

# EFFECTS OF DIFFERENT POISON FACTORS ON THE DEACTIVATION AND CHARACTERISTICS OF CATALYSTS

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**Abstract:** The activity of a commercial Pt-Pd catalyst for VOC decomposition and the effects of different poison factors on the deactivation of catalysts were investigated. The characteristics of fresh and reacted catalysts at different reaction conditions were also analyzed and compared. Experimental results showed that the conversion efficiency of C<sub>3</sub>H<sub>6</sub> by the catalysts were all up to 97.6% when the reaction condition was at 200-400°C without SO<sub>2</sub> gas. When the inflow gas contained 400ppm or 800ppm SO<sub>2</sub>, the conversion efficiency of C<sub>3</sub>H<sub>6</sub> significantly decreased to 72.4% and 11.9%, respectively. The poisoning effect of SO<sub>2</sub> on the catalysts was more obvious at low temperature (200°C). When the reaction temperature increased to over 300°C, the conversion efficiency of C<sub>3</sub>H<sub>6</sub> by the catalysts would increase up to 96%. From the BET, SEM, EDS, and XRD analysis results, the major poisoning mechanisms of the catalyst were carbon deposition, sintering, and the formation of metal sulfides. Moreover, the Taguchi Orthogonal Array method was utilized to evaluate the influences of different poison factors and find the best operating conditions for the catalysts. The results showed that the influence of different factors on the activity of catalysts flowed the sequence of reaction temperature, SO<sub>2</sub> concentration, and C<sub>3</sub>H<sub>6</sub> concentration. The best reaction condition for the Pt-Pd catalyst was 400°C, 0ppm SO<sub>2</sub>, and 1000ppm C<sub>3</sub>H<sub>6</sub>, where the conversion efficiency of C<sub>3</sub>H<sub>6</sub> was up to 99%.

**Keywords:** Catalyst, Deactivation, Poison Factor, Characteristic, Taguchi Orthogonal Array.

## I. INTRODUCTION

With the continuous development of industry and technology, various pollutants are generated and emitted, environmental pollution is becoming increasingly serious in many countries. Nevertheless, the raising public awareness of environmental protection and better living quality have pushed the regulations to be more rigorous. Therefore, many novel and efficient technologies for manufacturing and pollution control are continuously developed and utilized. One of the most popular technology is catalysis and many catalysts have been developed and widely applied in petroleum refining, chemical industry and pollution control.

As the catalysts are applied in the industrial manufacturing processes for periods of operation, they will be deactivated and must be renewed or regenerated. Catalyst deactivation means that the activity or selectivity of catalyst decreases over reaction time. The possible reasons cause the catalysts declined or deactivated include the thermal collapse, failure, or sintering due to the catalysts being operated at high temperatures, and the poisoning and fouling due to the inlet gas stream contained chemical substances such as sulfur, chloride, heavy metals and dust or ash, respectively [1-8]. Besides the activity and selectivity, the validity period of catalyst is also an important evaluation factor that should be taken into consideration. If the validity period of catalyst can be extended, the operation cost can be reduced and the economic value can be enhanced.

The deactivation and poisoning of a catalyst can be summarized as the following factors: fouling,

sintering, collapse, and poisoning. (1) Fouling: As the gas stream contained small particles, dust and pollutants, the surface and pores of catalyst may be covered and blocked. Moreover, some pollutants may also form the coke on the surface or in the pores of catalyst. The effective reaction sites and contact areas between catalysts and reactants were reduced, so the activity of catalysts was declined. (2) Sintering: Sintering is an irreversible physical change. Metals or ash on the catalyst surface would form temporary and movable molecular intermediate products at high temperature. The active metals dispersed on the supports would be slowly gathering and growing up. The active sites and effective surface area of the catalyst would decrease. The sintering rate was depended on the reaction temperature. The oxidizing environment is more likely to occur sintering than the reducing environment. (3) Collapse: The catalysts would be broken or collapsed as they subjected to hit, pressure, or overheating. The crystal structures of catalyst's supports would be destructed or changed due to overheating and water vapor. (4) Poisoning: Various chemical pollutants would react and adsorb on the surfaces of catalysts to cause the catalysts declined. The possible poisoning substances included phosphorus, sulfur, chlorine, lead, mercury, Sb, and Bi [9-17].

This study innovatively utilized the systematic approach method, Taguchi Orthogonal Array, to evaluate the effects of different poison factors on the activity and deactivation of catalysts. The results can provide useful information for practical applications of catalysts in many industrial processes and air pollution control system.

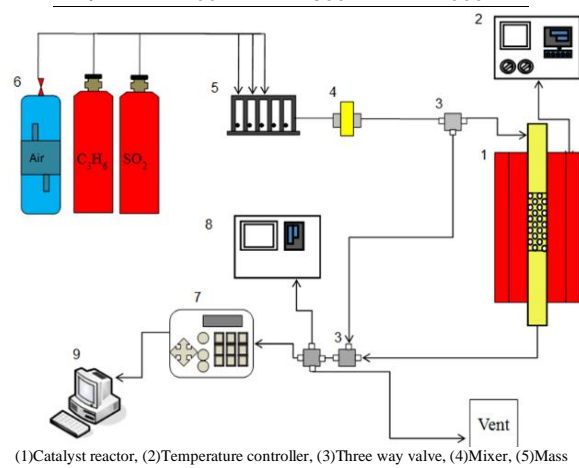
## II. DETAILS EXPERIMENTAL

### 2.1. Test Procedures of Catalyst Activity and Deactivation

The activity and deactivation of a commercial Pt-Pd catalyst were performed and evaluated in a laboratory scale catalyst reaction system. The experimental conditions of catalyst tests were arranged by using Taguchi orthogonal array method with three factors (reaction temperature,  $\text{SO}_2$  concentration, and  $\text{C}_3\text{H}_6$  concentration) and three levels (Table 1). Before the experiments, the commercial Pt-Pd catalyst was cut into a catalyst cuboid of 2 grams. Then it was put in the middle of a quartz tube and the tube inserted into the catalyst reactor. The schematic diagram of experimental apparatus was shown in Fig.1. The tests were carried out at different reaction conditions, including different reaction temperatures (200, 300, and 400°C), different concentrations of  $\text{SO}_2$  (0, 400, and 800 ppm), and different concentrations of  $\text{C}_3\text{H}_6$  (1000, 2000, 4000 ppm). The inflow gas contained  $\text{C}_3\text{H}_6$  or  $\text{SO}_2$  gases with air as the carrier gas. The flow rates and concentrations of the three gases were accurately controlled by mass flow meters. After the gases were well mixed in a mixing room, they were introduced into the catalyst reactor at constant pressure and constant flow rate. The total gas flow rate was 1.8L/min. Besides, the concentrations of  $\text{SO}_2$  and  $\text{C}_3\text{H}_6$  were intentionally set to be higher than those in normal conditions in order to accelerate and enhance the deactivation and poisoning reactions in the finite experimental time.

**Table 1: Experimental conditions of catalysts tests**

RUN	Temp.(°C)	$\text{SO}_2$ (ppm)	$\text{C}_3\text{H}_6$ (ppm)
1	200	0	1000
2	200	400	2000
3	200	800	4000
4	300	0	2000
5	300	400	4000
6	300	800	1000
7	400	0	4000
8	400	400	1000
9	400	800	2000



**Fig.1. Schematic diagram of experimental apparatus for catalyst tests**

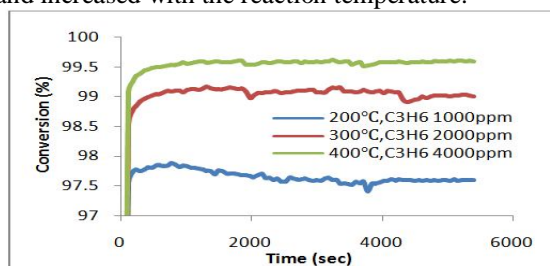
### 2.2. Catalyst Characteristics Analyses

The analysis items and methods for the characteristics of fresh and reacted catalysts were summarized as follows: (1) The specific surface area, pore volume, and pore size of catalysts were measured by a specific surface area analyzer by gas adsorption method. The system temperature was decreased to 77K with the aid of liquid nitrogen, and the amount of nitrogen gas by physical adsorption on the catalysts were measured. Finally, the BET (Brunauer-Emmett-Teller) formula was used to calculate the specific surface area, pore volume and pore size of catalysts. (2) Scanning Electron Microscope (SEM) was utilized to observe the surface morphology, pore distribution and the carbon deposition or sintering on the catalysts. Furthermore, the Energy Dispersion Spectrum (EDS) was used for qualitative and semi-quantitative analysis of the elements on the catalyst surface. (3) X-ray Powder Diffractometer (XRD) was used to identify the species of catalysts. The catalyst samples were pulverized in an agate mortar and pressed into test pieces for X-ray diffraction analysis. The scanning angle ( $2\theta$ ) ranged  $5^\circ \sim 75^\circ$  and the scanning step was  $4^\circ/\text{min}$ . In the excitation of incident rays, the specific diffraction spectrum of species was generated at different diffraction angles. The XRD patterns of catalysts were compared with the JCPDS (Joint Committee on Power Diffraction Standards) to identify the species on catalysts. (4) The compositions of elements (C, H, S, N) on the catalysts were analyzed by the Heraeus Elemental Analyzer.

## III. RESULTS AND DISCUSSION

### 3.1. Effect of different reaction temperature on the catalysts

The activity of catalyst was evaluated by the conversion efficiency of propylene at different reaction temperature (200, 300, 400 °C). As shown in Fig.2, the conversion efficiency of propylene increased with the rising temperature. At 200°C and 1000ppm propylene, the conversion efficiency of total hydrocarbons (THC) was only 97%. As the reaction temperature rose to 300°C, the conversion efficiency of total hydrocarbons increased to 99% and even to 99.6% at 400°C. Therefore, the conversion efficiency of VOC and the activity of catalyst were higher at high temperature and increased with the reaction temperature.



**Fig.2. Conversion efficiency of  $\text{C}_3\text{H}_6$  by catalyst at different reaction temperatures**

### 3.2. Effect of Different SO<sub>2</sub> concentration on the catalysts

The deactivation and poisoning tests of the catalysts were carried out at different concentrations of SO<sub>2</sub> (0, 400, and 800 ppm) and different temperature (200, 300, and 400°C). The results showed that SO<sub>2</sub> gas had significant impacts on the catalysts and the conversion efficiency of THCs declined quickly with increasing the concentration of SO<sub>2</sub> as the reaction temperature was 200°C (as shown in Fig. 3). Without SO<sub>2</sub>, the conversion efficiency of THCs was high as 99% and kept steady for a long time. However, the conversion efficiency of THCs decreased to 72.4% and reached steady after 45 minutes as the SO<sub>2</sub> concentration was 400 ppm. When the concentration of SO<sub>2</sub> increased to 800 ppm, the conversion efficiency of THCs declined quickly to be only 11.9% and reached steady after 15 minutes.

Therefore, the influences of SO<sub>2</sub> on the catalyst activity were increased with the concentration of SO<sub>2</sub>. SO<sub>2</sub> would cause the deactivation and poisoning of catalysts due to the generation of inactive metal sulfides. As compared the conversion efficiency of THCs at 200°C with those at 300°C and 400°C, the influence of SO<sub>2</sub> on the catalyst was found to decrease when the reaction temperature rose to over 300°C. The conversion efficiency of THCs at 300°C and 400°C were both improved and up to 96%. Therefore, high reaction temperature would alter the influence of SO<sub>2</sub> on catalysts by changing the condensation and accumulation of SO<sub>2</sub> on the catalysts as well as decreasing the reactions and formations of inactive metal sulfides. Moreover, the activity of catalyst was improved as the reaction temperature increased, as mentioned in section 3.1.

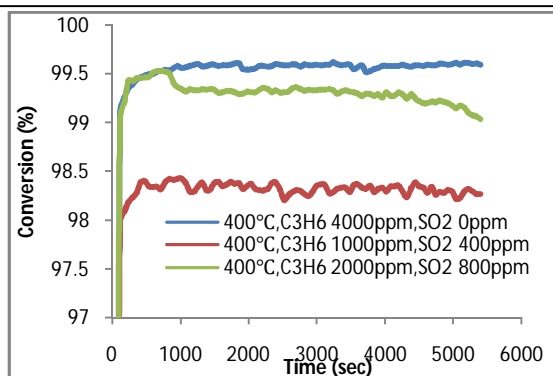
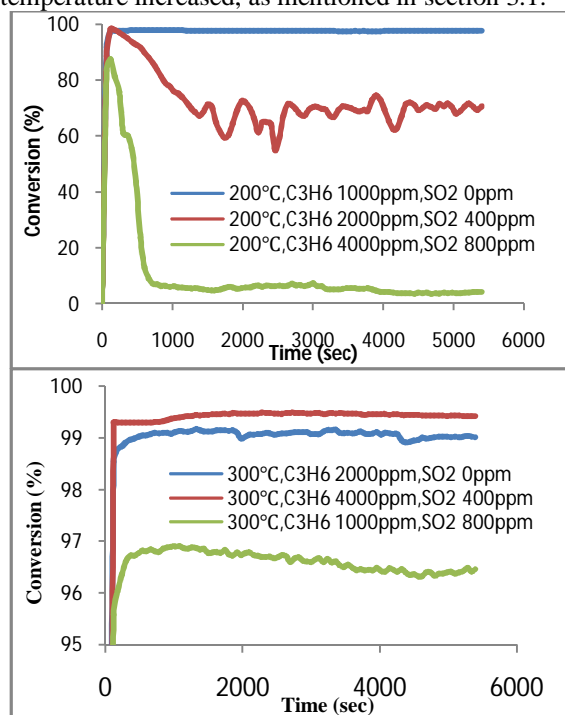


Fig.3. Conversion efficiency of C<sub>3</sub>H<sub>6</sub> by catalyst at different SO<sub>2</sub> concentrations

### 3.3. Characteristics of poisoned catalysts

The specific surface area and pore volume of the catalysts poisoned at constant concentration of SO<sub>2</sub> (800 ppm) but different temperatures (200, 300, 400°C) and different concentrations of C<sub>3</sub>H<sub>6</sub> (1000, 2000, and 4000 ppm) were analyzed and shown in Table 2. From the results, the specific surface area of catalyst poisoned at 200°C decreased to 29.25 m<sup>2</sup>/g from 38.55 m<sup>2</sup>/g and the pore volume decreased to 0.008 cm<sup>3</sup>/g from 0.012 cm<sup>3</sup>/g; the specific surface area of poisoned catalyst at 300°C decreased to 23.34 m<sup>2</sup>/g and the pore volume decreased to 0.006 cm<sup>3</sup>/g; the specific surface area of poisoned catalyst at 400°C decreased to 20.62 m<sup>2</sup>/g and the pore volume decreased to 0.005 cm<sup>3</sup>/g. From the above changes (Fig. 4), the specific surface area and the pore volume of catalysts would decrease with the temperature increased. The possible reason for the results might related to the carbon deposition and the sintering on the surface of catalysts.

Table 2: Surface characteristics of fresh and reacted catalysts

Catalysts	Specific Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Pore Diameter (Å)
VOC catalyst (fresh)	38.5451	0.0118	12.8901
Reacted catalyst (200°C, C <sub>3</sub> H <sub>6</sub> 1000ppm)	29.2520	0.007540	10.3110
Reacted catalyst (300°C, C <sub>3</sub> H <sub>6</sub> 2000ppm)	23.3393	0.005656	9.6930
Reacted catalyst (400°C, C <sub>3</sub> H <sub>6</sub> 4000ppm)	20.6184	0.005418	10.5113

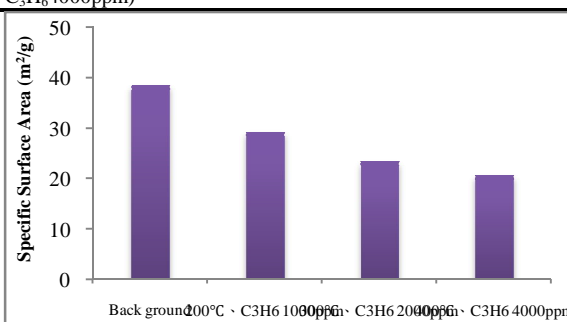


Fig.4. Specific surface areas of fresh and reacted catalysts at different reaction conditions

The XRD patterns of the poisoned catalysts at different conditions were shown in Fig.5. The major active species on the catalysts were  $\text{PtO}_2$  and  $\text{PdO}$ , and the major species of support were  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . During the catalytic tests, the active metals would react with  $\text{SO}_2$  to form sulfides which caused the poisoning and deactivation.  $\text{PdS}_2$  was found to be the major species of sulfides.

The SEM pictures and EDS analysis results of the catalysts reacted at different temperature without  $\text{SO}_2$  were shown in Fig.6 and Table 3. As the reaction temperature and the concentration of propylene increased, the weight percentage of carbon on the surface increased. Although the value of carbon was negative in Table 3(C), but Fig.5(C) showed the phenomenon of sintering on the surface of catalyst. Fig.7 and Table 4 show the SEM pictures and EDS analysis results of the catalysts poisoned at 400 ppm  $\text{SO}_2$ . There were many carbon deposited on the surface and the percentage of carbon increased. The changes of reaction temperature and  $\text{SO}_2$  concentration would decrease the conversion efficiency of THC's and increase carbon deposition. As the  $\text{SO}_2$  concentration increased to 800 ppm, the SEM pictures and EDS analysis results of the poisoned catalysts were shown in Fig.8 and Table 5. The surface morphology was rough and there were many particles on the surface. The carbon percentage in EDS analysis results was increased. Therefore, the carbon deposition on the catalysts was more serious if the catalyst reacted with  $\text{SO}_2$ . The carbon deposition was more obvious as the  $\text{SO}_2$  concentrations increased. Besides, Fig.8(b) and Fig.8(c) showed some parts of catalyst surface were smooth due to the sintering phenomenon.

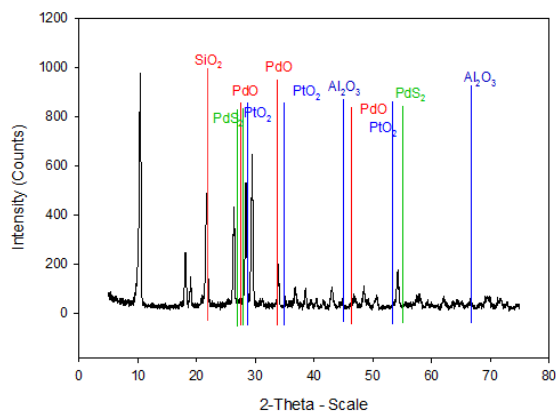
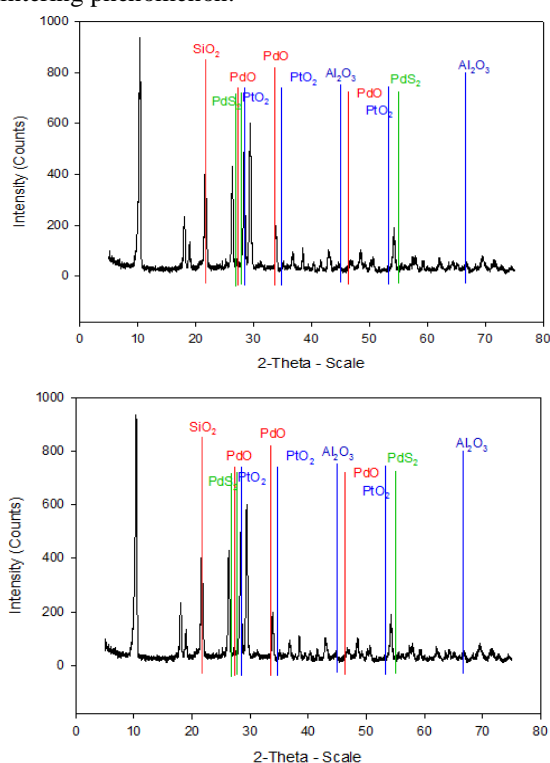


Fig.5. XRD patterns of reacted catalysts at different reaction conditions

(a) 200°C,  $\text{C}_3\text{H}_6$  400ppm,  $\text{SO}_2$  800ppm;  
 (b) 300°C,  $\text{C}_3\text{H}_6$  1000ppm,  $\text{SO}_2$  800ppm  
 (c) 400°C,  $\text{C}_3\text{H}_6$  2000ppm,  $\text{SO}_2$  800ppm

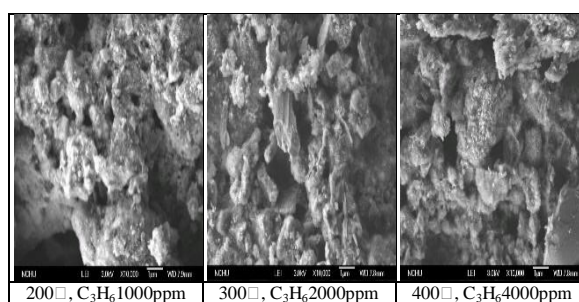


Fig.6. SEM pictures (10kX) of reacted catalyst at different conditions

Table 3: EDS analysis results of reacted catalysts at different conditions

Element	(A) 200°C, $\text{C}_3\text{H}_6$ 1000ppm		(B) 300°C, $\text{C}_3\text{H}_6$ 2000ppm		(C) 400°C, $\text{C}_3\text{H}_6$ 4000ppm	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
C K	1.43	2.12	5.03	9.81	-2.26	-3.88
O K	53.08	65.50	53.22	63.85	54.90	70.94
Al K	40.79	31.07	35.08	25.43	41.93	32.13
S K	0.75	0.49	0.04	0.03	0.02	0.01
Pd L	1.08	0.52	2.58	0.47	2.49	0.48
Pt M	2.87	0.30	4.05	0.41	2.91	0.31
Totals	100.0		100.0		100.0	

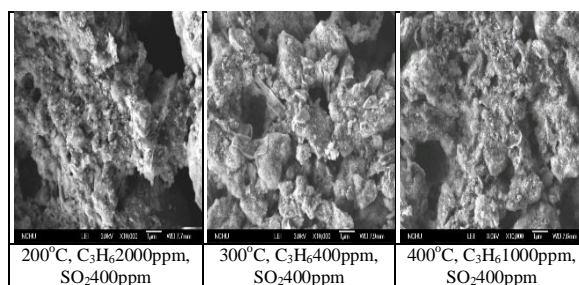
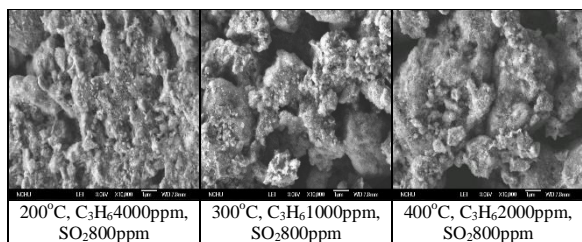


Fig.7. SEM pictures (10kX) of reacted catalyst at different conditions

**Table 4:EDS analysis results of reacted catalysts at different conditions**

Element	(A)200°C, C <sub>3</sub> H <sub>6</sub> 2000ppm, SO <sub>2</sub> 400 ppm		(B)300°C, C <sub>3</sub> H <sub>6</sub> 4000ppm, SO <sub>2</sub> 400 ppm		(C)400°C, C <sub>3</sub> H <sub>6</sub> 1000ppm, SO <sub>2</sub> 400 ppm	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
C K	8.59	13.20	-10.87	-19.65	3.21	5.20
O K	55.33	63.80	61.74	83.81	56.22	68.46
Al K	30.06	20.55	38.86	31.28	33.03	23.85
S K	3.84	2.21	5.57	3.77	3.07	1.86
Pd L	0.40	0.07	2.80	0.57	2.21	0.41
Pt M	1.77	0.17	1.89	0.21	2.26	0.23
Totals	100.0		100.0		100.0	

**Fig.8. SEM pictures (10kX) of reacted catalyst at different conditions****Table 5:EDS analysis results of reacted catalysts at different conditions**

Element	(A)200°C, C <sub>3</sub> H <sub>6</sub> 4000ppm, SO <sub>2</sub> 800 ppm		(B)300°C, C <sub>3</sub> H <sub>6</sub> 1000ppm, SO <sub>2</sub> 800 ppm		(C)400°C, C <sub>3</sub> H <sub>6</sub> 2000ppm, SO <sub>2</sub> 800 ppm	
	Weight %	Atomic %	Weight %	Atomic %	Weight %	Atomic %
C K	9.33	14.21	4.29	6.88	3.90	6.23
O K	54.78	62.68	55.98	67.36	55.60	66.78
Al K	30.83	20.92	31.07	22.17	33.93	24.17
S K	3.49	1.99	5.08	3.05	4.01	2.40
Pd L	0.53	0.09	2.31	0.42	2.02	0.36
Pt M	1.04	0.10	1.27	0.12	0.55	0.05
Totals	100.0		100.0		100.0	

### 3.4. Analysis of effect factors for catalyst activity

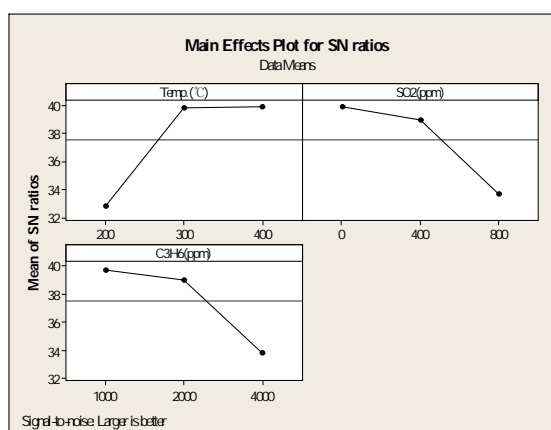
In order to evaluate the influences of different poison factors on the activity and deactivation of catalysts, MINITAB software was used to calculate the signal to noise ratios (S/N ratios) of different factors. The analysis results were shown in **Table 6**. The effects of different factors on the activity of catalyst followed the sequence of reaction temperature, concentration of SO<sub>2</sub>, and concentration of C<sub>3</sub>H<sub>6</sub>. From the experimental results, the conversion efficiency of THCs at different reaction temperature (200, 300, and 400°C) were quite different. Reaction temperature was the most important factor that influence the activity of catalyst for decomposing the total hydrocarbons.

**Fig. 9** showed the effects (S/N ratios) of different factorson the activity of catalysts. The results indicated that the best reaction conditions of catalysts for the conversion of C<sub>3</sub>H<sub>6</sub>were reaction temperature at 400°C and the concentrations of SO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub> was

0ppm and 1000ppm, respectively. The activity of catalysts for VOC conversion was increased with the rising reaction temperature, decreasing the concentration of SO<sub>2</sub>, and decreasing the concentration of C<sub>3</sub>H<sub>6</sub>.

**Table 6: S/N ratios of different factors on the activity of catalysts**

Level	Temp.(°C)	SO <sub>2</sub> (ppm)	C <sub>3</sub> H <sub>6</sub> (ppm)
1	32.83	39.89	39.78
2	39.85	39.00	39.02
3	39.92	33.71	33.80
Delta	7.09	6.18	5.98
Rank	1	2	3

**Fig.9. Effects (S/N ratios) of different factors on the activity of catalysts**

## CONCLUSIONS

The activity and deactivation of a commercial Pt-Pd catalyst were tested and studied at different reaction temperatures and concentrations of SO<sub>2</sub> and C<sub>3</sub>H<sub>6</sub>. Experimental results could be summarized as the following conclusions:

1. The VOC catalyst was easily poisoned by SO<sub>2</sub>, the conversion efficiency of THCs decreased with the rising concentrations of SO<sub>2</sub>. The conversion efficiency of THCs at 200 °C and 0, 400, 800ppm SO<sub>2</sub> was 97.64 %, 72.43 %, and 11.88%, respectively.
2. The influence and poisoning phenomenon of SO<sub>2</sub> on the catalysts was obvious at the condition of 200°C, 800ppm SO<sub>2</sub>, and 4000ppm C<sub>3</sub>H<sub>6</sub>.
3. When the reaction temperature was higher than 300°C, the activity of catalyst for C<sub>3</sub>H<sub>6</sub> conversion was increased. The best reaction temperature of the catalyst was 400°C. The conversion efficiency of THCs at 400°C could reach 98.3~99.55 %.
4. The Taguchi orthogonal array method was utilized to evaluate the influences of different factors on the activity of catalysts. From the results, the major factor influencing the activity of catalysts was reaction temperature, the second was the concentration of SO<sub>2</sub>, and the last was the concentration of C<sub>3</sub>H<sub>6</sub>.

5. The results of XRD analysis showed the major active metal species in the VOC catalyst were PdO and PtO<sub>2</sub>, which would react with SO<sub>2</sub> to form PdS<sub>2</sub> as the catalyst was poisoned.

## ACKNOWLEDGMENTS

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