Available online at www.sciencedirect.com
SCIENCE DIRECT®

Catalysis Today 87 (2003) 19–28

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Effects of support and additive on oxidation state and activity of Pt catalyst in propane combustion

Hisao Yoshida[*], Yoshiteru Yazawa, Tadashi Hattori

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho,
Chikusa-ku, Nagoya 464-8603, Japan

Abstract

The effects of support and additive on the oxidation state and catalytic activity of Pt catalyst in the low temperature propane combustion were systematically investigated on Pt/MgO, Pt/Al_2O_3 and Pt/SiO_2–Al_2O_3. The catalytic activity varied much with both support materials and additives. The catalyst on the more acidic support showed higher activity, and the catalytic activity on every support materials increased as the electronegativity of additives increased, while some additives decreased the activity. The oxidation state of platinum, estimated by white line intensity of Pt L_{III}-edge XANES spectrum, also varied with the support and additives, and additives with higher electronegativity greatly prevented the platinum from its oxidation under oxidising atmosphere. Among almost all the catalysts with various supports and various additives, a clear relationship was observed between the oxidation state of platinum and the catalytic activity; the more metallic platinum showed higher activity. Thus, it was concluded that the total electrophilic/electrophobic property derived from those of the support and additive controls the oxidation state of platinum, which intensively affects the catalytic activity; i.e. higher electrophilic property provides less oxidised platinum, resulting in high catalytic activity. The mechanism of this effect was also discussed on the basis of thermochemical data, and it was proposed that the electrophobic materials promote the noble metal oxidation since the noble metal oxo-anion such as $PtO_\alpha^{\delta-}$ is more stabilised with electrophobic cation.

Keywords: Electrophilic property; Electrophobic property; Electronegativity

1. Introduction

The catalytic property of supported noble metal catalysts can be modified with support materials and additives [1,2]. The acid–base property of support materials affects the electronic state of the metal [3–13], e.g. electron-deficiency of noble metal is enhanced on acidic support materials [3,4], while the structure of support also affects the structure of metal [14–23], e.g. epitaxial growths of noble metal particle on Al_2O_3 are observed [14,15]. On the other hand, the additive effect seems to be less systematically investigated, but it is recognised that electron density of the metal is increased by the addition of electrophobic alkaline and alkaline earth groups [24–30]. However, these observations are on the supported noble metal in metallic state, and these aspects could not necessarily be applied under oxidising atmosphere such as hydrocarbon combustion where supported noble metal can be oxidised.

In low temperature catalytic combustion over noble metal catalysts, the support effect on the catalytic performance has also been investigated [31–41], and there is a general consensus that the catalytic activity

---

[*] Corresponding author. Tel.: +81-52-789-4609;
fax: +81-52-789-3193.
E-mail address: yoshidah@apchem.nagoya-u.ac.jp (H. Yoshida).

0920-5861/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2003.10.001

of noble metals for hydrocarbon combustion varies with support materials. However, systematic investigations are not enough for the support and additive effect under oxidising atmosphere, and it has not been clarified how support materials and additives affect the catalytic property of supported noble metal.

Since we reported that the use of solid super acid as the support remarkably enhanced the catalytic activity of Pt in propane combustion [42,43] and that the self-inhibition effect of oxygen was much greater over basic support [44,45], we have investigated the support effect on Pt [44–48] and Pd catalyst [45,49] as well as the additive effect on Pt/Al_2O_3 [50,51]. In these studies, we have focused on the effect on the oxidation state of noble metals since the catalytic activity of noble metal varies with its oxidation state [52–54]. It is noted that these support and additive effects on the oxidation state of noble metal under oxidising atmosphere are quite opposite to that under the reducing one mentioned above. As acid strength of support materials is enhanced, noble metal is less oxidised under oxidising atmosphere, i.e. the oxidation-resistance of noble metal is improved by the electrophilic property of support materials [45–49]. The oxidation state of platinum also varies with the electronegativity of additives to more or less oxidised state compared with original Pt/Al_2O_3, and the oxidation-resistance of platinum is improved by the electrophilic property of additive [50].

In the present study, we report that the support and additive exhibit a combined effect on oxidation-resistance of Pt in propane combustion. The mechanism of the effect was also discussed on the basis of thermochemical data.

2. Experimental

The support materials used in this study were MgO, Al_2O_3 and SiO_2–Al_2O_3, all of which are the reference catalysts of Catalysis Society of Japan (MGO-1, ALO-4 and JRC-SAL-2) [55,56]. The sieved support material (25–50 mesh) was immersed in $Pt(NO_2)_2(NH_3)_2$ aqueous solution, and excess water was removed by rotary evaporator with suction at room temperature. After drying at 383 K for 12 h, the resultant materials were calcined at 673 K for 3 h, and then, reduced at 623 K for 3 h in a flow of hydrogen. 5 wt.% platinum catalysts thus obtained were further immersed in aqueous solutions of KNO_3, $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, NH_4VO_3, H_2WO_4 and H_2MoO_4. After drying and calcination in the same manner as mentioned above, the promoted catalysts were obtained, which are denoted as M/Pt/MgO, M/Pt/Al_2O_3 and M/Pt/SiO_2–Al_2O_3 (M: additive, the mole ratio $M/Pt = 4$).

The BET surface area of support materials was obtained from nitrogen uptake at liquid nitrogen temperature by using a conventional flow-type apparatus. The each BET surface area of MgO, Al_2O_3 and SiO_2–Al_2O_3 was 65, 177 and 532 $m^2\,g^{-1}$, respectively. The acid strength (H_0) of support materials was measured through the changes in colour of Hammett indicators adsorbed on support materials calcined at 773 K for 3 h. The acid strength of support materials was 22.3, 3.3 and −12.0, respectively.

The CO uptake of platinum catalyst was measured by pulse-adsorption of CO in a flow of helium [55,56]. The platinum catalyst was treated in a flow of oxygen at 673 K for 15 min to remove adsorbate on the catalyst, and reduced by hydrogen at 673 K for 15 min. The platinum catalyst was reduced by hydrogen at 823 K for 2 h, followed by helium purge at 823 K for 30 min before the pretreatment of the CO uptake measurement. By this treatment, the platinum catalyst will have similar dispersion after the pretreatment for the propane combustion, i.e. reduction at 823 K for 2 h.

The XAFS measurement of platinum catalyst was performed at the BL-10B station [57] at KEK-PF. Pt L_{III}- and L_{II}-edge XAFS spectra were recorded in transmission mode at room temperature with Si(3 1 1) channel cut monochromator. The catalysts were oxidised at 823 K for 2 h, and then immediately cooled to room temperature in oxygen. The oxidised catalysts were sealed in polyethylene packs under nitrogen atmosphere without exposure to air.

Catalytic test was performed with a conventional flow reaction apparatus, detailed elsewhere [49]. An amount of 0.03 g of platinum catalyst was used in the catalytic run with 1.5 g of the quartz granules as the diluent of catalyst to avoid local increase in the temperature. Before the catalytic run, the platinum catalyst was reduced in a flow of $He + H_2$ mixture ($He/H_2 = 4$) at 823 K for 2 h, and then, cooled to 423 K in a flow of helium. The catalytic activity was measured from 423 to 823 K with the interval of 50 K.

At each reaction temperature, the reaction conditions were kept for 30 min, and then, the products were analysed by gas chromatography. The composition of the reaction mixture was 0.25% of propane, 3.0% of oxygen and helium as a balance, and total flow rate was 200 ml min^{-1}.

3. Results

3.1. Propane combustion over the promoted Pt catalysts

Fig. 1 shows the catalytic activity of M/Pt/MgO (A), M/Pt/Al_2O_3 (B) and M/Pt/SiO_2–Al_2O_3 (C) in propane combustion, as a function of the reaction temperature. The activities of platinum catalysts with no additives, Pt/MgO, Pt/Al_2O_3 and Pt/SiO_2–Al_2O_3, are represented by open circle. The activity increased with the increase in the acid strength, electrophilic property, of support materials as already reported [44–48]. On each support materials, the catalytic activity varied with the additives. On M/Pt/Al_2O_3 (Fig. 1B), the potassium depressed the activity while the addition of tungsten, molybdenum and vanadium greatly enhanced it though the addition of aluminium or magnesium did not change the activity of the unmodified one as reported [50]. The activity increased with an increase of electronegativity of added element. However, note that the effect of additive differs from support to support. On M/Pt/MgO (Fig. 1A), the potassium addition greatly depressed the activity, the magnesium addition did not affect, while the others improved. On M/Pt/SiO_2–Al_2O_3, most of the additives reduced the catalytic activity more or less. Thus, an additive effect was exhibited both positively and negatively, which depended on the support material; e.g. the addition of Al enhanced the activity of Pt/MgO, but depressed that of Pt/SiO_2–Al_2O_3.

Fig. 2 depicts the activity of these as a function of the electronegativity of additives. Fig. 2A shows the propane conversion at 523 K. To compare the catalytic activity more strictly, the reaction rate at low conversion level (at 473 K) was also shown in Fig. 2B. The electronegativity of additives is obtained as that of oxides on the basis of the Sanderson concept [58] by using the electronegativity of the element defined by Pauling [59]. The horizontal line shows the catalytic activity of the unmodified catalyst. As mentioned above, the additive effect seems rather positive on the MgO support, while it seems negative on the SiO_2–Al_2O_3 (compare the plots to the horizontal line on each support). However, the catalytic activity on each support material clearly increased with the increase in the electronegativity of additives.

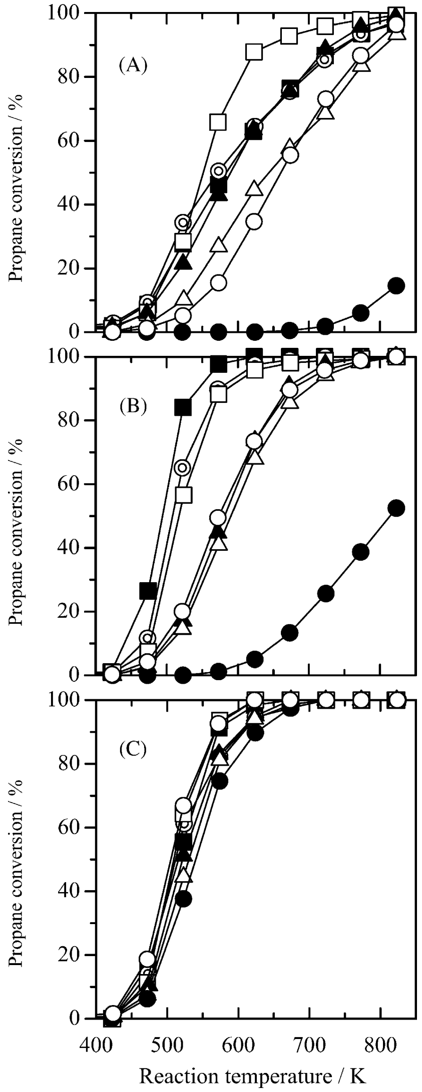

Fig. 1. The propane conversion over (A) M/Pt/MgO, (B) M/Pt/Al_2O_3 and (C) M/Pt/SiO_2–Al_2O_3 with no additives (open circles), potassium (closed circles), magnesium (open triangles), aluminium (closed triangles), vanadium (open squares), tungsten (closed squares) and molybdenum (double circles).

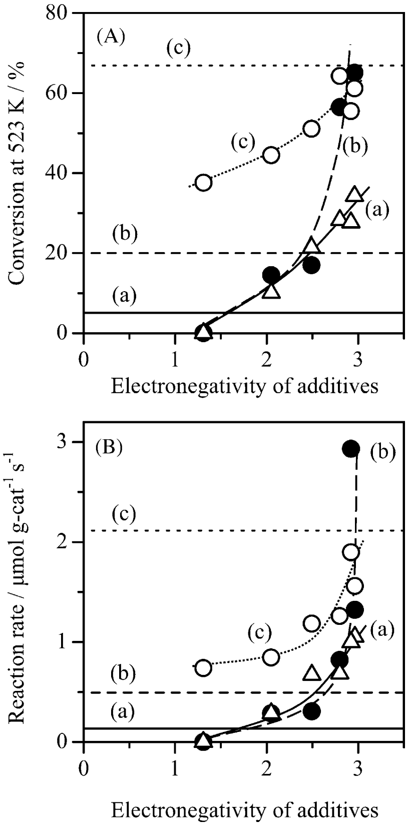

Fig. 2. Plots of propane conversion at 523 K (A) and reaction rate at 473 K (B) vs. electronegativity of additives on M/Pt/MgO (a, open triangles), M/Pt/Al_2O_3 (b, closed circles) and M/Pt/SiO_2–Al_2O_3 (c, open circles). The horizontal lines show the conversion and reaction rate on each catalyst without additives, Pt/MgO (a), Pt/Al_2O_3 (b) and Pt/SiO_2–Al_2O_3 (c), respectively.

3.2. CO uptakes of the promoted Pt catalyst

The CO uptakes on the Pt catalysts are summarised in Table 1. The CO uptake is represented by CO/Pt, which is the molar ratio of adsorbed CO to total platinum in the catalyst. The CO uptakes of K/Pt/Al_2O_3, Mg/Pt/Al_2O_3 and Al/Pt/Al_2O_3 were slightly larger than that of Pt/Al_2O_3, while the CO uptakes of V/Pt/Al_2O_3, W/Pt/Al_2O_3 and Mo/Pt/Al_2O_3 were smaller than that of Pt/Al_2O_3. As a whole, the additives with larger electronegativity more reduced the CO uptake on M/Pt/Al_2O_3. The CO uptakes on M/Pt/MgO were similar to one another and smaller than that of Pt/MgO. On M/Pt/SiO_2–Al_2O_3, the additives decreased the CO uptake, and the CO uptake decreased with an increase of the electronegativity of additives. Although the amount of additives was large enough to compare the platinum (M/Pt = 4), the CO uptake did not drastically decrease by additives, implying that large amount of the additives would be located on the surface of the support and might influence on the property of the support.

Table 1
The CO uptakes of M/Pt/MgO, M/Pt/Al_2O_3 and M/Pt/SiO_2–Al_2O_3

Additive	Electronegativity	CO/Pt		
		MgO	Al_2O_3	SiO_2–Al_2O_3
No additive		0.23	0.37	0.40
K	1.31	0.11	0.42	0.31
Mg	2.05	0.16	0.46	0.32
Al	2.49	0.16	0.45	0.27
V	2.80	0.10	0.21	0.15
W	2.92	–[a]	0.17	–[a]
Mo	2.96	0.11	0.15	0.06

[a] Not measured.

3.3. The oxidation state of platinum in the catalysts

Fig. 3 shows Pt L_{III}- and L_{II}-edge XANES spectra of M/Pt/MgO, M/Pt/Al_2O_3 and M/Pt/SiO_2–Al_2O_3 that are oxidised at 823 K, with those of Pt foil and PtO_2 as references. The energy offsets were 11 559 eV for L_{III}-edge and 13 267 eV for L_{II}-edge. Since the white lines, intense absorption peak at Pt L_{III}- and L_{II}-edge are mainly assigned to electron transition from $2p_{3/2}$ to $5d_{3/2}$ and $5d_{5/2}$, and from $2p_{1/2}$ to $5d_{3/2}$, respectively, the white line intensity at Pt L_{III}-edge is an informative indication for the oxidation state of platinum; large white line is observed on oxidised platinum due to the electron vacancy in d-orbital, while small white line is observed on reduced platinum due to lack of electron vacancy. All catalysts showed the relatively large white line, and the spectra were similar to that of PtO_2 rather than Pt foil. These would be partially oxidised platinum catalysts, which might contain some phases; metallic platinum, platinum dioxide (PtO_2) and others (e.g. PtO).

The white line intensity varied with both the support materials and additives. The white line of platinum catalysts with no additives became less intense with the acid strength of support materials enhanced in the

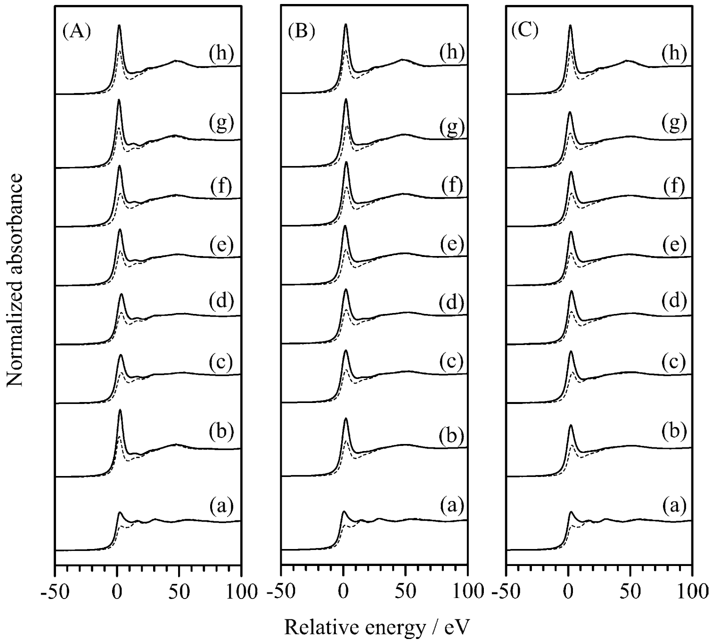

Fig. 3. Pt L_{III} (solid line) and L_{II} (broken line) edge XANES spectra of M/Pt/MgO (A), M/Pt/Al_2O_3 (B), M/Pt/SiO_2–Al_2O_3 (C); with no additives (b), molybdenum (c), vanadium (d), aluminium (e), magnesium (f) and potassium (g), and those of Pt foil (a) and PtO_2 (h) as a reference. Energy offsets were 11 559 eV for L_{III} edge and 13 267 eV for L_{II} edge.

order Pt/MgO (Fig. 3A (b)) > Pt/Al_2O_3 (Fig. 3B (b)) > Pt/SiO_2–Al_2O_3 (Fig. 3C (b)), which is consistent with the previous study [45–48]. On the XANES spectra of M/Pt/SiO_2–Al_2O_3 (Fig. 3C) the white line seems to be only a little changed by additives, while relatively large change was observed on the XANES spectra of M/Pt/MgO (Fig. 3A) and M/Pt/Al_2O_3 (Fig. 3B). On Pt/MgO and Pt/Al_2O_3, for example, the addition of molybdenum (c) obviously decreased the white line intensity, while it was intensified by the addition of potassium (g).

The white line area intensity of Pt L_{III} edge XANES spectrum was evaluated by a curve fitting analysis using an arctangent and a Gaussian function [60,61]. In the separate study [62], we confirmed a good linear relationship between the white line area intensity and the oxidation state described as O/Pt atomic ratio, where the XANES spectra of various oxidised supported Pt catalyst were recorded by a laboratory EXAFS instrument (Technos, EXAC-820) equipped with an in situ cell, and the oxidation state of the platinum treated at given condition (O/Pt) was determined by desorption amount of oxygen in temperature-programmed desorption (TPD) profile. Therefore, the white line intensity directly and linearly reflects the oxidation state of platinum (O/Pt).

In Fig. 4, the white line intensity of the present Pt catalysts, which indicates the platinum oxidation state, was plotted as a function of the electronegativity of additives. The horizontal line shows that of the catalyst with no additives. On every support materials, the oxidation state of platinum decreased with an increase in the electronegativity of additives, indicating that the additives with higher electronegativity prevent platinum from its oxidation. However, the effect of additives on the oxidation state of platinum is different from support to support; both positive and negative effects were observed (Compare the plots to the horizontal line on each support). In the case of M/Pt/Al_2O_3 (Fig. 4b) the electronegativity of ca. 2.6 was threshold; i.e. in the region of electronegativity smaller than ca. 2.6, the white line was enhanced, while it was smaller in the larger electronegativity region as already reported [50]. On the other hand, the additives made it larger on Pt/SiO_2–Al_2O_3 (Fig. 4c) and smaller on Pt/MgO (Fig. 4a). These

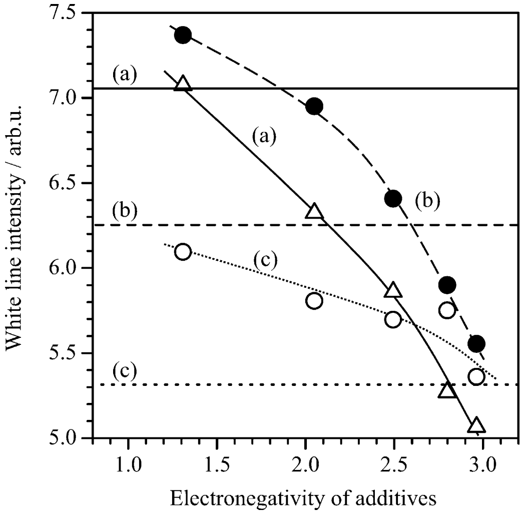

Fig. 4. The effect of electronegativity of additives on the oxidation state of M/Pt/MgO (a, open triangles), M/Pt/Al_2O_3 (b, closed circles) and M/Pt/SiO_2–Al_2O_3 (c, open circles). The horizontal lines represent the oxidation state of original catalyst with no additives; Pt/MgO (a), Pt/Al_2O_3 (b) and Pt/SiO_2–Al_2O_3 (c), respectively.

results indicate that the additives cannot determine the oxidation state independently, or in other words, the oxidation state of platinum is affected synergistically by both the support materials and additives.

The range of the variation in the oxidation state of platinum was different from support to support. This means that the variation range of the oxidation state by additives would be roughly determined by the properties of the support materials such as acid–base property and surface area. SiO_2–Al_2O_3 support has relatively larger BET surface area compared with Al_2O_3 and MgO, and thus, there may be less additives directly interacting with platinum particle.

4. Discussion

4.1. Additive effect on the catalytic activity of the Pt catalyst

The catalytic activity of M/Pt/MgO, M/Pt/Al_2O_3 and M/Pt/SiO_2–Al_2O_3 was obviously varied with additives (Figs. 1 and 2). Here, we will discuss how the additives modify the catalytic activity of platinum. At first, the effect of the platinum surface area on the catalytic activity must be checked, since the catalytic activity might be decreased by the reduction of the platinum surface area due to site blocking by the additives, and/or might vary with the particle size of platinum, which is known as the structure sensitivity: the catalytic activity of supported noble metal for hydrocarbon combustion, in terms of turnover frequency, is known to increase with the increase in its particle size [46,63–69]. As discussed in the previous study [50], the variation in the catalytic activity with additives on Pt/Al_2O_3 cannot be explained by either site blocking or structure sensitivity. The catalytic activity on Pt/MgO was enhanced by the additives except for potassium although the CO uptake was decreased by the additives (Table 1), indicating that the site blocking by additives is not applicable to the case. The CO uptakes on M/Pt/MgO were similar to one another, which were independent of the additives, and the variation in the activity was much larger than that in the CO uptake. For example, although K/Pt/MgO, V/Pt/MgO and Mo/Pt/MgO have almost the same CO uptake, the catalytic activity was drastically different from one another. On Pt/SiO_2–Al_2O_3, although both the catalytic activity and the CO uptake decreased by additives in any case, the decreases in the activity and those expected from the CO uptake seem to be out of harmony. Thus, the variations in the activity of M/Pt/MgO and M/Pt/SiO_2–Al_2O_3 also cannot be explained by the variation in the platinum surface area.

Since the catalytic activity of platinum catalyst for hydrocarbon combustion is known to decrease with the platinum oxidation proceeded, it must be discussed. Fig. 4 clearly shows the additive effect on the oxidation state of platinum. On every support materials, the oxidation state of platinum varied with additives; the platinum with the additives of the higher electronegativity was less oxidised. This indicates that the oxidation-resistance of platinum is more enhanced by more electrophilic additives. Since the catalytic activity of platinum on every support materials was enhanced as the electronegativity of additives increased (Fig. 2), it is expected that the oxidation state of platinum thus controlled on every support would be essentially responsible for the catalytic activity. In the previous study on Pt/Al_2O_3, it has been indicated that the variation in the catalytic activity of platinum arises from the variation in its oxidation state [50]. Fig. 5 shows the relation between the catalytic

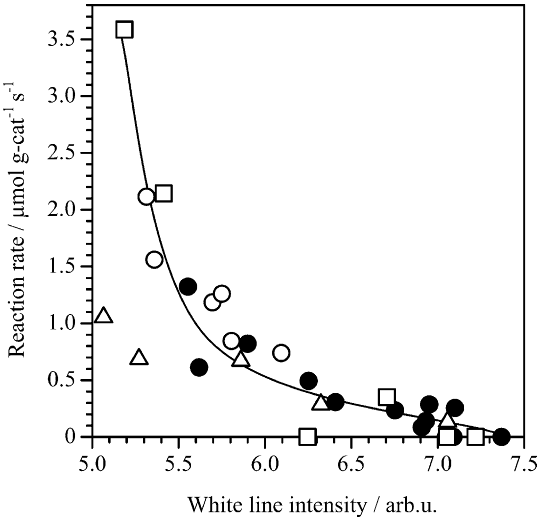

Fig. 5. The effect of the oxidation state of platinum on the catalytic activity for propane combustion at 473 K over Pt/MO_x (open squares), M/Pt/MgO (open triangles), M/Pt/Al_2O_3 (closed circles) and M/Pt/SiO_2–Al_2O_3 (open circles).

activity of platinum and its oxidation state (the white line intensity) on the Pt catalysts of each support. On every support, MgO (open triangle), Al_2O_3 (closed circle) and SiO_2–Al_2O_3 (open circle), the good relationships were observed between the oxidation state of platinum and the catalytic activity. This means that the activity of Pt catalyst is mainly determined by the oxidation state of platinum that is controlled by the electrophilic/electrophobic properties of additives. Electrophilic property of additives makes platinum less oxidised and, as a result, enhances the high catalytic activity in the propane combustion.

4.2. Effect of support and additive on the catalytic activity of the Pt catalyst

In Fig. 5, the platinum catalysts on other supports such as La_2O_3, ZrO_2, SO_4^{2-}–ZrO_2, which were investigated in the past study [47], are also plotted (open square) together with the catalysts supported by MgO, Al_2O_3 and SiO_2–Al_2O_3. Almost all samples are on one curve with a narrow deviation except for a few samples. This obviously shows that the oxidation state of platinum is one of the most important factors controlling the catalytic activity in propane combustion. Therefore, we here summarise the effect of support and additive on the catalytic activity of the Pt catalyst in propane combustion: *The total electrophilic property of support materials and additives improves the oxidation-resistance of noble metal, which results in high activity*. This proposes that the catalytic activity of noble metal catalysts under the oxidising atmosphere can be improved by the selection of the support materials and additives through adjusting the oxidation state of the noble metal catalyst. This fundamental feature would be extremely effective for the practical use of supported noble metal catalysts, since the selection of support materials is sometimes limited by some problems, e.g. the surface area and thermal- and/or poison-resistance of support materials.

4.3. Mechanistic cause of controlling the platinum oxidation state

In the previous study [47], the mechanism of support effect on the oxidation-resistance of noble metal was discussed, and it is suggested that the support effect comes from the variation of the stability of the binary oxide containing noble metal. These binary oxides containing noble metal are more stabilised than noble metal oxide such as PtO_2, and conjugation with alkali and alkaline earths is especially effective for stabilisation [70]. In the present study, the results clearly indicate that the total electrophilic/electrophobic property of both support materials and additives plays important role for controlling oxidation-resistance of platinum. Here, we discuss the mechanistic cause of controlling the platinum oxidation state on the basis of thermochemical data. To simplify, let us focus on the support effect at first. For thermochemical discussion, the formation of the binary oxide containing platinum is divided into two steps as follows:

$$\mathrm{Pt} + \mathrm{MO}_x + \mathrm{O}_2 \xrightarrow{\text{oxidation}} \mathrm{PtO}_2 + \mathrm{MO}_x \xrightarrow{\text{binary oxide formation}} \mathrm{MPtO}_\alpha \qquad (1)$$

where MO_x denotes the support oxide and $MPtO_\alpha$ denotes the binary oxide containing platinum. The first step is the PtO_2 formation from Pt and O_2. In this step the Gibbs energy of oxidation is independent of support materials (MO_x). The second step is the

Table 2
The decomposition temperature of binary oxide containing platinum[a]

Oxide	Electronegativity of MO_x in $MPtO_\alpha$	Decomposition temperature (K)
PtO_2	–	896–933
$CdPt_3O_4$	2.44	978–1162
$ZnPt_3O_4$	2.37	982–1165
$CaPt_3O_4$	1.87	1053–1307
$LiPt_3O_4$	1.52	1042–1135
$NaPt_3O_4$	1.41	1071–1241

[a] From Ref. [70].

binary oxide formation from PtO_2 and MO_x, where the change of Gibbs energy (ΔG_M) is expected to vary with MO_x. The variation in ΔG_M with MO_x is considered to bring about the variation in the oxidation state of platinum.

The thermal stability of such binary oxide containing platinum has been already reported [70], and summarised in Table 2. The electronegativity of MO_x in $MPtO_\alpha$ is calculated according to the Sanderson concept [58] by using the electronegativity for the element defined by Pauling [59], and also shown in Table 2. The thermal stability of binary oxide containing platinum is much higher than that of PtO_2, and clearly varies with the electronegativity of MO_x in $MPtO_\alpha$. The alkaline and alkaline earth group is effective for the stabilisation of $MPtO_\alpha$, and the thermal stability of $MPtO_\alpha$ seems to be improved with the decrease in the electronegativity of MO_x, implying that the electrophobic materials improve the thermal stability of binary oxide, or, in other words, the electrophobic materials promote the binary oxide formation. Thus, it is expected that the equilibrium of the reaction formula (1) leans to the system of formation, and that the electrophobic materials promote the platinum oxidation.

Since the thermochemical data of binary oxide containing iron, which is the same 8A group as noble metals, has been obtained much more systematically than that of binary oxide containing noble metal, the effect of the electronegativity of MO_x on the binary oxide formation is discussed hereafter in the case of iron as a substitute for noble metal. The Gibbs energy change (ΔG_M) in the binary oxide formation from Fe_2O_3 and MO_x for 1 mol of Fe in the compound is shown in Fig. 6 as a function of the electronegativity of MO_x. In almost all cases, ΔG_M is negative, and it obviously decreases with the decrease in the electronegativity of MO_x, indicating that the binary oxide formation is promoted as the electronegativity of counter oxide (MO_x) decreased. This result clearly indicates that the second step in the reaction formula (1) is promoted as the electrophobic property of MO_x is enhanced, and that the equilibrium of the total reaction leans to the system of formation. Further, since ΔG_M approaches zero as the electronegativity of MO_x increases, the electrophilic oxide cannot form the binary oxide, or, in other words, the electrophilic oxide can scarcely promote the oxidation of iron (or noble metal). Thus, the cause of the support effect is clearly verified thermochemically: the electrophobic support materials enhance the oxidation of noble metal through the stabilisation of the binary oxide containing noble metal. The electrophobic oxide would stabilise the oxo-anion of noble metal such as $PtO_\alpha^{\delta-}$ through the enhancement of the negative charge of oxo-anion by its electrophobic property.

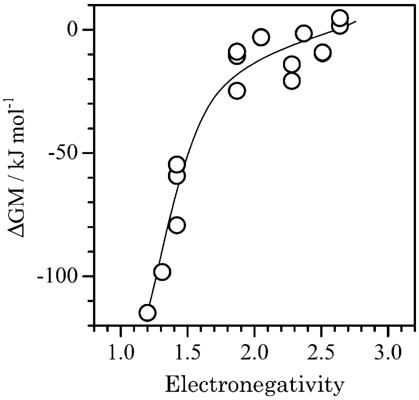

Fig. 6. The effect of the electronegativity of MO_x on the Gibbs free energy change for binary oxide formation from MO_x and Fe_2O_3 [48–59].

As for the additive effect, the same concept as above could be applied, judging from the results. However, since additives would be located on both metal and support surface, the electrophilic/electrophobic property of additives affects directly the metal and indirectly together with the support material.

5. Conclusion

From the above results and discussion, the effect of support and additive on oxidation state and activity of platinum catalyst in propane combustion is concluded as follows:

1. More metallic platinum shows higher catalytic activity. The electrophilic property of the support materials and the additives improved the oxidation-resistance of platinum, and as a result, the catalyst exhibits high catalytic activity.
2. The support and additive effects arise from the variations in the stability of oxo-anion of noble metal such as $\mathrm{PtO}_{\alpha}^{\delta-}$; the electrophobic materials promote the noble metal oxidation through the stabilisation of oxo-anion of noble metal.

These conclusions show the importance of the total electrophilic/electrophobic property of both support materials and additives for design of the active noble metal catalyst employed under the oxidising atmosphere.

Acknowledgements

The X-ray absorption experiment was performed under the approval of the Photon Factory Program Advisory Committee (Proposal no. 2001G093).

References

[1] G.C. Bond, in: B. Imelik, C. Naccache, G. Coudurier, H. Praliaud, P. Meriaudeau, P. Gallezot, G.A. Martin, J.C. Vedrine (Eds.), Metal–Support and Metal–Additive Effect in Catalysis, Elsevier, Amsterdam, 1982, p. 1.
[2] S.J. Thomson, J. Chem. Soc., Faraday Trans. I 83 (1983) 1893.
[3] T. Ishihara, K. Harada, K. Eguchi, H. Arai, J. Catal. 136 (1992) 161.
[4] A.Y. Stakheev, L.M. Kustov, Appl. Catal. A 188 (1999) 3.
[5] G. Larsen, G.L. Haller, Catal. Lett. 3 (1989) 103.
[6] A.P.J. Jansen, R.A. van Santen, J. Phys. Chem. 94 (1990) 6764.
[7] E. Sanchez-Marcos, A.P.J. Jansen, R.A. van Santen, Chem. Phys. Lett. 167 (1990) 399.
[8] M.G. Samant, M. Boudart, J. Phys. Chem. 95 (1991) 4070.
[9] W.M.H. Sachtler, A.Y. Stakheev, Catal. Today 12 (1992) 283.
[10] M. Sugimoto, H. Katsuno, T. Hayasaka, N. Ishikawa, K. Hirasawa, Appl. Catal. A 102 (1993) 167.
[11] W.M.H. Sachtler, B. Bunsenges, Phys. Chem. 99 (1995) 1295.
[12] B.L. Mojet, J.T. Miller, D.E. Ramaker, D.C. Koningsberger, J. Catal. 186 (1999) 373.
[13] D.C. Koningsberger, J. de Graaf, B.L. Mojet, D.E. Ramaker, J.T. Miller, Appl. Catal. A 191 (2000) 205.
[14] P. Briot, P. Gallezot, C. Leclercq, M. Primet, Microsc. Microanal. Microstruc. 1 (1990) 149.
[15] E. Garbowski, C. Feumi-Jantou, N. Mouaddib, M. Primet, Appl. Catal. A 109 (1994) 277.
[16] R.J. Emich, A.N. Mansour, D.E. Sayers, S.T. Mcmillan, J.R. Katzer, J. Phys. Chem. 89 (1985) 4261.
[17] K. Asakura, M. Yazawa, Y. Iwasawa, H. Kuroda, Chem. Lett. (1985) 511.
[18] D.C. Koningsberger, J.B.A.D. van Zon, H.F.J. van't Blik, G.J. Visser, R. Prins, A.N. Mansour, D.E. Sayers, D.R. Short, J.R. Katzer, J. Phys. Chem. 89 (1985) 4075.
[19] K. Asakura, Y. Iwasawa, H. Kuroda, Nihon Kagaku Kaishi (1986) 1539.
[20] Y. Izumi, K. Aika, J. Phys. Chem. 99 (1995) 10336.
[21] Y. Izumi, K. Aika, J. Phys. Chem. 99 (1995) 10346.
[22] J.B.A.D. van Zon, D.C. Koningsberger, H.F.J. van't Blik, R. Prins, D.E. Sayers, J. Chem. Phys. 99 (1995) 3914.
[23] D.I. Kochubey, S.N. Pavlova, B.N.N. Novgorodov, G.N. Kruova, V.A. Sadykov, J. Catal. 161 (1996) 500.
[24] E.L. Garfunkel, J.J. Maj, J.C. Frost, M.H. Farias, G.A. Somorjai, J. Phys. Chem. 87 (1983) 3629.
[25] S.C. Chuang, J.G. Goodwin Jr., I. Wender, J. Catal. 95 (1985) 435.
[26] S. Kesraoui, R. Oukaci, D.G. Blackmond, J. Catal. 105 (1987) 432.
[27] B.J. Kip, E.G.F. Hermans, R. Prins, Appl. Catal. 35 (1987) 141.
[28] R.G. Windham, M.E. Bartram, B.E. Koel, J. Phys. Chem. 92 (1988) 2862.
[29] F. Solymosi, M. Pasztor, G. Rakhely, J. Catal. 110 (1988) 413.
[30] S.R. de Miguel, A.A. Castro, O.A. Scelza, Catal. Lett. 32 (1995) 281.
[31] M. Niwa, K. Awano, Y. Murakami, Appl. Catal. 7 (1983) 317.
[32] T. Huizinga, J.V. Grondelle, R. Prins, Appl. Catal. 10 (1984) 199.
[33] C.P. Hubbard, K. Otto, H.S. Candhi, K.Y.S. Ng, J. Catal. 144 (1993) 484.
[34] Y. Li, J.N. Armor, Appl. Catal. B 3 (1994) 275.
[35] K. Muto, N. Katada, M. Niwa, Appl. Catal. A 134 (1996) 203.
[36] M. Haruta, Catal. Today 36 (1997) 153.
[37] H. Widjaja, K. Sekizawa, K. Eguchi, Chem. Lett. (1998) 481.
[38] K. Okumura, H. Tanaka, M. Niwa, Catal. Lett. 58 (1999) 43.
[39] K. Asakura, H. Nagahiro, N. Ichikuni, Y. Iwasawa, Appl. Catal. A 188 (1999) 313.
[40] R.W. van den Brink, M. Krzan, M.M.R. Feijen-Jeurissen, R. Louw, P. Mulder, Appl. Catal. B 24 (2000) 255.
[41] K. Eguchi, H. Arai, Appl. Catal. A 222 (2001) 359.
[42] A. Ishikawa, S. Komai, A. Satsuma, T. Hattori, Y. Murakami, Appl. Catal. A 110 (1994) 61.
[43] T. Sugaya, A. Ishikawa, S. Komai, A. Satsuma, T. Hattori, Y. Murakami, Trans. Mater. Res. Soc. Jpn. A 15 (1994) 103.
[44] Y. Yazawa, N. Kagi, S. Komai, A. Satsuma, Y. Murakami, T. Hattori, Catal. Lett. 72 (2001) 157.
[45] Y. Yazawa, H. Yoshida, N. Takagi, N. Kagi, S. Komai, A. Satsuma, Y. Murakami, T. Hattori, Stud. Surf. Sci. Catal. 130 (2000) 2189.

[46] Y. Yazawa, H. Yoshida, T. Hattori, Appl. Catal. A: Gen. 237 (2002) 139.

[47] Y. Yazawa, N. Takagi, H. Yoshida, S. Komai, A. Satsuma, T. Tanaka, S. Yoshida, T. Hattori, Appl. Catal. A 233 (2002) 103.

[48] H. Yoshida, Y. Yazawa, N. Takagi, A. Satsuma, T. Tanaka, S. Yoshida, T. Hattori, J. Synchrotron Radiat. 6 (1999) 471.

[49] Y. Yazawa, H. Yoshida, N. Takagi, S. Komai, A. Satsuma, T. Hattori, J. Catal. 187 (1999) 15.

[50] Y. Yazawa, H. Yoshida, S. Komai, T. Hattori, Appl. Catal. A 233 (2002) 113.

[51] Y. Yazawa, H. Yoshida, T. Hattori, J. Synchrotron Radiat. 8 (2001) 560.

[52] J. Volter, G. Lietz, H. Spindler, H. Lieske, J. Catal. 104 (1987) 375.

[53] J.G. Nunan, H.J. Robota, M.J. Cohn, S.A. Bradley, J. Catal. 133 (1992) 309.

[54] Y. Yazawa, H. Yoshida, N. Takagi, S. Komai, A. Satsuma, T. Hattori, Appl. Catal. B 19 (1998) 261.

[55] T. Hattori, H. Matsumoto, Y. Murakami, in: B. Delmon, P. Grange, P.A. Jacobs, G. Poncelet (Eds.), Preparation of Catalysts IV, Elsevier, Amsterdam, 1987, p. 815.

[56] T. Uchijima, in: S. Yoshida, N. Takezawa, T. Ono (Eds.), Catalytic Science and Technology, vol. 1, Kodansha, Tokyo/VCH, Weinheim, 1990, p. 393.

[57] N. Nomura, A. Koyama, KEK Report 89-16, 1989, p. 1.

[58] R.T. Sanderson, Chemical Bond and Bond Energy, Academic Press, New York, 1976.

[59] L. Pauling, Nature of Chemical Bond, 3rd ed., Cornell University Press, Ithaca, NY, 1960.

[60] J.A. Horsley, J. Phys. Chem. 76 (1982) 1451.

[61] S. Yoshida, T. Tanaka, in: Y. Iwasawa (Ed.), X-ray Absorption Fine Structure for Catalysts and Surface, World Scientific Series on Synchrotron Radiation Techniques and Applications, vol. 2, World Scientific, Singapore, 1998, p. 308.

[62] H. Yoshida, S. Nonoyama, Y. Yazawa, T. Hattori, submitted for publication.

[63] P. Chon, M.A. Vannice, J. Catal. 105 (1987) 342.

[64] P. Briot, A. Auroux, D. Jones, M. Primet, Appl. Catal. 59 (1990) 141.

[65] R.F. Hicks, H. Qi, M.L. Young, R.G. Lee, J. Catal. 122 (1990) 280.

[66] R.F. Hicks, H. Qi, M.L. Young, R.G. Lee, J. Catal. 122 (1990) 295.

[67] R. Burch, F.J. Urbano, Appl. Catal. A 124 (1995) 121.

[68] K. Muto, N. Katada, M. Niwa, Appl. Catal. A 134 (1996) 203.

[69] K. Fujimoto, F.H. Ribeiro, M. Avalos-Borja, E. Iglesia, J. Catal. 179 (1998) 442.

[70] D. von Bergner, R. Kohlhaas, Z. Anorg. Allg. Chem. 401 (1973) 15.