

PROPANE COMBUSTION OVER Pt CATALYSTS SUPPORTED ON ZEOLITES

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Abstract. We prepared Pt catalysts supported on various zeolites, viz. H-Y, Na-Y, H-ferrierite, and H- β , and applied them to propane combustion. Pt/H-Y showed a higher catalytic activity than Pt/Na-Y although both catalysts exhibited a similar Pt dispersion. In the case of Pt/H- β and Pt/H-ferrierite, the catalytic activity increased but the Pt dispersion decreased with increasing SiO₂/Al₂O₃ molar ratios of H-zeolites.

1. INTRODUCTION

Catalytic combustion has recently been paid much attention due to its merits such as high combustion efficiency, wide operation window of fuel/air ratios and low emission levels of pollutants. Propane is an attractive fuel because it can be delivered as the liquefied petroleum gas (LPG) through a well-developed infrastructure. Until now, various catalysts have been applied to propane combustion and noble metal catalysts have been reported to show a higher catalytic performance than transition metal oxide catalysts [1]. Although supported Ru [2], Rh [3], and Pd [4-7] catalysts have been examined, Pt-based catalysts were proposed as the suitable ones for this reaction due to its high catalytic activity especially at low temperatures [4,8-16].

In the case of Pt-based catalysts, some factors such as the preparation methods, the pretreatment conditions and the promoters have been reported to affect the catalytic activity. The reduced Pt catalyst showed the higher propane combustion activity compared with the oxidized one [8]. The effect of a sup-

port on the propane combustion was also examined. Kim *et al.* reported that the Pt catalyst supported on zirconia-incorporated silica showed a high activity and stability [9]. Ishikawa *et al.* compared the Pt catalysts supported on different supports such as La₂O₃, CeO₂, Al₂O₃, SiO₂, TiO₂, SiO₂-MgO, SiO₂-ZnO, SiO₂-ZrO₂, SiO₂-Al₂O₃, SO₄-ZrO₂, and SO₄-Al₂O₃, and reported that there was a close correlation between the catalytic activity and the acid strength of a support [10]. Kobayashi *et al.* suggested that the superior catalytic activity of Pt/TiO₂-SiO₂-WO₃ compared with those of Pt/TiO₂-SiO₂ and Pt/TiO₂ was attributed to the superior oxidation-resistance of Pt due to the higher acidity of a support [11]. Garetto *et al.* carried out the comparison work among Pt supported on MgO, alumina, KL, HY, H-ZSM-5, and H-BEA and reported that the much higher catalytic activity was obtained over Pt catalysts supported on zeolites [12,13]. They proposed that an additional reaction pathway might occur over Pt/zeolites through increasing the density of adsorbed propane molecules drastically in the interfacial region [12]. Since zeolites have some advantages

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Table 1. Physicochemical properties and catalytic performance of the supported Pt catalysts.

Catalyst	SiO ₂ /Al ₂ O ₃ ratio	Pt content(%) ^a	Surface Area (m ² /g) ^b	Amount of CO chemisorbed (μmol/g _{cat.}) ^c	[CO]/[Pt] ^c	The average Pt particle size (nm) ^d	T _{100%} (°C)
Pt/H-β(25)	25	0.87	5.4×10 ²	11.8	0.26	N.D.	165
Pt/H-β(350)	350	0.85	7.2×10 ²	3.7	0.08	7.2	160
Pt/H-ferrierite(20)	20	0.86	2.5×10 ²	12.4	0.28	3.0	180
Pt/H-ferrierite(55)	55	0.83	3.4×10 ²	6.3	0.15	3.5	160
Pt/Na-Y(5.5)	5.5	0.84	8.9×10 ²	6.8	0.16	3.6	175
Pt/H-Y(5.1)	5.1	0.84	5.1×10 ²	7.8	0.18	N.D.	155

^aThe Pt content was determined with an inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

^bThe surface area of catalyst was calculated with the BET method based on the N₂ physisorption data at liquid N₂ temperature.

^cThe CO chemisorptions were measured at 300K in He.

^dThe average Pt particle size was measured by TEM images.

such as their high surface area, acidity and regular microporosity, they have been utilized as supports or catalysts by themselves. Although there are some previous works on the propane combustion over Pt catalysts supported on zeolites, further works on the effect of a cation in zeolites and SiO₂/Al₂O₃ molar ratios in zeolites on the catalytic activity for propane combustion are required. In this work, we prepared Pt catalysts supported on various zeolites by an incipient wetness impregnation method and applied them to propane combustion.

2. EXPERIMENTAL

As a support, Na-Y ($S_{\text{BET}} = 910 \text{ m}^2/\text{g}$) was purchased from Tosoh Chem. and the other zeolites such as H- β (25) ($S_{\text{BET}} = 500 \text{ m}^2/\text{g}$), H- β (350) ($S_{\text{BET}} = 690 \text{ m}^2/\text{g}$), H-ferrierite(20) ($S_{\text{BET}} = 390 \text{ m}^2/\text{g}$), H-ferrierite(55) ($S_{\text{BET}} = 380 \text{ m}^2/\text{g}$), and H-Y ($S_{\text{BET}} = 630 \text{ m}^2/\text{g}$) were purchased from Zeolyst. All of the zeolites were pretreated in air for 3 h at 600 °C. All of the catalysts were prepared with an incipient wetness method from an aqueous solution of Pt nitrate, Pt(NH₃)₄(NO₃)₂ (Aldrich). The impregnated catalysts were further dried in air at 120 °C overnight and all of the dried catalysts were calcined in a stream of 10 vol.% O₂/He for 3 h at 500 °C. All of the catalysts were reduced in H₂ for 1 h at 400 °C before a reaction. The physicochemical properties of the prepared catalysts are listed in Table 1.

The BET surface area was calculated from N₂ adsorption data that were obtained using Autosorb-1 apparatus (Quantachrome) at liquid N₂ temperature. Before the measurement, the sample was degassed in vacuum for 4 h at 200 °C.

The Pt content of the prepared samples was analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, JY-70 Plus, Jobin-Yvon).

The CO chemisorptions were conducted in an AutoChem 2910 unit (Micromeritics) equipped with a thermoconductivity detector (TCD) to measure CO consumption. A quartz U-tube reactor was generally loaded with 0.20 ~ 0.40 g of samples, and the catalyst was pretreated by reduction in H₂ at 400 °C for 1 h, then cooled to room temperature. The CO chemisorptions were carried out at 30 °C in 30 ml/min of He stream through a pulsed-chemisorptions technique, in which 500 ml pulses of CO were injected.

Bright-field transmission electron microscopy (TEM) images were obtained using a JEM-2100 F (JEOL) operated at 200 kV. The images were used to determine the particle size of Pt metal. The

samples were ground in a mortar to fine particles and then dispersed ultrasonically in methanol. The sample was deposited on a Cu grid covered by a holey carbon film.

The catalytic activity measurements were carried out in a small fixed bed reactor with catalysts that had been retained between 45 and 80 mesh sieves. For screening tests, a standard gas of 1 mol.% C₃H₈ and 5 mol.% O₂ balanced with He was fed to the reactor, in which 0.10 g of catalyst without diluents was contacted with a reactant gas at a flow rate of 0.100 NL/min, at atmospheric pressure. The steady-state catalytic activity was measured at each temperature.

The gaseous products in the effluent stream were separated in the packed column filled with Carbosphere and the capillary Poraplot Q column and analyzed by a gas chromatograph (HP5890A) with a TCD and a flame ionization detector (FID). The C₃H₈ conversion was calculated using the following formulas:

$$\text{C}_3\text{H}_8 \text{ conversion (\%)} = \frac{[\text{C}_3\text{H}_8]_{\text{in}} - [\text{C}_3\text{H}_8]_{\text{out}}}{[\text{C}_3\text{H}_8]_{\text{in}}} \times 100.$$

The water trap was installed before a gas chromatograph to remove all water vapor formed by reactions.

3. RESULTS AND DISCUSSION

The physicochemical properties of all of the catalysts are listed in Table 1. The Pt dispersion determined by CO chemisorption appeared to be affected by the SiO₂/Al₂O₃ molar ratio even in the zeolites with the same structure. The Pt dispersion of Pt/zeolites decreased with increasing SiO₂/Al₂O₃ molar ratio of zeolites as long as the crystalline structure is same. On the other hand, little change in Pt dispersion was found between Pt/Na-Y and Pt/H-Y.

The steady-state catalytic activities of all of the catalysts were measured at different temperatures and the temperatures achieving 100% conversion of propane (T_{100}) are listed in Table 1. T_{100} was determined to be 155, 160, 160, 165, 175, and 180 °C for Pt/H-Y(5.1), Pt/H- β (350), Pt/H-ferrierite(55), Pt/H- β (25), Pt/Na-Y(5.5), and Pt/H-ferrierite(20). Interestingly, the catalytic activity decreased with increasing Pt dispersion for the Pt catalyst supported on the zeolites with the same structure. Even though Pt/Na-Y(5.5) and Pt/H-Y(5.1) had comparable Pt dispersions, Pt/H-Y showed much higher catalytic activity than Pt/Na-Y.

The promotional effect of zeolites for the combustion was explained by the enhanced alkane con-

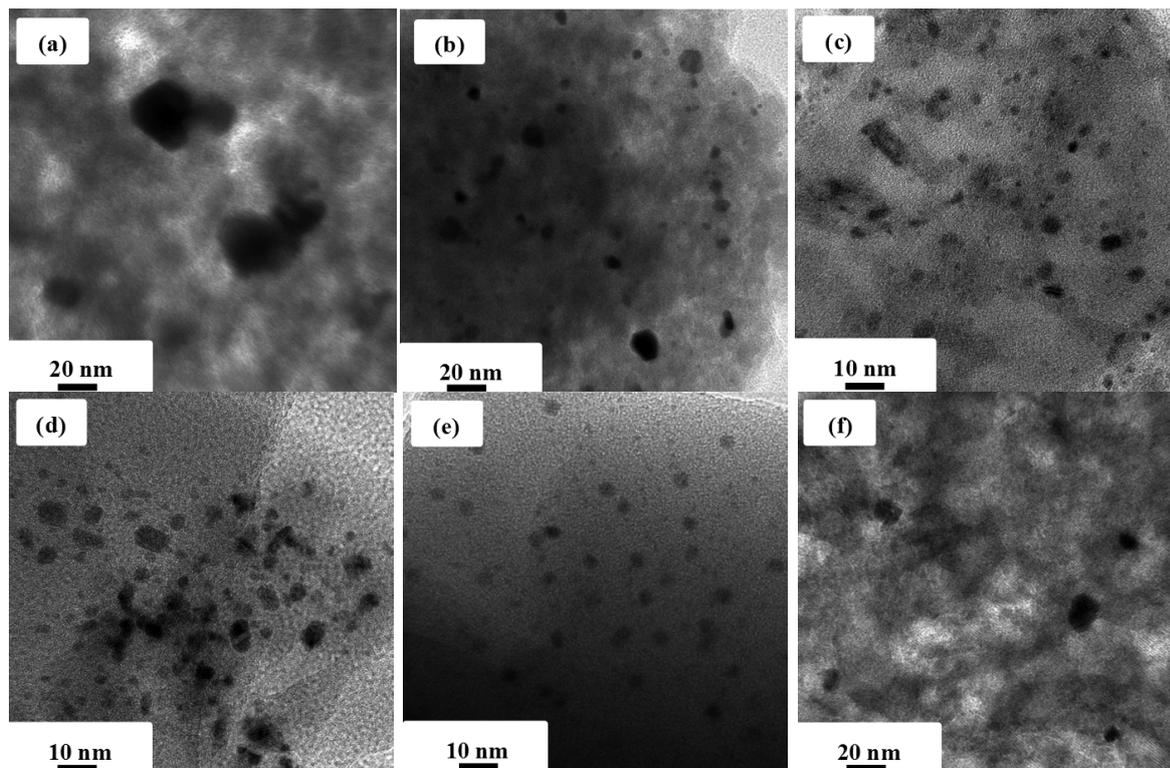


Fig. 1. The bright-field TEM images of (a) Pt/H- β (25), (b) Pt/H- β (350), (c) Pt/H-ferrierite(20), (d) Pt/H-ferrierite(55), (e) Pt/Na-Y(5.5) and (f) Pt/H-Y(5.1).

centration in zeolite cavities [13]. Among zeolites, Garetto *et al.* reported that Pt/H- β showed a much higher catalytic activity for the propane combustion than Pt/H-Y [12,13]. This seems to be inconsistent with our results in which Pt/H-Y(5.1) showed the slightly higher catalytic activity than Pt/H- β (350). However, it is worth mentioning that the Pt dispersion as well as the catalytic activity is strongly dependent on $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of zeolite with the same crystalline structure. Therefore, the catalytic activity over Pt/zeolite cannot be explained solely by the crystalline structure of zeolites. Yazawa *et al.* proposed that Pt would be chemically modified by the acid strength of support materials [14-16]. They also suggested that the oxidation-resistance of platinum increased with the acid strength of support materials during the propane combustion over Pt supported on non-zeolite supports [10,15]. On the other hand, Garetto *et al.* concluded that the acidic strength of support was not major factor to affect the catalytic activity for the propane combustion over Pt catalysts supported on zeolites [13]. However, no systematic work has been carried out for Pt catalysts supported on zeolites with different $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio. In the case of

Pt/H- β , the catalytic activity increased with increasing of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio from 25 to 350. This trend was also observed over Pt/H-ferrierite. It is generally accepted that the acid strength of zeolites increased with decreasing $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio. Therefore, we can say that the acid-strength is not the main factors to control the catalytic activity for Pt/zeolites. On the other hand, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio affected the Pt dispersion determined by CO chemisorption data and predominantly controlled the catalytic activity. The catalytic activity is inversely related to the Pt dispersion, which might be closely related to the oxidation-resistance of platinum because the smaller Pt particle can be oxidized easily than the larger Pt particle [17] and the metallic Pt is superior to the oxidized Pt for the oxidation reaction [8]. To determine the average particle size of Pt particles, TEM images were obtained for all of the Pt catalysts, as shown in Fig. 1. The average particle sizes of Pt metal in Pt/H- β (380), Pt/H-ferrierite(20), Pt/H-ferrierite(55) and Pt/Na-Y(5.1) were determined to be 3.1 ± 0.8 , 3.2 ± 0.7 , 8.0 ± 2.9 , and 8.7 ± 3.2 nm, respectively. In the cases of Pt/H- β (25) and Pt/H-Y(5.1), the average particle size

of Pt metal cannot be measured because of low resolution of Pt particles.

The negative effect of Na⁺ on the catalytic activity for the propane combustion cannot be explained by the change of Pt dispersion because there was no noticeable difference in Pt dispersion in between Pt/Na-Y and Pt/H-Y. Lewis acid sites and Bronsted acid sites are dominant in Na-Y and H-Y, respectively. The acid strength determined by NH₃-TPD is stronger for H-Y than for Na-Y. Besides surface acidity, Na⁺ can affect the chemical environment of Pt. Yoshida *et al.* examined the effect of promoters on the propane combustion and reported that the combustion activity was affected by the electronegativity of a promoter [14].

4. CONCLUSION

Pt/H-Y showed a higher catalytic activity for propane combustion than Pt/Na-Y although both catalysts exhibited a similar Pt dispersion based on CO chemisorptions data. In the case of Pt/H-b and Pt/H-ferrierite, the catalytic activity for propane combustion increased but the Pt dispersion determined by CO chemisorptions decreased with increasing SiO₂/Al₂O₃ molar ratios of H-zeolites.

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