Selective oxidation of glycerol over titania supported AuPd bimetallic catalysts

[1]Ainol Hayah Ahmad Nadzri, [2]Noraini Hamzah, [1]Aznira Alias, [1]Jumat Salimon and [1]Mohd Ambar Yarmo

***Abstract*—** Oxidation of glycerol to form various types of important short chain oxygenated derivatives became an important reaction to support biodiesel industries. In this study, a series of AuPd nanoparticles at different metal ratio which were 9:1 and 8:2 supported on titania (TiO_2) were successfully prepared, characterized and tested for its activity and selectivity in liquid phase oxidation reaction of glycerol. All the catalysts were prepared by deposition-precipitation method with decomposition of urea agents. Au_xPd_y/TiO_2 catalysts were characterized using XRD, TEM and XPS. The formation of alloy Au-Pd phase was ascertained by XRD and XPS analysis. TEM analyses have shown that the Au and Pd metal particles in the range of 10-30 nm in size were uniformly dispersed on the TiO_2 support with narrower size distribution. Higher catalytic activity observed for the catalysts was attributed to the presence of metallic Au^0 and PdO phases together with the 'synergistic' effect of Au-Pd alloy. The highest selectivity to tartronic acid (54.6%) was obtained by using Au_9Pd_1/TiO_2 catalyst after 8 h of reaction time at lower reaction temperature (50^{o}C).

***Keywords*:** *bimetallic catalyst; deposition-precipitation; gold; palladium*

I. INTRODUCTION

[1]*Ainol Hayah Ahmad Nadzri, Aznira Alias, Jumat Salimon and Mohd Ambar Yarmo are with School of Chemical Sciences and Food Technology, Faculty of Science and Technology, Universiti Kebangsaan Malaysia ,43600 Bangi, Selangor Darul Ehsan, Malaysia (phone: 013-6735193; fax: 03-89215410; e-mail: aries_wgurlz85@yahoo.com).*

[2]*Noraini Hamzah is with School of Chemical Science and Environment, Faculty of Applied Science, University of Technology MARA, 40450 Shah Alam, Malaysia (e-mail:norainihamzah@gmail.com).*

as a main by-product from transesterification of trigliseride into biodiesel in which the sources for trigliseride can be extracted from vegetables oils or animal fats [1].

Glycerol can be oxidized into various value-added chemicals such as glyceric acid (GLYA), tartronic acid (TARAC), hydroxypyruvic acid (HPYA), glycolic acid (GLYCA), dihydroxyaceton (DHA) and oxalic acid (OXALA) (Fig. 1) [2-4]. Every product has their own significant importance in our markets today. For instance, tartronic acid and mesoxalic acid is regarded as a potentially sequestrants that are important as intermediates in the synthesis of fine chemicals [1]. Furthermore, the esterified product of tartronic acid with high molecular weight of long chain and branching alcohols is defined as potentially source for synthesis of biolubricant.

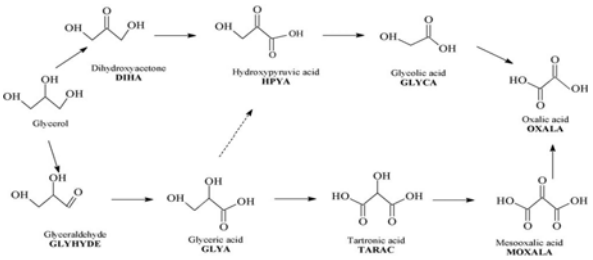


Fig. 1: General reaction pathways [2-4]

Bimetallic catalysts have been reported to be highly active and selective than monometallic catalysts for oxidation reaction of glycerol [5]. Bimetallic system mainly based on Au and Pd metals have several characteristics that may contribute to the good catalysts performance. This includes miscible properties of the two metals in almost all composition and high resistivity to oxygen poisoning [6]. Furthermore, the selectivity to glyceric and tartronic acids were enhanced by using these metals under basic condition [4]. The significant properties of bimetallic Au-Pd system is their "synergistic" effect which is contributes to the higher catalytic activity in oxidation reaction of glycerol [6]. This behaviour is strongly observed in a large range of Au/Pd ratio, being maximized for Au_8Pd_2 composition [7].

Most of the previous studies have employed the high surface area carbon and graphite to be used for depositing AuPd particles while lack of studies has been given to the metal oxide supports such as TiO_2 [3]. TiO2 is one of the promising support that can produce small and highly dispersed metal particles which contributes

Glycerol has emerged as a new attractive reactant for the production of a large number of valuable compounds for so many years due to its bioavaibility, renewability and non-toxic properties. It is well known that glycerol is obtained
liquid phase oxidation of alcohols using Au and Pd as the main metal.

Hence, in this study, we have synthesized bimetallic Au_9Pd_1 and Au_8Pd_2 supported on TiO_2 via deposition-precipitation method with urea. The main advantage of using urea is that all the gold present in solution is deposited on support surface, therefore leads to higher gold loading [10]. By using this method, it is possible to obtain small hemispherical metal particles with diameters below 5 nm [11]. Both of the catalysts were tested in liquid phase oxidation reaction of glycerol in order to know the effect of the Au-Pd ratio on catalysts performance and in particular turning the reaction pathway towards the desired products. Our target product is tartronic acid, so here, we performed the reaction at 50^{o}C and 100^{o}C with prolonged reaction time because previous studies by Porta & Prati [12] have reported that tartronic acid tend to form at high temperature and with increasing reaction time.

II. EXPERIMENTAL

2.1 Materials

$NaAuCl_4.2H_2O$, Na_2PdCl_4 of 99.99% purity and TiO_2 (99.8% anatase) were from Aldrich. Urea (99.0 % purity) was purchased from Systerm. NaOH of the highest purity (99.0%) was obtained from Fisher. Gaseous oxygen was 99.99% pure. Glycerol (99.99% purity) was obtained from Fisher, glyceric acid and all other standards were obtained from Aldrich.

2.2 Catalysts preparation

2.00 g of TiO_2 was added to 100 ml of aqueos solution containing urea (0.42 M) and mixture of Au and Pd precursor (molar ratio of Au/Pd: 8/2 and 9/1). The suspension thermostated at 80^{o}C was vigorously stirred for 18 h. The solid materials were gathered by centrifugation (5000 rpm for 10 min). The sample was washed in 100 ml of DI water under stirring for 10 min at 50^{o}C and followed by centrifugation. This operation was repeated for 4 times. The solids were then dried at 50^{o}C overnight. The catalysts were activated by calcinations under air at 673 K for 4 h.

2.3 Oxidation experiments

The reactions were carried out in a three rounded-neck flask (50 ml capacity) equipped with condenser, heater, mechanical stirrer, gas supply system and thermometer. An aqueous solution of glycerol (0.6 M, 10 ml total volume) together with the desired amount of NaOH and catalyst (glycerol/metal=200 by mol, NaOH/glycerol=4 by mol) was added into the glass reactor. The reactor was pressurized at 3 atm of O_2 and thermostated at the appropriate temperature (50 or 100^{o}C). When the required temperature was reached, the gas supply was switched to O_2. The reaction was conducted under stirring condition. The reaction samples were further taken at suitable intervals duration and analysed using HPLC with UV and Refractive Index (RI) detectors. An Altech OA 1000 column (300 nm x 6.5 nm) was used with aqueous H_3PO_4 0.1 % as the eluent. The column temperature was set at 25.0^{o}C with flow rate of 0.5 ml/min. The same eluent was used to dilute the samples before analysis. Identification of the products was done by comparison of their retention time with the authentic samples. The activity of the catalysts was measured based on turn over frequencies (TOF) [(mol of product)/(mol of total Au atom added)/per hour].

2.4 Catalysts characterization

a) For TEM investigations, the powder samples of the catalysts were ultrasonically dispersed in ethanol for 2 h and mounted onto a copper TEM grid. A Philips CM 12 electron microscope, operating at 100 kV was used for TEM observation.

b) The phase structures of the catalysts were determined by Bruker D8 Advance X-ray powder diffractometer using Cu Kα radiation (γ=0.154 nm). The diffraction data were collected between $20^o<2\theta<80^o$. The sample powder was grinded and pressed on the holder of diffractometer.

c) XPS spectra were recorded on an Kratos Axis ultra electron spectrometer equipped with a monochromatic Al Kα sources (1486.6 eV) and with a pass energy of 20 eV for narrow scan analysis. Samples was analysed at pressure in the analytical chamber at $1x10^{-9}$ Pa. The binding energy (BE) of C 1s peak was taken at 284.5 eV as an internal standard. A curve fitting procedure for the experimental spectra was done using software provide by Kratos Axis.

III. RESULTS AND DISCUSSIONS

3.1 Catalysts characterization

X-ray diffractograms of TiO_2 support, Au_9Pd_1/TiO_2 and Au_8Pd_2/TiO_2 catalysts at 673 K are shown in Fig. 2. As can be seen in the figure, the diffraction peaks at 38.2^o refer to the Au (111) plane, was the characteristic for pure metallic gold. This peak is quite underdeveloped because it is overlap with the anatase TiO_2 (112) plane at same Bragg angle. Note that, the other low intensity Bragg peak positioned at 44.4^o refer to Au (200) plane is seen as well. This peak also resemble the pure metallic gold having the fcc structure. According to Venezia et al. [13], formation of alloy Au_xPd_y with gold–enriched phase were occured between the (111) and (200) peaks of Au and Pd. We observed that the location for alloy Au_xPd_y were very close to the peaks of Au likely because of the higher gold content in both of the catalysts as we prepared. The crystallite particles size (L) of the nanoparticles in the studied samples can be estimated by Sherrer's equation as shown in equation below [14].

$$L = k\lambda / \beta \cos(\theta) \quad \text{..... Equation 1}$$

where k= 0.94, λ is the wavelength of the radiation, β is the full width at half maximum of the peak in radians and θ is the Bragg angle. The equation was applied to the peak of metallic gold (111) and (200) in the corresponding XRD patterns shown in Fig. 2. The calculated crystallite particles size for Au_9Pd_1/TiO_2 was determined to be 10.6 nm and 7.2 nm meanwhile for Au_8Pd_2/TiO_2, it was about 13.2 nm and 9.7 nm. The values of particle sizes determined by XRD are smaller as compared to TEM possibly because of an overestimation of the line broadening of the XRD peaks.

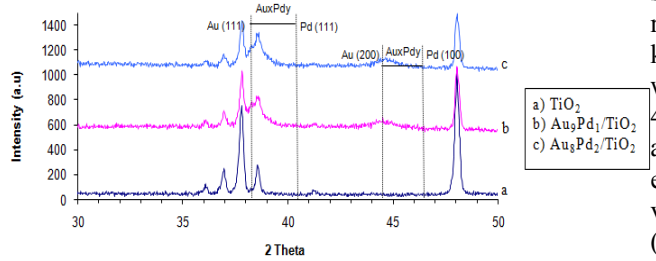
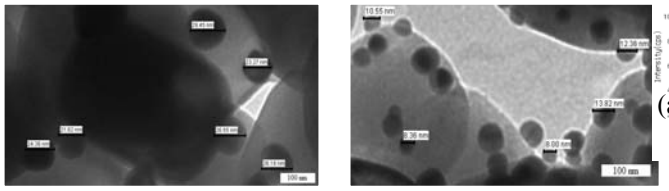


Fig. 2: X-ray diffractograms of a) TiO_2, b) Au_9Pd_1/TiO_2 and
c) Au_8Pd_2/TiO_2

Fig. 3 shows the TEM images of both the Au_9Pd_1/TiO_2 and Au_8Pd_2/TiO_2 catalysts. As shown, the semi-spherical AuPd particles on TiO_2 are uniform and well-dispersed. Note that, the Au_8Pd_2/TiO_2 catalyst has smaller mean particles diameter which the average is in between 10 to 15 nm. However, Au_9Pd_1/TiO_2 catalysts had a somewhat larger mean particles diameter, in the range of 20-30 nm. The uniform distribution of these particles combined with their small particles size leads to a good catalysts performance in our model oxidation reactions of glycerol.



(a) (b)

Fig. 3: TEM micrograph for a) Au_9Pd_1/TiO_2 and b) Au_8Pd_2/TiO_2 (Magnificent of 60000 X).

The surface properties and chemical states of the two metals were investigated by XPS technique. XPS derived data including Au $4f_{7/2}$ and Pd $3d_{5/2}$ binding energies together with Au/Ti and Au/Pd atomic ratios for both of the catalysts were listed in Table 1. As can be seen, the Au/Pd surface ratio for Au_9Pd_1/TiO_2 was much higher than Au_8Pd_2/TiO_2 therefore from qualitative point of view, we could suggest that Au_9Pd_1/TiO_2 have higher surface gold exposure than Au_8Pd_2/TiO_2. Apparently, the changing of the Au/Pd ratio from 9:1 to 8:2 lead to the decrease of the Au/Pd atomic ratio and a marked increased of Au/Ti atomic ratio.

Table 1

XPS Au $4f_{7/2}$ and Pd $3d_{5/2}$ binding energies (eV) and XPS derived (Au/Ti) and (Au/Pd) atomic ratios of Au_9Pd_1/TiO_2 and Au_8Pd_2/TiO_2 catalysts

Catalysts	Au $4f_{7/2}$	Pd $3d_{5/2}$	Au/Ti	Au/Pd
Au_9Pd_1/TiO_2	83.3	334.4 336.0	0.40	1.75
Au_8Pd_2/TiO_2	83.5	334.5 335.9	0.50	1.42

The experimental and fitted Au 4f and Pd 3d core-level spectra for both of the catalysts were shown in Fig. 4 and 5, respectively. The Au 4f peak will split into two spin-orbit components which is Au $4f_{7/2}$ and Au $4f_{5/2}$ that represent two different chemical species. It is commonly known that the Au $4f_{7/2}$ binding energy for metallic gold was at ~84 eV. The photoelectron binding energy for Au $4f_{7/2}$ and Au $4f_{5/2}$ in Au_9Pd_1/TiO_2 catalysts was 83.3 eV and 87.8 eV meanwhile for Au_8Pd_2/TiO_2, it was at 83.5 eV and 87.8 eV. Specially, all the peak at these BE values was the characteristics for gold in metallic state (Au^0). The negative shift of binding energy for Au^0 species obtained for these catalysts is indicative of Au-Pd alloy formation. Thus, it was suggested that all the charged gold species (Au^{III}) were reduced to zerovalent gold (Au^0).The A^0 species is considering the most important site that is responsible to boost the activity in oxidation reaction of glycerol [3].

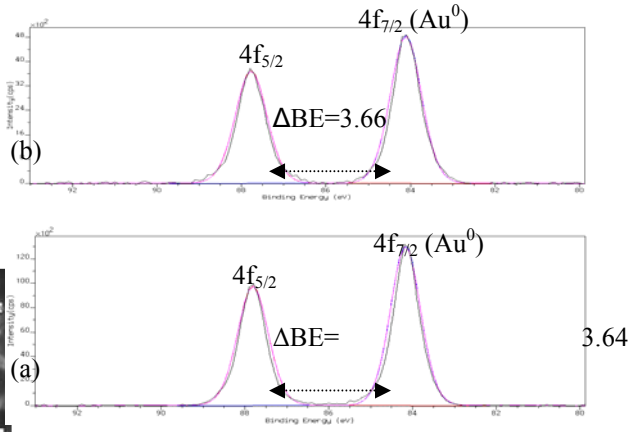


Fig. 4: XPS spectra of Au 4f of a) Au_9Pd_1/TiO_2 and b) Au_8Pd_2/TiO_2

The Pd 3d spectra of Au_9Pd_1/TiO_2 and Au_8Pd_2/TiO_2 (Fig. 5) catalysts also split into two spin-orbit components which is Pd $3d_{5/2}$ and Pd $3d_{3/2}$ with ΔBE values of 5.3 eV for Au_9Pd_1/TiO_2 and 5.4 eV for Au_8Pd_2/TiO_2. For the sake of simplicity, the following binding energy (BE) will be referred only to the peak of Pd $3d_{5/2}$. According to the literature, the binding energy for Pd^{2+} species was at 336.9 eV and 342.3 eV and for the metallic and/or Pd-Au alloy was at 335.3 eV and 341.4 eV [15]. Referring to the binding energy of our samples, the formation of metallic Pd and/or Pd-Au alloy was observed at the binding energy of 334.4 eV for both of the catalysts. A negative shift in the binding energy of metallic Pd 3d (335.3 eV) to 334.4 eV observed in the

two samples indicated the formation of gold rich bimetallic sample [16]. The component at around 335.7 eV for Au_9Pd_1/TiO_2 sample was due to the formation of PdO phase whereas for Au_8Pd_2/TiO_2, it was appeared at the binding energy of 336.0 eV.

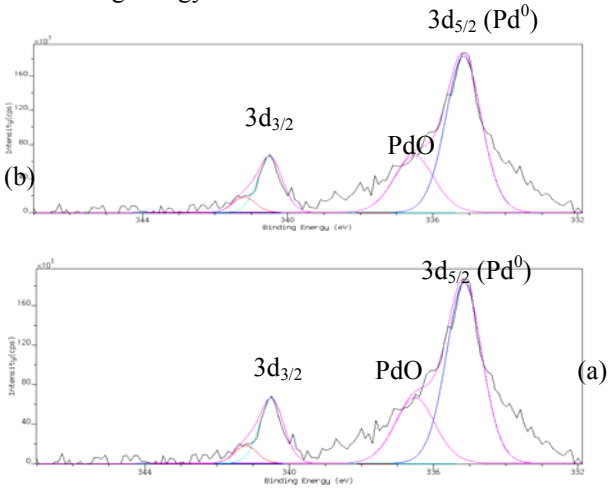


Fig.5: XPS spectra of Pd 3d of a) Au_9Pd_1/TiO_2 and b) Au_8Pd_2/TiO_2

3.2 Catalytic reaction evaluation

Both of the catalysts were tested in the selective liquid phase oxidation of glycerol under alkaline condition. The reaction conditions were as follow: 0.6 M glycerol, NaOH/glycerol=4 mol/mol, glycerol/metal=200 mol/mol and pO_2=3 atm. In order to evaluate the effect of reaction temperatures towards the activity and product distribution, we have performed the reaction at 50 and 100°C. Table 2 shows the results of the catalytic testing for both of the bimetallic Au_8Pd_2/TiO_2 and Au_9Pd_1/TiO_2 catalysts in the selective oxidation reaction of glycerol at 50°C and 100°C respectively.

Table 2
Oxidation of glycerol using bimetallic Au_xPd_y/TiO_2 catalysts at 50 and 100°C.

Catalysts	T°C	TOF (h^{-1})	Selectivity (%)			
			GLYA	TARAC	GLYCA	OXALA
Au_8Pd_2/TiO_2	50	523	28.21	13.11	34.02	20.00
	100	826	21.91	15.73	23.53	24.41
Au_9Pd_1/TiO_2	50	476	15.45	18.67	11.59	32.85
	100	676	21.11	16.47	24.48	26.03

Depending on reaction temperature and metal ratio of the catalysts, we observed that the activity and products distribution was different for each catalyst (Table 2). For example, at 50°C, glycolic acid was the main products for Au_8Pd_2/TiO_2 catalysts followed by formation of glyceric acid, oxalic acid and tartronic acid. The reaction profile of Au_8Pd_2/TiO_2 and Au_9Pd_1/TiO_2 at 50°C and 100°C are shown as an example (Fig. 6 and 7). The different trend was observed for Au_9Pd_1/TiO_2 catalyst because it favoured the formation of oxalic acid as the main products followed by tartronic acid, glyceric acid and glycolic acid. At 100°C, high and almost similar values of oxalic and glycolic acids were obtained for both of the catalysts. Noticed that, for both of the catalysts at each reaction temperature, as the reaction time increase, the selectivity to oxalic acid and tartronic acid was increased followed with the decreasing of selectivity to glycolic acid and glyceric acid, suggesting that the main loss of selectivity due to further oxidation of glycolic acid to oxalic acid and glyceric acid to tartronic acid.

For Au_9Pd_1/TiO_2, the temperature affected the reaction in a different way. At lower reaction temperature (50°C), we achieved the highest selectivity to tartronic acid if compared than at 100°C which was about 54.6 % after 8 h of reaction time. It can be seen that from their reaction profile (Fig. 7a) glyceric acid and glycolic acid suffered the significant loss of selectivity when the reaction time is increased. Another interesting point to mark is at each temperature, oxalic acid was the prominent product. This indicated that the formation oxalic acid was favoured at moderate and higher temperature, 50°C and 100°C. Following the reaction pathway of glycerol oxidation at Fig.1, we found that the formation of tartronic acid and oxalic acid were favoured by using Au_9Pd_1/TiO_2 catalysts at lower reaction temperature with longer reaction time. This indicated that the glyceric acid and glycolic acid were rapidly transformed to tartronic acid and oxalic acid. On the contrary, at higher reaction temperature, the secondary oxidation of glyceric acid and glycolic acid was found to be limited.

In terms of catalytic activity, both of the catalysts possessed only slightly different in activity. TOF data after 0.5 h of reaction (Table 2) have shown that their TOF values were in the range of 476-826 $^{h-1}$. The most active catalysts at 50°C and 100°C being Au_8Pd_2/TiO_2 catalyst with the TOF value of 523 $^{h-1}$ and 826 $^{h-1}$. In fact, at lower reaction temperature, the TOF decreased down to 1.6 times of magnitude. Au_8Pd_2/TiO_2 has higher TOF value than Au_9Pd_1/TiO_2 because of their smaller particles size (10-15 nm) as shown in TEM study. We also observed the same trend of activity for Au_9Pd_1/TiO_2 catalyst. This trend was in agreement with the study reported by Bianchi et. al [4] that higher reaction temperature will enhance the rate of glycerol oxidation. Looking at the conversion profiles for both of the catalysts, they almost reaching full conversion after 1 h of reaction time with their activity remain constant until reaction complete. This demonstrated that both of the catalysts were very active for the oxidation reaction of glycerol. The high activity for these catalysts was due to the presence of metallic Au^0 and alloy Au-Pd phase as showed by XRD and XPS analysis. It was generally accepted that "synergistic" effect that existed between the Au-Pd metal was the important criteria for high catalytic activity observed in this reaction [5]. In this study, we only prepared bimetallic catalysts with higher Au/Pd ratio because they have very high activity compared with those catalysts which have higher Pd contents [4]. Catalysts that contain higher palladium content also suffered a faster deactivation due to the tendency to undergo catalyst poisoning rapidly [4].

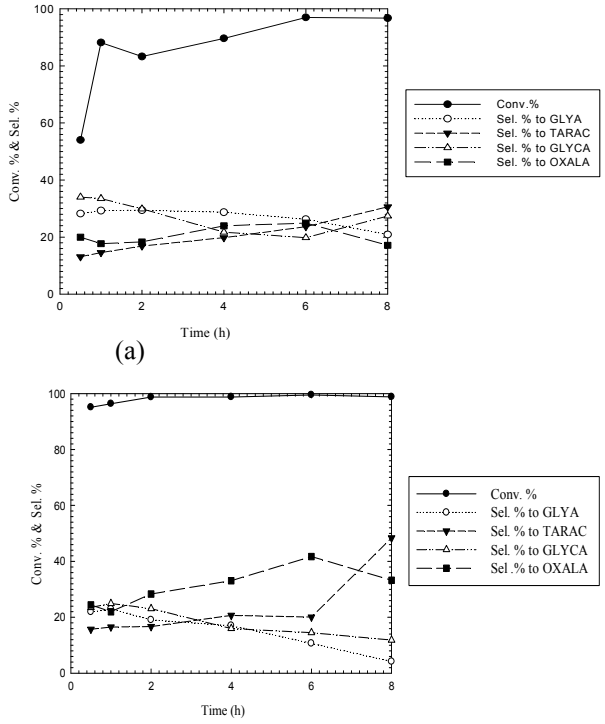


Fig. 6: Selective oxidation of glycerol in the presence of Au_8Pd_2/TiO_2 at: a) 50°C and b) 100°C. Reaction condition: 0.6 M glycerol, NaOH/glycerol=4 mol/mol, glycerol/M= 200 mol/mol and pO_2= 3atm

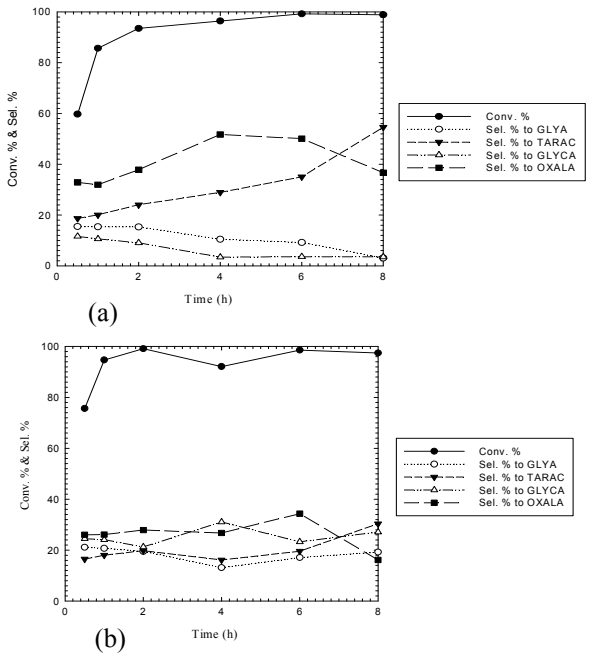


Fig. 7: Selective oxidation of glycerol in the presence of Au_9Pd_1/TiO_2 at: a) 50°C and b) 100°C. Reaction condition: 0.6 M glycerol, NaOH/glycerol=4 mol/mol, glycerol/M= 200 mol/mol and pO_2= 3atm

IV. CONCLUSION

Oxidation of glycerol towards various short chain oxygenated derivatives can be performed using bimetallic Au_9Pd_1/TiO_2 and Au_8Pd_2/TiO_2 catalysts. The conversion and selectivity of the products were found to be depended on the reaction conditions and nature of the metals. Higher catalytic activity of bimetallic Au_xPd_y/TiO_2 catalysts was due to the presence of metallic Au^0 and PdO phases as indicated by XRD and XPS analysis. Others, the "synergetic" effect between the Au and Pd and/or PdO phases also contributed to the activity of the catalysts.

In terms of selectivity to tartronic acid, we obtained the best result by using Au_9Pd_1/TiO_2 at 50°C (54.6% at 99% conversion) after 8 h of reaction time. At each temperature, the oxalic acid formed as major product suggesting that the selectivity to this acid was favoured at moderate (50°C) and higher temperature (100°C).

ACKNOWLEDGMENT

The authors would like to convey gratitude for financial support from University Kebangsaan Malaysia under GUP project, UKM-GUP-BTK-08-14-306, Malaysian Ministry of Science, Technology and Innovation (MOSTI) and CRIM, UKM for spectroscopy analysis.

REFERENCES

[1] C. Zhou, J. Beltramini, Y. Fang, and G. Lu, "Chemoselective catalytic conversion of glycerol as a biorenewable source to valuable commodity chemicals," *Chem. Soc. Rev.*, vol. 37, pp. 527-549, 2008.

[2] N. Dimitratos, J. A. Lopez-Sanchez, D. Lennon, F. Porta, L. Prati, and A. Villa, "Effect of particle size on monometallic and bimetallic (Au/Pd)/C on the liquid phase oxidation of glycerol," *Catal. Letters*, vol. 108, no. 3-4, pp. 147-153, 2006.

[3] N. Dimitratos, A. Villa, C. Bianchi, L. Prati, and M. Makkee, " Gold on titania: Effect of preparation method in the liquid phase oxidation," *Appl. Catal. A: Gen.*,Vol. 311, pp. 185-192, 2006.

[4] C. L. Bianchi, P. Canton, N. Dimitratos, F. Porta, and L.Prati, "Selective oxidation of glycerol with oxygen using mono and bimetallic catalysts based on Au, Pd and Pt metals," *Catal. Today*, vol. 102-103, pp. 203-212, 2002.

[5] A. Villa, C. Campione, and L.Prati, "Bimetallic gold/palladium catalysts for the selective liquid phase oxidation of glycerol," *Catal. Lett.*, Vol. 115, no. 3-4, pp. 133-136, 2007.

[6] L. Prati, A. Villa, F. Porta, D. Wang, and D. Su, "Single-phase gold/palladium catalyst:The nature of synergistic effect," *Catal. Today*, vol. 122, pp. 386-390, 2007.

[7] A. Villa, N. Janjic, P. Spontoni, D. Wang, D. S. Su, and L.Prati, "Au-Pd/AC as catalysts for alcohol oxidation: Effect of reaction parameters on catalytic

activity and selectivity," *Appl.* Catal. *A: Gen.*, vol. 364,
pp. 221-228, 2009.
[8] W. Li, M. Comotti, and F. Schuth, "Highly reproducible
synthesis of active Au/TiO_2 catalysts for CO oxidation
by deposition-precipitation or impregnation," *J. Catal.*,
vol. 237, pp. 190-196, 2006.
[9] D. I. Enache, J. K. Edwards, P. Landon, B. Solsona Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C.J.
Kiely, D. W. Knight, and G. J. Hutchings, "Solvent-free
oxidation of primary alcohol to aldehydes using Au-Pd/TiO_2 catalysts," *Science 311*, pp. 362-365, 2006.
[10] R. Zanella, S. Giorgio, C. H. Shin, C. R. Henry, and C.
Louis, "Characterization and reactivity in CO oxidation of gold nanoparticles supported on TiO_2 prepared by deposition- precipitation with NaOH and
urea," *J. Catal.*, vol. 222, pp. 357, 2004.
[11] S. Tsubota, D. Cunningham, Y. Bando, and M. Haruta, "CO oxidation over gold supported on TiO_2," *Stud. Surf. Sci. Catal.* vol. **77**, pp. 325-328, 1993.
[12] F. Porta, and L. Prati, "Selective oxidation of glycerol to sodium glycerate with gold-on-carbon catalysts: an insight into reaction selectivity," *J. Catal.*, vol. 224, pp. 397-403, 2004.
[13] A. M. Venezia, V. La Parola, V. Nicoli, and G. Deganello, "Effect of gold on the HDS activity of supported palladium catalysts," *J. Catal.*, vol. 212,
pp. 56-62, 2002.
[14] C. Suryanarayana, and M. G. Norton, "*X-ray diffraction: A practical approach*. New York: Plenum Press, 1998.
[15] B. Pawelec, A.M. Venezia, V. La Parola, E. Cano-Serrano, J.M. Campos-Martin, and J.L.G. Fierro, "AuPd alloy formation in $Au-Pd/Al_2O_3$ catalyts and its role on aromatics hydrogenation," *Appl. Surf. Sci.*, vol. 242, pp. 380, 2005.
[16] A. M. Venezia, L. F. Liotta, G. Pantaleo, V. La Parola, G. Deganello, A. Beck, Zs. Koppány, K. Frey, D. Horváth, and L. Guczi, "Activity of SiO_2 supported gold-palladium catalysts in oxidation. *Appl. Catal. A*, vol. 251, pp. 359-368, 2003.