CHAPTER III

SYNTHESIS OF SUPPORTED PLATINUM CATALYST
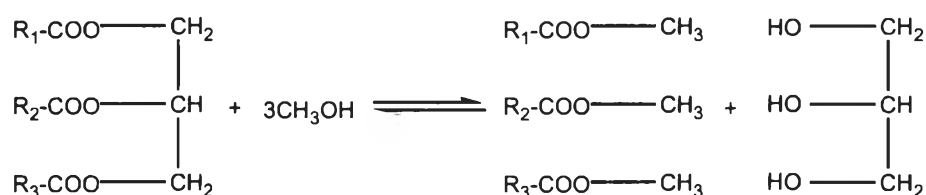## *VIA* GREEN NANOTECHNOLOGY

3.1 Introduction

Platinum metal has been used for a variety of catalyst applications (e.g., hydrogenation reaction and oxidation reaction).[6] Although, the Pt NPs has an advantage with high catalytic activity, however, homogeneous catalysts suffer from the problems of separation, recycling, and deactivation via the aggregation of Pt NPs during the reaction.[66] To overcome the drawback, the support materials such as activated carbon,[67] graphite,[67] silica,[68] and alumina[69] have been used. The most common methods for synthesis of supported platinum catalyst (heterogeneous catalyst) are the impregnation, deposition-precipitation and immobilization method. The preparation of very active platinum catalyst using immobilization method has been reported. This method involving of the metal nanoparticles or metal sols is generated by the reduction of metal precursor with a reducing agent. Next, they are immobilized on the support material. The advantages of this methodology are the reproducible variation of particles size and the control of particles sized distribution.[70] However, the stabilizer or protection agent is required. As mentioned in Chapter II that Pt NPs are generated by using soluble starch as both of reducing agent and stabilizer. Therefore, the developed synthesis method of Pt NPs is applied for the preparation of supported Pt NPs catalyst without external stabilizer requires.

Pt NPs have been reported as an oxidative catalyst especially for the alcohol oxidation. Li F. et al. (2009) reported a synthesis of Pt NPs by using $NaBH_4$ as a reducing agent and amino-terminated ionic liquid as a stabilizer.[71] The Pt NPs/glassy carbon exhibited high electrocatalytic activity toward reduction of oxygen and oxidation of methanol. Li S. et al. (2011) reported the Pt NPs decorated carbon nanotubes by using polyoxometalates served as both reducing and bridging molecules.[72] The nanohybrid showed a highly electrocatalytic activity towards

methanol oxidation reaction. Moreover, the platinum catalyst also shows the good activity in the oxidation of polyalcohol such as glycerol.
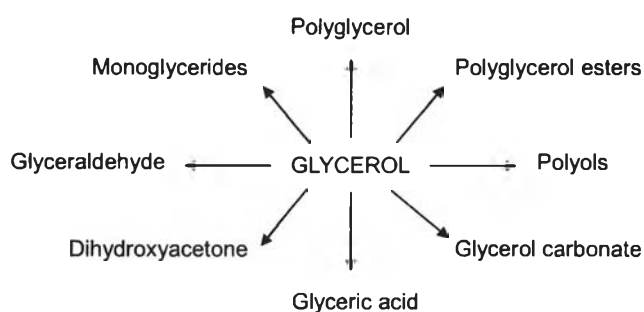
3.1.1 Glycerol

Glycerol is one of the by-products from industries especially, biodiesel industry (Scheme 3.1).

$$R_1\text{-COO}\text{——}CH_2 \qquad\qquad R_1\text{-COO}\text{——}CH_3 \quad HO\text{——}CH_2$$

$$R_2\text{-COO}\text{——}CH \ + \ 3CH_3OH \ \rightleftharpoons \ R_2\text{-COO}\text{——}CH_3 \ + \ HO\text{——}CH$$

$$R_3\text{-COO}\text{——}CH_2 \qquad\qquad R_3\text{-COO}\text{——}CH_3 \quad HO\text{——}CH_2$$

Scheme 3.1 Overall reactions for production of glycerol from biodiesel industry.[8]

Since there is an increase in biodiesel production, the crude glycerol generated from the process has also been produced in large quantities. There are wide applications of pure glycerol in food, cosmetics, and pharmaceutical industries. Many research projects have been conducted on the innovative utilizations of glycerol. According to its three hydroxyl groups, glycerol is a potential starting material for several high-valued fine chemicals.[8, 73] It could be transformed into a value-added chemical by employing different chemical reactions,[74] e.g., hydrogenolysis,[75, 76] dehydration,[77] and oxidation.[67, 70] Especially, oxidation reaction of glycerol provides a lot of value-added chemicals as shown in Scheme 3.2. However, the similarly reactive with molecular oxygen of the hydroxyl groups on the glycerol cause the poor selectivity. Therefore, a careful design of the catalyst is required to control the selectivity of the desired compounds.

Polyglycerol

Monoglycerides   Polyglycerol esters

Glyceraldehyde ⟵——— GLYCEROL ———⟶ Polyols

Dihydroxyacetone   Glycerol carbonate

Glyceric acid

Scheme 3.2 Products from oxidation reaction of glycerol.[78]

3.1.2 Literature reviews

Carrettin S. et al. (2003) prepared palladium, platinum, and gold nanoparticles supported on graphite and activated carbon (1-5% metal by weight of support) using formaldehyde as a reducing agent. Their catalytic activity was performed for oxidation of glycerol which showed some selective to glyceric acid product under reaction condition of 60°C and 1 bar oxygen pressure for batch reaction. When the reaction performed using an autoclave with pure oxygen at 3 bar pressure, it gave a significant improvement in reactivity for platinum and gold catalysts. However, in the absence of NaOH, the Au/C catalyst was inactive.[67]

Dimitratos N. et al. (2006) prepared gold and platinum mono- and bimetallic catalysts supported on carbon (Au/C and Pt/C) by sol immobilization. Polyvinyl alcohol was used as a protecting agent and $NaBH_4$, N_2H_4, and H_2 were used as a reducing agent. The catalytic performance of the synthesized catalysts was performed in the liquid phase oxidation of glycerol. The reaction was carried out with condition: glycerol solution (0.3 M and NaOH/glycerol ratio = 4, mol/mol), catalyst (glycerol/metal ratio = 500, mol/mol), oxygen pressure of 3 atm, 50°C. All the cases of monometallic Pt/C catalysts a deactivation progress took place during the reaction. To overcome this problem the Pt/C catalysts were modified with addition of gold. Finally, the most active bimetallic catalyst was obtained when H_2 was the reducing agent for platinum precursor.[70]

Liang D. et al. (2009) prepared a series of platinum/carbon (Pt/C) catalysts with different platinum particle size ranged from 1.2 to 26.5 nm reducing with at 50 °C for 1 h in a basic condition (with a final pH value of 9.0). It was found that the platinum dispersion depends on the surface properties of the support, the amount of reducing agent, and preparation temperature. The catalytic test was carried out for the oxidation of glycerol in a base-free aqueous solution. The reaction was performed under condition: glycerol solution (50 cm^3 of 0.1 g/cm^3), catalyst (0.5 g), constant flow of oxygen (150 cm^3/min), 60°C, 6 h. The bigger sized platinum particles (>10 nm) were less active while smaller sized ones (<6 nm) exhibited higher glycerol conversion, stable selectivity, and good recycled activity.[79]

Gao J. et al. (2009) prepared active carbon and multi wall carbon nanotube supported platinum (Pt/MWNTs and Pt/AC) catalyst using an aqueous solution of KBH_4 as a reducing agent. The oxidation of glycerol with molecular oxygen was catalyzed by Pt/MWNTs and Pt/AC in base free aqueous solution as the following conditions: glycerol solution (0.1 g/mL), catalyst (0.50 g), oxygen flow rate (150 mL/min), 60°C. The results found that Pt/MWNTs catalyst was more active than Pt/AC. It is due to the platinum particles mainly deposited on the external wall of MWNTs, which can contact easily with glycerol and/or oxygen.[80]

Hu W. et al. (2010) prepared activated carbon supported platinum bismuth (Pt-Bi/AC) catalysts by the sequential impregnation method. Catalysts with different loadings were prepared by using a constant molar ratio of Pt/Bi, and varying platinum from 2 to 10%. The Pt-Bi/C catalysis of Glycerol to dihydroxyacetone was investigated systematically in a semi-batch. A typical reaction was performed as the following conditions: catalyst (5 g), glycerol solution (1 M), oxygen pressure. The optimum catalyst composition which gave high glycerol oxidation rate and maximum DHA yield was determined to be 3 wt% platinum, 0.6 wt% Bi, supported on activated carbon. In addition, the optimum reaction conditions were identified as 80 °C, 30 psig, and initial pH 2. Under these conditions, a maximum DHA yield of 48% was obtained at 80% glycerol conversion.[81]

Tsuji A. et al. (2011) prepared hydrotalcite supported platinum catalyst using formaldehyde as a reducing agent. They were used as a catalyst for the oxidation of glycerol: glycerol (0.5 mmol), water (5 mL), glycerol/metal molar ratio up to 3125, O_2 flow (10 mL/min), 333 K, 6 h. It was found that high selectivity toward glyceric acid was obtained even at room temperature under air atmosphere. Moreover, the activity of the catalyst was greatly influenced by the Mg/Al ratio of hydrotalcite. The glycerol conversion increased with increasing the Mg/Al ratio of hydrotalcite.[82]

3.1.3 Green catalyst concept

Nowadays, many researches tend to make environmental friendly method for preparation of metal catalyst. Therefore, the simplification of the catalyst development in term of optimizing atom and energy efficiencies was referred to green

technology to overall process design the reaction or choose the environmental benign reagent.[83] In order to design the green oxidation reaction, the key design parameter for selective oxidation catalysis was adapted from green chemistry principle as shown in Scheme 3.3.
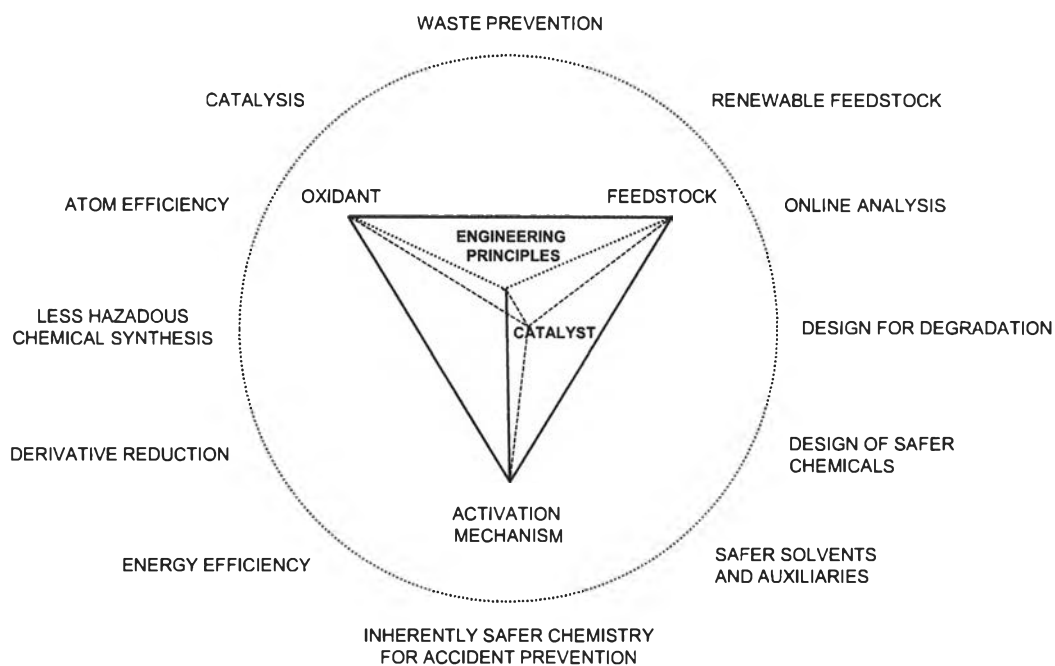
Scheme 3.3 Key design parameter for selective oxidation catalysis.[83]

From the viewpoint of green nanotechnology for oxidation reaction design, the molecular oxygen is the greener oxidant as well as the water is a media. Including, the energy efficient were designed if the reaction was performed using catalysis under atmosphere at nearly room temperature. Moreover, it is well known that the catalysis for oxidation reaction of primary alcohol strongly dependent on the basicity of the reaction medium leading to external base required. Consequently, the acid salt (e.g., glycerate) products were formed result in the solution needs additional neutralization and acidification in order to get the free product. Therefore, the carrying out of the alcohol oxidation in base-free reaction using drastically condition (i.e., oxygen flow rate 150 mL/min) or basic support material (i.e., hydrotalcite) was demonstrated.[80, 82]

3.2 The goal of the research

1. To apply the developed green synthesis method as mention in Chapter II for preparation of hydrotalcite supported Pt NPs (Pt NPs/HT) heterogeneous catalyst.

2. To investigate the catalytic performance of an obtained Pt NPs/HT catalyst for the selective oxidation of glycerol under base free aqueous solution.

3.3 Experimental section

3.3.1 Chemicals and materials

$H_2PtCl_6 6H_2O$ (99.9%) and soluble starch were purchased from Wako Pure Chemicals (Japan). NaOH was obtained from Kanto Chemicals (Japan). Hydrotalcite (HT, Mg/Al = 5) was purchased from Tomita Pharmaceutical (Japan).

3.3.2 Preparation of hydrotalcite supported Pt NPs catalyst (Pt NPs/HT)

Pt NPs were synthesized by the chemical reduction method using soluble starch as both the reducing agent and the stabilizer as shown in Chapter II. They were supported onto HT by the sol immobilization method at several reduction times. At first, a 2.5 mM platinum salt solution was prepared from hexachloroplatinic acid. The pH of the solution was adjusted to neutral with 1 M NaOH. Separately, 5 mL fractions of the solution were individually pH adjusted with 0.05 M NaOH. A 4% w/v soluble starch solution was prepared by dissolving 4 g of soluble starch in hot water (100 mL). After cooling down, 5 mL fractions of starch solution were mixed with 0.05 M NaOH. The platinum solutions and the starch solutions were heated at 100°C for 20 min before mixing under a vigorous stir. In addition, time-dependent studies on the generation of Pt NPs were conducted after a reduction time of 3 min (1st fraction), 7 min (2nd fraction), 10 min (3rd fraction), 15 min (4th fraction), and 20 min (5th fraction) reduction time. During each of the reduction time interval, HT (0.49 g) was added to each of the mixed solution samples under a continuous vigorous stirring and refluxed at 100°C for 1 hr. The amount of HT was calculated to have a metal loading of 1 wt% (HT:Pt metal = 100:1 wt%). Finally, the solution was cooled down to room temperature, filtered and washed with de-ionized water. The filtrate was dried overnight at 100°C.

3.3.3 Characterization

Pt NPs and Pt NPs/HT were characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), inductively coupled plasma atomic emission spectroscopy (ICP-AES), and X-ray absorption fine structure (XANES).

3.3.3.1 Transmission electron microscopy (TEM)

The Pt NPs/HT was dispersed in water and dropped onto a carbon-coated copper grid. The specimen was dried overnight in a desiccator. The morphology of Pt NPs was captured by TEM (H-7100, Hitachi High-Technologies Corporation) at 100 kV accelerating voltage.

3.3.3.2 X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) patterns were obtained with a Rigaku RINT2000 X-ray diffractometer using Cu $K\alpha_1$ radiation ($\lambda = 0.154$ nm) and a power of 40 kV and 20 mA.

3.3.3.3 X-ray photoelectron spectroscopy (XPS)

The Pt NPs/HT was placed on the carbon tape. The relative binding energies of NPs were measured with an XPS instrument (Shimadzu Kratos AXIS-ULTRA DLD).

3.3.3.4 X-ray absorption fine structure (XANES)

A 200 mg of catalyst was grained and pressed to a pellet ($\phi{\sim}10$ mm) for XANES analysis. Pt L_{III}-edge spectra were recorded at beamline BL01B1 of Spring-8. The oxidation state of platinum was estimated from the Pt L_{III}-edge XANES spectra. The linear relationship in the intensities of PtO_2 and platinum foil were assigned to be 0 and 100% Pt^0. The obtained XANES spectra were analyzed using the Rigaku REX2000 software (ver.2.5.7).

3.3.3.5 Inductively coupled plasma atomic emission spectroscopy (ICP-AES)

The concentration of Pt NPs for Pt NPs/HT (10 min) catalysts was determined by ICP (Shimadzu ICPS-7000).

3.3.4 Catalytic activity test

Catalytic test of Pt NPs/HT was evaluated for glycerol oxidation in a base-free aqueous solution using molecular oxygen as an oxidant. The reaction parameters and conditions were as follows: glycerol (0.5 mmol), H_2O (2 mL), catalyst (glycerol to metal of 400–1000 mol/mol), temperature (313–353 K), time (1–7 h) under a steady O_2 flow (5–30 mL/min). All were performed in a Schlenk tube attached to a reflux condenser. After the reaction, the vessel was cooled down to room temperature, and the catalyst was separated by filtration. The filtrate was analyzed by high performance liquid chromatography (HPLC) with an 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) with a flow rate of 0.5 mL/min and a column temperature of 323 K.

3.4 Results and discussion

3.4.1 Catalyst optimization

In this work, time dependent HT supported Pt NPs catalysts, namely, Pt NPs/ HT (3 min), Pt NPs/HT (7 min), Pt NPs/HT (10 min), Pt NPs/HT (15 min), and Pt NPs/HT (20 min) were employed as catalyst in the reaction of glycerol oxidation. The morphologies of all catalysts were characterized by TEM and XANES. TEM images and particles size distribution histograms of Pt NPs/HT are shown in Figure 3.1. The size of Pt NPs increased with increasing reduction times with the average size being 0.9, 1.4, 1.9, 1.9, and 2.1 nm for 3, 7, 10, 15, and 20 min, respectively. In addition, all of them showed a narrow size distribution. The estimated oxidation state of platinum (Pt L_{III}-edge XANES spectra) is shown in (Figure 3.2). The concentration of Pt^0 increased with increasing reduction times (Table 3.1). Moreover, the increase of Pt^0 concentration reflects a corresponding increase in the Pt NPs size. From the results, it is evident that the size and Pt^0 concentration of Pt NPs depends on the reduction times. Thus within this method, we can control the size of Pt NPs by controlling the reduction time.
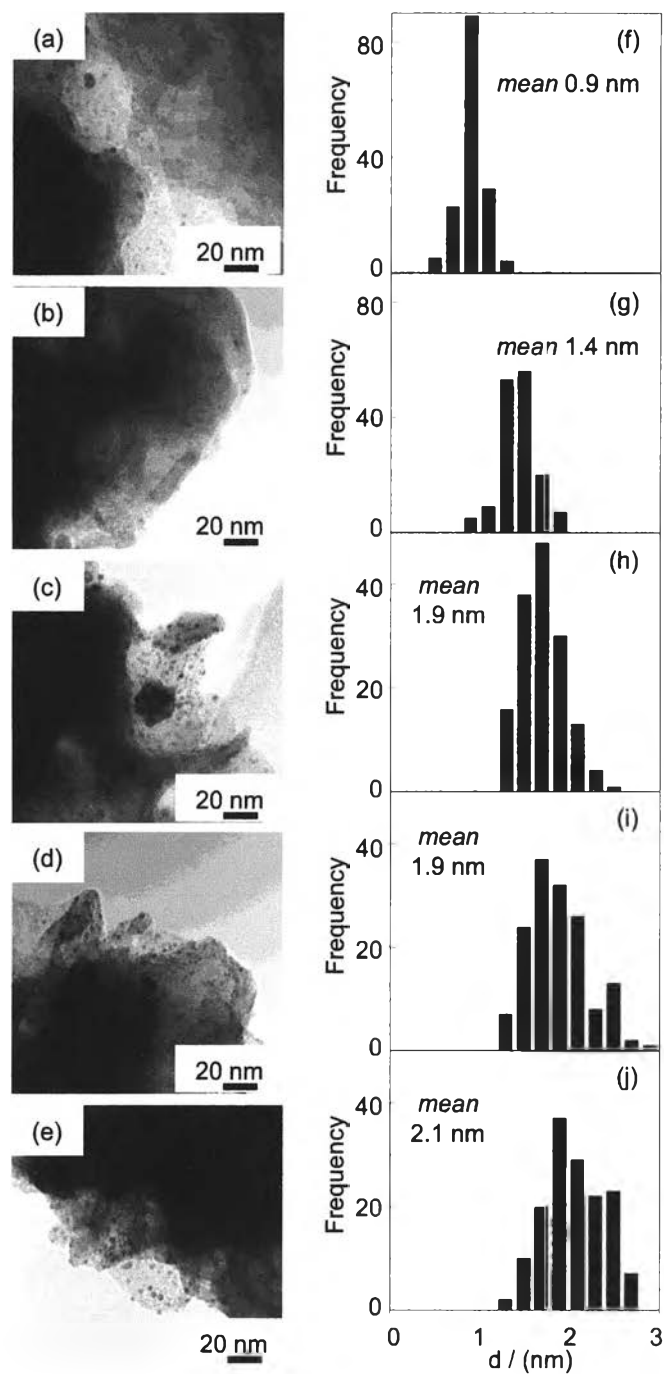
Figure 3.1 TEM images of HT supported Pt NPs at various reduction times: (a) 3 min, (b) 7 min, (c) 10 min, (d) 15 min, and (e) 20 min and (f)-(j) their particle size distribution histograms respectively.
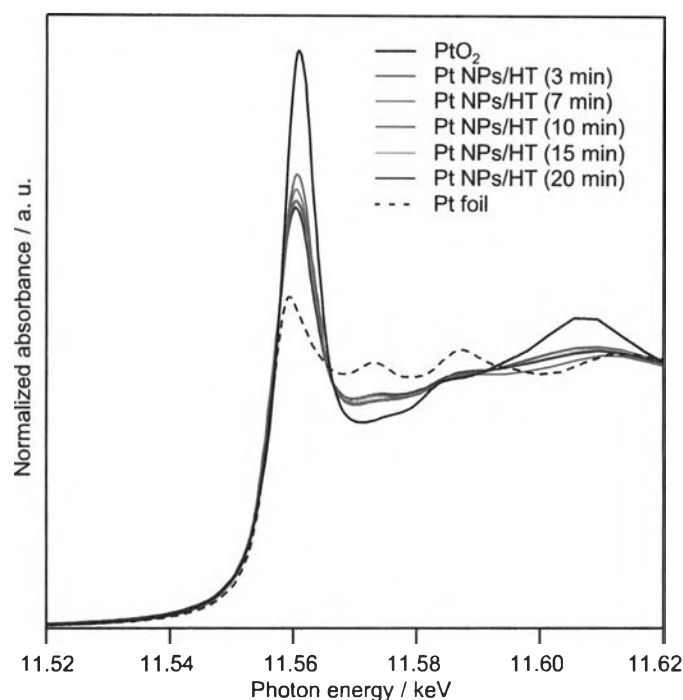
**Figure 3.2** Pt L$_{III}$-edge XANES spectra for Pt NPs/HT catalysts.

The evaluation of catalytic activity of Pt NPs/HT was performed for the selective oxidation of glycerol in a base-free solution using molecular oxygen as an oxidant under atmospheric pressure. The reaction was carried out in water at 333 K with a glycerol/metal molar ratio of 600. The results are shown in Table 3.1.

Table 3.1 Effect of initial glycerol concentration on glycerol oxidation catalyzed by Pt NPs/HT.[a]

Entry	Catalysts	Glycerol conversion (%)	Glyceric acid Yield (%)	Glyceric acid Selectivity (%)	Pt size (nm)	Pt^0 (%)
1	Pt/HT (3 min)	80	32	40	0.9	50.3
2	Pt/HT (7 min)	72	36	49	1.4	56.2
3	Pt/HT (10 min)	55	41	75	1.9	60.6
4	Pt/HT (15 min)	57	40	70	1.9	61.4
5	Pt/HT (20 min)	49	38	77	2.1	63.5

[a] Reaction conditions: glycerol (0.5 mmol), H$_2$O (5 mL), glycerol/metal = 600 (mol/mol), 1 wt% metal, under O$_2$ flow (10 mL/min), 333 K, 6 h. [b] Mg/Al = 5. [c] Reaction conditions: glycerol (0.05 mmol), H$_2$O (2 mL), glycerol/metal = 700 (mol/mol), 1 wt% metal, under O$_2$ flow (10 mL/min), 323 K, 6 h.

All of the catalysts show high catalytic activity towards glyceric acid. The possible reaction pathway of glycerol oxidation by Pt NPs/HT catalyst is shown in Scheme 3.4. The reaction was accomplished by the oxidation of glycerol molecule at the primary alcohol position to yield glyceraldehyde. Then it was further oxidized to glyceric acid (GA), tartronic acid (TA), glycolic acid (HA), and oxalic acid (OA).[82] The highest activity (80% conversion, Table 3.1, entry 1) as the glycerol oxidation was catalyzed under the molecular oxygen as an oxidant with a small size of Pt NPs. The catalytic activity decreased with increasing size of Pt NPs/HT (Table 3.1, entries 2–5). However, the selectivity to GA increased with decreasing size of Pt NPs. It indicated that the size of Pt NPs related to both of catalyst activity and selectivity for the oxidation reaction of glycerol. In order to select of the best catalyst, both of catalytic activity (glycerol conversion), selectivity to GA, and GA yield are considered. It was found that the best catalyst is Pt NPs/HT (10 min, Table 3.1, entry 3).
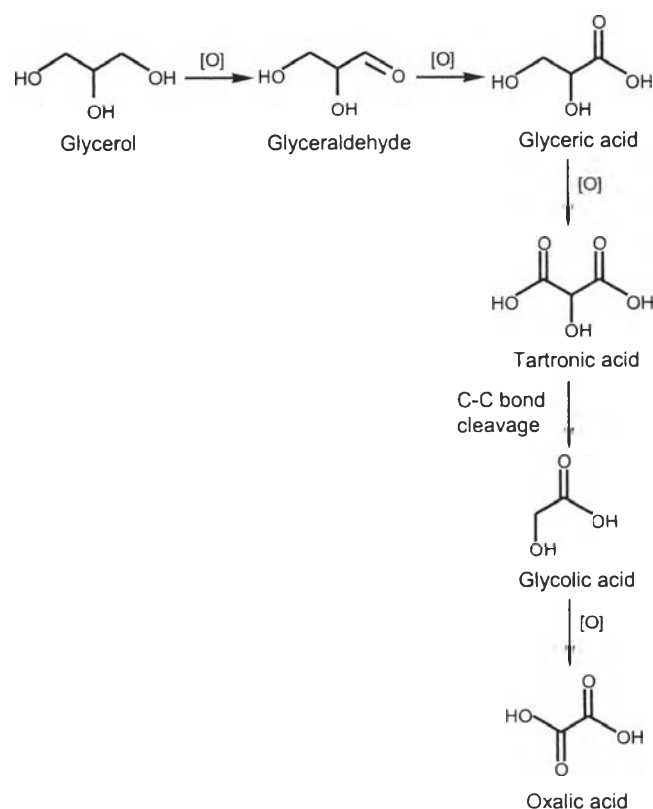
Scheme 3.4 A possible reaction pathway of glycerol oxidation catalyzed by Pt NPs/HT.

3.4.2 Catalyst Characterization

The crystal structure and oxidation state of Pt NPs (unsupported) were examined by XRD and XPS. The XRD diffraction peaks of face center cubic (fcc) crystal lattice of platinum were observed at 2θ of 39.5, 45.9, and 67.3 (Figure 3.3(A)).[82] Moreover, the XPS result in Figure 3.3(B) shows peaks at 71.8 ($Pt4f_{7/2}$) and 75.1 ($Pt4f_{5/2}$) representing the zero oxidation state of platinum (Pt^0) which confirms the formation of Pt NPs.[84] From above results, it is clear that, before immobilization on support, Pt NPs are formed as isolated particles with uniform size distribution. The morphologies of Pt NPs/HT (10 min) catalyst were characterized by TEM and XRD. The TEM image (Figure 3.4) confirmed that Pt NPs were obtained (Figure 3.4A1). Pt NPs were uniformly immobilized on the hydrotalcite surface (Figure 3.4B1). Moreover, Pt NPs size was unchanged after immobilization onto HT surface. The amount of loaded Pt of Pt NPs/HT (10 min) was estimated to be 0.9 wt%, as determined by ICP-AES.
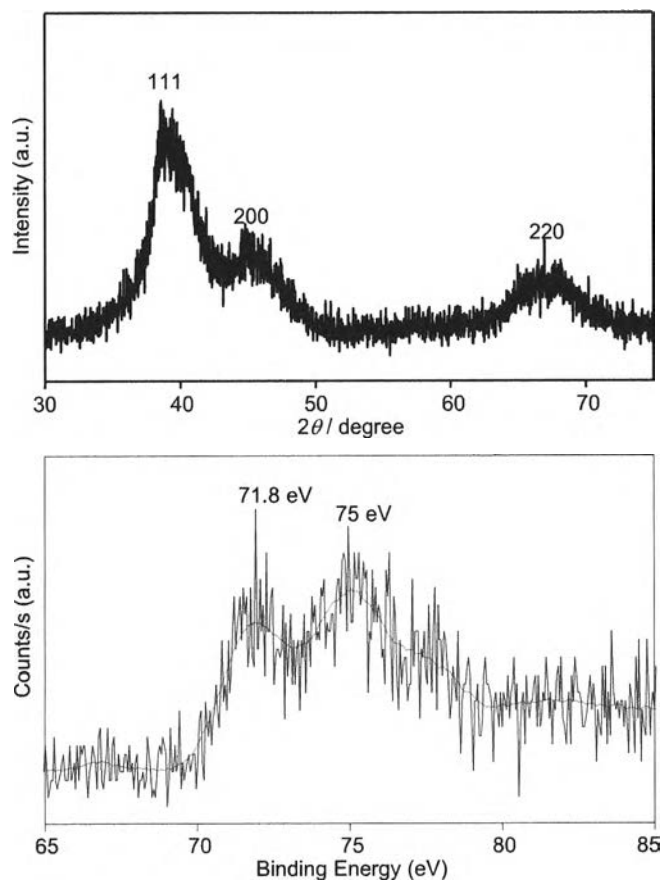

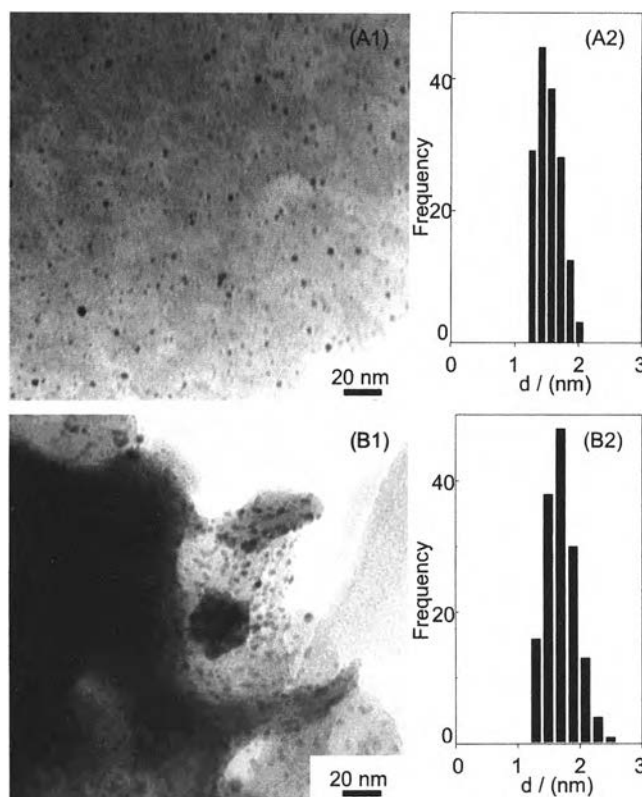**Figure 3.3** (A) XRD pattern and (B) XPS spectrum of Pt NPs.

Figure 3.4 (A1)–(B1) TEM images and (A2)–(B2) particle size distribution of Pt NPs and HT-supported Pt NPs, respectively.

3.4.3 Optimization of reaction condition

In order to optimize the glycerol oxidation to achieve high selectivity to glyceric acid, the different reaction conditions were evaluated: glycerol/metal ratio, temperature, oxygen flow rate, initial glycerol concentration.

3.4.3.1 Influence of the catalyst amount

The catalyst amount was calculated from the glycerol to metal molar ratio. It was varied in the range of 400–100 while the other reaction parameters were kept constant as follows: glycerol (0.5 mmol), H_2O (5 mL), 333 K, 6 h under a steady O_2 flow (10 mL/min). Figure 3.5 shows that the glycerol oxidation depends on the catalyst amount. Its amount in the range of 500–700 (mol/mol) shows nearly constant yield of glyceric acid, which is the highest yield point. However, the optimal desirable glycerol/metal ratio giving the highest selectivity towards glyceric acid is 700.
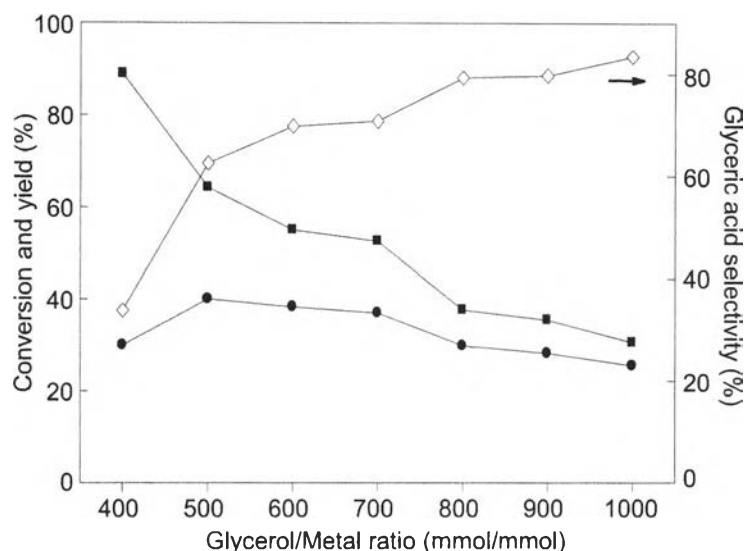
Figure 3.5 Reaction profile of glycerol oxidation catalyzed by Pt NPs/HT at various glycerol/metal ratios. Glycerol conversion (■: close square), glyceric acid yield (●: close circle), and glyceric acid selectivity (◇: open diamond).

3.4.3.2 Influence of the initial glycerol concentration

The influence of the initial glycerol concentration was evaluated by decreasing the total volume of the solution. Table 3.2 shows the increasing of glycerol conversion when initial glycerol is increased concentration from 0.1 M to 0.25 M. At all concentrations, the products produced were the same type. Moreover, the sum of product yield is nearly constant with glycerol consumed. As a result, it indicated that overoxidation occur significantly, although, the reaction was performed under high initial glycerol concentration.[82]

3.4.3.3 Influence of the oxygen flow rate

This investigation was to verify the dependency of the oxidation reaction and the catalyst selectivity on the oxygen flow rate. The reaction conditions were as follows: glycerol (0.5 mmol), H_2O (2 mL), glycerol/metal ratio of 700 mol/mol, 333 K, 6 h under a steady O_2 flow (10 mL/min). The oxygen flow rate was varied between 5 and 30 mL/min. Figure 3.6 reveals that increasing flow rate does not nearly influence on the reaction.

Table 3.2 Effect of initial glycerol concentration on glycerol oxidation catalyzed by Pt NPs/HT.[a]

Initial glycerol concentration [M]	Conversion [%] (glycerol consumed [mmol])	Yield [mmol]				Sum[i] (%)
		GA[e] (selectivity [%])	TA[f]	HA[g]	OA[h]	
0.1[b]	53 (0.26)	0.18 (71)	0.02	0.03	0.02	96
0.14[c]	64 (0.32)	0.21 (65)	0.03	0.05	0.03	>99
0.25[d]	63 (0.32)	0.21 (67)	0.03	0.06	0.02	>99

[a] Reaction conditions: glycerol (0.5 mmol), glycerol/metal = 700 (mol/mol), under O_2 flow (10 mL/min), 333 K, 6 h. [b] H_2O (5 mL). [c] H_2O (3.5mL). [d] H_2O (2 mL). [e] GA : glyceric acid. [f] TA : tartronic acid. [g] HA : glycolic acid. [h] OA : oxalic acid. [i] Sum of products (GA, TA, HA, and OA)/amount of glycerol consumed × 100.

It means that the selective oxidation reaction of glycerol is carried out at low molecular oxygen flow rate is equivalent to 10 mL/min. Moreover, it reveals that the catalyst retain stability although the reaction was performed under high oxygen flow rate. We suppose that starch stabilized Pt NPs suppress the oxygen poisoning from the platinum metal.
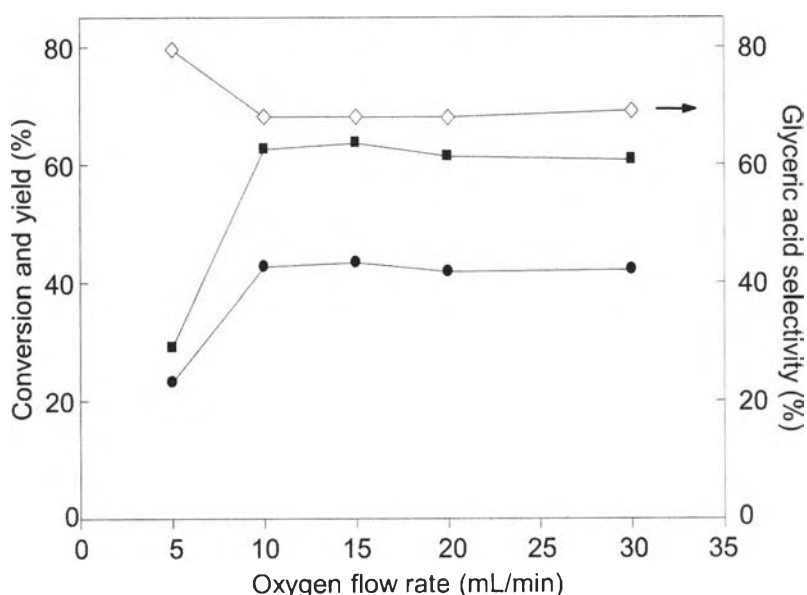

Figure 3.6 Catalytic activity of Pt NPs/HT at various oxygen flow rate. Glycerol conversion (■: close square), glyceric acid yield (●: close circle), and glyceric acid selectivity (◇: open diamond).

3.4.3.4 Influence of the reaction temperature

The influence of the reaction temperature was evaluated from 313 K (nearly room temperature) to 353 K. Table 3.3 clearly explains that the reaction temperature does not nearly influence the glycerol oxidation. However, it notifies that the catalytic activity decreases significantly as the temperature increases to 353 K. It also indicated that, under moderate temperature (353 K), the stabilizer does not obstruct the catalytic activity. It shows good catalytic performance in the oxidation reaction of glycerol. Nevertheless, we assume that the starch is more soluble (chain-extended starch) at high temperature (353 K) leading to the obstruction of the active site.[85]

Table 3.3 Effect of reaction temperature on glycerol oxidation catalyzed by PtNPs/HT.[a]

Temperature (K)	Conversion (%)	Selectivity GA (%)	GA[b] Yield (%)
313	46	78	36
323	63	68	43
333	64	67	43
343	65	66	43
353	64	63	40
[a] Reaction conditions: glycerol (0.5 mmol), H_2O (5 mL), glycerol/metal = 700 (mol/mol), under O_2 flow (10 mL/min), 6 h. [b] GA : Glyceric acid.			

3.4.4 The reaction profile under optimized reaction conditions

It was found, that the catalysis of glycerol oxidation with Pt NPs/HT (10 min) under the optimum conditions: glycerol (0.5 mmol), H_2O (2.0 mL), catalyst (700 mol/mol, 0.0139 g), 323 K, 6 h under a steady O_2 flow (10 mL/min). Result shows the glycerol conversion (63%) and selectivity (68%) to GA. Within the optimum reaction condition, the reaction time profile of glycerol oxidation catalyzed by Pt NPs/HT was evaluated as shown in Figure 3.7. At the initial stages of the reaction (1 h), a

considerably high selectivity of glyceric acid (78%) was obtained. The possible reaction pathway of glycerol oxidation by Pt NPs/HT catalyst is shown in Scheme 3.4. The reaction was accomplished by the oxidation at primary alcohol of glycerol to glyceraldehyde. Then further oxidize to glyceric acid (GA), tartronic acid (TA), glycolic acid (HA), and oxalic acid (OA). When the reaction time was increased to 7 h, the glycerol conversion increased to 60% and the selectivity toward glyceric acid gradually decreased to 71% with 42% GA yield. It clearly indicated that Pt NPs/HT synthesized by our method showed selectivity and high oxidation activity for the glycerol conversion to glyceric acid under such moderate reaction conditions, including a base-free aqueous solution and normal atmospheric molecular oxygen pressure.
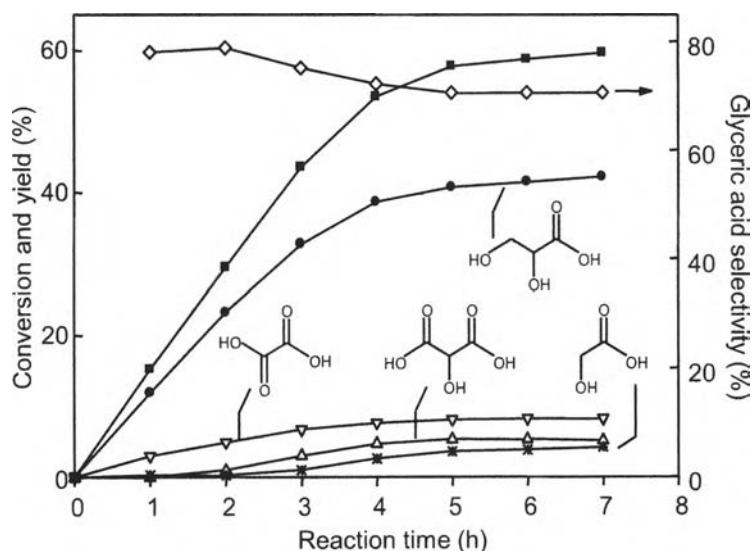

Figure 3.7 Reaction time profile of glycerol oxidation catalyzed by Pt NPs/HT. Glycerol conversion (■: close square), glyceric acid yield (●: close circle), tartronic acid yield (△: open up triangle), glycolic acid yield (▽: open down triangle), oxalic acid yield (∗: star), and glyceric acid selectivity (◇: open diamond).

3.4.5 Leaching test

The complete separation of catalyst after catalysis is essential to investigate. Therefore, the leaching test of Pt NPs/HT catalyst in glycerol oxidation was carried out under the optimum conditions: glycerol (0.5 mmol), H_2O (2 mL), catalyst (700 mol/mol), 323K under a steady O_2 flow (10 mL/min). Reaction time profile for leaching test of glycerol oxidation catalyst by Pt NPs/HT is shown in Figure 3.8. After

2 h, the catalyst was separated by hot filtration. The clear filtrate solution (absence of catalyst) was continually carried out. The reaction conversion did not significantly change although prolonged reaction. It means that no catalyst left in the filtrate solution. In other words, the catalyst was properly removed by simple filtration.

3.4.6 Recyclability

The above results revealed that our green synthesis method had an effect on the synthesis of Pt NPs/HT catalyst which showed good activity for selective oxidation of glycerol under moderate condition. However, the evaluation of the catalytic activity of catalyst was performed not only for the pure catalyst but also for the recycled catalyst. Therefore, the catalyst recycling test was carried out under the optimum conditions: glycerol (0.5 mmol), H_2O (2 mL), catalyst (700 mol/mol), 323 K under a steady O_2 flow (10 mL/min).
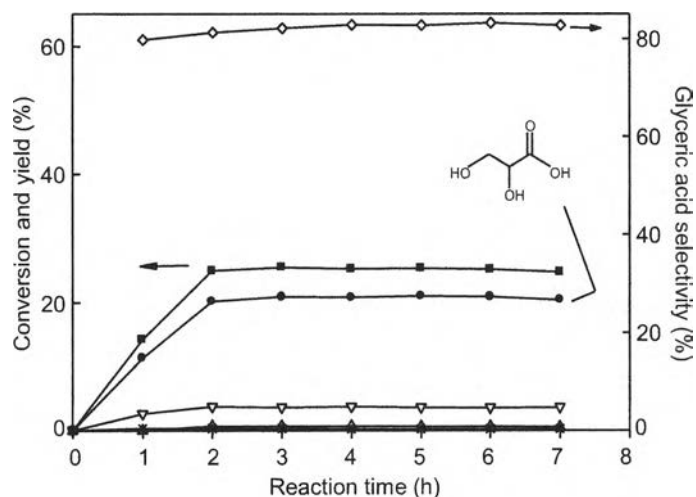

Figure 3.8 Reaction time profiles for leaching test of glycerol oxidation catalyzed by Pt NPs/HT. Glycerol conversion (■: close square), glyceric acid yield (●: close circle), tartronic acid yield (△: open up triangle), glycolic acid yield (▽: open down triangle), oxalic acid yield (✳: star), and glyceric acid selectivity (◇: open diamond).

The catalyst was totally 3 times recycled after catalysis for the oxidation reaction of glycerol. The result in term of glycerol conversion and GA yield is shown in Figure 3.9. It was found that, after three times of recycling there was slightly decrease in glycerol conversion (i.e., 63, 59, and 56% for 1st, 2nd, and 3rd used,

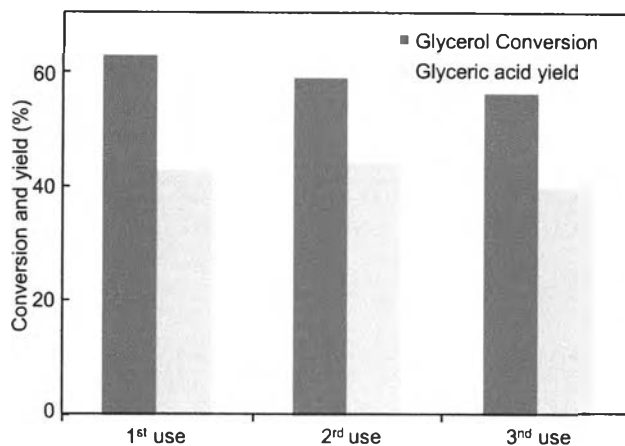respectively) by unchanging of selectivity to GA (e.g., 68 and 71% selectivity for 1st and 3rd used, respectively).
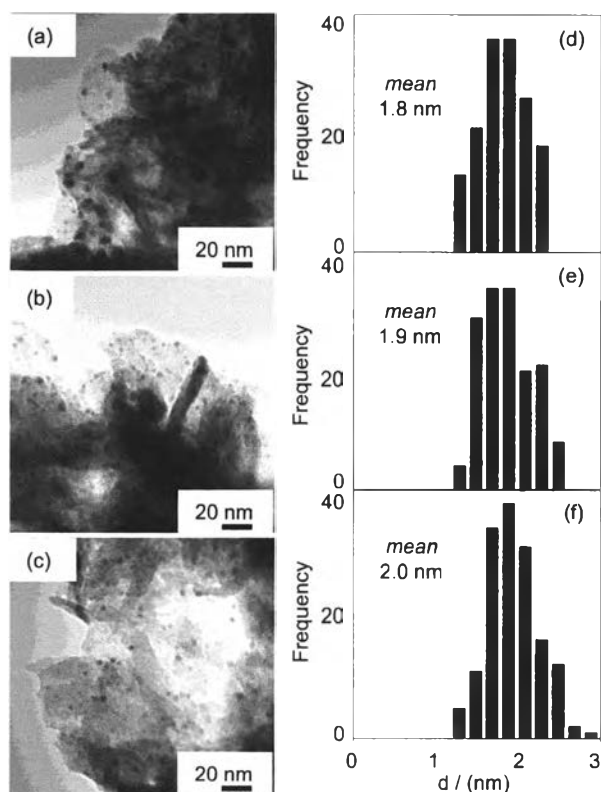

Figure 3.9 Recycling of Pt NPs/HT catalyst.

Figure 3.10 TEM images of recycled Pt NPs/HT catalyst: (a) Pt NPs/HT after 1st used, (b) Pt NPs/HT after 2nd used, (c) Pt NPs/HT after 3rd used. Particles size distribution histograms of Pt/HT catalyst: (d) after 1st used, (e) Pt NPs/HT after 2nd used, (f) Pt NPs/HT after 3rd used.

The morphologies of recycled catalysts were investigated by XRD and TEM as shown in Figure 3.10 and 3.11. The XRD patterns of recycled catalyst exhibited identical patterns as that of the initial catalyst. Additionally, the TEM images and histograms showing unchanged of recycle catalyst in term of particles size and particle size distribution.
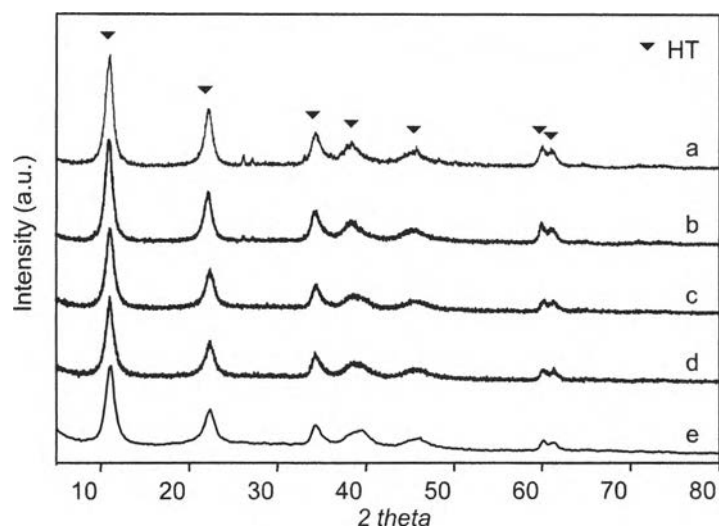

Figure 3.11 XRD patterns of HT supported Pt NPs catalyst before and after reused: (a) HT, (b) initial Pt NPs/HT, (c) Pt NPs/HT after 1st used, (d) Pt NPs/HT after 2nd used, (e) Pt NPs/HT after 3rd used.

3.5 Conclusion

We have successfully synthesized Pt NPs/HT heterogeneous catalyst using a "Green" synthesis approach. The reaction was performed under mild condition. Using soluble starch under alkaline treatment simultaneously employs as reducing and stabilizing agent. The catalyst shows high oxidation activity for the glycerol conversion (63%) to glyceric acid (68% selectivity) under moderate reaction conditions, including a base-free aqueous solution and normal atmospheric molecular oxygen pressure. After reaction, the catalyst easily removes by hot filtration and no catalyst left in the solution. Moreover, the catalyst remained highly activity although it was recycled three times.