INTERNATIONAL JOURNAL of RENEWABLE ENERGY RESEARCH
S. Mulijani et al., Vol.12, No.4, December 2022

Synthesis of Titanium Oxide Catalyst with Gold Nanoparticle as a Dopant for Ethanol Dehydration Application

Sri Mulijani*‡, Rohmat Ismail*, Aep Patah**, Karna Wijaya***, A.C. Wibowo****

*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Bogor Agriculture University, Bogor 16118-Indonesia

**Department of Chemistry, Faculty of Mathematics and Natural Sciences, Institute Technology Bandung, Bandung 40132-Indonesia

*** Department of Chemistry, Faculty of Mathematics and Natural Sciences, Gadjah Mada University, Yogyakarta 55281-Indonesia

****Department of Applied Science, College of Art and Sciences, Abu Dhabi University, Abu Dhabi 59911-United Arab Emirates

‡ Corresponding Author; First Author, Jalan Cemara Boulevard No. 4 Taman Yasmin, Bogor 16116-Indonesia

Tel: +628128362595,

Fax: +62 251 86234567, srimulijani@apps.ipb.ac.id

Received: 22.05.2022 Accepted:07.08.2022

Abstract- Designing specific method to investigate selective catalytic reaction of ethanol dehydration to produce diethy lether as a more valuable product is very challenging. In this study, four types of gold nano particles (AuNP) on TiO2 heterogeneous catalysts were prepared by hydrothermal (HT) and solvothermal (ST) methods, denoted as AuNP/TO-AHT; AuNP/TO-RHT; AuNP/TO-AST and AuNP/TO-RST(A = anatase and R = rutile phase). Further, their property of catalytic were investigated in terms of ethanol to diethyl ether conversion through dehydration reaction of ethanol. The catalyst product and diethyl ether (DEE) were then characterized to determine their characteristics and performance using FTIR, XRD, SEM and GCMS instruments. We discovered that the TO-HT revealed more amount of active acid positions and greater pore volume surface area than those of TO-ST. GCMS analysis showed that the highest transformation of ethanol to DEE was reached by the catalyst AuNP/TO-AHT (16.96%) followed by AuNP/TO-AST (0.97%), AuNP/TO-RHT (0.33%), and AuNP/TO-RST (0.07%).

Keywords Ethanol dehydration, diethyl ether, gold nanoparticle (AuNP), heterogenous catalyst, hydrothermal, solvothermal.

1. Introduction

In recent times, with rapid decline of fossil energy supply, the demand for energy fuel has increased. Therefore, development of a sustainable and environment friendly energy system is one of the most important challenges to fulfil a constantly growing energy need. Biomass can be considered as a renewable raw material to produce ethanol through fermentation. In addition, other researchers use livestock manure to produce biogas. It is also intended to produce renewable energy [1]. Researchers have been paying attention to the catalytic dehydration process in producing ethylene and diethyl ether (DEE) from ethanol since it is known that they can be operated at lower temperatures, minimize complications in the process, and produce fewer impurities [2]. In plastic industry, ethene or ethylene is one of the crucial basic materials to produce polyethene, ethene oxide, phenylethane, and poly(1-phenylethene). Currently, thermal cracking catalytic from product of petroleum, for example natural gas condensate or petroleum distillate, and dehydration of ethane from natural gas are two methods used to produce ethylene.

Apart from ethylene, ethanol dehydration also produces DEE through catalytic reaction using liquid H_2SO_4 as a catalyst. This process, however, requires further separation and purification process. A solid acid catalyst which is reusable and easily separated from the product is therefore highly desired. DEE is a very important chemical in transportation fuels for enhanced ignition additives in diesel and gasoline engines. Some of the valuable properties include octane number higher than 110, great volatility, cetane number higher than 125, low auto-ignition temperature, reasonable energy density for on-board storage, wide flammability limit, high oxygen content, and good miscibility, high in fuel of diesel and bioethanol [3][4].

As DEE is an important product for chemical industry and transportation, having a highly selective solid acid catalyst for DEE production would be ideal. Phung and Busca [2] used zeolite and alumina as catalysts to produce DEE from ethanol conversion. The dehydration of ethanol selectively to ethylene relatively occurs at high temperatures by means of elimination via breakdown of the ethoxy groups using those catalysts; it also occurs at lower temperatures in successive pathways through the formation and breakdown of DEE. Other researchers employed widely available and inexpensive metal oxide heterogeneous catalysts such as Al_2O_3, TiO_2, ZrO_2, ZnO [3]. Due to properties of TiO_2 i.e high thermal stability, adaptable surface, mechanical strength and good porous distribution, this material is a widely used as heterogeneous supporting catalyst in fuel processing. Incorporating noble metals such as platinum (Pt), gold (AuNP) and silver (Ag) onto TiO_2 has been widely used for enhancing stability, catalytic performance and its control [5][6][7]. In addition, Leal et al have reported that the Au/TiO_2 catalysts are capable of being used at low temperatures and shows excellent performance and high stability [6]. Au/TiO_2 catalyst is also used for several ethanol reactions, such as oxidation, dehydration to ethene and to ethanal at high temperature [8]. In the present study, catalyst of $AuNP/TiO_2$ anatase and rutile were prepared through hydrothermal and solvothermal methods. The catalyst was impregnated by H_2SO_4. Structure and performance of the catalyst were then examined by X-ray Diffraction, Scanning Electron Microscope (SEM), Gas Chromatography-Mass Spectroscopy (GC-MS) and Fourier Transform Infrared (FTIR).

2. Methodology

2.1. Preparation of Catalyst

For preparation of the catalysts, we used titanium oxide anatase and rutile purchased from Aldrich, $HAuCl_4.3H_2O$, ethanol (99.99%), H_2SO_4 concentrate, dimethyl formamide (DMF) as a solvent and HNO_3 were purchased from Merck Company Ltd., urea from Bratachem.

TiO_2 anatase and rutile were synthesized by hydrothermal and solvothermal methods [2,10]. Calcination of TiO_2 were carried out at temperature of 400 °C within 3 h. Then, TiO_2 calcinated was used for further hydrothermal and solvothermal process. The composition of the mixture consisting of the ratio between TiO_2, HNO_3 and water is 1: 0.5:50. Further, the mixture was transferred to a Teflon-lined autoclave after being stirred for 30 min, and the reaction of hydrothermal was carried out at 200 °C for 6 h. The resulted sample was dried at 80 °C. Further the sample is impregnated in to H_2SO_4 solution within 5 h to get the acid catalyst of titania sulfonate. However, solvothermal process used DMF as a solvent. The reaction was conducted at 100 °C within 6 h.

2.2. Synthesis of Gold Nano Particle (AuNP)

Synthesis of AuNP uses a reduction process with the citrate method. The reducing agent used is trisodium citrate. The process of reducing Au particles to nano can be seen visually by change in colour of the solution during the reduction process from a colourless solution to red. The AuNP solution must then be stored in a dark vial at 4 °C and then used for preparation of the AuNP/TO catalyst. The AuNP solution was characterized by a particle size analyser (PSA).

2.3. Impregnation Catalyst with AuNP

An amount of 2.5 g of calcined TiO_2 (anatase/rutile) was added into 50 ml of urea 0.42 M solution and 0.5 mL of 2% AuNP solution. The mixture solution was then homogenized and heated at 87 °C for 8 h and kept the pH constant. Then, the solution was filtered and then dried at a temperature of 80 °C, after that the dried precipitate was calcined at a temperature of 300 °C. According to the types of TiO_2 of anatase and rutile and 2wt% AuNP, the samples were labelled as AuNP/TO-AHT and AuNP/TO-RHT, AuNP/TO-AST and AuNP/TO-RST, respectively.

2.4. Determination of Performance of Catalyst

To determine the crystalline phase present in the catalyst as well as the chemical composition contained therein, measurements were made using X-ray diffraction (XRD) Rigaku, miniflex 600. The size of crystallite was assessed using the Scherrer formula,

$$c_s = \frac{k\lambda}{B\cos\theta} \tag{1}$$

here λ, β, and 2θ were the wavelength of the X-ray radiation, the half-height width of the diffractive peak, and the diffractive angle, respectively. The state of AuNP on the surface of TO was observed with a SEM JEOL operated at an acceleration voltage of 100 kV. The content of AuNP in AuNP/TO samples was determined by FTIR. The Au loading of the samples is stated in gram of Au per gram of sample: 2 wt% AuNP in TO. Diethyl ether obtained was evaluated with GC-MS GC Thermo Scientific type ISQ 1300 MS.

3. Result and Discussion

3.1. Characteristic of TiO_2-NP

Titanium oxide synthesized by hydrothermal process is white apparent. TiO_2 has been shown to be one of the favorable semi-conductors n-type because of its widespread band gap (3.2 eV) in UV light. In addition, it has extraordinary stable in chemical and physical properties in addition to have great refractive index which has made this material much investigated. Due to its optical and electronic properties, TiO_2 can be used in various subjects, such as basic material for solar energy application, catalysts, self-screening and cleaning in environment field. In electrochemistry, TiO_2 based materials play important part since of their great stability and conductivity in alkaline and acid solution.

Titanium oxide occurs in three forms of crystalline; rutile, anatase, and brookite. Anatase and rutile are the utmost usual forms, and the crystal size of rutile is constantly bigger than that of the anatase. Brookite is a third structural form, an orthorhombic structure, which is rarely used, and remains unattractive for most applications. Of the three phases, rutile phase is the most stable in thermal. Anatase and brookite crystals, above 600 °C undergo a phase transition and gets converted into the rutile phase. Generally, the transformation of anatase into the rutile phase occurs between 600 °C-700 °C, therefore the TiO_2 calcination was carried out at a temperature of 400 °C. However, for certain applications, TiO_2 anatase must be stable at temperatures of 900 °C.

The diffraction pattern of XRD in Fig.1 revealed that the TiO_2 obtained was established to form a pure anatase crystal structure (JCPDS # 00-021-1272). Three different diffraction peaks were perceived at 2 θ values of 25.31°, 37.79, and 48.04 ° according to (101), (004), and (200) of the crystal plane anatase.

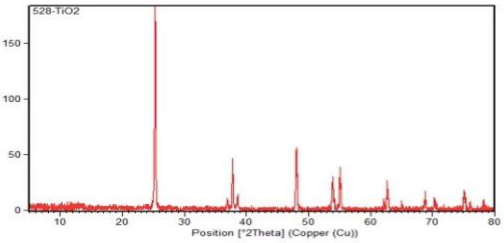


Fig. 1. Diffraction pattern of TiO_2-NP anatase

The crystal size obtained is calculated following the Scherrer formula with Cu Kα = 0.15406 nm, k is the taken constant of 0.94, θ is the diffraction angle, and B is the full width at half the maximum (FWHM) peak in radians. All diffraction peaks were calculated and a mean crystal size of 79 nm obtained. The incorporated process of Au on to TiO_2 produces a different diffraction pattern from pure TiO_2 anatase (Fig.2). It shows two characteristic peaks that correspond to the mixture of AuNP/TiO_2-anatase forms. The peak at 25.335° (2θ) corresponds to the anatase shape of TiO_2 (JCPDS # 01086-1156). It has a tetragonal structure with a body-centered cubic lattice. The peaks at 37,809°, 48,105° and 70,394° (2θ) were identified as coming from (004), (200) and (220) respectively to represent the Au diffraction pattern (JCPDS # 00-004-0784). This diffraction pattern can be indexed to space group Fm3m (225), a face-centered cubic structure with cell parameter a = 4.0786 Å. The average crystal grain size calculated using the Scherrer equation was found to be 43.9 nm. The pattern is comparable with the ones reported in the literature [9].

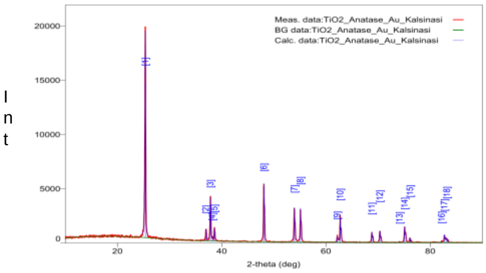
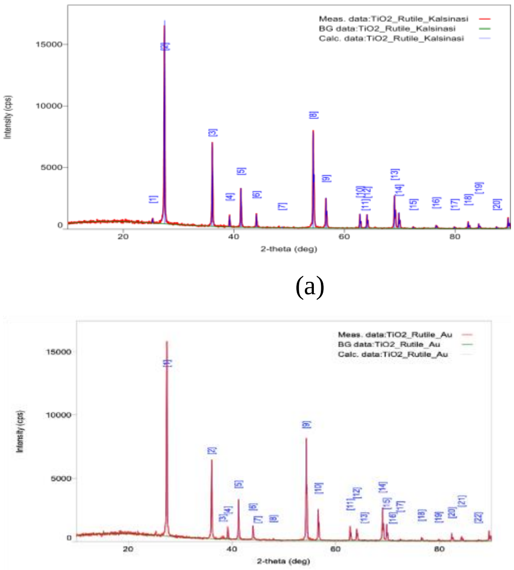


Fig. 2. Diffraction pattern of AuNP/TiO_2 anatase

Figure 3a exhibits the XRD diffraction pattern of the TiO_2 rutile type. The peaks corresponding to the rutile phase were confirmed by JCPDS # 01-076-0649 i.e. peak around 27.440°, 36.079°, 41.240°, 54.325° and 56.635°and it were also according to planes of the Miller indices (110), (101), (111), (211) and (301), respectively. This diffraction pattern is dealing in the space group P42/mnm (136), with a tetrahedral crystal form.



(a)

(b)

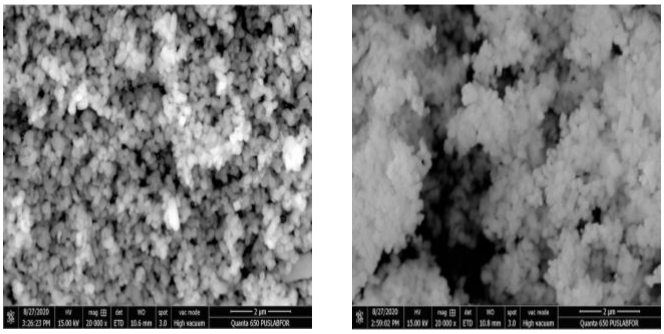
Fig. 3. Diffraction pattern of TiO_2-rutile (a); AuNP/TiO_2 rutile (b)

In contrast to AuNP/TiO_2-anatase, the addition of AuNP into TiO_2-rutile only shows a diffraction pattern with a small intensity (Fig. 3b). As can be seen that diffraction peaks around 41.24°, 39.19° and 56.63◦ corresponds to planes (111), (200) and (220) according to the cubic structure of metallic gold [13,14]. According to Martinez et al. [13][16], gold deposition by impregnation method did not affect the crystalline phase coexistence of TiO_2-anatase and rutile. In conclude, there is no significant change in XRD diffraction pattern when Au nanoparticles are combined with the resulting catalyst.

As shown in Fig. 2 and 3, the four samples of anatase and rutile have very similar shape and intensity of diffraction peaks, this indicates that the calcination at 400 °C for 5 h did not cause changes in the content and particle size of anatase and rutile in the sample. These results are in accordance with research obtained and reported by Tian et al. [11]

3.2. *Surface Morphology of Catalyst*

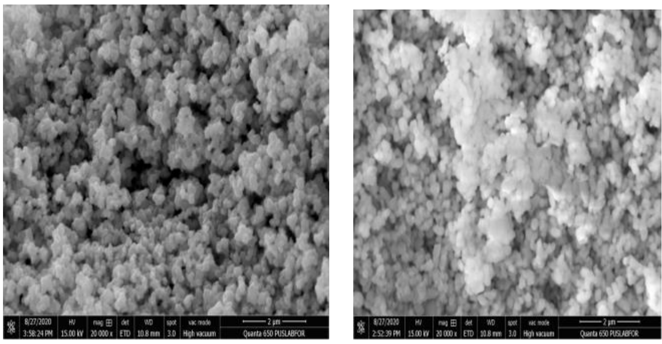
The morphology catalysts prepared by different methods and types revealed distinctive structures. Figure 4 shows the results of observations of the morphology of the catalyst TO-AHT and TO-RHT. The TO-AHT formed crystal uniformity (Fig. 4a) while TORHT appears to form aggregates (Fig. 4b). The outcomes are consistent with the results reported by Machin et al. that catalyst TiO_2 consist irregular spheric aggregates [8]. Anchale et al. have reported that impregnation of Noble metal on TiO_2 will exhibit more porous particle and increase the porosity of catalyst [2].



(a) (b)

Fig. 4. Morphology of TO-AHT (a) dan TO-RHT (b)

Meanwhile, the surface morphology of the solvothermal process catalysts exhibited clustered or aggregated crystals, either anatase (Fig. 5a) or rutile (Fig. 5b). The solvothermal process uses DMF solvent, in theory the addition of DMF solvent will stimulate an increasingly regular crystal form. But with the addition of excessive DMF and low temperature the desired crystal formation remains less than optimal so that larger aggregates are formed compared to the hydrothermal process. Beside, there is an effect sulfation process toward agglomeration form in both anatase and rutile. This is in accordance with the results obtained by Karna et.al, that particle size of the solvothermal product is larger than that of hydrothermal [17].



(a) (b)

Fig.5. Morphology of TO-AST(a) and TO-RST (b)

3.3. *Analysis Functional Group*

The FTIR spectra of TO-HT, AuNP/TO-HT and AuNP/TO-SO_4 are shown in Fig. 6. The presence of AuNP in TiO_2 causes a shift in the vibrational band at wave numbers 690 cm^{-1} to 721 cm^{-1} and a significant change in wave number 3400 cm^{-1} to 3600 cm^{-1} indicates the presence of H_2O arising from $HAuCl_4.3H_2O$. Vibration bands of about 3400 cm^{-1} and 1655 cm^{-1} present in the spectrum indicating the presence of a hydroxyl group attached to a titanium atom (Ti-O-H). Lee et al have reported peak growth at 2300 cm^{-1} proved the conversion of CO to CO_2 which corresponds to the C-O stretching mode of CO_2 [12]. Thus, it should be indicated that this reaction condition has occurred at low temperature, the signal is related to the carbon dioxide condensed on the titania support, not to the gas phase CO_2 as shown in the experiment at room temperature or above [9][11]. The presence of a vibration band at a wave number of 732 cm^{-1} even though its intensity is small shows that there is a bond between oxygen and Ti (Ti-O). Other vibration bands indicate Ti-OTi (1400 cm^{-1}) and Ti-O-O (500 cm^{-1}) [8][17].

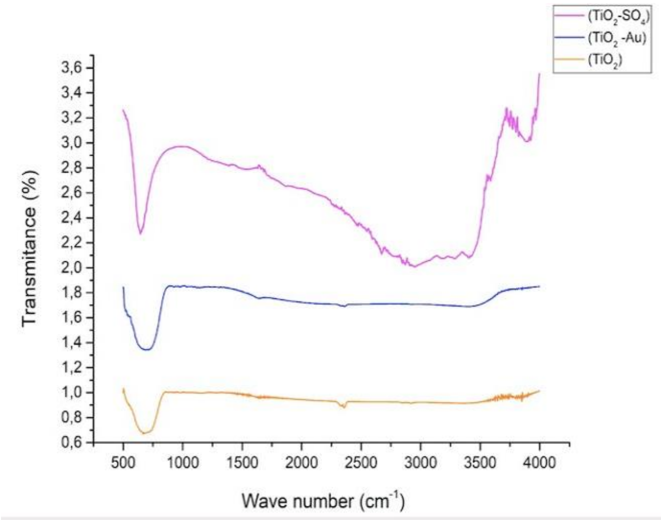


Fig. 6. Spectra TiO_2 and AuNP/TiO_2

3.4 *Performance of Catalyst*

The dehydration reaction that occurs in ethanol using this catalyst produces DEE that is not optimum. In result of GCMS determination showed that the highest ethanol conversion to DEE was achieved by the catalyst AuNP/TO-AHT(16.96%) then AuNP/TO-AST (0.97%), AuNP/TO-RHT (0.33%) while AuNP/TiO_2-RST (0.07%). The AuNP/TO-AHT catalyst has a larger surface area than other catalysts proven by the high active acid site. Therefore, ethanol dehydration reaction in the reactor is faster to be achieved due to the presence of AuNP/TO-AHT. Meanwhile AuNP/TiO_2-RST revealed the lowest DEE, due to the smaller acid active site and small pore surface area. This is in accordance with the results of the surface morphology image showing the presence of crystal agglomeration which inhibits the absorption of acid in the pore. The addition of Au onto TiO_2 will decrease gradually the reaction selectivity of dehydration ethanol to DEE [14] [15]. However, it has been reported that due to the reactivity of Au it can be used as a homogenous catalyst [18][19]. The evidence has come up in the result of GCMS, 3-Methylpentene and methylcyclopentene which are side products from dehydration ethanol reaction. The reaction that occurs is nucleophilic aliphatic substitution on saturated carbon where the nucleophile is alkoxide ion or phenoxide ion, so that it can produce alkene or cycloalkene compounds. In addition, alkenes as by-products can be obtained from aliphatic nucleophilic substitution reactions, as well as 1,2 eliminations between substrates containing beta hydrogen and alkoxide ions [20]. These results are in corresponding with the research conducted by Nadeem et al. [15] that due to the relationship between the desorption temperature and the interfacial length of the Au particles in TiO_2.

4. Conclusion

The synthesis of titania sulfate catalyst has been successfully carried out through hydrothermal and solvothermal processes. Hydrothermal and solvothermal methods can prepare anatase and rutile crystalline phase TiO_2 catalyst modification with impregnated AuNP. Both FT-IR and XRD analysis study evidenced that there occurred tough contact between AuNP and TiO_2. The crystallinity and sizes of samples altered on AuNP content, and the addition of AuNP in TiO_2 particle might excellently overwhelm the construction of rutile phase and the growing of the titanium dioxide crystals on calcination. The AuNP/TO-AHT showed better catalytic dehydration than that of pure AuNP/TO - RHT. Meanwhile, AuNP/TO-AST and AuNP/TO-RST exhibited low catalytic dehydration of ethanol. Therefore, it can be concluded that AuNP/TO-AHT prepared by hydrothermal method is very promising as a catalyst for catalytic ethanol dehydration.

Acknowledgements

The authors thankfully acknowledge the funding of IPB University through Indonesia Research Collaboration Program and BRIN. In addition, Dr.R.S. Rawal is highly acknowledged.

References

[1] M.A. Haque, AKM. A. Kabir, M. A. Hashem, M. A. Kalam Azad, M. K. J. Bhuiyan, M. M. Rahman, “Efficacy of Biogas Production from Different Types of Livestock Manures” International Journal Of Smart Grid. DOI. 10.20508/ijsmartgrid.v5i4 Vol. 5, No. 4, pp.158-166, 2021

[2] A. Tresatayawed, P. Glinrun, B. Jongsomjit, “Ethanol Dehydration over WO_3/TiO_2 Catalysts Using Titania Derived from Sol-Gel and Solvothermal Methods”, International Journal of Chemical Engineering, Hindawi, DOI: 10.1155/2019/4936292, Vol. 2019, pp. 1-11, 2019.

[3] T. K. Phung, G. Busca, “Diethyl ether cracking and ethanol dehydration: Acid catalysis and reaction paths”, Chemical Engineering Journal, DOI: 10.1016/j.cej.2015.03.008, Vol. 272 pp. 92-101, 2015.

[4] K. Wijaya, M. L. L. Malau, M. Utami, S. Mulijani, A. Patah, A. C. Wibowo, M. Chandrasekaran, J. R. Rajabathar and H. A. Al-Lohedan, “Synthesis, Characterizations and Catalysis of Sulfated Silica and Nickel Modified Silica Catalysts for Diethyl Ether (DEE) Production from Ethanol towards Renewable Energy Applications”, DOI: 10.3390/catal11121511, Vol. 11, pp. 1511, 2021.

[5] S. Bagheri, N. Muhd Julkapli, S. Bee Abd Hamid, “Titanium dioxide as a catalyst support in heterogeneous catalysis”, Scientific World Journal, DOI:10.1155/2014/727496, Vol. 2014, 2014.

[6] G.B. Leal, D.C.L. da Silva, B.N. Watacabe, L. Ciotti, R.M. Antoniassi, R. Giudici, M. Linardi, J.M. Vaz, E. V. Spinacé, “Au/TiO_2 catalysts prepared by borohydride reduction for preferential CO oxidation at near-ambient temperature”, Catalysis for Sustainable Energy, De Gruyter Publiher. DOI:10.1515/cse-2019-0002, Vol 6, pp. 6–12, 2019.

[7] F. Fu, F. Wang, T. Li, C. Jiao, Y. Zhang, Y. Chen, “Synthesis of TiO_2NWS@AuNPS composite catalyst for methylene blue removal”, Materials (Basel), DOI: 10.3390/ma11061022, Vol.11, pp. 1–13, 2018.

[8] A. Machín, M. Cotto, J. Ducongé, J.C. Arango, C. Morant, F. Márquez, “Synthesis and Characterization of Au@TiO_2 NWs and their Catalytic Activity by Water Splitting: A Comparative Study with Degussa P25”, American Journal of Engineering and Applied Science, DOI:10.3844/ajeassp.2017.298.311, Vol 10 pp. 298–311, 2017.

[9] A. Nuhu, “Ethanol Oxidation Over Au /TiO_2”, Bayero Journal of Pure and Applied Sciences, Vol. 2, pp. 88–94, 2009.

[10] Z. Li, B. Hou, Y. Xu, D. Wu, Y. Sun, “Hydrothermal synthesis, characterization, and photocatalytic performance of silica-modified titanium dioxide nanoparticles”, Journal of Colloid Interface Science, DOI: 10.1016/j.jcis.2005.02.082, Vol. 288, pp.149–154, 2005.

[11] B. Tian, J. Zhang, T. Tong, F. Chen, “Preparation of Au/TiO_2 catalysts from Au(I)-thiosulfate complex and study of their photocatalytic activity for the degradation of methyl orange”, Applied Catalysis B Environment, DOI: 10.1016/j.apcatb.2007.11.001, Vol. 79, pp. 394–401, 2008.

[12] I. Lee, F. Zaera, “Effect of metal nanoparticle size and titania crystallinity on the performance of Au/TiO_2

catalysts for the promotion of carbon monoxide oxidation at cryogenic temperatures", Journal of Chemical and Physics, DOI: 10.1063/1.5114928. Vol. 151, 2019.

[13] C. R. Martínez, A.E.G.Dominguez, F.G.Robles, R O.S. Diaz, J. G. Torres and CC. Fellipe, "Synthesis of Supported Metal Nanoparticles (Au/TiO_2) by the Suspension Impregnation Method", Journal of Composite Science, MDPI, DOI: 10.3390/jcs4030089 Vol. 4 (2020), pp. 89, 2020.

[14] Adib A.S. Pavón, G.Torres-Torres, J. C. A. Perez, A.C. Uribe, Z.Guaerra-Que, A.C. GraciaA.E.de los Monteros amd J.N. Beltramini, "Effect of gold addition by recharge method on silver supported catalyst in catalytic wet air oxidation (CWAO) of phenol" Royal Society of Chemistry Advance, DOI: 10.1039/c9ra00540d, Vol. 9, pp. 11123-11134, 2019.

[15] M. A. Nadeem, I. Majeed, G. I. N.Waterhouse and H. Idriss, "Study of ethanol reaction on H_2 reduced Au/TiO2 anatase and rutile: efect of metal loading on reaction selectivity", *Catalyst, Structure and Reactivity*,. DOI 10.1179/2055075814Y.0000000008, Vol. 1, pp. 1-10, 2015.

[16] J. Quesada, R. Arreola-Sánchez, L. Faba, E. Díaz, V.M. Rentería-Tapia, S. Ordóñez, " Effect of Au nanoparticles on the activity of TiO_2 for ethanol upgrading reactions", Applied Catalysis A: General, DOI: 10.1016/j.apcata.2017.12.004, Vol.551, pp23-33, 2018.

[17] K. Wijaya, R. A. Pratika, E. R. Fitri, P. F. Prabani, Y. Candrasasi, W. D. Saputri, S. Mulijani, A. Patah, and A. C. Wibowo, "Effect of Sulfation on Physicochemical Properties of ZrO_2 and TiO_2 Nanoparticles", Korean Journal Material Research, DOI: 10.3740/MRSK.2022.32.3.125, Vol. 32, No.3 pp.125-130, 2022.

[18] A. Stephen K.H., T. D. Ramamurthi, F. Rominger, "Synthesis, structure and reactivity of organogold compound of relevance to homogeneous gold catalysis", DOI : 10.1016/j.jorganchem.2008.11.054, Vol.

[19] Y. Huang, B. Wang, H. Yuan, Y. Sun, D. Yang, X. Cui and F. Shi, "The catalytic dehydrogenationof ethanol by heterogeneous catalyst", Catalysis Science &Technology, Royal Society of Chemistry, DOI: 10.1039/d0cy02479a, Vol 11, pp. 1652-1664, 2021.

[20] B. Yang, R. Burch, C. Hardcare, G. Headdock, and P. Hu, "Origin of the increase of activity and selectivity of Nickel doped by Au, Ag and Cu for acetylene hydrogenation", ACS Catalysis, DOI: 10.1021/cs2006789, April 18, 2012, Vol.2, No.6. pp.1027-1032.