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Low-temperature deactivation and oxidation state of Pd/γ-Al_2O_3 catalysts for total oxidation of *n*-hexane

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Abstract

Five weight percentage of Pd/γ-Al_2O_3 catalysts were used for the oxidation of *n*-hexane. The activities of catalysts were greatly influenced by pre-treatments. The hydrogen-treated catalysts mainly with metallic palladium showed higher oxidation activities than the air-treated catalysts mostly with palladium oxide, even if the palladium oxide was known to be the active phase for high-temperature combustion of methane. The XPS and XRD analyses suggested that the oxidation state of palladium did not change during oxidation reaction at lower temperature of 180 °C. The reduced catalysts whose initial activities at lower temperatures were higher than the oxidized catalysts showed a gradual deactivation. This kind of low-temperature deactivation was attributed to the deposit of carbonaceous intermediates, which were evidenced through temperature-programmed analyses such as TGA and TPO.

Keywords: VOCs; Palladium catalyst; Oxidation state; Deactivation

1. Introduction

The catalytic oxidation of hydrocarbon is becoming of increasing importance to control the emission of the volatile organic compounds (VOCs) [1]. The primary advantage of catalytic combustion processes is that they can be operated below the lower flammability limits of fuel oxidizer mixtures. In addition, catalytic oxidation leads to lower thermal NO_x emissions because the temperatures involved are relatively low. Catalysts typically used for VOC incineration are noble metals such as platinum or palladium, and many catalytic processes have been commercialized and successfully operated by using the noble metal catalysts [2–7].

Even if the palladium catalysts have been widely applied for the combustion process for VOC removal, the effects of oxidation state of palladium on the catalytic activity are still under debate [8–14]. It is now widely accepted that a Pd-based catalyst supported on alumina can readily undergo oxidation/reduction transformations and these transformations can lead to rapid changes in apparent catalyst activity. There is a general consensus that PdO/Al_2O_3 is more active than Pd/Al_2O_3 for high-temperature combustion of methane [9]. Recent studies, however, have shown that supported metallic palladium catalyst was more active than oxidized palladium for combustion of some VOCs such as methanol, ethanol, acetaldehyde, formic acid, and acetic acid [15].

In the present work, the oxidation of *n*-hexane was carried out over Pd/γ-Al_2O_3 catalysts. *n*-Hexane is one of the paraffinic VOCs difficult to oxidize and very often encountered in the work place environment [16]. The catalysts were treated with two different methods; one was hydrogen-treatment (reduced catalyst) and the other was air-treatment (oxidized catalyst). The effects of different pre-treatments on the catalytic activities were investigated by obtaining light-off curves. The change of oxidation state was analyzed with XPS, and the nature of low-temperature deactivation was investigated through TGA and TPO.

2. Experimental

2.1. Catalysts and characterization

Five weight percentage of Pd/γ-Al_2O_3 catalysts from Aldrich were used for this work. All the catalysts with particle size between 74 and 125 μm were calcined at 500 °C

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for 2 h before pre-treatment. The calcined catalysts were heated to a specific pre-treatment temperature at a rate of 5 °C/min using nitrogen, then they were held at this temperature for 1 h in a flow of gas (air or H_2). The catalysts treated with hydrogen at 500 °C for 1 h were denoted as Pd(R) and those with air at 500 °C for 1 h as Pd(O). The surface areas of the pre-treated catalysts were measured by nitrogen adsorption method with a Micromeritics ASAP 2010C. Before the measurement, each sample was degassed at 150 °C for 3–5 h in vacuum. Pore size distribution was calculated form the desorption branch of nitrogen adsorption isotherm using the Barrett–Joyner–Halenda (BJH) formula. CO chemisorption measurements at 35 °C were carried out using a Micromertics ASAP 2010C. Before the chemisorption experiment, the samples were reduced in situ at 350 °C for 2 h and then degassed for 1 h at the same temperature. The composition, BET surface areas, average pore size and CO chemisorption data were summarized in Table 1.

The crystal structures of catalysts were confirmed by powder X-ray diffraction pattern using monochromic Cu Kα radiation (Rigaku, D/MAX III). XPS data were obtained using a photoelectron spectrometer (VG Scientific, ESCALAB MK II) equipped with a magnesium anode (1253.6 eV). During data processing of the XPS spectra, binding energy (BE) values were referenced to the C 1s peak (284.6 eV). The curves were resolved using a Gaussian function and an appropriate combination of peak height, line-width and peak position.

2.2. Catalytic oxidation of n-hexane

The catalytic activities were measured in a fixed bed apparatus with a reaction feed of air stream containing 250 ppm of *n*-hexane. 0.1 g of catalyst was loaded in the reactor heated with an electric furnace, and the flow rate of gas mixture through the reactor was 180 cm^3/min. To obtain the light-off curves, the catalysts were pre-treated and then stabilized. Pre-treatment was performed at 500 °C for 1 h with air (50 cm^3/min) or H_2 (80 cm^3/min). Stabilization was achieved by letting the reaction proceed for 270 min at 160 °C. The conversion was measured after this period. Then, the temperature was increased by a step of 20 °C at a rate of 2 °C/min until complete combustion was obtained. Sampling was made after 30 min at each temperature.

The catalytic activities were also measured sequentially as function of the reaction time for Pd/γ-Al_2O_3 treated at three different conditions. First, the catalyst was treated with air at 500 °C for 1 h and cooled in air to the reaction temperature (Step A), and then the activity of this catalyst was investigated at this reaction temperature (T_R) for 5 h. Second, the catalyst was heated in nitrogen, treated with hydrogen at 500 °C for 1 h and cooled in nitrogen to the reaction temperature (Step B), and the activity was investigated at T_R for 5 h. Finally, this hydrogen-treated catalyst was re-treated with air by Step A and the activity was investigated. The product was analyzed by a gas chromatography (HP 6890 GC) equipped with FID (HP 624 capillary column for hydrocarbon) and TCD (Carboxen 1006 PLOT capillary column for CO, CO_2).

2.3. Temperature-programmed experiments

Temperature-programmed oxidation (TPO) of used catalysts was carried out with a PulseChemiSorb 2705 of Micromeritics. 0.04 g of catalyst was charged in the microreactor and the flow rate of gas mixture into the reactor was 40 cm^3/min. The samples were degassed at 100 °C for 2 h in helium. After the stabilization at 40 °C for another 1 h, temperature was raised to 600 °C at a rate of 2 °C/min under the flow of 5 vol.% O_2/He (50 cm^3/min). The desorbed CO_2 was analyzed by quadrupole mass spectrometer (VG Gaslab 300). TPO was also performed by thermogravimetric method using a Cahn-2000 balance with a stream of air (100 cm^3/min) for the catalysts before and after reaction to determine whether there had been an accumulation of reaction intermediates during the reaction. Before the measurement, each sample was degassed at 110 °C for 2 h with nitrogen.

3. Results and discussion

3.1. Catalytic activities of Pd(O) and Pd(R) catalysts

Fig. 1 shows the light-off curves of supported palladium catalysts for the oxidation of *n*-hexane. For all the catalysts, the hydrogen-treated catalysts [Pd(R)] were more active than the air-treated catalysts [Pd(O)] at lower reaction temperatures (<240 °C).

The oxidation states of palladium which should have been affected by pre-treatment were analyzed with XPS and XRD. In general, XPS peaks from oxidized and metallic state of Pd appear at 336.6 and 334.8 eV, respectively [17]. The broader Pd ($3d_{5/2}$) peak was fitted with two Gaussian functions each of which is characteristic of metallic Pd and PdO component, respectively (Fig. 2(a)). Palladium in the Pd(R)

Table 1
Phyisco-chemical properties of prepared catalysts

Catalyst[a]	BET area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (Å)	CO chemisorbed (cm^3/g_{cat})
Five weight percentage of Pd(O)/Al_2O_3	123	0.28	72	3.2
Five weight percentage of Pd(R)/Al_2O_3	122	0.29	74	1.8

[a] Calcined at 500 °C for 2 h.

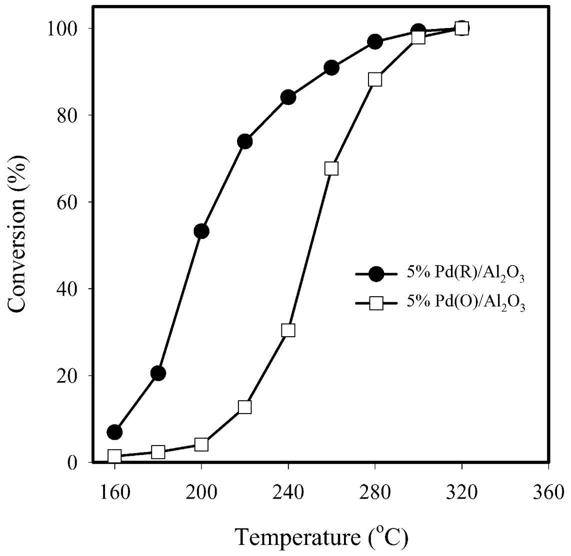

Fig. 1. Light-off curves of *n*-hexane over 5% Pd/Al_2O_3. Pd(O): treated with air at 500 °C for 1 h, Pd(R): treated with H_2 at 500 °C for 1 h.

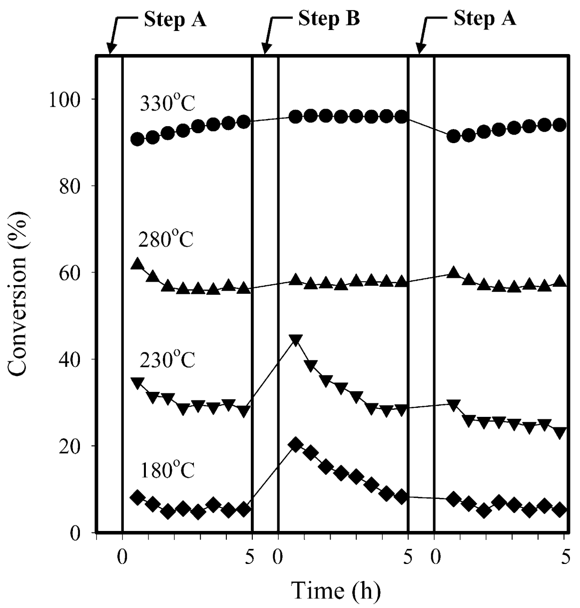

Fig. 3. Temporal conversion of *n*-hexane over 5% Pd/Al_2O_3 (Step A: air treatment at 500 °C, Step B: H_2 treatment at 500 °C).

catalysts treated with hydrogen were mainly metallic (Pd^0), and the palladium in the Pd(O) catalysts treated with air were mainly oxide (PdO). This result was also confirmed with XRD peaks (see Fig. 2(b)). The Pd(R) catalysts exhibited the reflections of γ-Al_2O_3 (JCPDS 10-0425) and peaks of Pd^0 at about 40°, 46° and 68° (JCPDS 46-1043), respectively. And Pd(O) catalysts exhibited the reflections of γ-Al_2O_3 and peaks of PdO at about 34°, 42°, 55°, 60°, and 72° (JCPDS 75-0584), respectively. Even though the XRD and XPS analyses indicated the presence of mixed Pd–PdO species, it should be noted that palladium catalysts treated with hydrogen were predominantly metallic form and that those treated with air were predominantly oxidized form. Therefore, metallic palladium (Pd^0) seems to be more active than oxidized palladium (PdO) for oxidation of *n*-hexane. These results are in good agreement with earlier reports from Cordi and Falconer [15], in which metallic Pd was more active than PdO for VOCs oxidation.

3.2. Sequential catalytic oxidation of *n*-hexane with different pre-treatments

Fig. 3 shows the temporal conversion of *n*-hexane at fixed temperatures. The conversions were higher at higher oxidation temperature as expected. Even if there were no differences in catalytic activity between Step A and Step B at higher temperatures (280 and 330 °C), initial activities of reduced catalysts by Step B were higher than those of oxi-

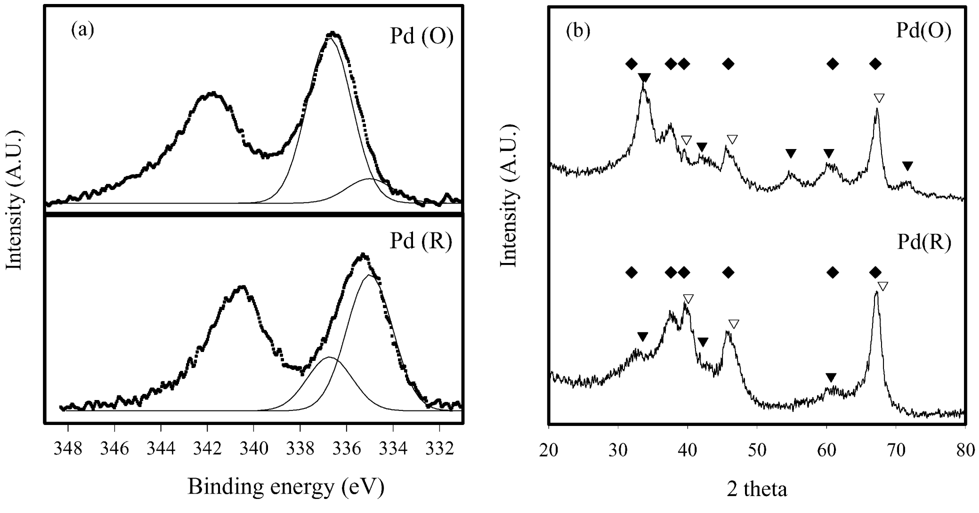

Fig. 2. (a) XPS spectra of Pd(O) and Pd(R) catalysts—334.8 eV: Pd^0 (metallic Pd), 336.6 eV: Pd^{2+}(PdO). (b) XRD patterns of Pd(O) and Pd(R) catalysts—◆ (γ-Al_2O_3), θ (PdO) and σ (Pd).

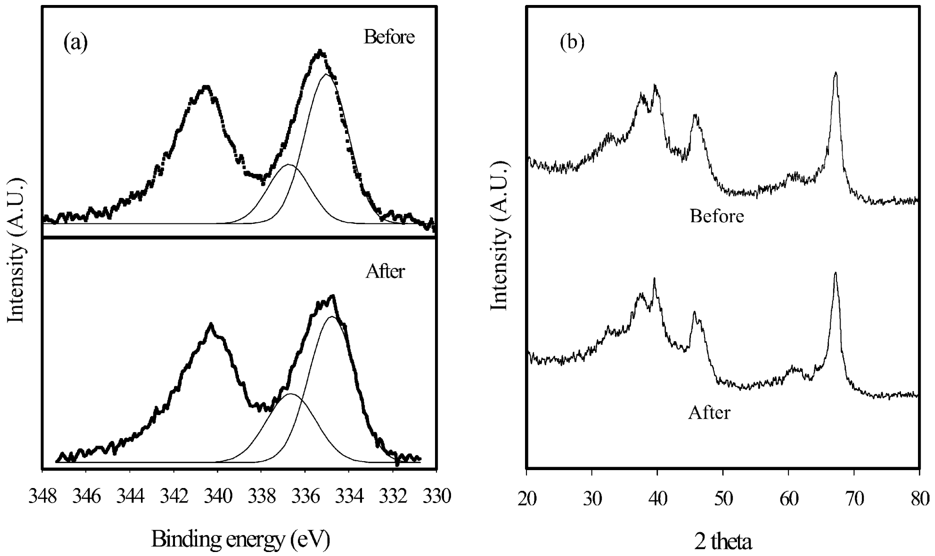

Fig. 4. (a) XPS spectra and (b) XRD patterns of Pd(R) catalysts before and after *n*-hexane oxidation at 180 °C, respectively.

dized form by Step A at the lower temperature of 180 and 230 °C. However, the activity of reduced catalysts gradually decreased during oxidation reaction at 180 and 230 °C and became equivalent to the activity of oxidized catalysts.

It was reported that the phase transformation of palladium (Pd ↔ PdO) might affect the activity of palladium catalyst for methane combustion [12,13,18] and that the decrease in activity of oxidized catalysts was ascribed to the transformation of $PdO \rightarrow Pd + 1/2\,O_2$ and metal sintering [19]. However, the oxidation state of palladium in Pd(R) catalyst remained unchanged after reaction at 180 °C for *n*-hexane, as confirmed by XRD and XPS (Fig. 4). The possible re-oxidation of reduced palladium may not be the origin of this kind of low-temperature deactivation.

On the contrary, it was observed that re-oxidation occurred after the reaction at higher temperature of 280 and 330 °C as shown in Fig. 5. The peak close to 336.6 eV is responsible for particulate (bulk) PdO. The highest binding energy of Pd (337.3 eV) can be attributed to deficiently coordinated PdO which is highly dispersed Pd in intimate contact with the alumina support. These re-oxidation at high-temperatures seemed to be the reason why there were no differences in catalytic activity between oxidized and reduced palladium in the reaction at high-temperatures which was shown in sequential experiments (Fig. 3).

It was suggested that this low-temperature deactivation was ascribed to the deposition of partially oxidized organics on the active sites [20]. Catalyst deactivation by VOCs, by their oxidation products, or by particulates in the gas is the

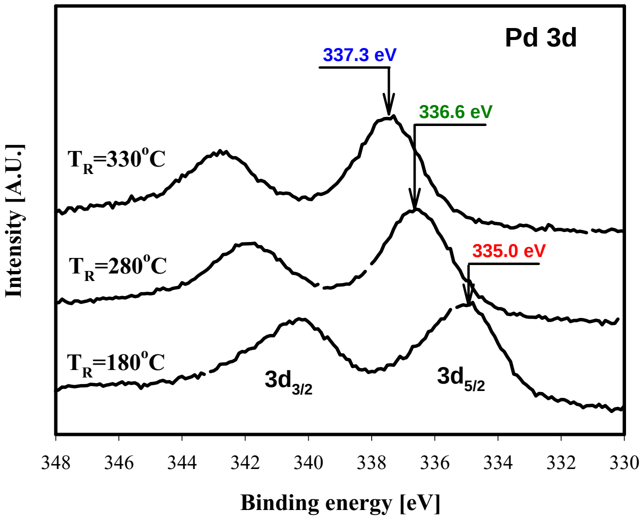

Fig. 5. XPS spectra of 5 wt.% Pd(R) catalysts after *n*-hexane oxidation at 180, 280 and 330 °C.

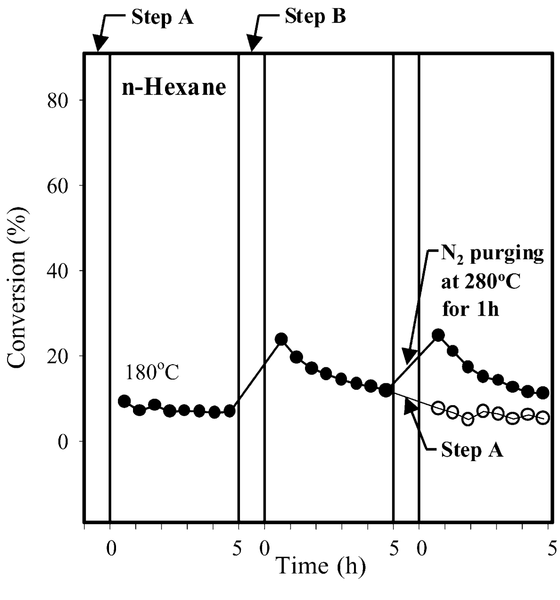

Fig. 6. Temporal conversion of *n*-hexane oxidation over 5% Pd/Al_2O_3 at 180 °C after purging with N_2 at 280 °C for 1 h (Step A: air treatment at 500 °C, Step B: H_2 treatment at 500 °C).

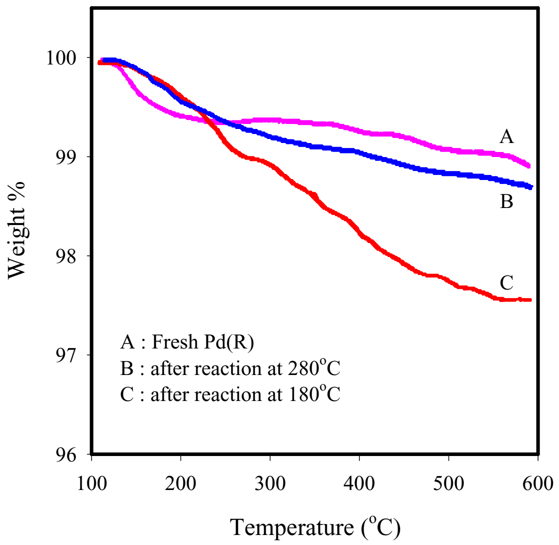

Fig. 7. TGA results of reduced Pd(R) catalysts by Step B before and after *n*-hexane oxidation at 180 and 280 °C, respectively.

main problem in the use of catalytic incineration [20–22]. After reaction at 180 °C over reduced palladium catalyst by Step B, the catalyst was purged continuously with inert nitrogen at 280 °C for 1 h and the activity was measured at 180 °C. It can be seen in Fig. 6 that the activity of the deactivated catalyst was recovered by the nitrogen purging. Fig. 7 shows the TGA results where the weight of catalyst after reaction at 180 °C for 5 h decreased more significantly than that at 280 °C. This weight decrease of used catalysts could be an evidence of the deposition of reaction intermediates during the low-temperature reaction. The temperature-programmed oxidation (TPO) of used catalysts in Fig. 8 showed that CO_2 was observed from the catalyst used at 180 °C, not from that used at 280 °C. The carbonaceous intermediates deposited during the low-temperature reaction at 180 °C must be oxidized to CO_2 during the TPO. Pd ↔ PdO equilibrium could be affected by carbonaceous deposits keeping the palladium in reduced state in case of low-temperature reaction at 180 °C.

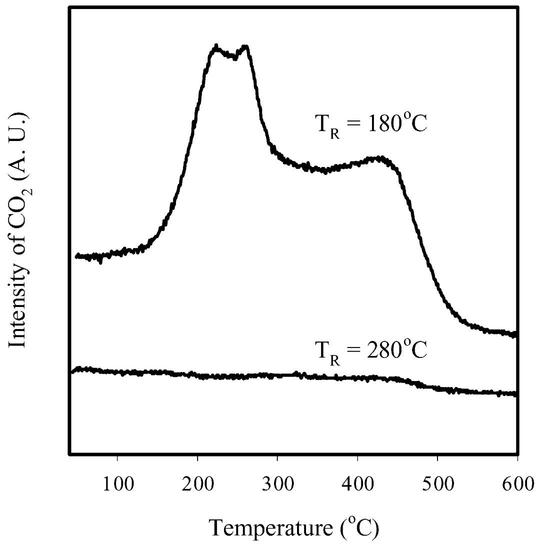

Fig. 8. TPO profiles of reduced Pd(R) catalysts by Step B after *n*-hexane oxidation at 180 and 280 °C, respectively.

4. Conclusion

The oxidations of *n*-hexane were carried out over 5 wt.% Pd/γ-Al_2O_3 catalysts. It was observed that hydrogen-treated catalysts (mainly with metallic Pd) were more active at low-temperatures than air-treated catalysts (mainly with palladium oxide), even if the palladium oxide is known to be an active phase for high-temperature combustion of methane. The activity of reduced palladium catalysts decreased gradually during oxidation reaction at lower temperatures and became equivalent to the activity of oxidized palladium catalysts. The oxidation state of palladium remained unchanged after reaction as confirmed by XRD and XPS. TPO and TGA analysis showed that the low-temperature deactivation was attributed to the deposition of carbonaceous intermediates during reaction.

Acknowledgements

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