Influence of physicochemical treatments on iron-based spent catalyst for catalytic oxidation of toluene

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Abstract

The catalytic oxidation of toluene was studied over an iron-based spent and regenerated catalysts. Air, hydrogen, or four different acid solutions (oxalic acid ($C_2H_2O_4$), citric acid ($C_6H_8O_7$), acetic acid (CH_3COOH), and nitric acid (HNO_3)) were employed to regenerate the spent catalyst. The properties of pretreated spent catalyst were characterized by the Brunauer Emmett Teller (BET), inductively coupled plasma (ICP), temperature programmed reduction (TPR), and X-ray diffraction (XRD) analyses. The air pretreatment significantly enhanced the catalytic activity of the spent catalyst in the pretreatment temperature range of 200–400 °C, but its catalytic activity diminished at the pretreatment temperature of 600 °C. The catalytic activity sequence with respect to the air pretreatment temperatures was 400 °C > 200 °C > parent > 600 °C. The TPR results indicated that the catalytic activity was correlated with both the oxygen mobility and the amount of available oxygen on the catalyst. In contrast, the hydrogen pretreatment had a negative effect on the catalytic activity, and toluene conversion decreased with increasing pretreatment temperatures (200–600 °C). The XRD and TPR results confirmed the formation of metallic iron which had a negative effect on the catalytic activity with increasing pretreatment temperature. The acid pretreatment improved the catalytic activity of the spent catalyst. The catalytic activity sequence with respect to different acids pretreatment was found to be oxalic acid > citric acid > acetic acid ≥ nitric acid > parent. The TPR results of acid pretreated samples showed an increased amount of available oxygen which gave a positive effect on the catalytic activity. Accordingly, air or acid pretreatments were more promising methods of regenerating the iron-based spent catalyst. In particular, the oxalic acid pretreatment was found to be most effective in the formation of FeC_2O_4 species which contributed highly to the catalytic combustion of toluene.
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1. Introduction

Volatile organic compounds (VOCs) are not only major contributors to air pollution because of their toxicity; their malodorous, mutagenic, and carcinogenic nature; but also as main precursors of ozone and smog formation [1–8]. In many countries, including USA, EU, Japan and Korea, stringent legislations have been passed to abate VOCs emission requiring that VOCs emission from various industrial processes be controlled. It is also recognized that catalytic oxidation is a potent method of controlling emissions of VOCs owing to its low thermal NO_x emissions, low operating cost, and high destructive efficiency [9–11]. At present, the catalysts used for reducing VOC emissions can be divided into two categories: noble metals and metal oxides. The noble metal catalysts such as Pt and Pd [12–17] are generally more active than metal oxides catalysts [18–20]. Despite having less catalytic activity than noble metals at low temperatures, metal oxides are much cheaper, allowing a higher catalyst loading which leads to a higher active surface area in the metal oxide bed, thus letting the metal oxide catalysts be only slightly less active than noble metals in the oxidation of hydrocarbon [21].

On the other hand, various kinds of commercial catalysts used in chemically related applications have been disposed off as an industrial waste when the activity of catalysts is too weak to achieve its optimum yield. It has been generally known that main reasons of catalytic deactivation are fouling, poisoning and thermal degradation (or sintering). Fouling involves deposition

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of materials (e.g., coke deposition) on a catalyst surface to block the active sites. Poisoning involves strong chemical interaction of a component (e.g., sulphur) of the feed or products with active sites on the catalyst surface. Thermal degradation decreases the catalyst active sites by agglomerations [22]. In addition, the spent catalyst disposal or utilization of deactivated catalyst by regeneration (reuse) or its other applications are closely connected with chemical, economical, and environmental matters. Even though the activity and selectivity of the regenerated catalysts are not quite efficient enough to re-apply in the original process, they could be employed as catalysts for the catalytic oxidation of VOCs [23].

Tseng and Chu [24] have reported an excellent metal oxide catalyst (MnO/Fe_2O_3) for the catalytic oxidation of styrene, and Spinicci et al. [25] have also found perovsikite catalyst ($LaMO_3$, M = Mn, Co, Fe, Sr) as one of the effective iron-based catalyst for the incineration of VOCs. However, little attention has been given to the catalytic oxidation using spent catalyst.

We focused on the iron-based spent catalyst for the catalytic oxidation after a proper regeneration method, and also on the findings of reliable regeneration methods for spent catalyst to assess if they are justified in the viewpoint of economic utilization, prolonging life time of resources, and environmental issues.

The present work examines the optimum pretreatment method for iron-based spent catalyst for the removal of VOC to assess the possibility of iron-based spent catalyst for the VOC removal. The chosen VOC probe molecule was toluene, which is a commonly used solvent in chemical and processing industries and presents an important POCP (Photochemical Ozone Creativity Potential). Therefore, toluene emission in the atmosphere needs to be controlled [4,6]. Several pretreatment methods such as air, hydrogen and four different acids ($C_2H_2O_4$, $C_6H_8O_7$, CH_3COOH and HNO_3) were employed, and a proper regeneration method was selected by comparing the catalytic activity of the different pretreated spent catalysts.

2. Experimental

2.1. Catalysts

Iron-based spent catalysts, disposed off as an industrial waste, were obtained from Namhae chemical company. They had been used for ammonia synthesis process. Fresh catalyst consists of 89 wt% Fe_2O_3, 9 wt% Cr_2O_3 and balance Al_2O_3 with a BET surface area of $12.4 \, m^2 \, g^{-1}$ according to data sheet provided by company. Catalyst was crushed to $1.2 \, mm \times 1.2 \, mm$ size prior to use. To examine the influence of gas treatments for spent catalysts, they were pretreated for 1 h with at $100 \, ml \, min^{-1}$ flow rate of air or hydrogen at three different temperatures (200, 400, and $600 \, °C$, respectively). In addition, a 0.1N solution of four different kinds of acids was also used to pretreat the spent catalysts (oxalic acid ($C_2H_2O_4$), citric acid ($C_6H_8O_7$), acetic acid (CH_3COOH), nitric acid (HNO_3)). The acid treatments were performed in a 100 ml Erlenmeyer flask. In each experiment, 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 firstly washed with deionized water until the pH of the solution reached 7 and thereafter dried at $120 \, °C$ for 24 h.

2.2. Characterization of catalysts

The Brunauer Emmett Teller (BET) surface areas of the spent catalyst (parent) and the pretreated samples were determined by nitrogen adsorption at $-196 \, °C$ using a Micromeritics ASAP 2020 analyzer. Prior to sorption analysis, all the samples were degassed under vacuum (5×10^{-3} mmHg) for 6 h at $150 \, °C$. The crystal structures of 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. The samples used were investigated in the 2θ range of 20–90° at a scanning speed of $70° \, h^{-1}$. To determine the elemental compositions of the spent and its pretreated catalysts, inductively coupled plasma atomic emission spectroscopy (ICP) was employed using a Perkin-Elmer OPTIMA 4300DV. Before the analysis, the samples were prepared using microwave assisted acid (a mixture of HCl and HNO_3) digestion method. The surfaces of the samples were studied using a Bio-Rad FTS 60A Fourier transform infrared spectrophotometer (FTIR). Grazing angle-FTIR was performed under a nitrogen purge and spectra were recorded from 400 to $4000 \, cm^{-1}$. Temperature programmed reduction (TPR) used a ChemBET 3000 setup. The gas mixture (10% H_2 and 90% He) was passed through the catalyst sample (0.4 g) at a rate of $60 \, ml \, min^{-1}$, while the temperature was increased up to $600 \, °C$ at a rate of $10 \, °C \, min^{-1}$.

2.3. Catalytic oxidation

The catalytic oxidations were carried out using a conventional fixed bed flow reactor as described in our previous work [23]. 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 consisted of a vertical tube of diameter 1.2 and 35 cm length, fitted within an electrical heating system controlled by a proportional integral derivative (PID) controller. In order to get an accurate measurement of the catalyst temperature, a K-type thermocouple was positioned in the catalyst bed. A catalyst sample of 1.0 g was loaded in the middle of the reactor supported by quartz wool. Toluene was purchased from Fisher and used without further treatment. An air stream bubbling through a saturator filled with toluene carried its vapor. For accurate and stable controlling the gas flow rates, mass flow controllers (UNIT Instrument, UFC-8100) were employed. The concentration of toluene was 1000 ppm, controlled by the temperature of the saturator and mixed with another air stream. The reactant flows were tuned to a gas hourly space velocity (GHSV) of $7500 \, h^{-1}$. All lines were heated sufficiently at $120 \, °C$ to prevent the adsorption and condensation of reactant and product in the tubes. Experimental data were collected after ensuring the steady state condition in each step.

The concentration of inlet and outlet gas stream was determined using a gas chromatograph, GC-14A model (Shimadzu) equipped with thermal conductivity detector (TCD). The chromatographic column used was composed of a 5% bentone-34 and 5%DNP/simalite (60–80 mesh, 3 mm $\Phi \times$ 3 m) for toluene analysis, and a porapak Q (50–80 mesh, 3 mm $\Phi \times$ 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, most experimental conditions produced only CO_2 and H_2O and other by-products were not detected. The conversion was calculated on the basis of toluene consumption.

3. Result and discussion

3.1. Influence of pretreatments

3.1.1. Effect of gas treatment

To examine the effect of gas treatment for the spent catalyst, air and hydrogen pretreatment methods were employed. The XRD and the BET surface area measurement were carried out to examine the properties of the gas treated samples. The XRD patterns of air treated spent catalysts (a) and hydrogen treated spent catalysts (b) at three different temperatures (200, 400 and 600 °C) are presented in Fig. 1. The XRD profiles of the air pretreated iron-based spent catalysts revealed the diffraction peaks only for Fe_2O_3 and Al_2O_3 phases, and there was no change in XRD profiles at three different pretreated temperatures. In contrast to the air pretreatment, the metallic iron diffraction peak appeared in the hydrogen pretreatment methods at temperatures in excess of 400 °C. Table 1 compares the BET surface areas of the air pretreated and the hydrogen pretreated spent catalysts. The results indicate that the air or hydrogen treatment has an insignificant effect on the BET surface areas of spent catalyst.

Fig. 2 exhibits light-off curves of toluene oxidation as a function of reaction temperature on the iron-based spent catalyst pretreated with air (a) and hydrogen (b) at different temperatures. The experimental results indicate that the activity of the pretreated samples is closely related to the treatment method. The conversion profiles for air pretreated samples shift to lower temperatures when the pretreatment temperature for the spent catalyst is raised from 200 to 400 °C. However, the profile shifts to a higher temperature when the pretreatment temperature of the spent catalyst is above 600 °C. For example, the reaction temperatures for T_{50} conversion (the value of the temperature when conversions approach 50%) of toluene are 295, 270 and 420 °C, respectively, compared to 307 °C for the parent. This experimen-
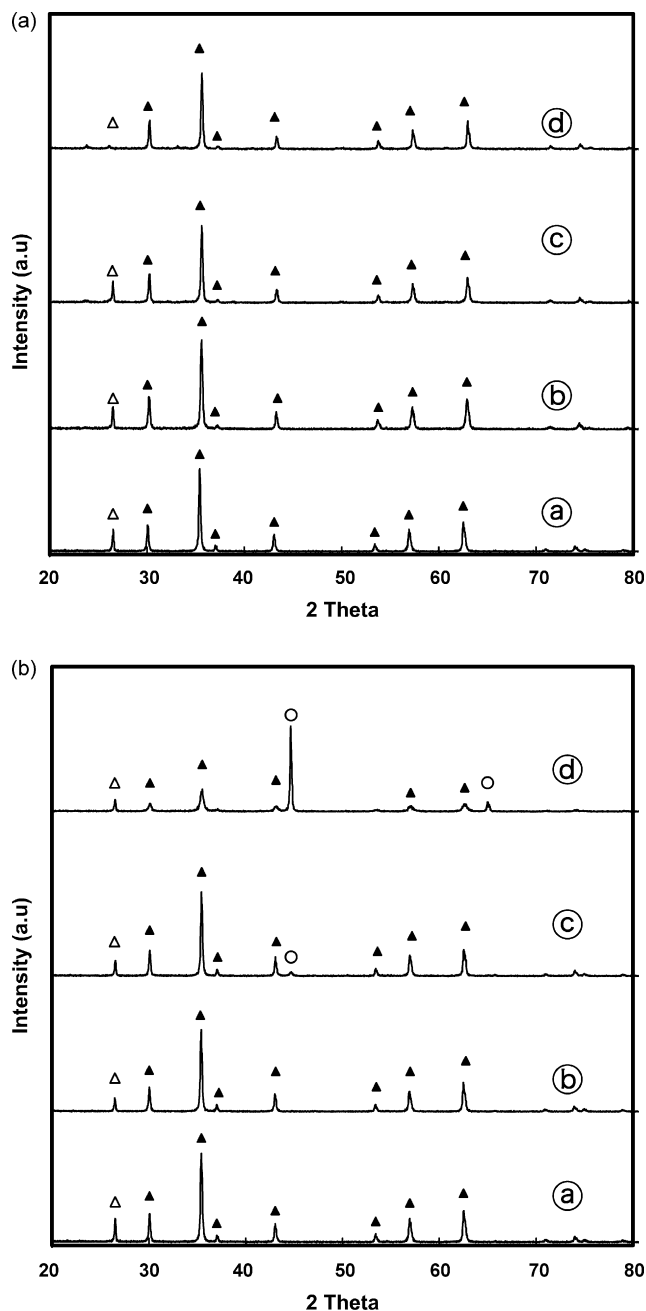

Fig. 1. XRD patterns of iron-based spent catalyst treated with air (a) and hydrogen (b). (▲) Fe_2O_3, (△) Al_2O_3, (O) Fe. (a) ⓐ Parent, ⓑ 200 °C, ⓒ 400 °C, and ⓓ 600 °C. (b) ⓐ Parent, ⓑ 200 °C, ⓒ 400 °C, and ⓓ 600 °C.

tal result reveals that the catalytic activity of the air pretreated spent catalyst is highly dependent on the pretreatment temperature. The order of catalytic activity for toluene oxidation was: 400 °C > 200 °C > 600 °C. These findings led us to conclude that the air pretreatment is efficient enough to regenerate the iron-based spent catalyst at the optimum pretreatment temperature of 400 °C.

The conversion curves of toluene oxidation on the hydrogen treated catalysts are considerably different from the results of the air treated samples. The conversion profiles for the hydrogen treated samples shift to higher temperatures when the pretreat-

Table 1
BET surface area of iron-based spent catalyst (Fe–S) further to air (–A) or hydrogen (–H) pretreatment

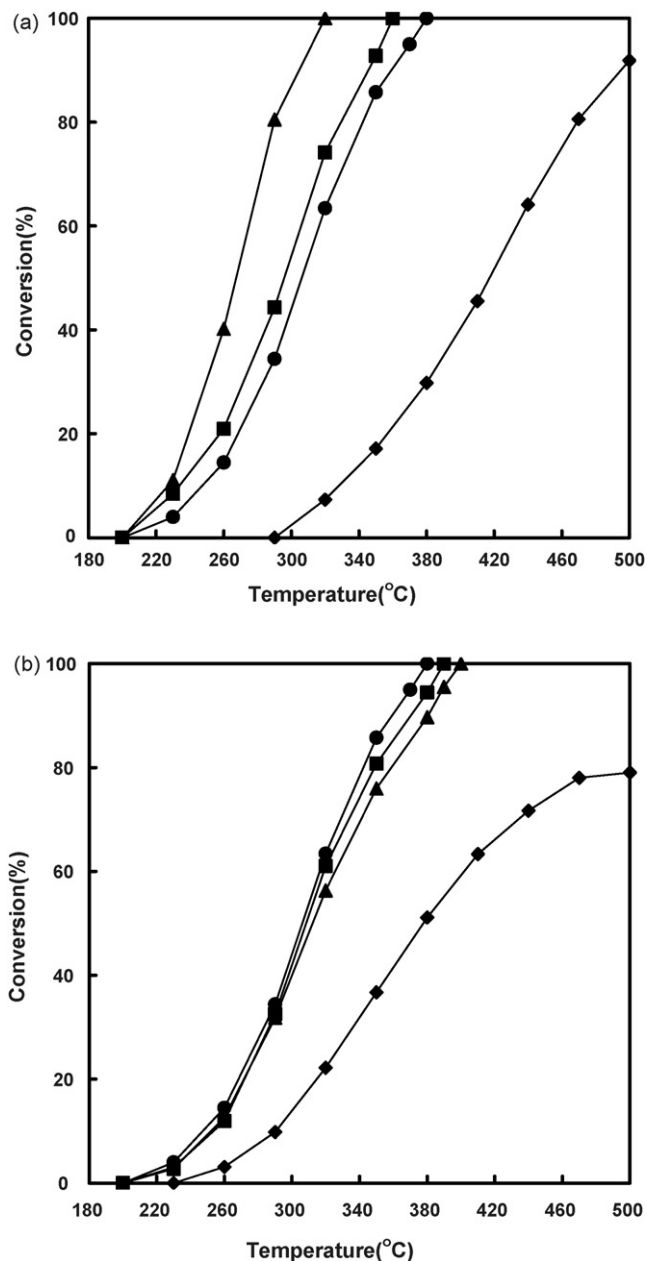| BET surface area ($m^2\,g^{-1}$)			
Air treatment		Hydrogen treatment	
Fe–S–A (200 °C)	12.5	Fe–S–H (200 °C)	12.4
Fe–S–A (400 °C)	13.1	Fe–S–H (400 °C)	12.7
Fe–S–A (600 °C)	12.9	Fe–S–H (600 °C)	12.6

Fig. 2. Conversion profiles of toluene oxidation on the air (a) and hydrogen (b) pretreated spent catalysts. (a) (●) Parent, (■) 200 °C, (▲) 400 °C, and (♦) 600 °C. (b) (●) Parent, (■) 200 °C, (▲) 400 °C, and (♦) 600 °C.

Fig. 3. XRD pattern of iron-based spent catalysts treated with different acids. (▲) Fe_2O_3, (△) Al_2O_3. ⓐ parent, ⓑ $C_2H_2O_4$, ⓒ CH_3COOH, ⓓ $C_6H_8O_7$, ⓔ HNO_3.

shown in Fig. 3. As shown Table 2, the acid treatment also has an insignificant effect on the BET surface areas of spent catalyst.

Fig. 4 shows the activity curves for the acid treated (0.1N of $C_2H_2O_4$, CH_3COOH, $C_6H_8O_7$ and HNO_3) spent catalysts. The toluene oxidation was initiated at about 210 °C on all the treated samples, and then the temperature was slowly increased up to 230 °C. The complete oxidation temperature of the oxalic acid treated sample was 270 °C which was considerably lower (50 °C) than that of the other treated catalysts. Based on T_{50}, the catalytic activity of acid treated samples was observed to decrease in the following order: $C_2H_2O_4$ (250 °C) > $C_6H_8O_7$ (276 °C) ≥ CH_3COOH (278 °C) ≥ HNO_3 (280 °C) > parent (307 °C). As a whole, after being pretreated with acid aqueous solution, the activity of modified spent catalysts increased significantly as compared to the spent catalyst. The oxalic acid treatment was superior to other acid treatment methods.

3.2. Physical properties of pretreated catalysts

The decrease of the catalyst activity is caused by poisoning of the active material [26]. The amounts of poisonous elements

Table 2
BET surface area of acid pretreated catalysts

	BET surface area ($m^2\,g^{-1}$)
0.1N HNO_3	13.8
0.1N CH_3COOH	13.3
0.1N $C_2H_2O_4$	14.6
0.1N $C_6H_8O_7$	13.1

ment temperature for the spent catalyst is raised from 200 to 600 °C. For example, the reaction temperatures T_{50} for the conversion of toluene are 310, 315 and 386 °C, respectively. The catalytic activity of toluene oxidation over the hydrogen treated samples is in the order of 200 °C > 400 °C > 600 °C. These findings strongly support that the hydrogen pretreatment produces the metallic Fe form and negatively affects the toluene oxidation.

3.1.2. Effect of acid treatment

All the acid treated samples exhibited only the Fe_2O_3 and Al_2O_3 crystalline phases, and no changes were observed in the peak sizes that show the intensities of the pretreated catalysts as
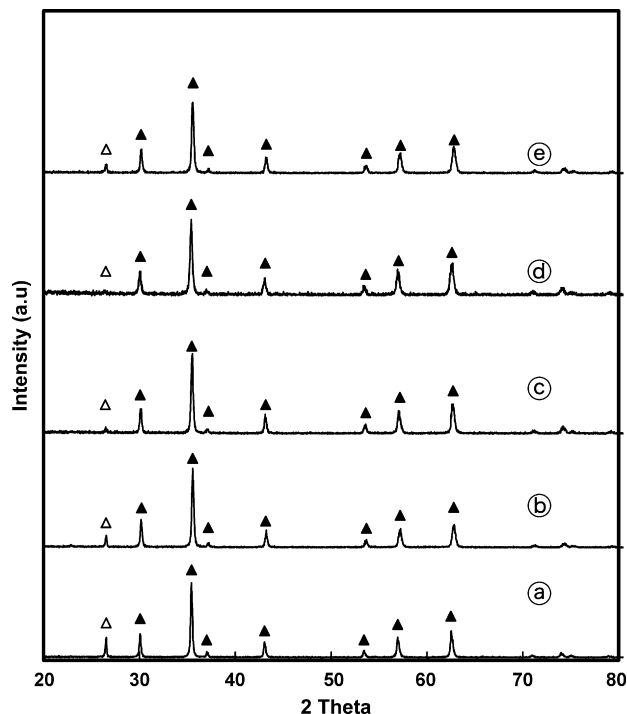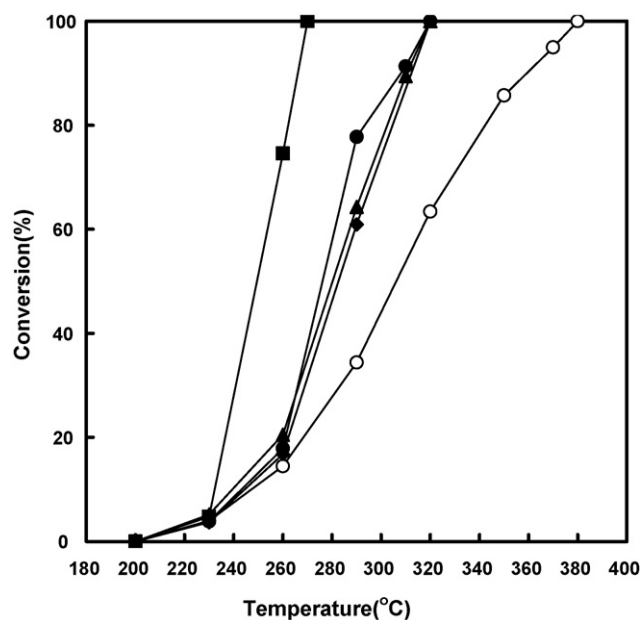
Fig. 4. Conversion profiles of toluene oxidation on acid pretreated spent catalysts. (○) Parent, (■) $C_2H_2O_4$, (▲) CH_3COOH, (●) $C_6H_8O_7$, and (♦) HNO_3.

other than the original compositions of catalyst were determined by ICP measurements and the ratios of metal to iron are presented in Table 3. The regeneration method may lead to a reduction in poisonous materials such as Si, P, S and Pb. As can be seen in Table 3, even though air, hydrogen or acid pretreatment reduces the amounts of Si, P, S and Pb in the spent catalyst, each activity of the pretreated samples is observed to be insignificantly associated with the amounts of Si, P, S and Pb.

In order to check the influence of pretreatment methods on the TPR pattern, the TPR experiments were performed on the spent catalysts pretreated with air, hydrogen and acids. Fig. 5(a–c) represents the TPR patterns of air, hydrogen and acid treated spent catalysts, respectively. As can be seen Fig. 5, TPR patterns strongly depend on the treatment methods. The starting reduction temperature (SRT), the temperature of TPR peak (TTP), and the end of reduction temperature (ERT) values of all the

Table 3
ICP analyses on the spent catalyst and the samples pretreated with air, hydrogen and acid

| Treatment	Si/Fe ($\times 10^3$)	P/Fe ($\times 10^3$)	S/Fe ($\times 10^3$)	Zn/Fe ($\times 10^3$)	Pb/Fe ($\times 10^3$)
Parent	0.961	0.097	0.201	0.931	0.128
Fe–S–A (200 °C)	0.960	0.091	0.197	0.942	0.128
Fe–S–A (400 °C)	0.932	0.093	0.187	0.928	0.126
Fe–S–A (600 °C)	0.933	0.087	0.125	0.930	0.116
Fe–S–H (200 °C)	0.962	0.094	0.195	0.929	0.127
Fe–S–H (400 °C)	0.971	0.092	0.168	0.927	0.123
Fe–S–H (600 °C)	0.969	0.091	0.161	0.926	0.117
0.1N CH_3COOH	0.862	0.083	0.161	0.925	0.104
0.1N HNO_3	0.851	0.078	0.146	0.923	0.095
0.1N $C_2H_2O_4$	0.829	0.069	0.121	0.930	0.101
0.1N $C_6H_8O_7$	0.821	0.064	0.154	0.926	0.105
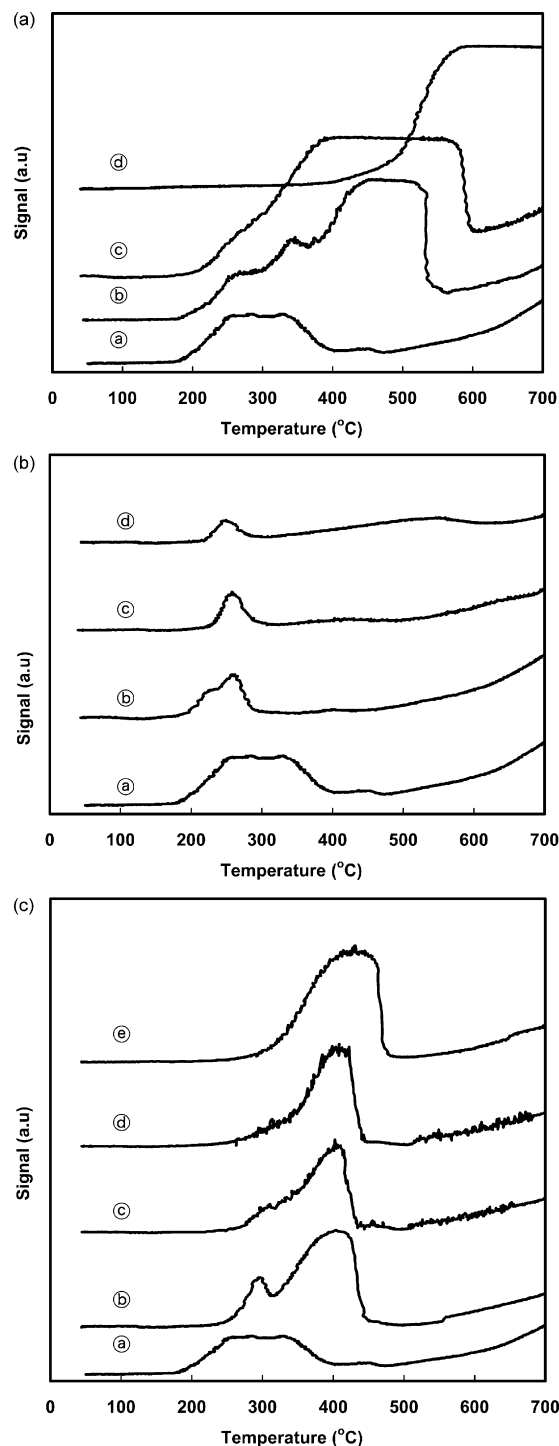
Fig. 5. TPR profiles of air (a), hydrogen (b) and acid (c) pretreated spent catalysts. (a) ⓐ Parent, ⓑ 200 °C, ⓒ 400 °C, ⓓ 600 °C. (b) ⓐ Parent, ⓑ 200 °C, ⓒ 400 °C, ⓓ 600 °C. (c) ⓐ Parent, ⓑ $C_2H_2O_4$, ⓒ CH_3COOH, ⓓ $C_6H_8O_7$, ⓔ HNO_3.

pretreated spent catalysts are summarized in Table 4. In the case of air pretreatment, SRTs of the pretreated spent catalysts at 200 and 400 °C are 164 and 165 °C, respectively, and they are almost similar to the spent catalyst. However, that of the spent catalyst pretreated at 600 °C considerably increased to 400 °C. The TTP value of the spent catalyst is 250 °C, and the sample pretreated

Table 4
TPR data of iron-based spent and its pretreated catalysts

Catalyst	Starting reduction temperature (°C)	Temperature of TPR peak (°C)	End of reduction temperature (°C)
Parent	164	250	415
Air treatment			
Fe–S–A (200 °C)	164	253[a], 345[b], 440[c]	550
Fe–S–A (400 °C)	165	380	590
Fe–S–A (600 °C)	400	545	–
Hydrogen treatment			
Fe–S–H (200 °C)	164	265	310
Fe–S–H (400 °C)	217	264	310
Fe–S–H (600 °C)	217	253	310
Acid treatment			
$C_2H_2O_4$	240	298[a], 407[b]	468
$C_6H_8O_7$	240	410	468
CH_3COOH	240	407	468
HNO_3	240	407	485

[a] 1st peak.
[b] 2nd peak.
[c] 3rd peak.

at 200 °C shows three TTPs (253, 345, and 440 °C). The samples pretreated at 400 and 600 °C show the 380 and 545 °C TTP values, respectively. The ERT of the spent catalyst is 415 °C, and those of the samples pretreated at 200, 400 and 600 °C are 550, 590 and ≫640 °C, respectively. In addition, the intensity of the TPR peak according to treatment temperature was also observed in the order of 600 °C > 400 °C > 200 °C > parent. The reduction temperature shifts to a higher temperature and the increment in the amount of hydrogen consumed with respect to the increasing pretreatment temperature may mean a decrease of oxygen mobility (an increase in the strength of the Fe–O bonds) and an increase in the amount of available oxygen on the catalyst, respectively. Therefore, the results indicate that conferring the highest activity to the iron-based spent catalyst is obtained when pretreating at 400 °C; the catalytic activity of toluene oxidation seems to be correlated with both the oxygen mobility [27] and the amount of available oxygen. In other words the higher the oxygen mobility and the amount of available oxygen on the catalyst, the higher the catalytic activity. In the case of hydrogen pretreatment, the increasing pretreatment temperature resulted in decreasing the intensity of the TPR peak, subsequently, decreasing the catalytic activity. In the case of acid treatment, SRTs of all the acid pretreated samples are the same (240 °C) and are higher than that of the spent catalyst (164 °C). The TTPs of the spent catalyst pretreated with citric acid, acetic acid, and nitric acid are the same (407 °C); however, the sample pretreated with oxalic acid shows two TTPs (298 and 407 °C). The ERTs of the spent catalyst pretreated with oxalic acid, citric acid and acetic acid are the same (468 °C), and that of the sample pretreated with nitric acid is 485 °C. In addition, the acid pretreatment resulted in considerably increasing the intensity of the TPR peak. Especially, the TPR profile of the spent catalyst pretreated with oxalic acid presented a shoulder which appeared on the low temperature (298 °C) and a main peak (407 °C). Therefore, the results indicate that the catalytic activity of toluene oxidation seems to be correlated with the

shoulder peak, conferring its highest activity of the oxalic acid treated sample.

The FTIR spectrums of the acid treated samples are shown in Fig. 6. Fig. 6 exhibits the following features: (i) the broad band at 3458 cm^{-1} represents an OH stretch; (ii) the band at 1687 cm^{-1} is indicative of the carbonyl in the oxalate molecule; (iii) the two bands at 1319 and 1363 cm^{-1} correspond to the symmetric and asymmetric stretching of the C–C–O$^-$ structure in the oxalate molecule [28]. This result indicates that the FeC_2O_4 species is formed on the spent catalyst pretreated with oxalic acid [28,29]. Accordingly, the shoulder peak of the TPR of the oxalic acid treated sample is related to the possible reduction of FeC_2O_4
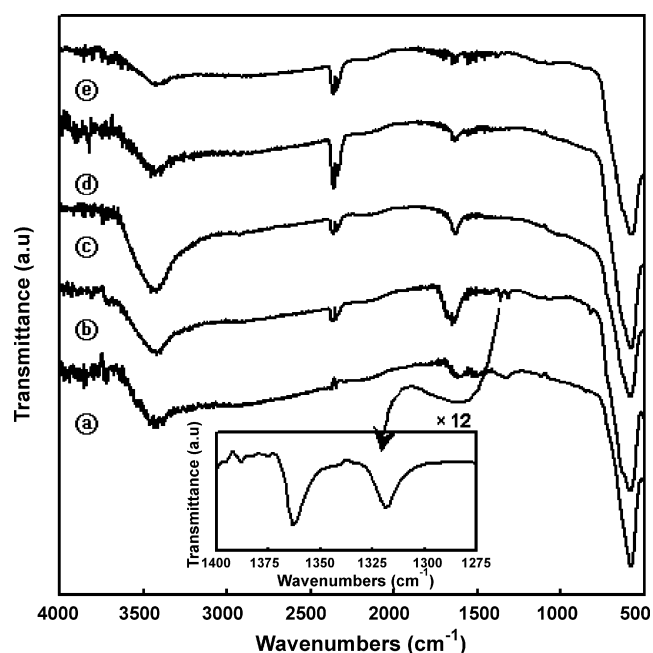

Fig. 6. FIPR spectra of different acid pretreated spent catalysts. (a) Parent, (b) $C_2H_2O_4$, (c) CH_3COOH, (d) $C_6H_8O_7$, (e) HNO_3.

species. It seems to have a great beneficial effect on the catalytic activity.

4. Conclusion

The catalytic oxidation of toluene over the iron-based spent catalyst treated with air, hydrogen or acid was carried out to explore the possibility of recycling spent catalyst. The results obtained from the catalytic activity of toluene revealed that the pretreated spent catalyst has a good VOC-conversion ability despite the reduction in relative value as a commercial catalyst. Moreover, the activities of the pretreated spent catalyst were highly dependent on the treatment method. The air or acid pretreated catalysts showed high conversions. However, in the case of hydrogen pretreated samples, the conversions significantly decreased compared to that of the parent catalyst because of the formation of metallic species.

Based on the light-off curve study results, the air and acid pretreatment methods were chosen as a means of regenerating the spent catalyst. In the case of air pretreatment, the TPR results indicate that the catalytic activity was correlated with both the oxygen mobility and the amount of available oxygen. Consequently, the catalytic activity sequence that followed the air pretreatment temperatures was $400\,^{\circ}C > 200\,^{\circ}C > parent > 600\,^{\circ}C$. In addition, the TPR results showed that the acid pretreatment increased the amount of available oxygen, and consequently the catalytic activity increased. Especially, the oxalic acid pretreatment proved itself to be the best method for regenerating the iron-based spent catalysts probably because of the formation of FeC_2O_4 species.

Acknowledgement

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