Kinetic study of support effect in the propane combustion over platinum catalyst

Yoshiteru Yazawa *, Noriko Kagi, Shin-ichi Komai, Atsushi Satsuma, Yuichi Murakami and Tadashi Hattori

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan
E-mail: y_yazawa@mbox.media.nagoya-u.ac.jp

Received 21 September 2000; accepted 8 January 2001

The support effect on the low-temperature propane combustion over platinum catalysts was investigated by kinetic study. The catalytic activity of supported platinum catalysts varied with the support material, and $Pt/SiO_2–Al_2O_3$ showed much higher activity than Pt/ZrO_2, as already reported. The reaction order for oxygen was negative and that for propane was positive. The reaction order for propane and oxygen also greatly depended on the support material: Pt/ZrO_2 gave anomalous reaction orders, i.e., −2.9 for oxygen and 3.4 for propane. Further, oxidized Pt/ZrO_2 showed a long-term change of the catalytic activity with time-on-stream, compared with oxidized $Pt/SiO_2–Al_2O_3$. From these results, it was concluded that high catalytic activity of platinum on acidic support is attributed to high ability to maintain the metallic state of platinum with high oxidation-resistance and high reducibility of platinum oxide.

KEY WORDS: support effect; propane combustion; platinum catalyst

1. Introduction

The catalytic combustion of hydrocarbons is regarded as an important technology for energy production (e.g., gas turbines) and for emission control (e.g., automotive exhausts). It is widely accepted that supported noble metal catalysts, especially palladium and platinum catalysts, are the most active for catalytic combustion [1,2]. The property of supported noble metal catalysts is known to be significantly modified by the support materials in many catalytic reactions. There are some investigations of the support effect on the catalytic property for supported platinum catalysts for low-temperature catalytic combustion [3–6]. However, the support effect on the catalytic activity of platinum is not systematically investigated, and it is ambiguous what property of support material affects the property of supported platinum.

In the previous study, it was shown that high catalytic performance is attained by using $SO_4^{2-}–ZrO_2$, solid super acid, as a support material for propane combustion over supported platinum catalysts, which suggested the importance of the acid strength of support materials to control the catalytic activity [7]. Since platinum is deactivated by its oxidation in catalytic combustion [8,9], it was suggested that acidic support material prevent platinum from oxidation thus leading to higher catalytic activity. In this study, the effect of the support on the catalytic activity of supported platinum catalysts is investigated by kinetic study.

* To whom correspondence should be addressed.

2. Experimental

The support materials employed were $SiO_2–Al_2O_3$ and ZrO_2, listed in table 1. $SiO_2–Al_2O_3$ is the reference catalyst of the Catalysis Society of Japan (JRC-SAL-2) [10]. The preparation procedure of ZrO_2 is described elsewhere [7,11]. Support materials were sieved to 25–50 mesh. These support materials employed are stable under the reaction conditions. Supported platinum catalysts were prepared by impregnating support materials with an aqueous solution of $Pt(NO_2)_2(NH_3)_2$ followed by drying at 383 K for 12 h, calcining at 673 K for 3 h, and reducing at 623 K for 3 h in flowing H_2. The platinum loading was 0.5 wt% as platinum.

The BET surface area of the support oxide was measured through N_2 adsorption at liquid nitrogen temperature by using a conventional flow-type adsorption apparatus. The acid strength of the support was measured through the changes in color of Hammett indicators adsorbed on the support calcined at 773 K for 3 h.

The dispersion of platinum was measured through pulse-adsorption of CO in a flow of He [10,12]. The catalyst surface was cleaned up by heating in flowing oxygen at 673 K for 15 min, and then reduced in flowing hydrogen at 673 K for 15 min. The dispersion of platinum was calculated from

Table 1
The property of support materials and the dispersion of supported platinum.

Support	Surface area of support ($m^2\ g^{-1}$)	Acid strength of support (H_0)	Dispersion of supported Pt (%)
$SiO_2–Al_2O_3$	543	−11.99	43
ZrO_2	66	9.3	20

1011-372X/01/0400-0157$19.50/0

the total CO uptake by assuming that carbon monoxide was adsorbed on surface platinum atoms at a 1 : 1 stoichiometry.

The catalytic run was conducted by using a conventional flow reaction apparatus, detailed elsewhere [7,11]. The platinum catalysts were dispersed 1.0 g of fused alumina granules to prevent a local increase of temperature.

In the measurement of the temperature dependence of the catalytic activity, the catalyst was reduced in a flow of $N_2 + H_2$ mixture ($N_2/H_2 = 4$) at desired temperature for 2 h (623 K for Pt/SiO_2–Al_2O_3 and 823 K for Pt/ZrO_2), and then cooled to 473 K in flowing nitrogen. The reaction temperature was raised stepwise from 473 K. At each step, after the bed temperature attained the desired value, the reaction condition was kept for 30 min, and then the products were analyzed by gas chromatography. The concentrations of propane and oxygen in the reaction mixture were 0.25 and 1.25%, respectively. Nitrogen was used as a balance gas, and total flow rate was 200 ml/min.

In the measurement of the time course of the catalytic activity, the catalyst was pre-treated at 623 K for 2 h in the mixture of $N_2/H_2 = 4$ (reduction) or at 823 K for 2 h in the mixture of $N_2/O_2 = 4$ (oxidation), and then cooled to the desired temperature in flowing nitrogen. In experiments where kinetic data were acquired, the catalyst weight was chosen to keep propane conversion less than 20%.

3. Results and discussion

3.1. The temperature dependence of the catalytic activity

Figure 1 shows the catalytic activity of supported platinum catalysts as a function of reaction temperature. The catalytic activity of supported platinum depended on the support material, and Pt/SiO_2–Al_2O_3 showed much higher activity than Pt/ZrO_2. In propane combustion, Ishikawa et al. [7] showed that platinum on the support having stronger acid strength exhibits higher catalytic activity. In this study, a similar result was obtained, though our reaction conditions were different from theirs.

Apparent activation energies were obtained from this result within the propane conversion less than 20%. The activation energy on Pt/ZrO_2 was twice larger than that on Pt/SiO_2–Al_2O_3, that is, activation energies were 215 kJ/mol on Pt/ZrO_2 and 100 kJ/mol on Pt/SiO_2–Al_2O_3. The activation energy on Pt/ZrO_2 was obviously high compared with reported activation energies ranging from 71 to 105 kJ/mol [13–18]. This unusual activation energy may suggest that additional reactions, e.g., oxidation of supported platinum, occur over the Pt/ZrO_2 catalyst.

3.2. The time course of the catalytic activity

The time course of the catalytic activity was recorded in a propane-rich mixture and an oxygen-rich mixture after pre-reduction and pre-oxidation. In the case of Pt/SiO_2–Al_2O_3, shown in figures 2 (A) and (B), the activity of the reduced catalyst slightly decreased in both reaction conditions, whereas the activity of the pre-oxidized catalyst gradually increased with the reaction time. Steady activity was obtained within ca. 120 min in every cases. These results indicate that the oxidation state of platinum is varied in the reaction condition; the pre-reduced catalyst is gradually oxidized and in contrast, the pre-oxidized catalyst is gradually reduced. This is because the catalytic activity of supported platinum varies with its oxidation state; metallic platinum shows higher activity than oxidized platinum [8,9].

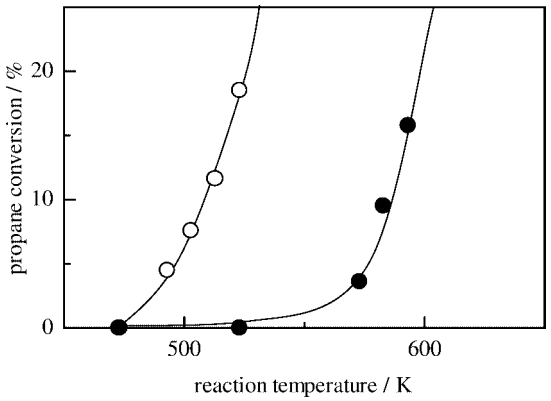

Figure 1. The activity of platinum catalysts supported on SiO_2–Al_2O_3 (○) and ZrO_2 (●).

In oxygen-rich mixture on Pt/ZrO_2, shown in figure 2(C), the activity of pre-oxidized catalyst did not change with time-on-stream, contrary to the case of Pt/SiO_2–Al_2O_3 (figure 2(A), open circle). On the other hand, in the case of the pre-reduced catalyst, the initial activity was higher than that after pre-oxidation, but gradually decreased and reached the steady activity which was the same as that of pre-oxidized catalyst. In propane-rich mixture on Pt/ZrO_2, shown in figure 2(D), the activity of the pre-reduced catalyst gradually increased when the catalyst was pre-reduced at the same temperature as Pt/SiO_2–Al_2O_3, i.e., at 623 K. The steady activity was obtained from the beginning of the reaction only when the catalyst was pre-reduced at 823 K. The activity after pre-oxidation continued increasing, and did not reach to the steady state even after 240 min of reaction. These peculiar behaviors indicate that the oxidized Pt/ZrO_2 is difficult to be reduced as compared with Pt/SiO_2–Al_2O_3.

3.3. Reaction orders

Figure 3 shows the reaction rate of propane combustion in the various reaction mixtures. The reaction rate depended both on the oxygen and propane partial pressure, and the logarithm of reaction rate had a curved relation with the logarithm of oxygen and propane partial pressure. The reaction orders, obtained by assuming a linear relation in the propane-rich and the oxygen-rich conditions, respectively, are shown in table 2. The reaction orders clearly depended both on the kind of support materials and the reaction mixture. The reaction order for propane varied in the region from 0.2 to 3.4, and that for oxygen varied

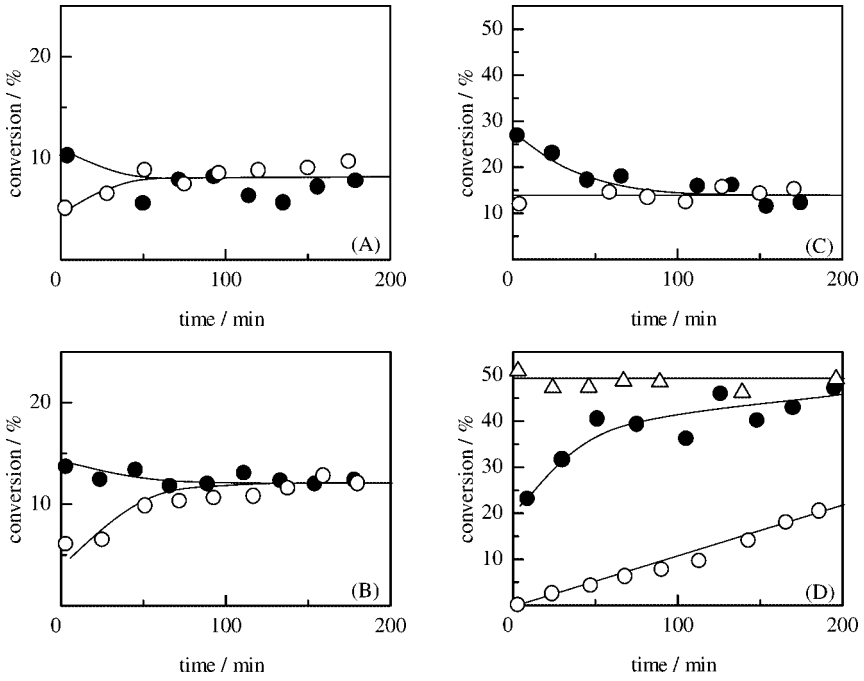

Figure 2. Time course of the activity of $Pt/SiO_2–Al_2O_3$ at 493 K in the oxygen-rich (C_3H_8 0.25%, O_2 3.0%) mixture (A) and in the propane-rich (C_3H_8 0.5%, O_2 1.25%) mixture (B), and that of Pt/ZrO_2 at 573 K in the oxygen-rich (C_3H_8 0.25%, O_2 3.0%) mixture (C) and in the propane-rich (C_3H_8 0.5%, O_2 1.25%) mixture (D). The platinum catalysts were oxidized at 623 K (○), reduced at 623 K (●) and reduced at 823 K (△) before the catalytic run.

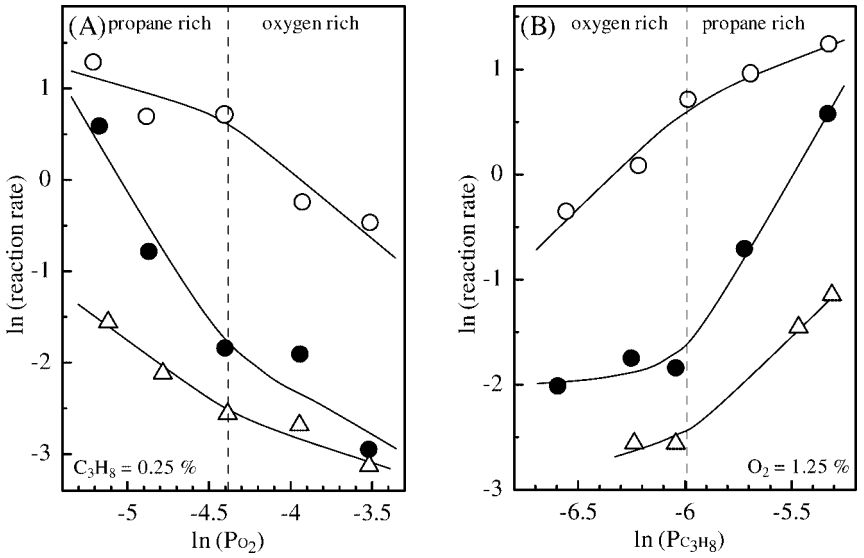

Figure 3. Dependence of reaction rate on the O_2 partial pressure (A) and the C_3H_8 partial pressure (B) over $SiO_2–Al_2O_3$ (○) and ZrO_2 (●). The initial reaction rate of Pt/ZrO_2 oxidized at 623 K is also shown (△).

Table 2
Reaction order for propane combustion over platinum catalysts.

Catalyst	Oxygen		Propane	
	Propane rich	Oxygen rich	Propane rich	Oxygen rich
$Pt/SiO_2–Al_2O_3$	−0.52	−1.5	0.80	2.0
Pt/ZrO_2	−2.9	−1.0	3.4	0.22

from −2.9 to −0.5. The negative reaction orders for oxygen, indicating that oxygen inhibits the propane combustion over supported platinum catalysts, cannot be explained by a Mars–van Krevelen mechanism. The reaction orders over Pt/ZrO_2 in the propane-rich mixture (−2.9 for oxygen and 3.4 for propane) and over $Pt/SiO_2–Al_2O_3$ in the oxygen-rich mixture (−1.5 for oxygen and 2.0 for propane) cannot be interpreted by a Langmuir–Hinshelwood mechanism, either. These values are unusual as compared with reported values; from 0.4 to 1 for propane, from −0.9 to 0.4 for oxygen [18,19]. Since the change in the catalyst itself is taken into account in neither Mars–van Krevelen nor Langmuir–Hinshelwood mechanism, it is suggested that the state of supported platinum changes in the reaction conditions. These unusual reaction orders may be rationalized

by assuming that the inhibition by oxygen includes the oxidation of bulk platinum, since the combustion activity of platinum decreases as platinum is oxidized [8,9]. This explanation is supported by other experimental results. The initial activity of pre-oxidized Pt/ZrO_2 is also shown in figure 3 (open triangles). The reaction rates were much smaller than that in steady state, as already mentioned. The tentative reaction orders obtained from the initial reaction rate were different from that obtained at steady state, and especially in propane-rich condition, the inhibition by oxygen was much weakened compared with steady state. This difference of the reaction orders at initial and steady state may come from the variation of the oxidation state of platinum supported on ZrO_2; at the beginning of the reaction, the variation of the oxidation state of platinum in each reaction condition should be smaller than that at the steady state, resulting in smaller inhibition by oxygen at the initial state than at the steady state.

In the propane-rich mixture, the reaction order for propane over Pt/ZrO_2 (3.4) is much larger than that over Pt/SiO_2–Al_2O_3 (0.80), and that for oxygen over Pt/ZrO_2 (-2.9) is much smaller than that over Pt/SiO_2–Al_2O_3 (-0.52). These results clearly indicate that the inhibition by oxygen over the basic support is much greater than that over the acidic one, and that propane combustion over Pt/ZrO_2 is strongly inhibited by oxygen even in the propane-rich mixture. From the above discussion, the stronger inhibition by oxygen over Pt/ZrO_2 indicates that platinum on ZrO_2 is more easily oxidized than that on SiO_2–Al_2O_3, i.e., platinum on SiO_2–Al_2O_3 is prevented from the oxidation. The difference in the reaction orders between propane-rich mixture and oxygen-rich mixture also supports this explanation. In the oxygen-rich mixture, the reaction order for oxygen over Pt/ZrO_2 (-1.0) is larger than that in the propane-rich mixture, showing that the reaction inhibition by oxygen is weakened. In contrast, in the case of Pt/SiO_2–Al_2O_3, the reaction order in the oxygen-rich mixture (-1.5) is much smaller than that in the propane-rich mixture, showing that the reaction inhibition is more pronounced in the oxygen-rich mixture. These results indicate that Pt/ZrO_2 is almost oxidized even in the propane-rich mixture, and that Pt/SiO_2–Al_2O_3 is not oxidized unless the oxygen concentration in the reaction mixture increases to some extent.

In the previous study, the authors investigated the support effect on the oxidation resistance by Pt $L_{III,II}$-edge XAFS using a series of support materials, and showed that the acidic support material prevents the oxidation of supported platinum after oxygen treatment at 823 K [20,21]. In this study, it is indicated by the kinetic investigation that platinum on ZrO_2 is more easily oxidized than on SiO_2–Al_2O_3, which is in good agreement with the previous observation obtained by the spectroscopic method. Thus, it is concluded that the platinum on acidic support materials keeps its metallic state more than that on basic materials under the reaction condition of propane combustion. This support effect furnishes the platinum on acidic support with a much higher catalytic activity and smaller inhibition, compared with that on basic support, since platinum catalysts for propane combustion are deactivated by their oxidation [8,9].

4. Conclusion

The support effect on the low-temperature propane combustion over platinum catalysts was investigated. The reaction inhibition, including the oxidation of bulk platinum, over Pt/ZrO_2 is much greater than that over Pt/SiO_2–Al_2O_3, and it is indicated that platinum on the basic support is more easily oxidized than that on the acidic one. Further, it is indicated that platinum oxide on basic support is more difficult to be reduced than that on acidic one. Thus, the high catalytic activity of platinum on acidic support is attributed to a high ability to maintain the metallic state of platinum with high oxidation resistance and high reducibility of platinum oxide.

Acknowledgement

YY acknowledges support by the Research Fellowship of the Japan Society for the Promotion of Science for Young Scientists.

References

[1] R.B. Anderson, K.C. Stein, J.J. Feenan and L.J.E. Hofer, Ind. End. Chem. 53 (1961) 809.
[2] G.I. Godoiets, Stud. Surf. Sci. Catal. 15 (1983) 465.
[3] T. Huizinga, J.V. Grondelle and R. Prins, Appl. Catal. 10 (1984) 199.
[4] Y. Li and J.N. Armor, Appl. Catal. B 3 (1994) 275.
[5] M. Niwa, K. Awano and Y. Murakami, Appl. Catal. 7 (1983) 317.
[6] C.P. Hubbard, K. Otto, H.S. Candhi and K.Y.S. Ng, J. Catal. 144 (1993) 484.
[7] A. Ishikawa, S. Komai, A. Satsuma, T. Hattori and Y. Murakami, Appl. Catal. A 110 (1994) 61.
[8] J. Volter, G. Lietz, H. Spindler and H. Lieske, J. Catal. 104 (1987) 375.
[9] J.G. Nunan, H.J. Robota, M.J. Cohn and S.A. Bradley, J. Catal. 133 (1992) 309.
[10] T. Uchijima, *Catalytic Science and Technology*, Vol. 1 (Kodansha/VCH, Tokyo/Weinheim, 1990) p. 393.
[11] Y. Yazawa, H. Yoshida, N. Takagi, S. Komai, A. Satsuma and T. Hattori, J. Catal. 187 (1999) 15.
[12] T. Hattori, H. Matsumoto and Y. Murakami, Stud. Surf. Sci. Catal. 31 (1987) 815.
[13] R. Prasad, L.A. Kennedy and E. Ruckenstein, Catal. Rev. Sci. Eng. 26 (1984) 1.
[14] K. Otto, J.M. Andino and C.L. Parks, J. Catal. 131 (1991) 243.
[15] A. Schwartz, L. Holbrook and H. Wise, J. Catal. 21 (1971) 199.
[16] L. Hiam, H. Wise and S. Chaikin, J. Catal. 10 (1968) 272.
[17] Y. Morooka, Y. Morikawa and A. Ozaki, J. Catal. 7 (1967) 23.
[18] R. Burch, E. Halpin, M. Hayes, K. Ruth and J.A. Sullivan, Appl. Catal. B 19 (1998) 199.
[19] A. Chiba, M. Komada, T. Kosumi, T. Nanba, N. Azuma and A. Ueno, Chem. Lett. (1999) 801.
[20] H. Yoshida, Y. Yazawa, N. Takagi, A. Satsuma, T. Tanaka, S. Yoshida and T. Hattori, J. Synchrotron Rad. 6 (1999) 471.
[21] Y. Yazawa, H. Yoshida, N. Takagi, N. Kagi, S. Komai, A. Satsuma, Y. Murakami and T. Hattori, Stud. Surf. Sci. Catal. 130 (2000) 2189.