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Regeneration of Spent Catalysts with Ozone

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***Abstract*—**This study investigates the in-situ regeneration of deactivated Pt-Pd catalyst in a laboratory-scale catalysis reactor. Different regeneration conditions are tested and the activity and characteristics of regenerated catalysts are analyzed. Experimental results show that the conversion efficiencies of C_3H_6 by different regenerated Pt-Pd catalysts were significantly improved from 77%, 55% and 41% to 86%, 98% and 99%, respectively. The best regeneration conditions was 52ppm ozone, 500°C, and 10min. Regeneration temperature has more influences than ozone concentration and regeneration time. With the comparisons of characteristics of deactivated catalyst and regenerated catalyst, the major poison species (carbon, metals, chloride, and sulfate) on the spent catalysts can be effectively removed by ozone regeneration.

***Keywords*—**Catalyst, deactivated, ozone, regeneration.

I. Introduction

ALONG with the fast development and wide application of catalysis technology, more and more catalysts are used in many industrial processes. As the catalysts are deactivated or poisoned after periods of operation, they are discarded as spent catalysts. The amounts of different spent catalysts are increased year by year. These spent catalysts usually contain many valuable metals their characteristics are varied depended on the catalysis processes. Nowadays the major treatment methods of the spent catalysts in Taiwan are recovering the precious metals by metallurgy processes or direct reuse them as the construction materials. These methods not only waste the valuable resources, but also consume more energy. If the spent catalysts can be regenerated and activated effectively, they can be reused with higher economic benefits [1]-[3].

The spent catalysts can be regenerated or reactivated by different physical, chemical and thermal methods [4]-[8]. Most spent catalysts are regenerated off-site, the catalysis reactors and processes have to stop for disassembling off the deactivated catalysts and transport them to the regeneration factory. This way is inconvenient and delays the continuous operation of industrial processes. On the contrary, the in-situ regeneration of deactivated catalysts is more convenient and attractive. They are carried out by heating or injecting hot steam, hydrogen, oxygen, and different oxidants, reductants, or organic solvents into the catalysis reactor [9]-[12]. There are few studies investigating the in-situ regeneration of deactivated catalysts. The regeneration efficiency of different methods and catalysts as well as the effects of different operation conditions need to further explorations.

This study investigates the in-situ regeneration of deactivated Pt-Pd catalyst in a laboratory-scale catalysis reactor. The commercial Pt-Pd catalysts are used for the removals of volatile organic compounds (VOCs) in the air pollution control processes of organic solvent industries and plastics industries. Different regeneration conditions are tested and the activity and characteristics of regenerated catalysts are analyzed.

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II. Experimental Processes

A. Regeneration Method

The Pt-Pd catalysts supported on honeycomb ceramics were used to perform the deactivation experiments with different poisons (ash, SO_2, and HCl). The characteristics of spent catalysts were observed and analyzed before regeneration experiments. The samples for catalyst regeneration were taken from the deactivated catalysts and the weight of each sample was 2 gram. The regeneration of deactivated catalysts was carried out by ozone oxidation method. Each sample was put into the catalysis reactor and in-situ regenerated by injecting ozone into the flowing gas. The effects of different ozone concentrations (17, 38, and 52ppm), different temperatures (300, 400, and 500°C) and different regeneration times (10, 20, and 30mins) were tested and investigated.

TABLE I
Regeneration Conditions for Spent Catalysts

Run No.	Deactivated Catalysts	Ozone Concentration (ppm)	Temperature (°C)	Time (min)
O_3-1	Cat-30	38	300	30
O_3-2	Cat-30	17	400	20
O_3-3	Cat-30	52	500	10
O_3-4	Cat-60	38	300	30
O_3-5	Cat-60	17	400	20
O_3-6	Cat-60	52	500	10
O_3-7	Cat-90	38	300	30
O_3-8	Cat-90	17	400	20
O_3-9	Cat-90	52	500	10

B. Catalyst Analysis and Activity Test

The physical and chemical characteristics of deactivated and regenerated catalysts were analyzed and compared. The Brunauer–Emmett–Teller (BET) surface area and pore size diameter of the catalysts were measured at 77K by the gravimetric methods with a vacuum microbalance (Micromeritics: Gemini 2360). The surface structure and the accumulation of contaminants on the surface of catalysts were observed by a scanning electron microscope (SEM, TOPCON:

ABT-150S). The compositions and relative amounts of elements on the surface of catalysts were determined by an energy dispersive spectroscopy (EDS, LINK: exLII) with a Kevex superdry detector. An X-ray powder diffractometer (XRPD, SIEMENS: D5000) with a Cu Kα radiation was used to identify the crystalline species on the catalysts.

A catalysis reactor was set up to measure the activity of deactivated and regenerated catalysts. The experimental equipments are composed of pure gas cylinders (C_3H_6 and air), mass flow meters, a quartz reaction tube, an electric heater, and a programmable temperature controller. An on-line FID analyzer of VOCs (Thermo Scientific, TVA-1000B) and a NDIR analyzer of flue gas (HORIBA, PG-250) were used to continuously monitor the concentrations of C_3H_6, CO, O_2, CO_2, and NO in the effluent. The total flow rate and concentration of C_3H_6 gas were controlled at 1.03l/min and 800ppm, respectively. The reaction temperature was controlled at 400 ^oC.

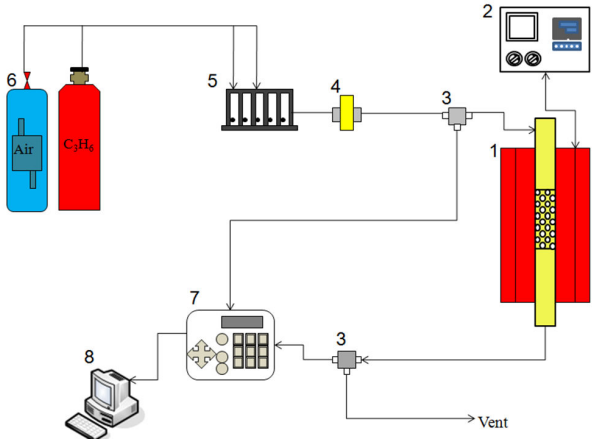


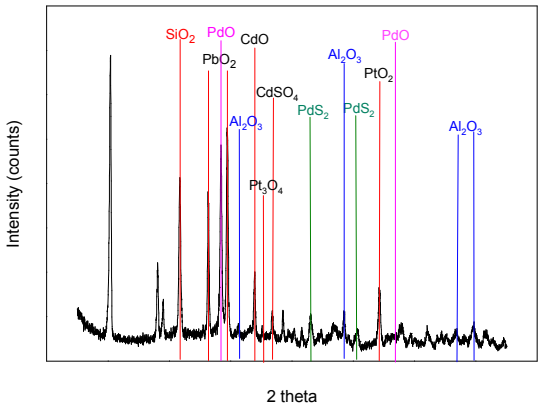
Fig. 1 Catalyst regeneration and activity test system. (1) Catalytic reactor, (2) Temperature controller, (3) Three way valve, (4) Mixer, (5) Gas flow meter, (6) Gas cylinders, (7) THCs analyzer, (8) Data Log system

III. Results and Discussions

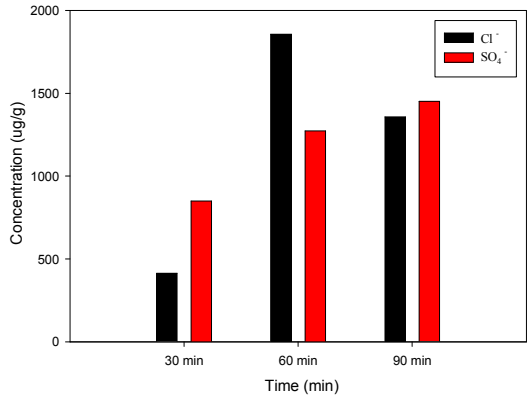
A. Characteristics of Spent Catalysts

The dominated species of active and deactivated metals on the spent catalysts were identified by high-resolution X-ray diffratometer (HRXRD). The HRXRD patterns of spent catalysts illustrated that the major poisoned species on the spent catalyst were PbO_2, CdO, and $CdSO_4$ with the specific peak at 2θ= 25.3°, 32.9°, and 37.5° respectively. The active metal Pd was poisoned by sulfur to form PdS_2 with specific peak at θ= 43.8° and 49.8°. The contents of chloride and sulfate on the spent catalyst were 414-1359μg/g and 850-1452μg/g respectively, depending on the reaction time.

With the comparisons of fresh catalyst and deactivated catalyst, the major elements which deactivated the Pt-Pd catalyst were Pb, Cd, and S. The active sites on the catalyst were obstructed by the poisoned species or the active metals were reacted with the poison elements to form metal species with less activity.



(a)



(b)

Fig. 2 HRXRD pattern (a) and Cl, S contents of spent catalyst (b)

B. Regeneration Efficiency of Spent Catalysts

The activities of Pt-Pd catalysts before and after ozone regeneration at different conditions were shown in Fig. 3. The conversion efficiency of C_3H_6 by spent catalyst (Cat-30) was 77%, and that was increased to 85-86% after ozone regeneration. The conversion efficiency of C_3H_6 by spent catalyst (Cat-60) was 55%, and that was improved to 95-98% after ozone regeneration. The conversion efficiency of C_3H_6 by spent catalyst (Cat-90) was 41%, and that was much improved to 96-99% after ozone regeneration. These results illustrate that the poison species (carbon, metals, chloride, and sulfate) on the spent catalysts can be effectively removed by ozone generation. The activities of regenerated catalysts were improved significantly.

As to the effects of different generation conditions, the results show that the best conversion efficiencies of regenerated Pt-Pd catalysts were occurred at the regeneration conditions of 52ppm ozone, 500^oC, and 10min. The second one is occurred at 17ppm ozone, 400^oC, and 20min, and the last one is occurred at 38ppm ozone, 300^oC, and 30min. Above results also indicate that regeneration temperature has more influences than ozone

concentration and regeneration time.

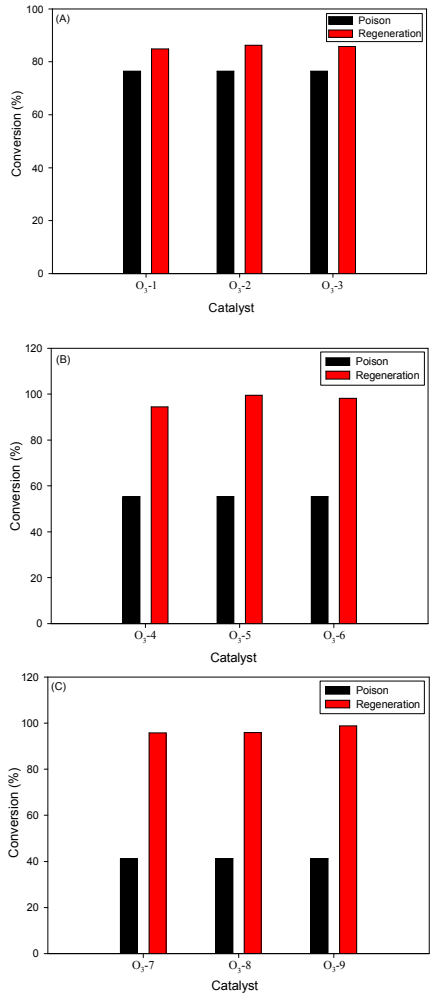


Fig. 3 Activities of Pt-Pd catalysts (a) before (b) and after (c) ozone regeneration at different conditions (The regeneration condition of each spent catalyst please refers to Table I)

C. Characteristics of Regenerated Catalysts

The major species of active metals on the regenerated catalysts were identified and compared with the spent catalysts. The HRXRD patterns of regenerated catalysts illustrated that the peak intensities of metal sulfides decreased and the peak intensities of active metal oxides increased after regeneration. The active metals were converted to PdO, PtO, and PtO_2. The contents of chloride and sulfate on the regenerated catalyst were decreased from 414-1359 to 20-88μg/g and from 850-1452μg/g to 40-130 respectively.

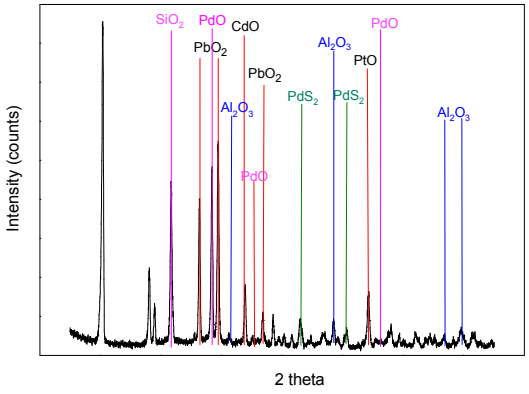


Fig. 4 HRXRD pattern of regenerated Pt-Pd catalyst

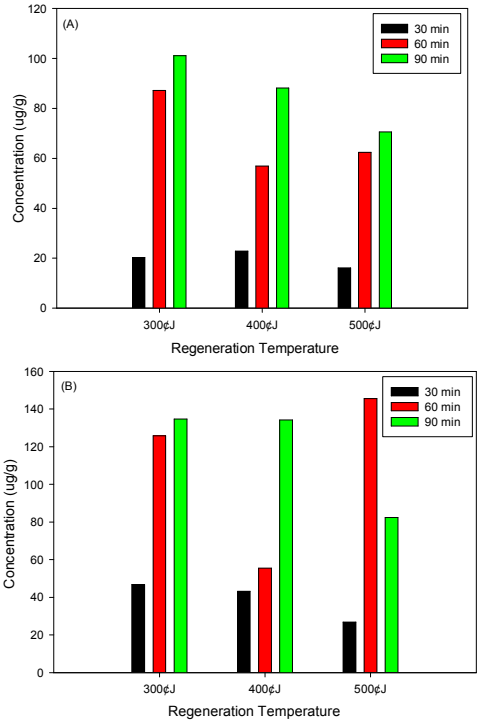


Fig. 5 Contents of Cl (a) and S (b) in regenerated Pt-Pd catalyst

IV. Conclusions

This study investigates the in-situ regeneration of spent Pt-Pd catalysts with ozone injection. The conversion efficiencies of C_3H_6 by different regenerated Pt-Pd catalysts were significantly improved from 77%, 55% and 41% to 86%, 98% and 99%, respectively.

The best regeneration conditions were 52ppm ozone, 500°C, and 10min. The second one is occurred at 17ppm ozone, 400°C, and 20min, and the last one is occurred at 38ppm ozone, 300°C, and 30min. Regeneration temperature has more influences than ozone concentration and regeneration time.

With the comparisons of characteristics of deactivated catalyst and regenerated catalyst, the major poison species

(carbon, metals, chloride, and sulfate) on the spent catalysts can be effectively removed by ozone regeneration.

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