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Influence of physicochemical treatments on spent palladium based catalyst for catalytic oxidation of VOCs

Sang Chai Kim [a,*], Seung Won Nahm [a], Wang Geun Shim [b], Jae Wook Lee [c], Hee Moon [b]

[a] *Department of Environmental Education, Mokpo National University, 61 Dorim Ri, Cheonggye Myeon, Muan 534-729, Republic of Korea*
[b] *Center for Functional Nano Fine Chemicals (BK21 CFN) and Faculty of Applied Chemical Engineering, Chonnam National University,*
300 Yongbong Dong, Buk-Ku, Gwangju 500-757, Republic of Korea
[c] *Department of Chemical Engineering, Seonam University, 720 Gwangchi Dong, Namwon 590-170, Republic of Korea*

Abstract

To recycle the spent catalyst for the removal of VOCs, the benzene, toluene, and xylene (BTX) complete oxidations were studied over pretreated palladium based spent catalyst in a fixed bed flow reactor system at atmospheric pressure. Two different pretreatment methods with gas (air and hydrogen) and acid aqueous solution (HCl, H_2SO_4, HNO_3, H_3PO_4 and CH_3COOH) were used to investigate the catalytic activity of spent catalyst. The properties of the spent and pretreated Pd based catalyst were characterized by XRD, BET, TEM, ICP, and XPS. The results of light-off curves indicate that the catalytic activity of toluene oxidation for pretreated samples is in the order of hydrogen > air > HNO_3 > CH_3COOH > H_2SO_4 > H_3PO_4 > HCl. In addition, the air and the acid aqueous pretreated catalyst activities were significantly decreased compared to that of the spent (or parent) catalyst. Moreover, hydrogen pretreated (or reduced) catalysts having mainly metallic form show the best performance in removing the toluene vapours compared to other pretreated samples. The reduction temperature made a significant difference in the catalytic performance of the spent catalyst pretreated with hydrogen. XPS results clearly supported that the palladium state of the spent catalysts pretreated at 300 °C was shifted more toward metallic form than other reduced catalysts. Furthermore, the results of a long-term test and catalytic activity of aromatic hydrocarbons also supported that the hydrogen pretreated spent catalyst was a good candidate for removing toxic compounds.
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Keywords: Catalytic oxidation; Palladium; Pretreatment; Spent catalyst; VOCs

1. Introduction

Volatile organic compounds (VOCs) have been extensively used in a variety of industrial and commercial applications for specific purposes, and they are known as one of the harmful pollutants because of their toxicity, malodorous nature, and a relatively high vapor pressure. Therefore, the proper control, removal, and reduction of the emission of VOCs are a crucial task for the protection of the environment [1,2]. Among the well-established destructive methods such as oxidation and biofiltration, catalytic oxidation has been reported to be more suited for the complete destruction of VOCs owing to its low thermal NO_x emissions, high feasibility, low operating cost, and highly destructive efficiency. At present, the catalysts such as supported noble metals, mixtures of noble metals and metal oxides, and metal oxides or supported metals are being extensively used in treating VOCs with various advantages and limitations [3–10].

On the other hand, various commercial catalysts used in chemical related applications have been disposed as an industrial waste when the catalytic activity of catalysts was not good enough to achieve an optimum yield. Previous studies have shown that the main causes of catalytic deactivation can be classified into three factors: (1) fouling, (2) poisoning, and (3) thermal degradation (or sintering). In addition, the utilizations of deactivated catalysts such as regeneration (reuse), disposal, and other applications have a close connection with the chemical, economical, and environmental matters. For environmental and economical considerations, the spent catalyst should be regenerated and used for the various purposes, although its activity is not as good as fresh catalyst [11,12].

As described above, spent catalysts containing noble and metal oxides are still applicable to catalytic oxidation by applying the proper treatment method: namely (1) physical (gas), and

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* Corresponding author. Tel.: +82 61 450 2781; fax: +82 61 450 2780.
E-mail address: gikim@mokpo.ac.kr (S.C. Kim).

(2) chemical (acid solution) treatment. Therefore, search for reliable regeneration methods for spent catalysts is justified from the viewpoint of economic utilization and environmental protection [11]. However, little attention has been given to the investigation of the regeneration methods of deactivated catalysts and the catalytic performance of regenerated catalysts. Therefore, systematic approaches are required to assess the possibility of those materials in the applications of catalyst based processes.

In the present work, to reuse and regenerate the spent catalyst for the removal of VOCs, the benzene, toluene, and xylene (BTX) complete oxidations have been studied on the spent Pd based catalyst modified by pretreatment techniques in a fixed bed flow reactor system at atmospheric pressure. Two different pretreatment methods, namely, gas (air and hydrogen) and five different acid aqueous solutions (HCl, H_2SO_4, HNO_3, H_3PO_4 and CH_3COOH) have been employed to compare with the catalytic activity of spent catalyst.

2. Experimental

2.1. Catalysts

The spent Pd based catalyst that has been disposed as an industrial waste was obtained from YNCC Corporation, South Korea. Its basic properties are summarized in Table 1. To examine the influence of gas treatments for spent catalysts, the spent catalysts were pretreated with a 100 cm^3/min flow rate of hydrogen and air at three different temperatures of (200, 300, and 400 °C) for 2 h, respectively. In addition, five different aqueous acid solutions with 0.1N (HNO_3, CH_3COOH, H_2SO_4, HCl, and H_3PO_4) were also used to pretreat the spent catalyst. The acid aqueous treatments were performed in a 100 ml Erlenmeyer flask. In each experiment, a 2.0 g of the spent catalyst was put into the flask containing 50 ml of acid aqueous solution and then the mixture was stirred in a shaker (KMC-8480SF, Vision Scientific Co., Korea) at a rate of 150 rpm at room temperature for 5 h. The acid treated samples were washed further with de-ionized water until the pH of the solution reached 7 and dried at 120 °C for 24 h.

2.2. Characterization of catalysts

The BET surface areas of the parent and pretreated samples were determined by nitrogen adsorption at 77 K using a Micromeritics ASAP 2020 analyzer. The crystal structures of the samples used in this work were examined by X-ray diffraction (XRD) data using a Phillips PW3123 diffractometer equipped

with a graphite monochrometer and Cu Kα radiation of wavelength 0.154 nm wavelengths. The samples used were investigated in the 2θ range of 20–90 °C at a scanning speed of 70 °/h. The coke deposition was measured by using elemental analyzer (1110, CE Instruments). To determine the net amount of palladium over the parent and pretreated samples, ICP was employed using a Perkin-Elmer OPTIMA 4300DV. An XPS analysis was conducted using a photoelectron spectrometer VG Scientific MultiLab 2000 system equipped with a non-monochromatic Mg Kα radiation of 1253.6 eV. The C 1s peak (285.0 eV) was used to calibrate the binding energy values. The pressure in the analytical chamber was about 10^{-9} Pa. In this study, the TEM images of prepared catalysts were obtained using a JEOL JEM-2000FAXII transmission electron microscope with an acceleration voltage of 200 kV.

2.3. Catalytic oxidation of VOCs

The catalytic oxidations were carried out using a conventional fixed bed flow reactor as shown Fig. 1. The reactor has three major sections: (1) apparatus for preparation of vapors, (2) fixed bed flow reactor in a heating system and (3) apparatus for the analysis of reactants and products.

The catalytic reactor (quartz tube with the shape of a (Y)) consisted of a vertical tubular of 1.2 cm diameter and 35 cm length in an electrical heating system controlled by a proportional integral derivative (PID) controller. To get the accurate measurement of the catalyst temperature, a K type thermocouple was positioned in the catalyst bed. A catalyst sample 1.0 g was loaded in the middle of the reactor supported by quartz wool. The BTX was purchased from Fisher and used without further treatment. Xylene was an *ortho*-isomer. An air stream bubbling through a saturator filled with liquid hydrocarbon carried an individual vapor. For accurate and stable controlling the gas flow rates, mass flow controllers (UNIT Instrument, UFC-8100) were used. The concentration of toluene was 1000 ppm, controlled by the temperature of the saturator and mixed with another air stream. The flow rate of the gas mixture through the reactor was 100 STP cm^3/min. All lines were heated sufficiently at 120 °C to prevent the adsorption and condensation of the reactant and the product in the tubes. The catalytic activities of the selected samples were examined in the temperature range of 120–300 °C with an interval of 20 °C. Experimental data were collected after a steady state condition was ensured in each step.

The concentration of inlet and exit gas stream was determined using a gas chromatograph GC-14A model (Shimadzu) equipped with thermal conductivity. The chromatographic column was composed of a 5% bentone-34 and 5% DNP/simalite (60–80 mesh, Ø3 mm × 3 m) for BTX analysis, and a porapak Q (50–80 mesh, Ø3 mm × 3 m) was used for CO_2 separation. The GC/MS (Shimadzu, QP5050) was also employed for the quantitative and qualitative analysis of the products and by-products. In the present work, the products were CO_2, H_2O, and other by-products were not found under most experimental conditions. Thus, the conversion was calculated based on the hydrocarbon consumption. In other words, the conversion of BTX was defined

Table 1
The basic properties of the Pd based spent catalyst

Catalyst	Pd/Al_2O_3
Shape	Sphere
Size (mm)	3.0
Color	Dark blue
BET surface area (m^2/g)	34.5
Pd content (wt.%)[a]	0.64

[a] Pd content measured with ICP.

1.Helium Cylinder 6.Mass Flow Controller 11.Three way cock 16.Bubble trap
2.Air Cynlinder 7.Check Valve 12.Temp.controller 17.Data Process analyzer
3.Nitrogen Cylinder 8.Constant Temperature Bath 13.Furnace 18.Printer
4.Hydrogen Cylinder 9.Evaporator 14.Reactor 19.Mass Flow Meter
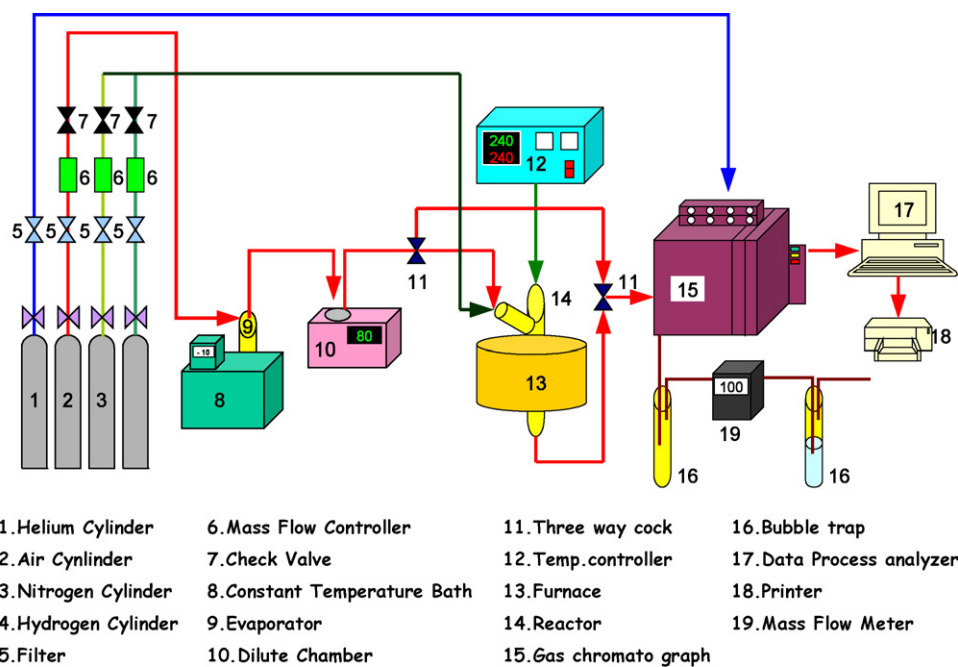5.Filter 10.Dilute Chamber 15.Gas chromato graph

Fig. 1. Schematic diagram of the experimental apparatus.

as follows:

$$\text{conversion, } X(\%) = \frac{\text{moles of product}}{\text{moles of feed}} \times 100$$

A blank test was conducted without a catalyst to examine the effect of quartz wool and the quartz reactor. No activity (homogeneous reaction) was observed below 600 °C. This result indicates that the employed system may be applied for analyzing the catalytic oxidation of VOCs.

3. Results and discussion

Pd based catalyst as well as Pt has been widely applied in various types of practical systems including the catalytic oxidation of VOCs because of their high thermal stability, high activity, and low volatility. However, from the viewpoint of cost, performance and stability of the catalyst, palladium is better than that of platinum catalyst [4].

The spent catalyst used in this study consists of 0.64 wt.% Pd with a BET surface area of 34.47 m^2/g. TEM image and XRD spectra of the spent catalyst prior to physicochemical treatment are presented in Fig. 2. As shown in this figure, the results from the TEM analyses show that the parent sample has a particle size in the range of 4–40 nm. Although XRD was used to examine the crystallinity of Pd, the spent catalyst showed the reflections of δ-Al_2O_3 alone. It has been reported that the reflections of lower Pd loading on relatively high surface area supports are hardly observed because of their highly dispersed surface phase [8,13]. Thus, the results revealed that the palladium particles on the support are well dispersed.

The light off curve (or temperature conversion profile) that gives valuable information for understanding the catalytic activity with a simple plot of conversion and temperature (or time) is widely employed in the catalysis related area. Fig. 3 shows

the light off plots of the spent catalyst for the complete oxidation of toluene with the function of temperature. As described in the experimental section, thermal oxidation (or homogeneous reaction) was not occurred at temperature below 600 °C. However, toluene oxidation started at 180 °C on the spent catalyst and a complete conversion was achieved at 210 °C. The results demonstrate that the spent catalyst used has a relatively high potential in applying the catalytic oxidation system when these commercial catalysts lost their values.
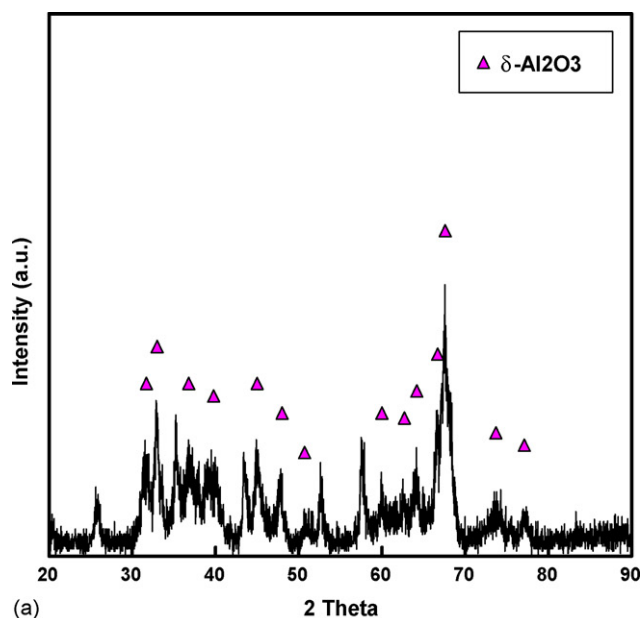
3.1. Influence of pretreatments

3.1.1. Effect of chemical treatment method

To further examine the nature of chemical treatment for the deactivated catalyst, five different acid aqueous pretreatment methods were employed. As shown in Fig. 4(a), all the acid treated samples exhibited δ-Al_2O_3 crystal peaks and their intensity insignificantly changed.
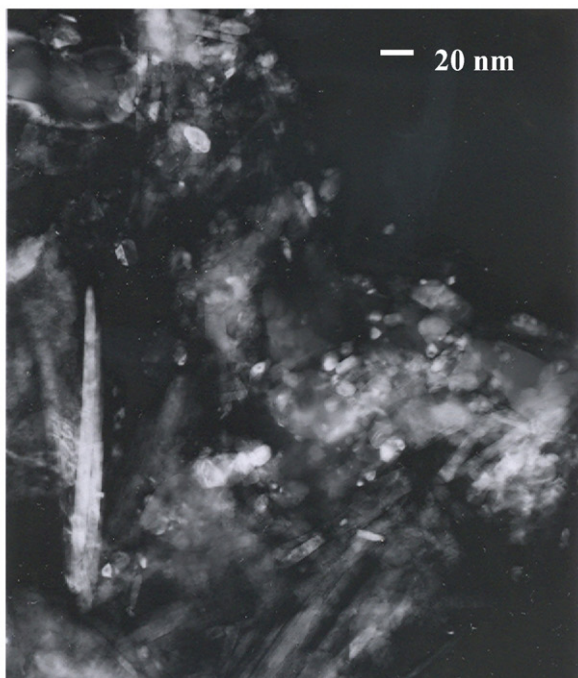
The BET surface area and the palladium content of the acid aqueous pretreated samples are summarized in Table 2. For all the treated catalysts, the BET surface areas moderately increased. In contrast, the palladium contents dropped significantly. For example, in the case of the deactivated catalyst treated with acetic acid having weak acidity, the BET surface

Table 2
BET surface area and Pd content of acid aqueous solution pretreated catalysts

	BET surface area (m^2/g)	Pd content (wt.%)
0.1N HNO_3	39.5	0.63
0.1N H_3PO_4	39.4	0.62
0.1N HCl	37.5	0.55
0.1N CH_3COOH	36.3	0.54
0.1N H_2SO_4	37.9	0.22

Fig. 2. XRD pattern (a) and TEM photograph (b) of spent Pd based spent catalyst.
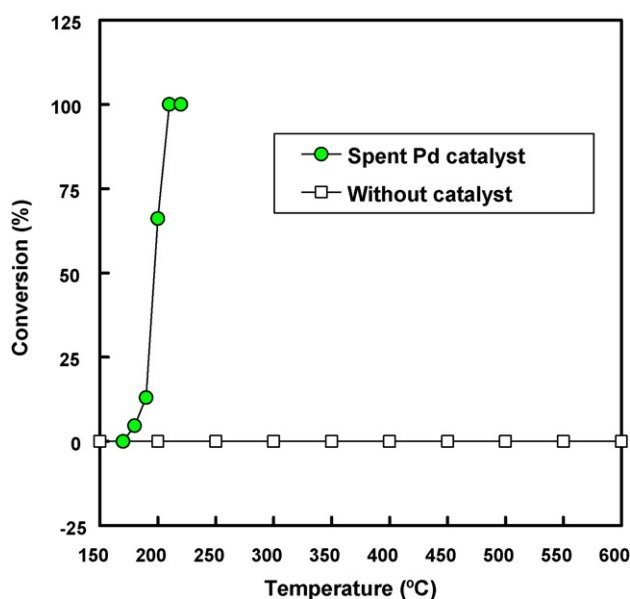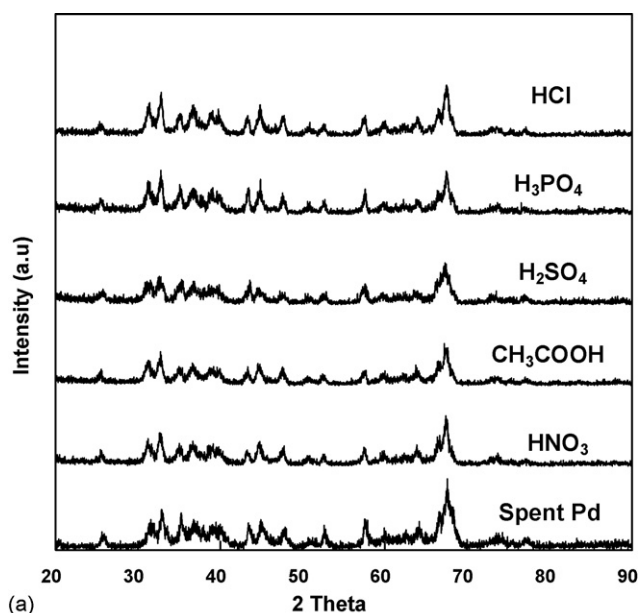

Fig. 3. Conversion profile of toluene oxidation on the spent Pd based spent catalyst.

initiated at about 190 °C on the treated samples, and then the temperature was slowly increased up to 210 °C. As shown in this figure, the complete oxidation temperature of the HCl treated sample was 240 °C which was slightly higher (10 °C) than that of other treated catalysts. Generally, T_{50}, defined as the value of the temperature at conversion approaches 50%, has been extensively used as a standard criterion to compare the catalyst activities. It can be seen that the catalytic activity of chemical treated samples decrease in the following order: CH_3COOH (213 °C) > HNO_3 (214 °C) > H_2SO_4 (221 °C) > HCl (222 °C) > H_3PO_4 (223 °C). As a whole, after being pretreated with acid aqueous solution, the activity of modified catalysts decreased severely compared to the parent catalyst, even though the BET surface areas slightly increased owing to the removal of impurities from the surface and pores of the spent catalysts. Accordingly, the acid aqueous pretreatment had a negative effect on the catalytic activity. In addition, no clear relation between the catalytic activity and the amount of remaining palladium content was observed in the activity tests, and acid pretreatment had a negative effect on the activity of the parent catalyst.
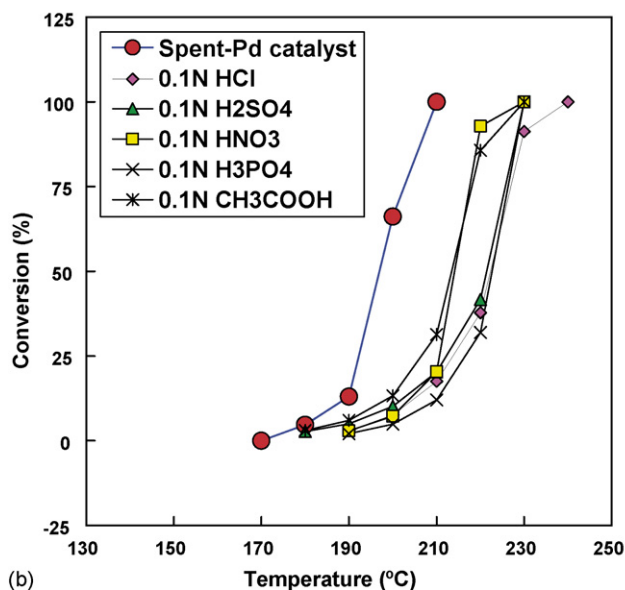
3.1.2. Effect of gas treatment method

The XRD and the BET surface area measurement were also carried out to examine the properties of the gas treated samples. The XRD patterns of preoxidized (top) and prereduced (bottom) spent catalysts at three different temperatures (200, 300, and 400 °C) are presented in Fig. 5. Although the intensities of the peaks slightly increased after pretreating the samples with two different gases (air and hydrogen) at three different temperatures, no distinctive peaks of metallic Pd (40°, 46°, and 68°) and PdO (34°, 55°, 60° and 71°) could be observed. Table 3 compares the BET surface areas of the air treated and the hydrogen treated spent catalysts. The results indicated that the BET surface areas for the air treated samples moderately increased ($34.8 \rightarrow 37.3$ m^2/g) with increasing oxidation temperature. In

area and the palladium content obtained were 36.3 m^2/g and 0.54 wt.%, respectively. In addition, the lowest palladium content was obtained with sulfuric acid. The BET surface area and Pd content listed in Table 2 also indicated that among the acid aqueous pretreatments, the nitric acid aqueous treated method seems to be the most helpful technique for regenerating the deactivated heterogeneous catalysts. However, distinctive relations between acid strengths, BET surface area and palladium content were not found.

Fig. 4(b) shows the activity curves for acid aqueous pretreated (concentration = 0.1N, HNO_3, CH_3COOH, H_2SO_4, HCl, and H_3PO_4) samples over spent catalyst. The toluene oxidation
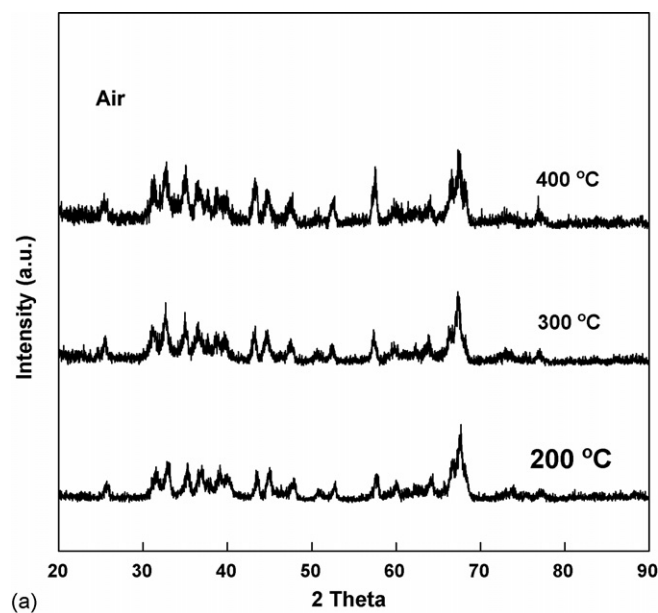
Fig. 4. XRD patterns (a) and conversion profiles (b) of toluene oxidation of acid aqueous solution pretreated spent catalysts.

Fig. 5. XRD patterns of air (a) and hydrogen (b) pretreated spent catalysts.
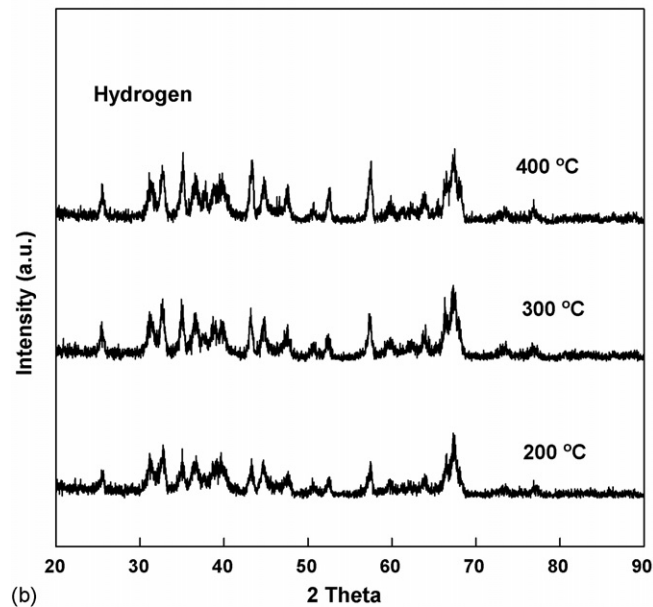
addition, as summarized in Table 4, the amount of coke deposition on the surface of the air treated spent catalyst decreased (2.17 → 0.32 wt.%) with an increase in pretreatment temperature, revealing that the removal of carbon might result in an increase in the BET surface area. However, in the case of hydrogen treated catalysts, the BET surface area slightly decreased (36.1 → 34.7 m^2/g) with increasing treatment temperature. This

result is in good agreement with those reported by Muller et al. [14], in which the reduction temperatures apparently play an important role in the catalytic behavior.

Fig. 6 exhibits comparison of light-off curves of toluene oxidation as a function of reaction temperature on Pd pretreated with air (a) and hydrogen (b) gases at different temperatures. The experimental results indicate that the activity of pretreated

Table 3
BET surface area (m^2/g) of air and hydrogen pretreated catalysts

Air treatment		Hydrogen treatment	
Pd–S–A (200 °C)	34.8	Pd–S–H (200 °C)	36.1
Pd–S–A (300 °C)	38.5	Pd–S–H (300 °C)	35.3
Pd–S–A (400 °C)	37.3	Pd–S–H (400 °C)	34.7

Table 4
Coke deposition of the parent and air pretreated catalysts

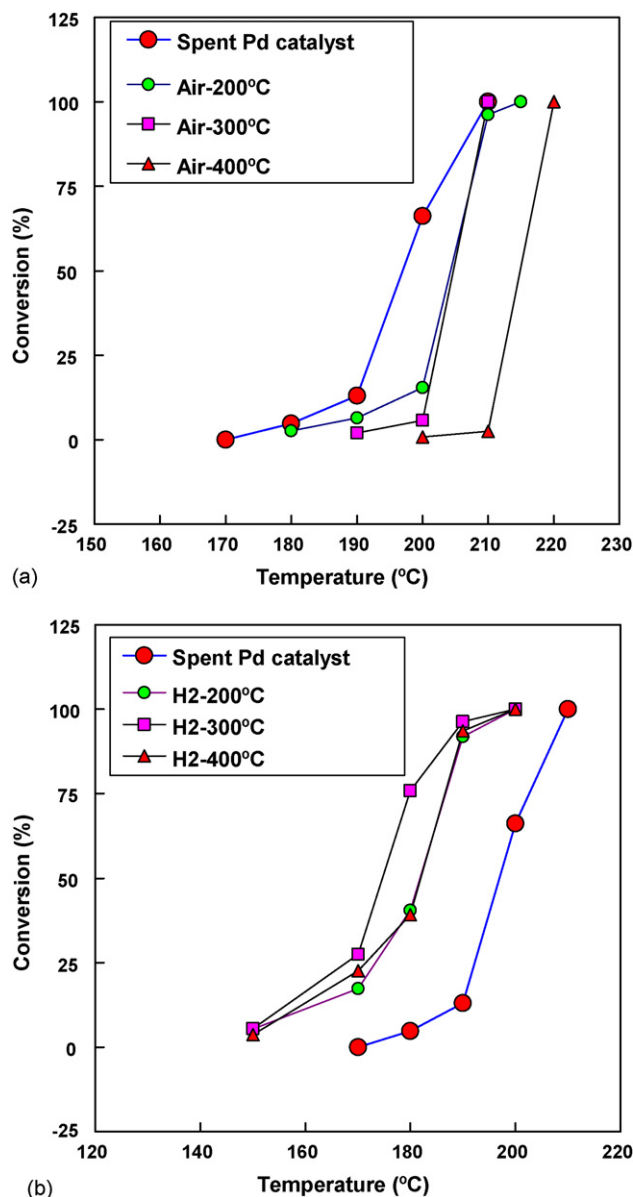|	The amount of coke deposition (wt.%)
Parent (spent)	2.17
Pd–S–A (200 °C)	1.34
Pd–S–A (300 °C)	1.17
Pd–S–A (400 °C)	0.32

Fig. 6. Conversion profiles of toluene oxidation on the air (a) and hydrogen (b) pretreated spent catalysts.

samples is closely related to the treatment method. The conversion profiles for air treated samples shift to higher temperatures when the pretreated temperature of the parent catalyst is raised. For example, reaction temperatures for T_{50} conversion of toluene are 204, 205, and 215 °C, respectively. This experimental result also revealed that the catalytic activity of the air treated spent catalyst is highly dependent on the pretreatment temperature. On the whole, the oxidized samples are less active than the spent catalysts. It was noticed that the order of catalytic activity for toluene oxidation was: 200 °C > 300 °C > 400 °C. These results suggested that air pretreatment was not efficient to regenerate the Pd based spent catalyst, although the removal amount of carbon increased with the temperature.

In contrast, the conversion curves of toluene oxidation on hydrogen treated catalysts, as shown in this figure, were considerably different from the results of the air treated samples.

In other words, the catalytic oxidation occurs at about 150 °C and then achieves a full oxidation at 200 °C for all the hydrogen treated samples. Compared to those of air treated catalysts, the temperatures required for the complete oxidation of toluene by hydrogen-pretreated catalysts are significantly decreased. It clearly demonstrates that the hydrogen treated catalysts enhance the catalytic oxidation of toluene, and the sample pretreated at 300 °C shows the highest activity. The catalytic activity of toluene oxidation on hydrogen treated samples is in the order of 300 °C > 400 °C ≥ 200 °C, although the differences in conversion between the samples are minor. The findings strongly support that the hydrogen pretreatment endowing the metallic form had significant beneficial effects on the VOCs oxidation, and that the pretreated temperatures were a crucial factor for applying the regeneration of spent catalysts.

3.2. XPS examination

XPS analysis widely used in the determination of physico-chemical changes of materials provides important information about the heterogeneous catalyst. To examine the influence of gas (hydrogen and air) treatment, XPS investigations were first applied to characterization of the Pd based spent catalyst. Fig. 7(a) shows the XPS spectra of the Pd based spent catalyst. The binding energy (BE) of Pd 3d for the spent samples was 336.4 eV, which represents the characteristic of oxidized state (PdO/Pd^{2+}) of Pd catalyst. The result indicates that the spent catalyst used largely oxidized.

However in the hydrogen treated catalyst, as shown in Fig. 7(b) the Pd 3d BE (334.4 eV) is characteristic of Pd catalyst in a reduced (or metallic) state (Pd^0). In addition, the BE of the catalyst after pretreated with air at 300 °C (Fig. 7(c)) was about 336.2 eV corresponding to the PdO state. These results show that Pd state of air treated sample is very similar to that of the catalyst disposed in commercial processes. Moreover, the results of XPS suggest that the surface states of catalysts are highly dependent on the pretreatment method, and a metallic form seems to be more desirable than the PdO state for treating the toluene vapor. The above trend coincides highly with the data reported in the literature over 5 wt.% Pd/γ-Al$_2$O$_3$ catalysts [15].

As noted in the catalytic activity test, the hydrogen treated catalyst at 300 °C has the highest conversion efficiency. To examine the influence of the reduction temperature of Pd based catalyst, the XPS also was measured as shown in Fig. 8. The binding energies of the spent catalysts reduced at three different temperatures of 200, 300, and 400 °C were 334.85, 334.40, and 334.90 eV, respectively. These data reveal that the binding energy of Pd 3d$_{5/2}$ presents a minimum at 300 °C. It is interesting to note that in the case of hydrogen treated samples, the pretreatment temperature is highly related to the catalytic activity. Recently, Ferreira et al. [7], Venezia et al. [16], and Demoulin et al. [17] have reported that the variations of catalytic activities are closely related to the particle size and support, although the effect of the size on the catalytic reaction is still arguable. In addition, hydrogen treated palladium particles have a relatively small size compared to that of aged or fresh samples. On the
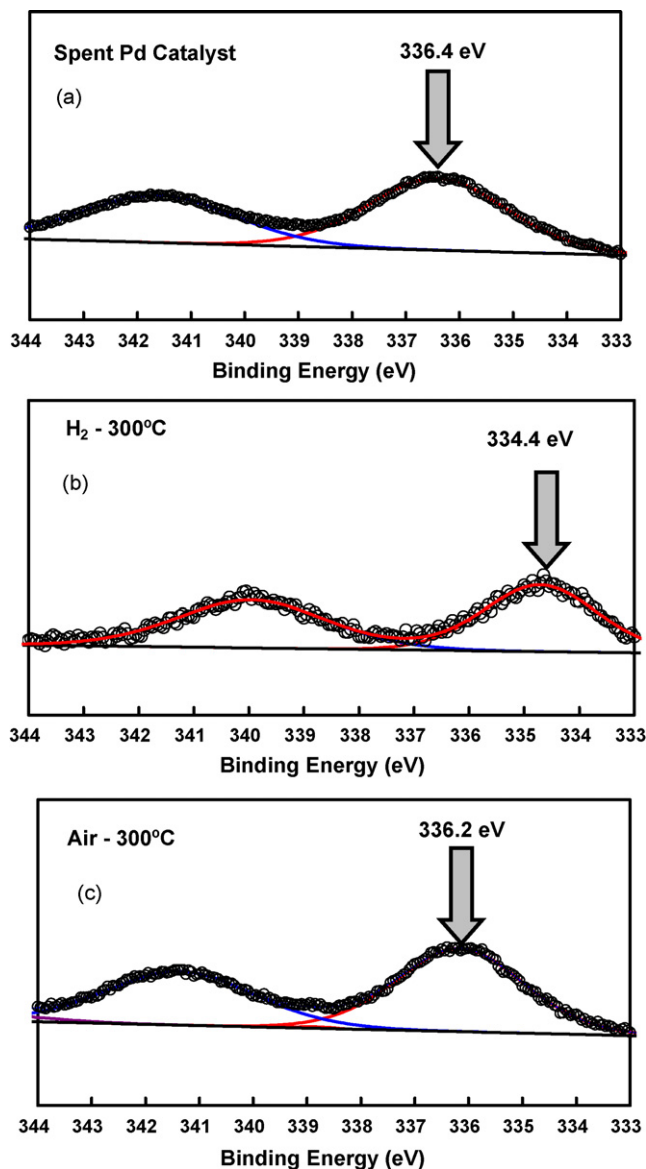
Fig. 7. XPS spectra of Pd based spent catalyst: parent (a), air pretreated (300 °C) (b), and hydrogen pretreated (300 °C) (c).

Fig. 8. XPS spectra of Pd based spent catalyst after hydrogen pretreatment at 200 (a), 300 (b), and 400 °C (c).

other hand, Muller et al. [14] and Matsumura et al. [18] also observed that the particle sizes of prereduced palladium particles increase with an increasing reduction temperature, and that a relatively higher increase in the catalytic activity of the palladium sample prereduced at lower temperature has been obtained. These authors pointed out that the enhancement of catalytic activity of the catalyst is directly related with the surface area of metal and the particle size. Furthermore, as the reduction temperatures increase the average particle size of metallic palladium exponentially increases. In other words, the particle size remained almost constant below the certain temperature and then significantly increased above the specific reduction temperature [14]. Similar trends were found in present study, as shown in Fig. 9 (TEM). The results showed that the average particle sizes of the palladium were between 4 and 8 nm for the case of samples that were pretreated below 300 °C, whereas an enlargement of the palladium particle sizes between 6 and
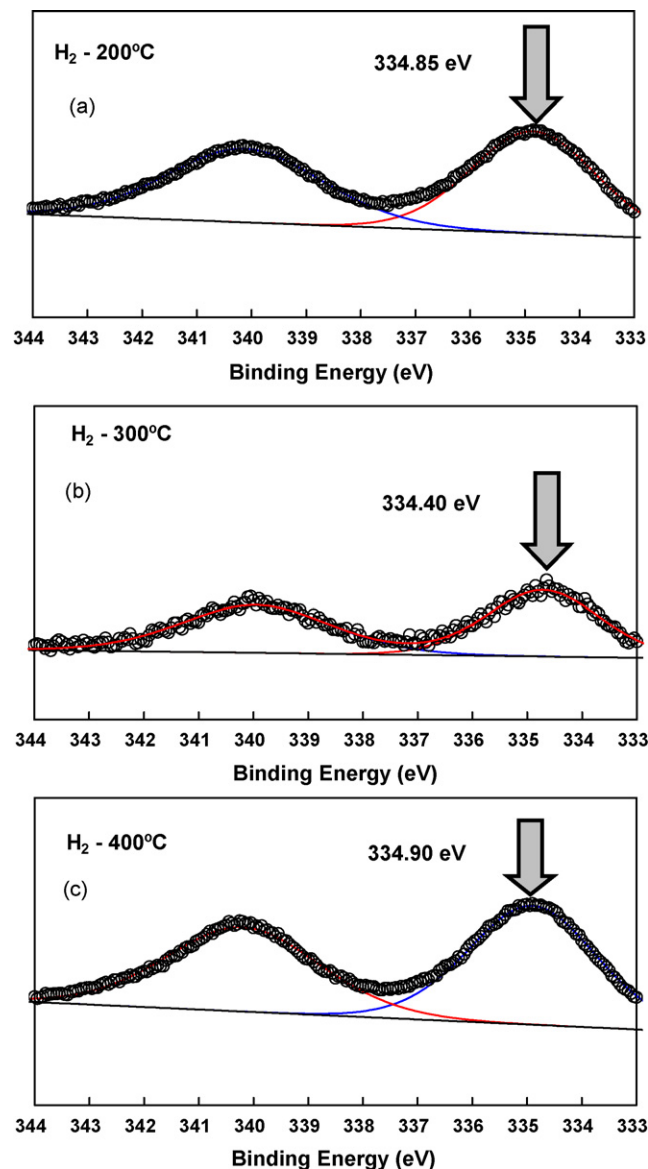
18 nm were appreciably noticed at 400 °C. It was also observed that the Pd particle size of hydrogen pretreated sample was reduced, compared to that of the spent catalyst without hydrogen pretreatment (Fig. 2(b)). However, in this work, the relation between the Pd particle size and the toluene oxidation was not clear.

Considering the Pd $3d_{5/2}$ binding energy shift, which was calculated with pure Pd metal (334.4 eV), the values of palladium in the samples reduced at 200, 300, and 400 °C were 0.45, 0.0, and 0.50 eV, respectively. These findings indicate that the palladium particles in the spent catalyst pretreated at 300 °C seems to have more metallic character than at other temperatures although the particle sizes observed have a similar range of prereduced Pd at 200 °C. Furthermore, as presented in Table 5, among the spent catalysts prereduced, the BE of Pd–S–H (300 °C) was relatively lower than that of other pretreated samples and also the Pd state was still kept after toluene oxidations unlike the other prereduced
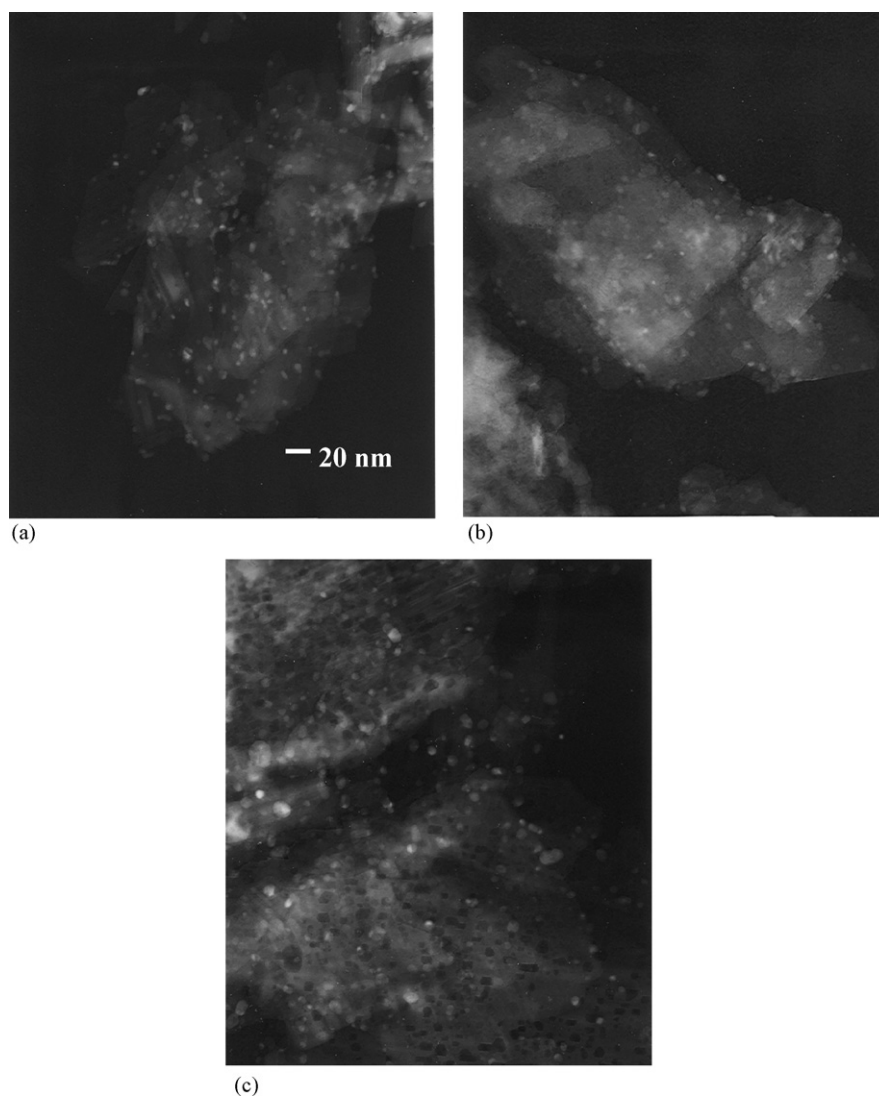
Fig. 9. TEM photographs of hydrogen pretreated catalyst: (a) 200 °C; (b) 300 °C; (c) 400 °C.

catalysts. Therefore, the results obtained from the catalytic performance and the XPS clearly indicated that the spent catalysts prereduced at 300 °C are the most active in toluene oxidation because of the relatively stable existence of metallic state.

Table 5
Binding energies (BE) of the Pd $3d_{5/2}$ for spent, air, and hydrogen pretreated catalysts

| Samples		BE Pd $3d_{5/2}$ (eV)	
Parent (spent)		336.41	
Pretreatments		Before reaction	After reaction
Air (300 °C)		336.16	336.09
Hydrogen	(200 °C)	334.85	335.14
	(300 °C)	334.40	334.80
	(400 °C)	334.90	335.31

3.3. Evaluation of prereduced Pd–S catalyst stability and oxidation of other aromatic reactants

In general, evaluating the stability of a catalyst and evaluating the catalytic behavior of different VOCs are very important in assessing, understanding and optimizing the catalytic applications [19]. Thus, a long-term test was carried out to examine the stability of the catalytic behavior of a pretreated spent catalyst at a reaction temperature of 200 °C for 48 h. Fig. 10(a) shows the long-term stability of Pd–S catalyst pretreated with hydrogen at 300 °C for the oxidation of toluene at a concentration of 1000 ppm. It was observed clearly that the conversion of toluene over a prereduced catalyst was moderately well maintained in the range of 80–100% and was also continuously fluctuating during the stability test. According to the previous studies [4,24], the oscillations in catalytic activity were attributed to (1) surface reconstruction of palladium species and (2) changing the pathway of oxygen activation. In addition, Ferreira et al. [7], Vassileva et al. [25], and Garcia et al. [26] reported a relationship between oscillation in catalytic behavior and redox (reduction
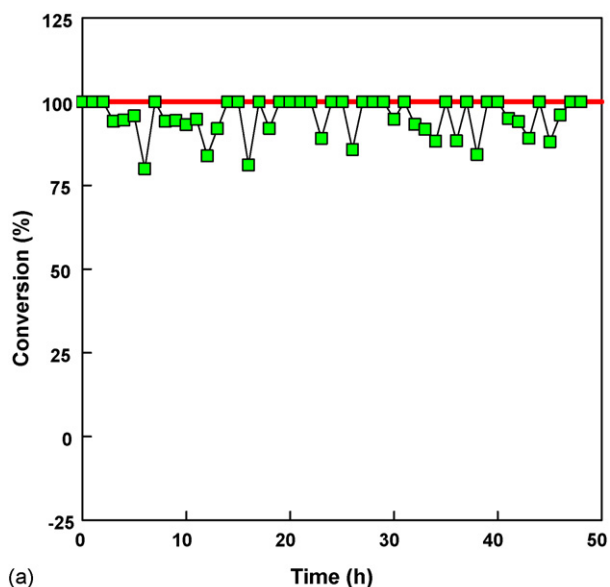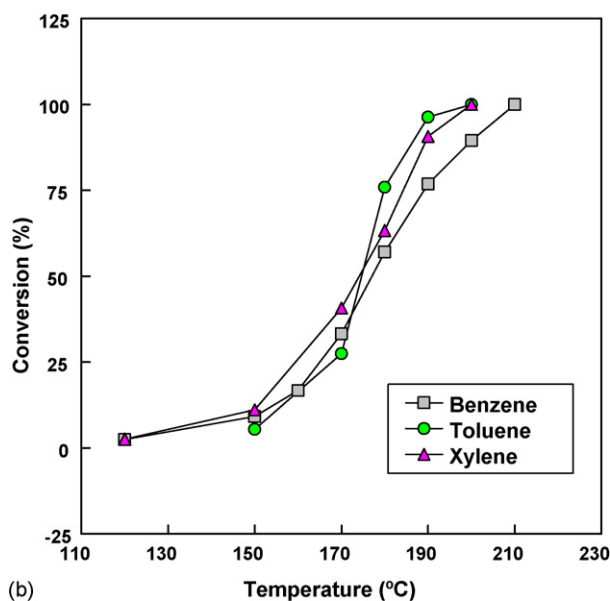
Fig. 10. Stability test of hydrogen pretreated Pd based spent catalyst (300 °C) of toluene oxidation (a) and conversion profiles of BTX oxidation on hydrogen pretreated Pd based spent catalyst (300 °C) (b). Reaction condition: catalyst weight = 1.0 g, BTX concentration = 1000 ppm in air; total flow rate = 100 cm^3/min.

and oxidation) cycle of Pd^0/PdO. Thus, the oscillatory behaviors (or the oxidation/reduction cycle) were closely related to the state of the palladium surface. It is evident from the results of light-off curve for toluene oxidation that the metallic Pd (Pd^0) is more active than the oxidized state (PdO). Namely, the catalytic activity gradually increased when the metallic Pd dominate the surface, while the contrary happened when the PdO control the system. Hence, the oscillations are probably attributing to the continual (or constant) transformation of Pd^0/PdO during the reaction.

On the other hand, previous studies have shown that performance of a catalytic system is highly dependent on the com-

bination of characteristics between the catalyst and the VOCs [10]. The catalytic activities in complete oxidation of benzene, toluene, and xylene (BTX) on platinum based catalysts are in the order of benzene > toluene > xylene [19,20]. However, in the case of palladium and metal oxide based catalysts, the order of catalytic ability for BTX was toluene > xylene > benzene [21–23]. These results suggested that the strength of adsorption, the order of ionization potential, and the strength of the VOC weakest C···H bond seem to be the key factors in controlling the catalytic system [10,19,20]. However, as shown in Fig. 10(b), the behavior of BTX conversion over the pretreated spent catalyst could be classified into two main parts. In other words, the order of activity for BTX oxidation above T_{50} was identical to that of the previous report (toluene > xylene > benzene) shows the relation between the catalytic activity and the ionization potentials of methyl derivatives, but below T_{50} the behavior was the inconsistent (xylene > benzene > toluene). The result also revealed that the pretreated spent catalyst has a good efficiency for treating the aromatic hydrocarbons.

4. Conclusions

The catalytic oxidations of VOCs over the Pd based spent catalyst modified by different pretreatment techniques are carried out to assess the possibility of recycling the spent catalyst. The results obtained from the catalytic activity of toluene revealed that the employed spent catalyst has a good conversion ability although the relative value as a commercial catalyst decreased. Moreover, the activities of the pretreated spent catalyst were highly dependent on the treatment methods. The hydrogen treated catalysts showed high conversions and steep increases in the catalytic activity with the rising reaction temperature. However, in the case of air or acid treated samples, the conversions significantly decreased compared to that of the parent catalyst, subsequently, air or acid pretreatment had a negative effect on the its catalytic activity.

From the screening of the results examined from the light-off curve study, the hydrogen pretreatment method was chosen as the best techniques of regenerating the deactivated catalyst because of the role of metallic state formation mainly in the spent catalyst surface. The catalytic performance of the spent catalyst pretreated with hydrogen was significantly different depending on the reduction temperature. Especially, the catalysts pretreated at 300 °C showed the highest conversion among other pretreated temperatures. The XPS results clearly supported that palladium state of the spent catalysts pretreated at 300 °C was shifted more toward metallic form than to other reduced catalysts. Moreover, the prereduced spent catalyst kept up a favorably high conversion in a long-term stability test and was also fairly good for removing other aromatic reactants.

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