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Description	

Green synthesis of platinum/gold bimetallic nanoparticles supported onto hydrotalcite surface as heterogeneous catalyst for selective oxidation of glycerol

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Abstract

Platinum/Gold bimetallic (Pt/Au) nanoparticles were successfully synthesized by green synthesis method in aqueous solution under mild condition using polysaccharide as a protecting agent as well as a reducing agent. The metal nanoparticles were supported on hydrotalcite (HT) surface by sol immobilization method and further utilized as heterogeneous catalyst. The surface morphology and compositions of supported platinum/gold (PtAu/HT) were analyzed by XRD and ICP-MS. The lattice parameter calculated from XRD diffraction pattern (111) of Pt_mAu_{100-m} exhibited linearly with their compositions only at low Pt concentrations (i.e., 20 and 40% Pt). However the result XRD pattern support that Pt/Au metal might be formed the partially alloy or partially phase segregation at high Pt concentrations, (i.e., 60, 80, and 90% Pt). The catalysis of Pt_mAu_{100-m}/HT (1 wt%) were evaluated for glycerol oxidation in base-free aqueous solution using molecular oxygen as an oxidant (glycerol/metal = 700 mol/mol). The moderate activities of Pt_mAu_{100-m}/HT also remain with increasing of Au amount to 20%, in addition, the increasing of Au amount more than this value resulting decreased of an activity. It is due to the Pt_mAu_{100-m}/HT particles size become larger with Au amount. However, the increasing of glycerol/metal ratio to 500 mol/mol was clearly seen that the presence of Au in Pt metal improved the selectivity toward glyceric acid, especially, $Pt_{80}Au_{20}/HT$ catalyst. This phenomenon is explained by the synergistic effect of Pt/Au bimetallic resulting in the decreasing of the undesired product.

Introduction

Glycerol can be obtained from biomass as the by-product, the production of biodiesel by tranesterification of triglyceride causes the output of glycerol approximately 10 wt% of the total product. Therefore, it would be of significantly advantage if the glycerol could be transformed to value-added chemical. Glycerol is an intermediate in the synthesis of a large number of compounds used in industry, therefore, there are many catalytic processes which transformed glycerol to valuable products, e.g., hydrogenolysis, polymerization, esterification, dehydration, and oxidation.(1-3) Especially, all glycerol oxygenates derivatives are value-added products. However, the similarly reactive with molecular oxygen of both hydroxyl groups cause the poor selectivity. Therefore, supported metal such as Pt/AC, Pt/MWNTs, Au/C, Pd/C, Au/TiO₂, Au/Fe₂O₃, Rh/AC, Au/graphite, Pd/graphite, Au/TiO₂, Nb₂O₅, Au/MgAl₂O₄, and Pt/HT catalyst have been used for catalysis of the glycerol oxidation reaction toward desired product.(4-13) However, the drawback for utilizing of monometallic as a heterogeneous catalyst in the liquid phase with oxygen as an oxidant is the sensitivity in deactivation due to over oxidation and poisoning from by-product.(13)

Recently, the publications have been reported that the bimetallic structure is of interest in heterogeneous catalysis, since they have different activity and selectivity comparable to that of monometallic because the presence of foreign metal atoms at the surface change its electronic and structures.(14, 15) Several bimetallic catalyst have been exhibited more active than either of their individual metals. For instance, the bimetallic catalyst of Au and Pd exhibit very high alcohol oxidation rate and selectivity in both solvent-free and aqueous solution reaction.(16-17) In particularly Pt/Au bimetallic catalyst, it was reported that their bimetallic has proved to be beneficial, performing better than platinum alone in oxygen reduction at the fuel cell cathode and in selective oxidation of polyol.(18, 19) Hence, Pt/Au bimetallic could provide a synergistic catalytic effect that involves the suppression of adsorbed poisonous species and a change in electronic band structure for modifying the strength of the surface adsorption.(20)

In this work we focused on the development of a simple method for synthesis of Pt/Au bimetallic nanoparticles in aqueous solution by using polysaccharide as a reducing agent as well as protecting agent and further supported HT surface (PtAu/HT) by sol immobilization method. Hydrotalcite, $Mg_6Al_2(OH)_{16}CO_3 \cdot nH_2O$ (Mg-Al- CO_3), consists of a positively charged two dimensional Brucite-like layer, with anionic species in the interlayer to form neutral material. One of an interest in characteristic of HT is the surface basicity.(21) Furthermore, we evaluated the catalytic activity of an obtained PtAu/HT bimetallic heterogeneous catalysts by glycerol oxidation in base-free aqueous solution using molecular oxygen as an oxidant under atmospheric pressure. It is well-known that the oxidation reaction of primary alcohol requires the alkaline condition therefore the selection of hydrotalcite as a supporter has an advantage for carrying out the reaction under the absence of homogeneous base.

Experiment

Material: $H_2PtCl_6 \cdot 6H_2O$ (99.9%), $HAuCl_4 \cdot 4H_2O$ (99.9%) and polysaccharide were purchased from Wako Pure Chemicals. NaOH (90.0%) was obtained from Kanto Chemicals. Hydrotalcite (HT), Mg/Al = 5, was purchased from Tomita Pharmaceutical.

Preparation of platinum and gold monometallic supported on hydrotalcite catalyst (Pt/HT and Au/HT): Pt and Au nanoparticles were synthesized with chemical reduction method by using the polysaccharide simultaneously as protecting agent as well as reducing agent and were supported HT by sol immobilization method. The desired concentration (2.5 mM, 5 mL) of $H_2PtCl_6 \cdot 6H_2O$ and $HAuCl_4 \cdot 4H_2O$ were prepared in aqueous solution. $H_2PtCl_6 \cdot 6H_2O$ and $HAuCl_4 \cdot 4H_2O$ were pH adjusted with NaOH until the solution became neutral (pH 7), and then mixed with NaOH solution (0.05 M, 5 mL). The polysaccharide (4 wt%) were dissolved in hot water, then, that solution (5 mL) were mixed with NaOH solution (0.05 M, 5 mL). The above two solutions were heated at 100°C for 20 min. Then, their solution were mixed together and continuously stirred at 100°C for 10 min. Within 10 min after sol generation, HT (Mg/Al = 5, 0.49 g) was added into the solution under the continuously stirred and refluxed at 100°C for 1 h. The amount of HT required was calculated to have a metal loading of 1 wt%. After that, the solid solution were cooled down at room temperature, filtered and washed with water. The filtrated was dried overnight at 100°C.

Preparation of platinum and gold bimetallic supported on hydrotalcite catalyst (PtAu/HT): PtAu bimetallic nanoparticles were synthesized and supported HT with the same method of monometallic catalyst. The desired concentration (2.5 mM of total metal loading, 5 mL)

of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ were prepared in aqueous solution, the several metal contents in bimetallic nanoparticles were listed in **Table 1**. H_2PtCl_6 and HAuCl_4 were pH adjusted with NaOH until the solution became neutral (pH 7). The NaOH solution (0.05 M, 5 mL) was added into the mixed solutions of H_2PtCl_6 and HAuCl_4 . In parallel, 5 mL of polysaccharide solution (4 g/100 mL H_2O) were also mixed with NaOH solution (0.05 M, 5 mL). The above two solutions were heated at 100°C for 20 min. Then, their solution were mixed together and continuously stirred at 100°C for 10 min. Within 10 min after sol generation, HT (Mg/Al = 5, 0.50 g) was added into the solution under the continuously stirred and refluxed at 100°C for 1 h. The amount of HT required was calculated to have a metal loading of 1 wt%. After that, the solid solution were cooled down at room temperature, filtered and washed with water. The filtrated was dried overnight at 100°C .

Catalyst characterization: Samples were characterized by X-ray diffraction (RINT-2000), and the metal contents in catalyst were analyzed by inductively coupled plasma atomic emission spectroscopy (ICPS-7000).

Catalytic testing: Catalytic test of Pt/HT and $\text{Pt}_m\text{Au}_{100-m}/\text{HT}$ were evaluated for glycerol oxidation in base-free aqueous solution using molecular oxygen as an oxidant. The reaction of glycerol solution (0.5 mmol), 2 mL of water and 1 wt% of Pt/HT $\text{Pt}_m\text{Au}_{100-m}/\text{HT}$ heterogeneous catalyst were carried out at 323 K for 5 h under oxygen flow (10 mL/min). All performed in a Schlenk tube attached with reflux condenser. After the reaction, the vessel was cooled down to room temperature and catalyst was separated by filtration. The filtrated were analyzed by using high performance liquid chromatography (HPLC) with a Aminex HPX-87H column from Bio-Rad Laboratories and refractive index (RI) detector. The analysis conditions were set as follows: the eluent was an aqueous solution of H_2SO_4 (10 mM), flow rate 0.5 mL/min and column temperature 323 K.

Results and Discussion

The results are divided into two sections, first section, we are discussing the morphology and compositions of Pt, Au mono- and bimetallic nanoparticles along with the support of their metal. Second section, we discuss the catalytic activity of supported-Pt mono- and bimetallic for glycerol oxidation.

1. Morphology and compositions of Pt, Au mono- and bimetallic nanoparticles

The bimetallic of Pt/Au was synthesized by green synthesis method using polysaccharide as a reducing agent as well as protecting agent. The various metals loading ($\text{Pt}_m\text{Au}_{100-m}$) were calculated in 1 wt% total metal loading with HT support. The calculations of metal loading for $\text{Pt}_m\text{Au}_{100-m}/\text{HT}$ are shown in **Table 1**, along with the obtainable of their metal loading that were analyzed by ICP-MS.

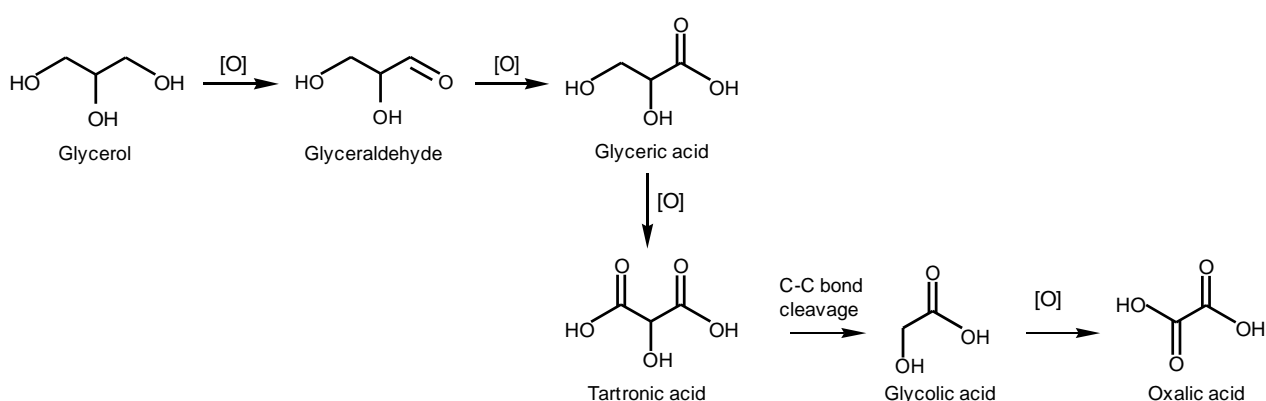
Figure 1(A) shows the XRD pattern of HT supported- $\text{Pt}_m\text{Au}_{100-m}$ nanoparticles. The diffraction patterns of Pt and Au metal could not be observed, since they overlapped with the HT peaks. Therefore, we are considering the diffraction patterns of $\text{Pt}_m\text{Au}_{100-m}$ nanoparticles without supportive material that was shown in **Figure 1(B)**. There revealed that the diffraction pattern of $\text{Pt}_m\text{Au}_{100-m}$ located between the patterns of Pt ($2\theta = 39.7$) and Au ($2\theta = 38.3$).⁽²²⁾ The peak position of the (111) reflection of $\text{Pt}_m\text{Au}_{100-m}$ nanoparticles shifted to lower angle with increasing of Au amount, i.e., $2\theta = 39.7, 39.6, 39.4, 39.1, 38.8, 38.5,$ and 38.3 for $\text{Pt}_{100}, \text{Pt}_{90}\text{Au}_{10}, \text{Pt}_{80}\text{Au}_{20}, \text{Pt}_{60}\text{Au}_{40}, \text{Pt}_{40}\text{Au}_{60}, \text{Pt}_{20}\text{Au}_{80},$ and Au_{100} , respectively. The broadening of (111) diffraction peak of

Pt₁₀₀ becomes narrower and sharper with increasing of Au amount. It is well-known that the increasing in the particles size results in a narrowing of diffraction peak.

Table 1. Composition of Pt mono- and PtAu bimetallic nanoparticles.					
Entry	Sample ⁽¹⁾	Metal loading		Nanoparticles ⁽²⁾	
		Pt	Au (%)	Pt	Au (%)
1	Pt	100	-	90	-
2	Pt ₉₀ Au ₁₀	90	10	84	10
3	Pt ₈₀ Au ₂₀	80	20	72	20
4	Pt ₆₀ Au ₄₀	60	40	57	34
5	Pt ₄₀ Au ₆₀	40	60	41	47
6	Pt ₂₀ Au ₈₀	20	80	24	65
7	Au	0	100	-	85

(1) Total amount of metal/HT = 1 wt%. (2) Analysis by ICP-MS.

Nevertheless, the lattice parameter calculated from XRD diffraction pattern of (111) reveals that the presence of Au increased the lattice distance of Pt. **Figure 1(C)** show the lattice parameter of Pt_mAu_{100-m} nanoparticles that exhibited linearly with their compositions at low Pt concentrations (i.e., 20 and 40% Pt). It indicated that the obtained Pt_mAu_{100-m} could be formed the completely bimetallic alloy only at low Pt concentrations. However, the result XRD pattern support that Pt/Au metal might be formed the partially alloy or partially phase segregation at high Pt concentrations, (i.e., 60, 80, and 90% Pt). Mott et al., proposed that bimetallic between Pt and Au could be formed not only completely alloy, but also partially alloy or partially phase segregation and completely phase segregation.(23)



Scheme 1. A possible reaction pathway of glycerol oxidation catalyzed by Pt_mAu_{100-m} heterogeneous catalyst.

2. Catalytic activity testing (glycerol oxidation)

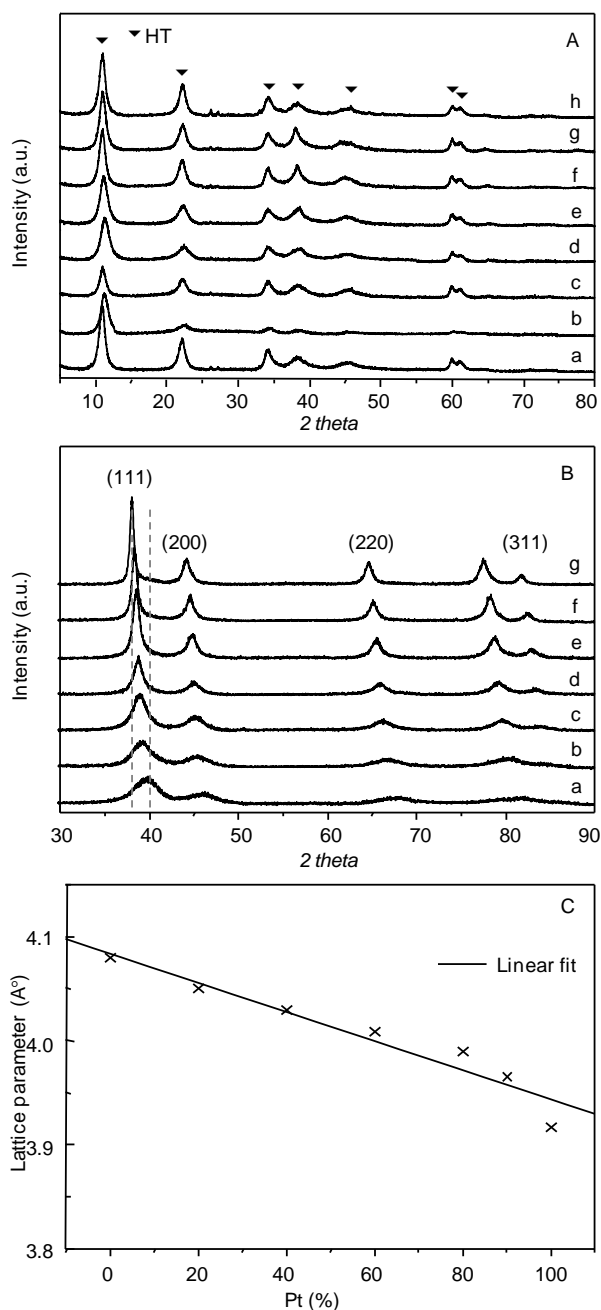


Figure 1. (A) XRD patterns of HT supported Pt_mAu_{100-m} nanoparticles: (a) Pt_{100}/HT , (b) $Pt_{90}Au_{10}/HT$, (c) $Pt_{80}Au_{20}/HT$, (d) $Pt_{60}Au_{40}/HT$, (e) $Pt_{40}Au_{60}/HT$, (f) $Pt_{20}Au_{80}/HT$, (g) Au_{100}/HT , and (h) HT ($Mg/Al = 5$). (B) XRD patterns of Pt_mAu_{100-m} nanoparticles (without support): (a) Pt_{100} , (b) $Pt_{90}Au_{10}$, (c) $Pt_{80}Au_{20}$, (d) $Pt_{60}Au_{40}$, (e) $Pt_{40}Au_{60}$, (f) $Pt_{20}Au_{80}$, and (g) Au_{100} . (C) Dependence of the lattice parameters for Pt_mAu_{100-m} nanoparticles on the relative composition of Pt% (cross mark on solid line).

52% yield) while the selectivity toward GA was constant.

For further comparisons of the catalytic activity of Pt/HT and $Pt_{80}Au_{20}/HT$ catalyst, the reaction time courses were performed by using glycerol/metal = 500 mol/mol, glycerol (0.5 mmol), H_2O (2 mL), under oxygen flow (10 mL/min), 323 K. The reaction time courses of glycerol oxidation catalyzed by Pt/HT and $Pt_{80}Au_{20}/HT$ catalyst are shown in **Figure 2.** and **3.** Their Figures presented of the two different important issues, the first one is the initial reaction rate and the second one is the occurrence of the undesired product. Firstly, we discussed the initial reaction rate,

The catalytic activity testing of Pt_mAu_{100-m} was carried out by glycerol oxidation in base-free aqueous solution under atmospheric oxygen pressure and the results were shown in **Table 2.** The possible reaction pathway of glycerol oxidation catalyst by Pt_mAu_{100-m}/HT catalyst was shown in **Scheme 1.** The reaction was accomplished with the oxidation at hydroxyl group (primary alcohol) of glycerol to glyceraldehyde further oxidized to glyceric acid (GA), tartronic acid (TA), glycolic acid (HA), and oxalic acid (OA). The catalytic activity of Pt_mAu_{100-m} for glycerol/metal = 700 mol/mol revealed that the glycerol conversion maintained with increasing of Au amount to 20% (entry 1, 3, and 5) and continuously decrease with increasing the amount of Au to 100% (entry 7, 8, 9, and 10). This results compatible with previously reported values that the catalytic activity showed a limitation when metal particle size increased.⁽²⁴⁾ However, the selectivity toward GA was boosted to 76 and 74% for 10 and 20% Au, respectively. In addition, it is obviously observed that not only the selectivity toward GA was increased, but also GA yields. The glycerol conversion did not occur for the reaction that was carried out without catalyst (entry 11). It indicated that the bimetallic of Pt and Au improved the selectivity toward GA, although, Au itself scarcely had selectivity toward GA. These improvements are clearly seen with increasing the amount of glycerol/metal = 500 mol/mol. In case of Pt/HT (entry 2), the glycerol conversion sharply increased to 80% along with the decreasing of selectivity toward GA to 60%. For $Pt_{90}Au_{10}/HT$ (entry 4) and $Pt_{80}Au_{20}/HT$ (entry 6), the increasing rate of glycerol conversion increasing smaller than that of Pt/HT . Especially $Pt_{80}Au_{20}/HT$ catalyst, it was found that slightly increasing of the conversion (64 to 69%) was mostly transformed to GA (47 to

it was found that the reaction catalyzed by Pt₈₀Au₂₀/HT showed the higher initial reaction rate than that was catalyzed by Pt/HT.

Table 2. Results of glycerol oxidation catalyst by Pt/HT and PtAu/HT in base free aqueous solution using molecular oxygen as an oxidant.⁽¹⁾

Entry	Catalysts	Conversion (%)	Selectivity (%)				GA Yield (%)
			GA	TA	HA	OA	
1	Pt/HT	63	68	10	16	6	43
2	Pt/HT ⁽²⁾	80	60	14	17	9	48
3	Pt ₉₀ Au ₁₀ /HT	61	76	7	12	5	47
4	Pt ₉₀ Au ₁₀ /HT ⁽²⁾	71	70	12	13	6	49
5	Pt ₈₀ Au ₂₀ /HT	64	74	8	14	4	47
6	Pt ₈₀ Au ₂₀ /HT ⁽²⁾	69	75	10	8	7	52
7	Pt ₆₀ Au ₄₀ /HT	39	86	3	10	1	33
8	Pt ₄₀ Au ₆₀ /HT	12	87	-	11	2	11
9	Pt ₂₀ Au ₈₀ /HT	4	67	-	28	6	2
10	Au/HT	2	39	-	46	15	1
11	Blank	1	30	-	9	3	-

(1) Reaction conditions: glycerol (0.05 mmol), H₂O (2 mL), glycerol/metal = 700 (mmol/mmol), total amount of metal/HT = 1 wt%, Mg/Al = 5, under O₂ flow (10 mL/min), 323 K, 7 hr. (2) Glycerol/metal = 500 (mmol/mmol).

This phenomenon can explain in term of the electronic interaction between Pt and Au. Generally, the feature of the accepted mechanism for metal catalyzed dehydrogenation process in aqueous solution involves hydride subtraction and subsequent oxidation by oxygen.⁽¹⁸⁾ Firstly, the hydride subtraction at alcohol position has occurred further toward alkoxide. After that, there are formed bonding with metal site toward to glyceraldehyde and undergo oxidized to GA. This step, the electronic interaction between Pt and Au atoms located in close proximity to each other cause a partially of electron transfer from Au to Pt, with the cause of, increasing of the back-donation of electrons from the filled *d* orbitals of Pt to the -CO⁻.⁽²⁵⁾ Consequently, the desorption of alkoxide toward glyceraldehyde is faster, therefore, the initial reaction of glycerol oxidation catalyzed by PtAu/HT is faster than Pt/HT. Secondly, we discuss the synergistic effect of Pt and Au bimetallic to the lower production of undesired products (i.e., TA, HA, and OA) The possible effect of the lower production of undesired products revealed the changing of *d* spacing in crystal structure of metal particles. It has been reported for the Au-Pd system, Au acted as promoter to isolate Pd monomer sites thus also limiting oxygen coverage, in other words, Au improved the geometric of Pt surface. This means that the presented of Au could enhance the resistance to oxygen poisoning. Gold also reported to reduce Pt self poisoning.^(18,26) As a result, we can say that the bimetallic nanoparticles in the presence of Au in Pt can improve the activity of PtAu/HT catalyst for glycerol oxidation by the synergistic effect electronic and geometric.

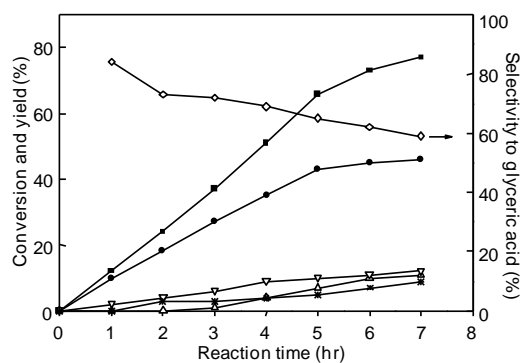


Figure 2 Reaction time profile of glycerol oxidation catalyst by Pt/HT in water used O₂ as an oxidant. Reaction condition: glycerol (0.5 mmol), H₂O (1.5 mL), 1wt% Pt/HT (Mg/Al = 5), glycerol/metal = 500 (mol/mol), under O₂ flow (10 mL/min), 323 K. Glycerol conversion (■ : close square), glyceric acid yield (● : close circle), tartronic acid yield (△ : open up triangle), glycolic (▽ : open down triangle), oxalic acid yield (* : star), and glyceric acid selectivity (◇ : diamond).

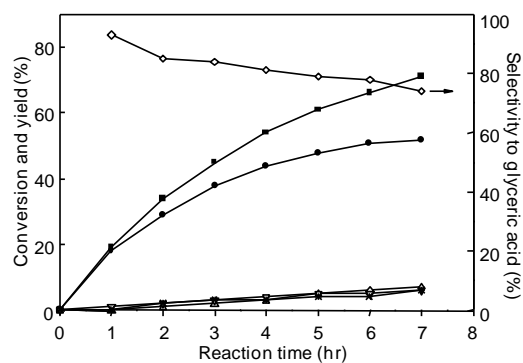


Figure 3 Reaction time profile of glycerol oxidation catalyst by PtAu/HT in water used O₂ as an oxidant. Reaction condition: glycerol (0.5 mmol), H₂O (1.5 mL), 1wt% PtAu/HT (Mg/Al = 5), glycerol/metal = 500 (mol/mol), under O₂ flow (10 mL/min), 323 K. Glycerol conversion (■ : close square), glyceric acid yield (● : close circle), tartronic acid yield (△ : open up triangle), glycolic (▽ : open down triangle), oxalic acid yield (* : star), and glyceric acid selectivity (◇ : diamond).

Conclusion

Green synthesis of HT supported-Pt/Au bimetallic nanoparticles was successfully synthesized by reduction of Pt and salt utilizing polysaccharide as a reducing agent as well as protecting agent. The analysis of metal morphology reveals that the Pt and Au formed a partially alloy onto the HT surface. The activity of Pt_mAu_{100-m}/HT as a heterogeneous catalyst for glycerol oxidation in base-free aqueous solution with atmospheric pressure O₂ flow as an oxidant showed that the glycerol conversion decreased with increasing of Au amount, since, the increasing of particles. However, the Pt₈₀Au₂₀/HT exhibited the best catalytic activity (considered both of conversion and selectivity) under these conditions. Even though, the presentation of Au in Pt is not formed the completely alloy, but the experimental result revealed that the PtAu/HT showed the synergistic effect to the improvement of selectivity toward GA.

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