that benzoic acid may be yielded through the deep oxidation reaction of benzaldehyde [17, 20].

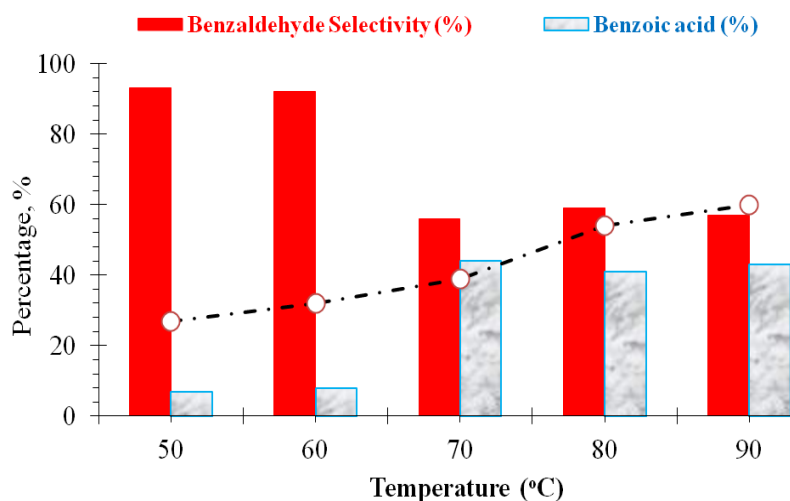


Figure 5. Correlation between temperature on substrate conversion and product distribution over 20.4 wt.% Cr₂O₃/sepiolite (4 h, C₆H₅CH₂OH/TBHB = 1/1.5).

In practice, it was generally observed that the oxidation of benzyl alcohol happens in a series of continuous conversion steps from benzaldehyde to benzoic acid, benzyl benzoate [7, 9, 23]. Raising up reaction temperature would promote some deep oxidation of benzyl alcohol to carboxylic and its derivatives because the activation energy for the oxidation of aldehyde to carboxylic acid, in general, is higher than that of alcohol to aldehyde [5, 19, 20]. Thus, the most suitable reaction temperature for the transformation between benzyl alcohol to benzaldehyde in the present work was found at 60-70 °C.

4. CONCLUSIONS

Two chromium oxide/sepiolite catalysts with different Cr₂O₃ loadings synthesized by precipitation route had finely dispersed Cr₂O₃ particles on the magnesium silicate. The prepared materials possessed high surface area and porosity and were used as catalysts for the oxidation reaction between C₆H₅CH₂OH and *t*-BuOOH at milder conditions. The catalyst exhibited a good activity in conversion of benzyl alcohol to benzaldehyde. In present experimental conditions, Cr₂O₃ component was rather active for the selective oxidation of benzyl alcohol into benzaldehyde. The alcohol conversion approached 40-60 % with the benzaldehyde selectivity of 86%. The substrate conversion and product selectivity were found to vary with on reaction time, temperature.

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REFERENCES

1. Weng Z., Liao G., Wang J., Jian X. - Selective oxidation of benzyl alcohol with hydrogen peroxide over reaction-controlled phase-transfer catalyst, *Catal. Commun.* **8** (2007) 1493–1496.
2. Cainelli G., Cardillo G. - *Chromium Oxidants in Organic Chemistry*, Springer-Verlag, Berlin, 1984.
3. Yadav G.D., Mehta P.H., Haldavanekar B.V. - Capsule membrane phase transfer catalysis: selective alkaline hydrolysis and oxidation of benzyl chloride to benzyl alcohol and benzaldehyde, *Stud. Surf. Sci. Catal.* **78** (1993) 503-512.
4. Mobley J. K. and Crocker M. - Catalytic oxidation of alcohols to carbonyl compounds over hydrotalcite and hydrotalcite-supported catalysts, *RSC Adv.* **5** (2015) 65780-65797.
5. Burange A.S., Jayaram R. V., Shukla R., Tyagi A.K. - Oxidation of benzylic alcohols to carbonyls using *tert*-butyl hydroperoxide over pure phase nanocrystalline CeCrO₃, *Catal. Commun.* **40** (2013) 27–31.
6. Yang X., Wu S., Hu J., Fu Peng X., L., Kan Q., Huo Q., Guan J. - Highly efficient N-doped magnetic cobalt-graphene composite for selective oxidation of benzyl alcohol, *Catal. Commun.* **87** (2016) 90–93.
7. Zhang Y. and Xu Y.-J. - Bi₂WO₆: A highly chemoselective visible light photocatalyst toward aerobic oxidation of benzylic alcohols in water, *RSC Adv.* **4** (2014) 2904–2910.
8. Ayari F., Mhamdia M., Hammedia T., Alvarez-Rodriguez J., Guerrero-Ruizb A.R., Delahayc G., Ghorbe A., - Influence of the parent zeolite structure on chromium speciation and catalytic properties of Cr-zeolite catalysts in the ethylene ammoxidation, *Appl. Catal. A* **439–440** (2012) 88–100.
9. Lounis, A. Riahi, F. Djafri, Muzart J. - Chromium-exchanged zeolite (CrE-ZSM-5) as catalyst for alcohol oxidation and benzylic oxidation with t-BuOOH, *Appl. Catal. A* **309** (2006) 270–272.
10. Garcia-Romero E., Suarez M. - Sepiolite–palygorskite: Textural study and genetic considerations, *Appl. Clay Sci.* **86** (2013) 129–144.
11. Suarez M., Garcia-Romero E. - Variability of the surface properties of sepiolite, *Appl. Clay Sci.* **67–68** (2012) 72–82.
12. Ma Y., Zhang G. - Sepiolite nanofiber-supported platinum nanoparticle catalysts toward the catalytic oxidation of formaldehyde at ambient temperature: Efficient and stable performance and mechanism, *Chem. Eng. J.* **288** (2016) 70–78.
13. Mahmoud H.R. - Highly dispersed Cr₂O₃–ZrO₂ binary oxide nanomaterials as novel catalysts for ethanol conversion, *J. Mol. Catal. A* **392** (2014) 216–222.
14. Ugurlu M., Karaoglu M.H. - TiO₂ supported on sepiolite: Preparation, structural and thermal characterization and catalytic behaviour in photocatalytic treatment of phenol and lignin from olive mill wastewater, *Chem. Eng. J.* **166** (2011) 859–867,
15. Tartaglione G., Tabuani D., G. Camino - Thermal and morphological characterisation of organically modified sepiolite, *Micro. Meso. Mater.* **107** (2008) 161–168.

16. Tuler F.E., Portela R., Avila P., Banus E.D., Miro E.E., Milt V.G. - Structured catalysts based on sepiolite with tailored porosity to remove diesel soot, *Appl. Catal. A* **498** (2015) 41-53.
17. Jia L., Zhang S., F. Gu, Ping Y., Guo X., Zhong Z., F. Su - Highly selective gas-phase oxidation of benzyl alcohol to benzaldehyde over silver-containing hexagonal mesoporous silica, *Micro. Meso. Mater.* **149** (2012) 158-165.
18. Behera G.C., Paridam K.M. - Liquid phase catalytic oxidation of benzyl alcohol to benzaldehyde over vanadium phosphate catalyst, *Appl. Catal. A* **413- 414** (2012) 245-253.
19. Ozturk O.F., Zumreoglu-Karan B., Karabulut S. - Solvent-free oxidation of benzyl alcohol over chromium orthoborate, *Catal. Commun.* **9** (2008) 1644-1648
20. Zhan G., Huang J., Du M., Sun D., Abdul-Rauf I., Lin W. , Hong Y., Li Q. - Liquid phase oxidation of benzyl alcohol to benzaldehyde with novel uncalcined bio-reduction Au catalysts: High activity and durability, *Chem. Eng. J.* **187** (2012) 232-238.
21. Melody K., Mohd M., Hadi J., Suh C., - Bimetallic Cu-Ni nanoparticles supported on activated carbon for catalytic oxidation of benzyl alcohol, *J. Phys. Chem. Sol.* **112** (2018) 50-53.