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Recovery of spent alumina-supported platinum catalyst and reduction of platinum oxide via plasma sintering technique

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A B S T R A C T

A thermal plasma process for the recovery of the spent alumina-supported platinum catalyst (Pt/Al_2O_3) and reduction of platinum oxide (PtO_2) was developed. The spent Pt/Al_2O_3 and PtO_2 catalysts were sintered at >1500 K under plasma condition and were reformed or reduced to metallic platinum, which were proven by XRD and EDX. Results from SEM and BET specific surface area analyses indicated that the organic tar with the intermolecular and intramolecular water on the surface of the spent catalysts was decomposed and converted to syngas (CO, CO_2, and H_2), which might be the reducing agents in the process. Time-programmed hydrogenation study of urocanic acid was carried out to compare the catalytic efficacy of recovery and fresh Pt/Al_2O_3 catalysts. The experimental result indicated that the plasma sintered Pt/Al_2O_3 catalyst showed the similar catalytic efficacy with respect to the fresh catalyst.

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1. Introduction

Platinum metals are in extensive use for catalysis reaction, electronic devices, space material, *etc.* (Mhaske and Dhadke, 2001). Recently research of platinum metal has focused on (i) the auto exhaust and electronic catalysts (Guerrero et al., 2009; Mhaske and Dhadke, 2001; Starz et al., 1999), (ii) the environmental materials (Barefoot, 1999; Ek et al., 2004; Jarvis et al., 2001; Moldovan et al., 2003; Mzereini et al., 1997; Turner et al., 2006) and (iii) their biological impacts (Cosden et al., 2003; de Vargas et al., 2004; Moldovan et al., 2001; Ravindra et al., 2004; Zimmermann et al., 2003). Moreover, alumina-supported platinum (Pt/Al_2O_3) and platinum oxide (PtO_2) catalyst (Kotzian et al., 2007) are the important catalysts in a variety of organic reactions, including Baeyer-Villiger oxidation (Greggio et al., 2008), coupling reaction (Akba et al., 2009), cyclization (Gerdin et al., 2008; Yoshida et al., 2008), dehydrogenation (He et al., 2008; Morán et al., 2007), isomerization (Wang et al., 2009a,b), and hydrogenation (Smith and March, 2007).

Due to the high cost and increasing demand of manufacturing industry, many processes have been developed for the recovery of platinum metal (Barakat and Mahmoud, 2004; Chassary et al., 2005; de Sá Pinheiro et al., 2004; Galisteo et al., 2005; Jafarifar et al., 2005; Okhlopkova, 2009; Ravindra et al., 2004). The reforming strategies of the spent platinum materials included the adsorption by conventional ion exchange and chelating resins (Chanda and Rempel, 1990), the solvent extraction (Inoue et al., 1990), a more benign and microwave-accelerated leaching methods (Yong et al., 2003), and pyro- or hydrometallurgical processes (Benson et al., 1999). However, the methods are the pollution-generating and energy-consuming process.

Sintering significantly contributes to the deactivation of the spent catalysts. Sintering is a complex process, which is controlled by many factors such as sintering temperature, catalyst composition and structure, and support morphology. The most important parameters are the sintering temperature and atmosphere over the catalyst. Increase of the reaction temperature and the presence of water can be able to accelerate the sintering process (Sehested et al., 2001). Plasma sintering gasification has been widely used in a number of fields such as ceramics and the metallurgy industry because of the characteristics of high temperature (usually up to 5000 °C) with high densities of ions and electrons (Pfender, 1999; Silva et al., 1997; Tanahashi et al., 2001; Wehrer et al., 2004). These diverse active species with the high energy radiation capability of

the plasma can help to enhance the chemical reactions substantially and to make some reactions possible. Owing to the multiple hydrotreating reactions, the surface of metallic oxide-supported catalyst was completely covered with organic tar and the catalysts lost its catalytic efficiency. In the reforming reaction, the plasma gasification technique has successfully converted organic tar to syngas (CO and H_2) as a reducing agent to recover and reduce the spent nickel oxide (NiO/SiO_2) and cobalt–molybdenum oxide (Co_3O_4–MoO_2/Al_2O_3) catalysts to metallic nickel and cobalt–molybdenum (Wong et al., 2006, 2008) respectively. Herein, we reported the utilization of plasma and gasification technique to recover the spent platinum catalyst and reduce platinum oxide (PtO_2) to metallic platinum by means of the syngas (CO and H_2).

2. Experimental

2.1. Sample preparation

The spent and fresh platinum-based aluminum oxide catalyst (Pt/Al_2O_3, ~0.8 wt% in Al_2O_3) was obtained from Chinese Petroleum Co. Platinum (IV) oxide hydrate ($PtO_2 \cdot xH_2O$, PtO_2 purity 80–82%) was purchased from Strem Chemical Co. The spent alumina-supported platinum (Pt/Al_2O_3) and platinum oxide (PtO_2) catalysts were ground in an agate mortar to the particle size of 300–500 mesh with a mean particle size of 400 mesh to serve as the model sample. The sample was placed in a graphite crucible with a diameter of 5.0 cm and a thickness of 1.0 cm. The outside wall of the graphite crucible was coated with refractory material and treated in an inductively coupled thermal plasma torch in the plasma furnace.

2.2. Sintering of the sample by plasma

The experimental plasma apparatus consisted of thermal coupler, plasma furnace and plasma-torch assembly. The temperature sensors were located on the plasma furnace close to the plasma-torch junction. The sintering of the sample by plasma was performed on a plasma furnace with an effective volume of 1.0 L and equipped with an A.C. transferred-type tungsten/copper (W/Cu) alloy torch. The masses of the bricks of the furnace consisted of 30 wt% graphite and iron, ranging 1.0–2.5 kg and 0.25–1.0 kg, respectively. A high-voltage A.C. power supply for the plasma was used, with a maximum voltage of 10 kV, a frequency of 10–20 kHz, and a power of 10–15 kW. The torch current was 110–120 amps and torch voltage was 210–220 V. A thermocouple, purchased from Peat International Co., was equipped in the plasma furnace (vacuum side) close to the torch for monitoring temperature. Constant flow of N_2 was used as the central plasma gas (flow rate 7 L min^{-1}). The power of the plasma was carefully adjusted to maintain the oven temperature at >1500 K and the sample was heated in the graphite crucible for 2–3 h. After the sintering process was completed, the furnace was cooled to ambient temperature and the sample was separated from the furnace and weighted.

2.3. Sintering of the sample in high temperature oven without plasma

The comparable experiment was carried out by sintering the sample in a muffle furnace (model MF-40, supplied by Channel Co.). The temperature was raised to 1200–1300 °C at a heating rate of 10 °C/min under the atmosphere and the sample was held at >1200 °C for 2–3 h, then cooled to ambient temperature. The residual sample was separated from the furnace and weighted.

2.4. Sample analysis

Thermochemical analysis was performed on a PerkinElemer Pyris Diamond differential thermogravimetric analyzer with a heating rate of 10 °C/min in N_2. X-ray diffraction (XRD) spectra were measured on a Bruker D8A Series XRD spectrometer. EDX and scanning electron microscopy (SEM) spectra were measured on a Hitachi S-3000N spectrophotometer. BET (Brunauer–Emmett–Teller, Beckman Coulter SA3100) isotherm obtained by nitrogen adsorption at 77 K was used to determine the specific surface area of the fresh and sintering alumina-supported platinum catalysts (Pt/Al_2O_3).

2.5. Gas chromatography

Gas samples were collected by a gas sampling port and then injected into Hewlett Packard GC 6850A series equipped with thermal couple detector for characterization. The analyses of H_2, N_2, CO, and CH_4 were conducted at 50 °C with a 2 m column packed with granular 5A molecular sieve and argon (99.99 vol%) as the carrier gas. The analyses of CO_2 were conducted at 40 °C with a 2 m column packed with GDX-104 molecular sieve and hydrogen (99.99 vol%) as the carrier gas. The gas standards for comparison were purchased from San Fu Chemical Co.

2.6. Time-programmed hydrogenation

Time-programmed hydrogenation experiments were performed to determine the catalytic activity of the reformed platinum catalyst from thermal plasma technique. A solution of urocanic acid (**1**, 1.03 g, 7.49 mmol) containing 20% (w/w) fresh or reformed platinum catalysts (Pt/Al_2O_3, 206 mg, based on urocanic acid **1**) in acetic acid (40 mL) was hydrogenated in a Parr apparatus at room temperature for 12 h. During the time-programmed reduction, the reaction mixture was sampled, filtered through Celite bed, and concentrated under reduced pressure to remove the acetic acid. The ratio of conversion product 3-(imidazol-4-yl)propionic acid (**2**)/urocanic acid (**1**) was identified by ^{1}H NMR spectroscopy technique for the hydrogenation reactivity.

Urocanic acid (**1**): ^{1}H NMR (CDCl$_3$, 300 MHz) 6.30 (d, 1H, J = 15.6), 7.38 (d, 1H, J = 15.6), 7.41 (s, 1H,), 7.75 (s, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 116.35, 123.21, 134.46, 136.32, 139.56, 169.84.

3-(Imidazol-4-yl)propionic acid (**2**): mp 206–208 °C; ^{1}H NMR (D$_2$O, 300 MHz) δ 2.35 (t, 2H, J = 9.0 Hz, –CH$_2$), 2.75 (t, 2H, J = 9.0 Hz, –CH$_2$), 6.99 (s, 1H), 8.33 (s, 1H); ^{13}C NMR (D$_2$O, 75 MHz) δ 20.64, 35.54, 114.89, 132.45, 133.12, 180.54; IR (neat) 3139 (b), 1572 (s, C=O), 1346 (m), 1253 (m), 1073 (m), 855 (m), 733 (m) cm^{-1}; MS m/z (relative intensity) 141 (M$^+$, 20), 139 (11), 138 (29), 137 (52), 136 (54), 120 (9), 107 (12), 89 (9), 77 (8), 63 (3), 51 (3); Anal. Calcd for C$_6$H$_8$N$_2$O$_2$: C, 51.42; H, 5.75; N, 19.99. Found: C, 51.39; H, 5.74; N, 19.96.

3. Result and discussion

3.1. Thermogravimetric analysis

The untreated spent catalyst (975 mg) was dried at 150 °C for 24 h. The weight loss of the spent catalyst was 12.3 mg and water content was ~1.3%. The spent catalyst samples before/after drying were then individually identified by thermogravimetric analysis (TGA). The TGA results (Figs. 1 and 2) indicated the onset of weight loss at 30 °C and an acceleration of weight loss at 1000 °C. No significant change of weight was observed at the temperature >1250 °C. From TGA results, the reasonable content of water and organic materials including tar and water in the untreated spent catalyst was considered as ~1.5% and 8.7% (Fig. 1), respectively.

When untreated sample (10.7 g) was sintered in high temperature oven at >1200 °C under atmospheric pressure for 2–3 h, the weight loss was 916 mg (8.6%). For the study of spent alumina-supported platinum (Pt/Al_2O_3) upon sintered by plasma, model
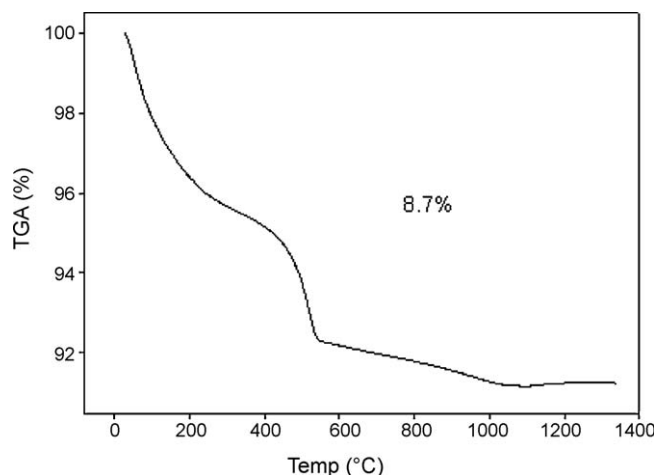
Fig. 1. TGA data of the weight loss of the untreated spent platinum catalyst (10 °C/min).
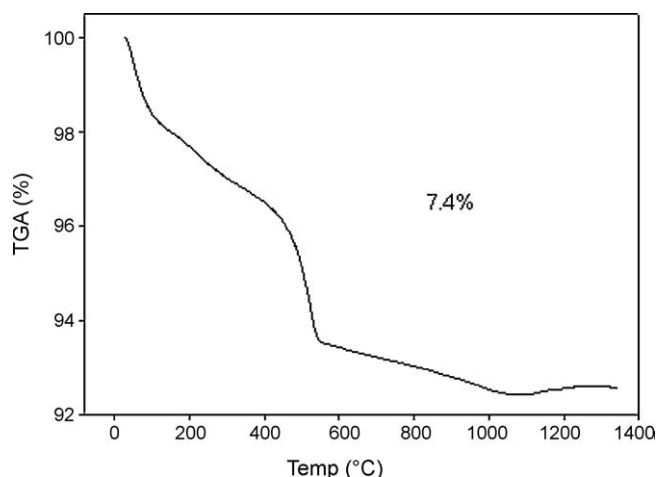

Fig. 2. TGA data of the weight loss of the dried spent platinum catalyst (10 °C/min).

Fig. 3. TGA data of the weight loss of the platinum (IV) oxide hydrate (10 °C/min).

Table 1
The weight loss of platinum oxide catalyst after sintered in the different conditions.

The heating condition	TGA study	Treating in high temperature oven	Sintering under thermal plasma
Weight (before heating, mg)	7.07	312	256
Weight (after heating, mg)	6.16	271	189
Weight loss (%)	12.9	13.3	26.2

3.2. Characterization of the sintered products by XRD

For identification of the products formed without the plasma, we performed X-ray power diffraction (XRD) technique for the analysis. The XRD spectrum of spent catalyst (line 1), heating sample in the high temperature oven (line 2), and sintering sample under thermal plasma (line 3), showed approximately identical peaks (see Fig. 4), which possessed the main reflection peak characterized as Al_2O_3 and Pt (2θ). The spent platinum samples after sintering both showed the characteristic peaks at 20–100° (2θ), which was consistent with the reported data of Al_2O_3 and Pt. Results of XRD with Al_2O_3 and Pt characteristic peaks are summarized in Table 1. The XRD patterns for the platinum catalyst show five significant variable reflection peaks at 39.98°, 46.67°, 68.15°, 81.56° and 86.30° (2θ, Fig. 4) and the index to {1 1 1}, {2 0 0}, {2 2 0}, {3 1 1}, and {2 2 2} planes (Liu et al., 2008) of the Pt face-centered cubic (fcc) crystal structure which was consistent with the reported data (see Table 2, Brandão et al., 2008; Liu et al.,

sample (10.2 g) was put in the graphite crucible and sintered in N_2 atmosphere under plasma condition at >1500 K for 2–3 h. The weight of the residue was found to be 9.3 g and the weight loss was 8.8%. The weight loss of the untreated sample in high temperature oven at atmospheric pressure and sintered in N_2 atmosphere under plasma condition is consistent with the result of TGA (8.7%).

The TGA data for platinum (IV) oxide hydrate ($PtO_2 \cdot xH_2O$, purity Pt 80–82%) indicated the onset of weight loss at 30 °C and an acceleration of weight loss at 600 °C (see Fig. 3). No significant change of weight was observed at 800 °C. According to the resulting data, the reasonable intramolecular and intermolecular water content was ~12.9%.

When platinum (IV) oxide hydrate (312 mg) was heated at >1200 °C in a high temperature oven under atmospheric pressure for 2–3 h, the weight loss was 41 mg (13.3%). The weight loss of platinum (IV) oxide hydrate sample in high temperature oven at atmospheric pressure is consistent with the result of TGA (12.9%, see Table 1, Punnoose et al., 2001). For the further plasma sintering study of platinum (IV) oxide hydrate, model sample (256 mg) was placed in the graphite crucible and sintered in N_2 atmosphere at >1500 K for 2–3 h. The weight of the residue was found to be 189 mg and the weight loss was 26.2%. Compared with the weight loss because of heating the sample without plasma, additional weight loss (~13%, see Table 1) was observed. We regarded this difference as the reduction of platinum oxide catalyst to metallic platinum with a loss of oxygen atom.
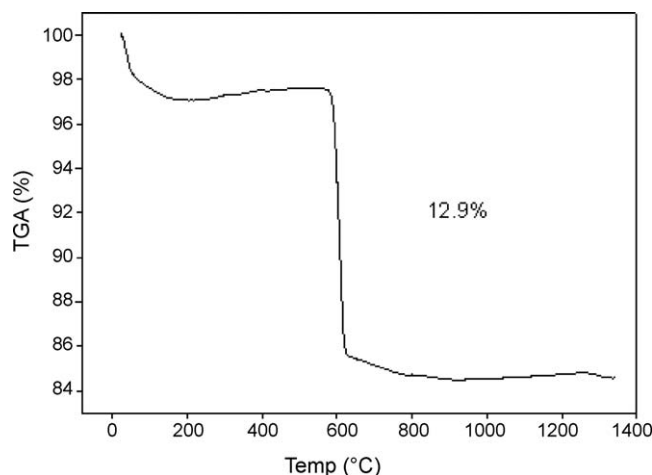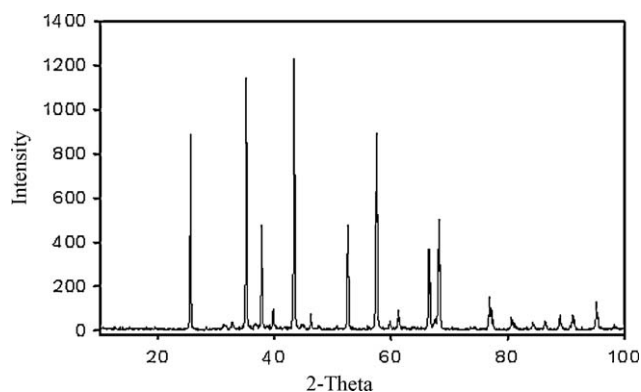

Fig. 4. X-ray diffraction patterns of the spent platinum catalyst in different heating conditions.

Table 2
XRD peaks for the spent platinum catalyst (Pt/Al$_2$O$_3$) and platinum oxide (PtO$_2$, Kuribayashi et al., 2004).

Metal or Metal Oxide	2θ	[h k l] or Structure
Pt	39.98	1 1 1 (fcc)
	46.67	2 0 0 (fcc)
	68.15	2 2 0 (fcc)
	81.56	3 1 1 (fcc)
	86.30	2 2 2 (fcc)
α-Al$_2$O$_3$	25.46	0 1 2
	35.27	1 0 4
	37.82	1 1 0
	43.26	1 1 3
	50.36	0 2 4
	57.42	1 1 6
	61.31	2 1 1
	65.75	2 1 4
	68.37	3 0 0
	76.73	0 1 0
	77.09	1 1 9
PtO$_2$	33.33	1 1 0
	55.93	1 2 1

Fig. 6. Scanning electron micrograph taken from the surface of the spent alumina-supported Pt catalyst (scale in 100 μm, magnification ×500).

2008; Wang *et al.*, 2009a,b). Based on the X-ray power diffraction (XRD) identified result, the spinel platinum was provided and formed in the presence of high temperature plasma sintering procedure for long time.

When platinum (IV) oxide hydrate was sintered under the thermal plasma condition for 2–3 h and identified by X-ray power diffraction (XRD) technique, the resulting XRD data showed the corresponding peak positions at 39.98°, 46.67°, 68.15°, 81.56° and 86.30° (2θ, Fig. 5), which was consistent with the reported metallic Pt data (see Table 2). The XRD data indicated that PtO$_2$ was reduced to metallic Pt under thermal plasma condition. We considered the reduction of PtO$_2$ to metallic Pt which did not take place upon sintering without plasma.

3.3. Quantitative analysis

From scanning electron micrograph of the untreated spent alumina-supported platinum catalyst (Pt) as shown in Fig. 6, we found its surface was completely covered with organic tar. After it was sintered at >1200 °C in the high temperature oven under atmospheric pressure for 2–3 h, the SEM results indicated that most of the small particles of organic tar were vaporized. However, some big particles were still observed on the surface of the spent catalyst (see Fig. 7). When the sintering process was carried out in A.C. plasma conditions under nitrogen atmosphere for 2–3 h, alumina-supporting material and metallic cobalt–molybdenum
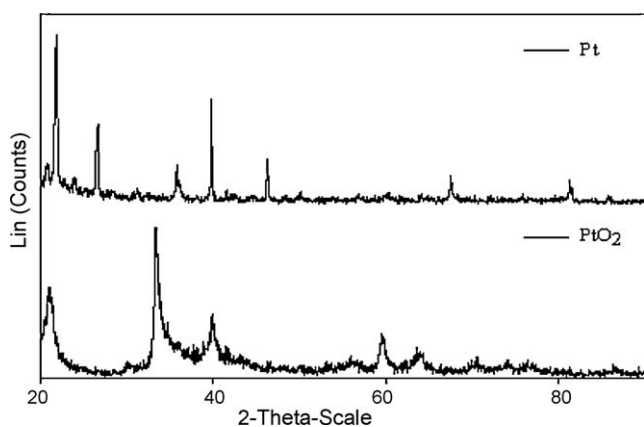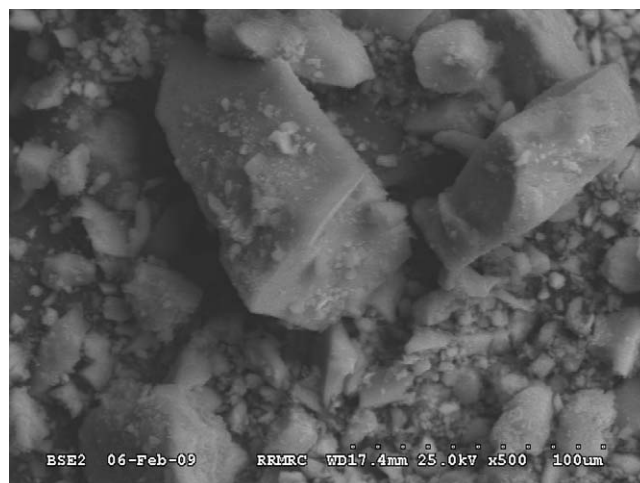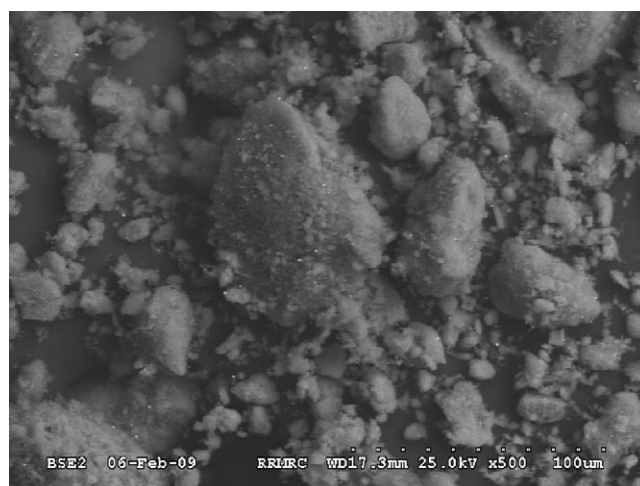

Fig. 7. Scanning electron micrographs taken from the surface of the sintered alumina-supported Pt sample in high temperature oven (scale in 100 μm, magnification ×500).
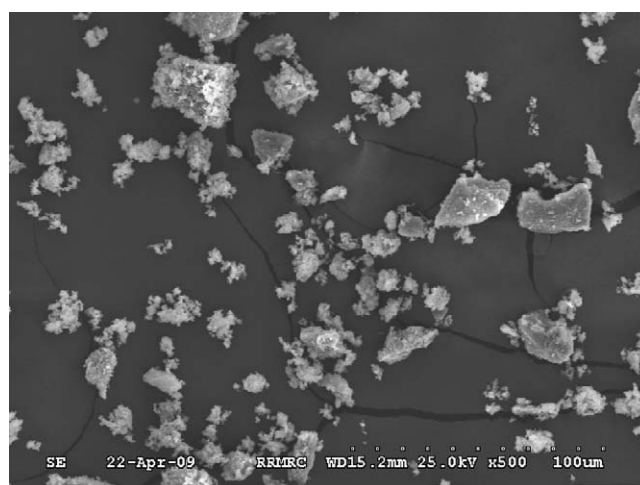

Fig. 5. X-ray diffraction patterns of platinum oxide (PtO$_2$) and the reduction sample (Pt) by sintering under thermal plasma condition.

Fig. 8. Scanning electron micrograph taken from the surface of the sintered alumina-supported Pt sample in N$_2$ medium under plasma condition (scale in 100 μm, magnification ×500).

Fig. 9. Scanning electron micrograph taken from the surface of the sintered alumina-supported Pt sample in N_2 medium under plasma condition (scale in 10 μm, magnification ×500).
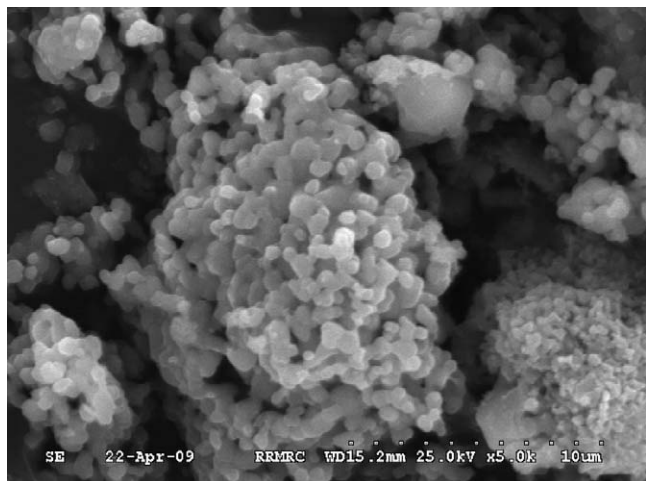
Table 3
Chemical composition of the spent catalyst and the sintered sample by EDX.

Element	Weight (%)		
	The spent catalyst	The sintered product in high temperature oven	The sintered product in N_2 medium under plasma condition
O	61.57	58.11	58.18
Al	35.29	39.32	38.74
Cl	2.26	–	–
Pt	0.89	2.57	3.08
Total	100	100	100

particles were clearly observed (see Figs. 8). The spent alumina-supported platinum catalyst (Pt) was believed to be significantly reformed and recovered under thermal plasma condition.

The EDX results of spent alumina-supported platinum catalyst (Pt) and the sintered samples with or without plasma were identified, and their quantitative analyses are summarized in Table 3 and Figs. 10–12. In the samples after sintering with or without plasma, most organic tar was vanished. For the samples treated under plasma conditions, its platinum content significantly increased from 0.89% to 3.08% (wt%). However, the platinum content of the sintered samples in the high temperature oven only increased from 0.89% to 2.57% (wt%). As a result, the spent platinum catalyst under plasma treatment can be significantly purified and the organic tar was removed to reform the metallic platinum.
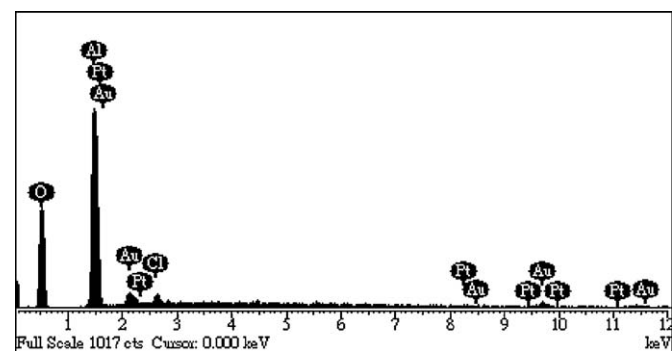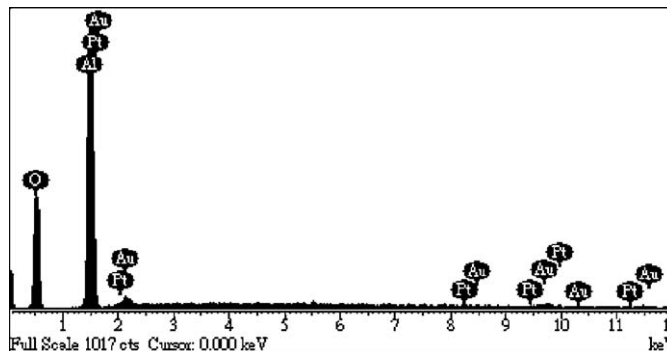

Fig. 10. EDX spectra of the spent Pt catalyst.

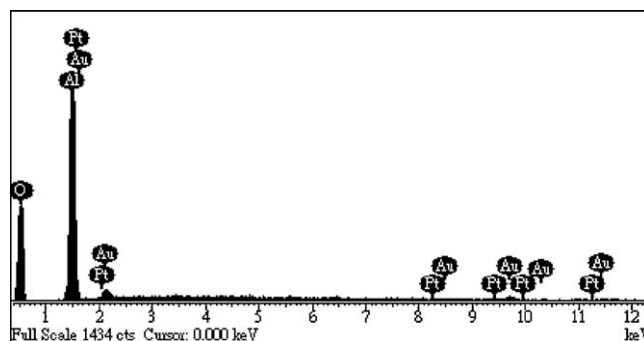**Fig. 11.** EDX spectra of the sintered Pt sample in the high temperature oven.

Fig. 12. EDX spectra of the sintered Pt sample in N_2 medium under plasma condition.

Scanning electron micrograph of the fresh platinum oxide (PtO_2) catalyst is shown in Fig. 13. When the sintering process was carried out in A.C. plasma conditions under nitrogen atmosphere for 2–3 h, metallic platinum skeleton was clearly observed (see Fig. 14).

The EDX results of fresh platinum (IV) oxide catalyst and the sintered sample with plasma were identified, and their quantitative analyses are described in Table 4. For the samples treated under plasma conditions, their oxygen content significantly decreased from 13.60% to 1.03% (wt%, see Figs. 15 and 16). As a result, the platinum oxide (PtO_2) catalyst was reduced to metallic platinum by plasma treatment.
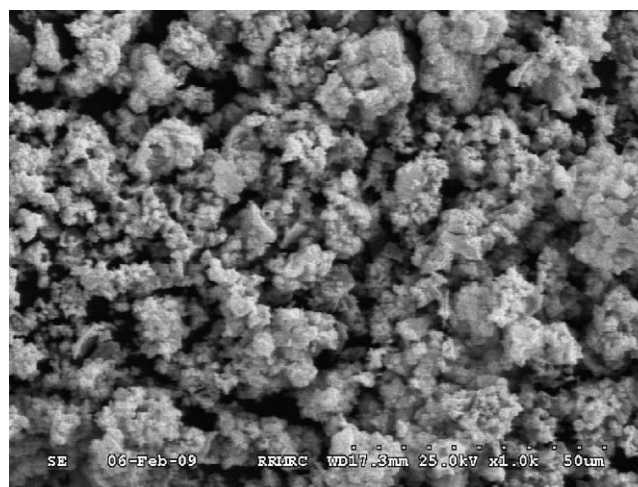

Fig. 13. Scanning electron micrograph taken from the surface of the fresh PtO_2 catalyst (scale in 50 μm, magnification ×500).
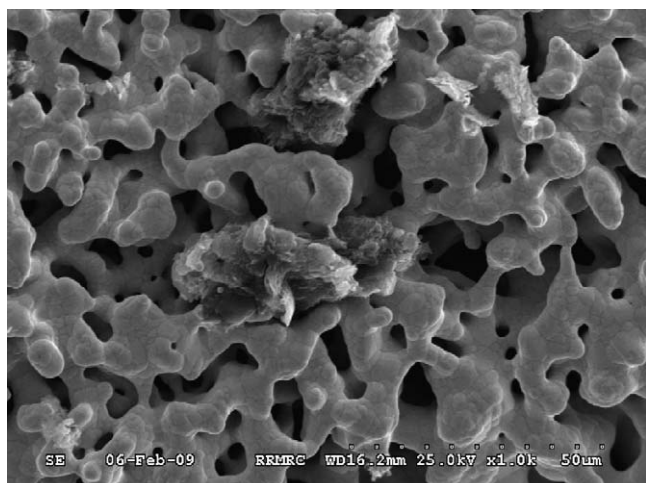
Fig. 14. Scanning electron micrograph taken from the surface of the sintered PtO_2 sample in N_2 medium under plasma condition (scale in 50 μm, magnification ×500).

Table 4
Chemical composition of the platinum oxide (PtO_2) catalyst and the sintered sample by XRD.

Element	Weight (%)	
	The fresh PtO_2 catalyst	The sintered product in N_2 medium under plasma condition
O	13.60	1.03
Pt	86.40	98.97
Total	100	100

Fig. 15. EDX spectra of the fresh PtO_2 catalyst.
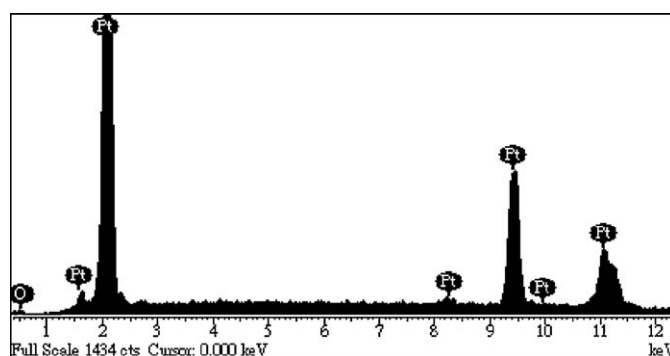
Fig. 16. EDX spectra of the sintered PtO_2 catalyst sample in N_2 medium under plasma condition.

3.4. BET surface area of alumina-supported platinum catalyst

To realize surface area change from the spent to reforming samples, we used BET surface area method (Guemini and Rezgui, 2008) to measure their specific surface areas. The results showed that the sample treated under thermal plasma condition provided the minimum BET surface area (see Table 5 and Fig. 17). The untreated spent platinum sample, however, provided the higher BET surface area for that it was completely covered with organic tar. The phenomenon was consistent with the observations from scanning electron micrograph (see Figs. 6–9).

3.5. Proposed mechanism for gasification and reduction of platinum oxide (PtO_2) catalyst

To realize the mechanism of the reduction process for the platinum oxide (PtO_2) catalyst under plasma conditions, the gases produced were analyzed by GC and peaks in the chromatogram were compared with the standards with and without spike. Except for the N_2 gas from the furnace, two additional peaks were found and assigned as H_2 and H_2O. Syngas (H_2) was found in sintering
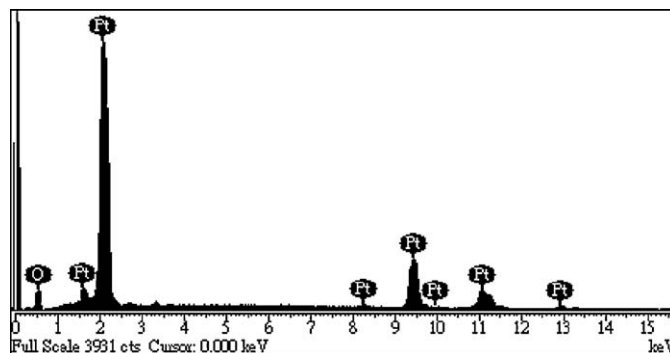
process, which might serve as the reducing agent for the reduction of platinum oxide (PtO_2) to metallic Pt.

The major component of carrier gas N_2 was found to produce stable, excited and radical intermediate (N atoms, N radical, and N_2^+ ion) species in the plasma (He et al., 2004). These species would react with intramolecular or intermolecular H_2O of platinum oxide to produce syngas in radical or atomic type reactions. Because the plasma gasification is performed without oxygen, we considered that the pyrolysis took place rather than combustion. Oxygen was decomposed to form O atoms, OH radical, and H_2O in pyrolysis process. Accordingly, we proposed a mechanism of the process into two-stage reactions as shown in Scheme 1. At the first stage, nitrogen gas was electrified to form active species such as N_2^+ and N intermediates, and water was dissociated into OH radicals and H radicals upon A.C. plasma (from (1) to (3)). The reaction of the active species might take place and result in the formation of new active intermediates such as NH and O atoms ((4) and (5)). The interaction of the active species from the first two stages was displayed in the second stage, which contained the formation of H_2 and H_2O in parallel- or chain-type reactions (from (6) to (7)). The net reaction of the second stages was the formation of syngas which contained H atom and H_2. The platinum oxide catalyst was thus reduced to metallic platinum (Pt) by H_2 (Lin and Chen, 2004),

Table 5
The BET surface area of the spent sample, sintered sample in the high temperature oven, and sample treated under thermal plasma condition.

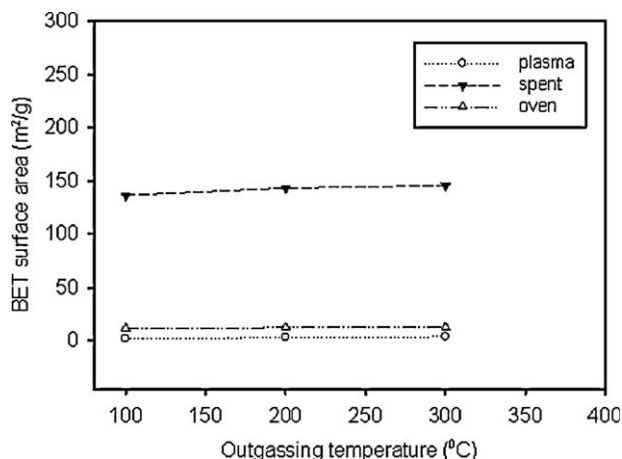| Temperature (°C)	BHT surface area (m²/g)		
	The spent catalyst without the sintering treatment	The sintered product in high temperature oven	The sintered product in N_2 medium under plasma condition
100	136.4	12.0	2.28
200	143.2	12.6	3.38
300	145.7	12.7	4.33

Fig. 17. The BET surface area results of the spent catalyst without the sintering treatment (▼), sintering in the high temperature oven (○), and thermal plasma condition (□).

H radicals, and electrons under plasma sintering process (from (8) to (9)).

3.6. Time-programmed hydrogenation study for catalytic performance of the reforming platinum
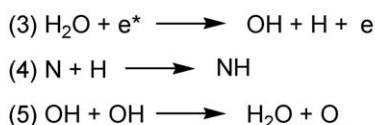
The catalytic activity of the reformed platinum catalyst by treating with thermal plasma was identified by the time-programmed hydrogenation experiments. Urocanic acid **1** was

The first stage

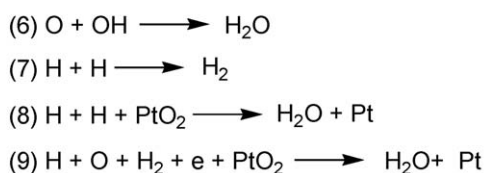#### (a) Active species in plasma at the initial step

(1) $N_2 + e^* \longrightarrow N_2^+ + 2e$

(2) $N_2 + e^* \longrightarrow 2N + e$
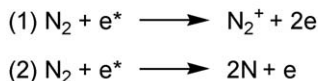
(b) Active species in the presence of water

(3) $H_2O + e^* \longrightarrow OH + H + e$

(4) $N + H \longrightarrow NH$

(5) $OH + OH \longrightarrow H_2O + O$

The second stage

(c) Reduction of PtO₂ and gases formed in the system

(6) $O + OH \longrightarrow H_2O$

(7) $H + H \longrightarrow H_2$

(8) $H + H + PtO_2 \longrightarrow H_2O + Pt$

(9) $H + O + H_2 + e + PtO_2 \longrightarrow H_2O + Pt$

Scheme 1. A possible mechanism for the reduction of platinum oxide in nitrogen medium under plasma conditions.
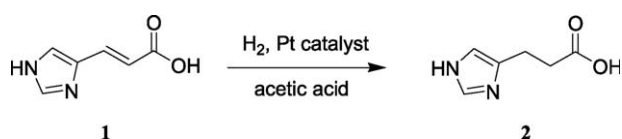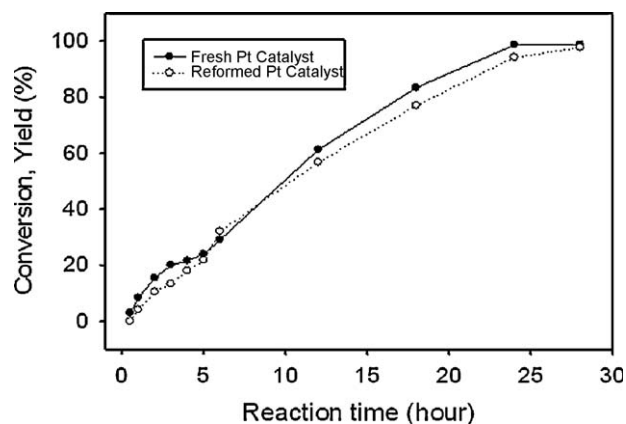

Scheme 2.

Fig. 18. Time-programmed hydrogenation experiments of urocanic acid (**1**) by fresh and reformed platinum catalysts.

Table 6
Conversion ratio of 3-(imidazol-4-yl)propionic acid (**2**)/urocanic acid (**1**) by fresh and reformed platinum catalysts.

Reaction time (h)	Conversion (**2/1**, %)	
	Fresh Pt catalyst	Reformed Pt catalyst
0.5	3.0	0.0
1.0	8.4	4.1
2.0	15.4	10.5
3.0	20.0	13.3
4.0	21.6	18.1
5.0	24.0	21.8
6.0	29.1	32.2
12	61.2	56.7
18	83.4	77.4
24	98.7	94.2
28	98.8	97.8

used as a probe molecule to test hydrogenation activity of the fresh and reformed platinum catalysts (see Scheme 2).

Fig. 18 shows the hydrogenation of urocanic acid **1** over fresh and reformed platinum catalysts (20% (w/w) based on urocanic acid **1**) with an atmospheric H_2 pressure in a Parr apparatus at room temperature (Altman et al., 1984). During the time programmed hydrogenation, the reaction mixture was sampled, filtered through Celite bed, and concentrated to remove the acetic acid under reduced pressure. The sampling reaction mixture was detected by proton NMR spectroscopy technique to identify the conversion of urocanic acid (**1**) to 3-(imidazol-4-yl)propionic acid (**2**). For time programmed hydrogenation result of the fresh platinum catalyst, the hydrogenation reaction was initiated at 1 h and fully converted at about 28 h (98.8%). By employing the same condition for reformed platinum catalyst, we were able to observe the similarly result (see Table 6 and Fig. 18). After the hydrogenation was performed 28 h, most of urocanic acid (**1**, 97.8%) was converted to the hydrogenation product 3-(imidazol-4-yl)propionic acid (**2**). The catalytic activity of the reformed platinum catalyst by plasma was similar to the fresh platinum catalyst.

4. Conclusions

Recovery of spent catalyst has been an enthusiastically investigated subject in recent years (van Deelen et al., 1989; Jong and Siemens, 1986). Due to economical and chemical reasons, we investigated the thermal plasma gasification technology to treat the spent platinum catalyst. This method could provide the convenient and efficient process and reduce the chemical

hazardous waste issues. We have developed a new method to recover the spent alumina-supported platinum catalyst (Pt_/ Al$_2$O$_3$) and reduce platinum oxide (PtO$_2$) to platinum under A.C. plasma conditions. This convenient and efficient technique might be applicable for the reform and recovery of the spent metal catalyst and reduction of metallic oxide catalyst in industries.

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