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Stabilization of high oxidation state of platinum over basic support oxide examined by in situ laboratory XANES and temperature programmed desorption of oxygen

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ABSTRACT

Support effect on the oxidation state of Pt nanoparticles was investigated by in situ laboratory XANES and O_2-TPD. The support oxides used were MgO and Al_2O_3. In oxidizing condition, the surface of Pt nanoparticles supported on Al_2O_3 was rapidly oxidized to become the oxidation state of $Pt(s)_2O$ to Pt(s)O stoichiometry, where Pt(s) stands for the surface Pt atom, but further oxidation was not observed even at high temperature. On the other hand, Pt supported on MgO was highly oxidized in two steps at high temperature; rapid oxidation exceeding the stoichiometry of Pt(s)O, and slow further oxidation toward the stoichiometry of PtO_2. The Pt particles on MgO would be redispersed and stabilized through the formation of *atomically dispersed platinate anions*, which would be tetravalent Pt cations coordinated by some oxygen anions, by the influence of the electrophobic cation of the support at high temperature and through the formation of *Pt oxide cluster anions*, $(PtO_x)_n{}^{y-}$, where x would be less than two, at lower moderate temperature.

1. Introduction

It is widely accepted that the support materials can remarkably affect the catalytic property of supported precious metal through the modifications of their structure and electronic state [1]. We have systematically investigated the effect of acid/base property of support and additive on propane combustion over Pt [2–10] and Pd [4,11,12] catalysts, and on methane combustion over Pd catalyst [13]. In these previous studies, it was clearly indicated that the oxidation state of the precious metal varied with the acid strength of the support materials and the additives. This effect on the oxidation state of the noble metal under oxidizing atmosphere is quite opposite to the well-known support effect under the non-oxidative condition. Under non-oxidative condition where the precious metals can exist in the metallic state, the basic property of the support materials increases the electron density of the precious metal, i.e., the metal is reduced, and acid property of support decreases the electron density of the metal, i.e., the metal is oxidized [1]. On the other hand, under oxidizing atmosphere in the presence of oxygen, as the acid strength of the support materials was enhanced, the noble metal was less oxidized by the gaseous oxygen, i.e., the oxidation-resistance of the noble metal is improved by the electrophilic (acidic) property of the support materials [3–5,7,9–14].

As for the mechanism of the support effect on the oxidation of the precious metals by gaseous oxygen, we have proposed, from thermodynamic consideration of the formation of mixed oxides, that the precious metal oxide particles are stabilized as *highly oxidized oxo-anion species of precious metal* such as $PtO_x{}^{y-}$ [10] and/or *metal oxide-like cluster anion species* such as $(PdO)_n{}^{y-}$ [13] by the presence of the electrophobic cations in a similar way to the formation of mixed oxides containing precious metal. In other words, the electrophobic cations such as alkaline and alkaline earth ions promote the formation of the mixed oxides through the stabilization of the oxo-anion of precious metal by their electrophobic properties.

Although the oxidation state under non-oxidative condition are controlled by the acid strength of the support materials, the effect of the oxidation state on the catalytic activity differed from metal to metal and also from reaction to reaction. For example, in the propane combustion, the catalytic activity of Pt was higher on acidic support or with acidic additives [2–10] and the use of solid super acid as the support remarkably enhanced the catalytic activity [2]; these results show that the metallic state of Pt is suitable for the propane combustion. Similarly in the case of heptane combustion on Pt catalyst the catalytic activity is higher on reduced Pt catalyst [15], while in the case of olefin oxidation the opposite results were reported [16]. In the case of Pd catalyst, partially oxidized Pd species exhibited high activity in the propane combustion [11,12] and in the methane combustion [13].

Our conclusion, i.e., the oxidation-resistance of noble metal was improved by the acidic property of the support materials, is con-

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sistent with the results in several papers reported so far. Wu et al. reported that the increase in the acid strength of support lowered the light-off temperature of Pt catalyst for propane and CO combustion [17]. Kobayashi et al. obtained an excellent propane combustion activity of Pt by using TiO_2–SiO_2–WO_3 as the support, which was attributed to the superior oxidation-resistance of Pt due to the higher acidity of the support [18]. Fridell and co-workers reported that a presence of NO_x storage component such as BaO lowered the specific activity of Pt for oxidation reaction, which was rationalized by the formation of platinum oxides [19,20]. As for the relation between the oxidation state of Pt and the support, Asakura et al. reported that Pt cations are stabilized on the surface of MgO under oxidizing condition [21]. Nagai et al. reported that the oxidation state of Pt increased as the electron density of oxygen in the support increased, and proposed that the strong interaction between the platinum oxide species and the support stabilizes the higher oxidation state of Pt [22]. There are also, however, some results for Pd catalysts that lead contradictory conclusion to ours one [23].

On the contrary, the oxidation of platinum by gaseous oxygen has been extensively studied for both single crystal and supported catalysts. It has been suggested for the single crystals of platinum that the oxidation was limited to the surface layer below 800 K; atomically adsorbed oxygen became the main adsorbate above 160 K and desorbed from platinum surface above 650 K. Subsurface oxide was formed through penetration of atomically adsorbed oxygen into subsurface region above 800 K [24]. In the case of supported catalysts, although the formation of metal oxide particles was proposed for highly dispersed catalysts [25], it is also widely accepted that only the surface layer was oxidized by dioxygen [24,26,27]. The extent of oxidation should be limited to form the surface oxides with a stoichiometry ranging from $Pt(s)_2O$ to $Pt(s)O_2$, where Pt(s) stands for the surface Pt atom. Thus, the extent of oxidation significantly depends on the dispersion of Pt and the oxidation temperature, i.e., highly dispersed platinum can be much oxidized, while larger particles only partially oxidized [9]. However, actually the platinum particles on the basic support materials were deeply oxidized as mentioned above [7,9,10].

In the present study, we simply focussed the oxidation state of Pt on MgO as basic support. To observe the oxidation of the moderately large particles, we prepared the samples of 60% and 30% dispersion of Pt. For comparison, we also prepared Al_2O_3-supported Pt catalysts, on which the dispersion was controlled to be the same as that of each Pt/MgO sample to rule out the effect of the initial dispersion. Then, the variation of oxidation state of supported Pt catalyst was quantitatively measured by using in situ laboratory X-ray absorption near edge structure (XANES) in the presence of oxygen, and further discussion was made on the stabilization of high oxidation state of Pt over the basic support in the light of temperature programmed desorption of oxygen (O_2-TPD).

2. Experimental

The support materials used in the present study were Al_2O_3 (a reference catalyst of Catalysis Society of Japan [28,29], JRC-ALO-4) and MgO (JRC-MGO-1) listed in Table 1. The acid strength by the Hammett indicator method and the surface area of the supports were reported previously [7].

Two groups of the supported platinum catalysts shown in Table 1 were prepared: One contained 2 wt% of Pt with ca. 60% dispersion and another had 5 wt% of Pt with ca. 30% dispersion. The sieved support material (25-50 mesh) was impregnated with an aqueous solution of $Pt(NO_2)_2(NH_3)_2$, and excess water was removed by a rotary evaporator with suction at room temperature. After drying at 383 K for 12 h, the resultant powder was calcined at 673 K for 3 h, and then, reduced at 623 K for 3 h in a flow of hydrogen. Additional reduction at 623 K for a moderate period was carried out on some samples in order to control the platinum dispersion. The CO uptake of the platinum catalyst was measured by the CO pulse-adsorption method in a flow of helium at room temperature [28,29]. The platinum dispersion was calculated from the total CO uptake by assuming that CO was adsorbed on the surface platinum atom at a 1:1 stoichiometry. PtO_2 and Pt foil previously employed [30] were used for reference in XANES and TPD experiments.

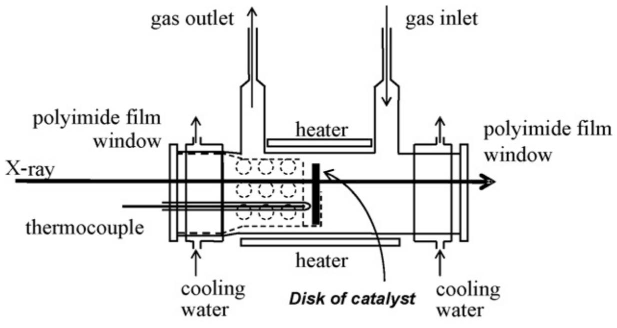

Fig. 1. Cross section of the in situ EXAFS cell.

The Pt L_{III}-edge XANES spectra of the samples were recorded in a transmission mode by a laboratory EXAFS instrument [30,31], EXAC820 (Technos Co. Ltd) in a flow of O_2 (100%) or a mixture of O_2 (5%) and He at selected temperature (473, 673 or 823 K). The X-ray source was a rotating anode X-ray generator (22 kV, 200 mA, the target anode: Mo, the filament: LaB_6). A single monochromator was employed using a Johansson-type Ge(400) bent crystal curved with Rowland circle geometry ($R = 300$ mm) and the 1st order of the reflection was used. The catalyst was pressed into a self-supporting disk and mounted into an in situ EXAFS cell with polyimide windows shown in Fig. 1. The catalyst amount was 0.6 g for the 2% Pt catalyst and 0.3 g for the 5% Pt catalyst, respectively. Before the measurement, the sample was treated in H_2 (67 kPa) at 823 K for 1 h followed by He purge. The X-ray intensity before passing the sample, I_0, was detected with a semi-transmitting sealed proportional counter (S-PC) filled with 50 kPa of Ar and the intensity after passing the sample, I, was detected with a pure-Ge solid-state detector (SSD). The energy steps for the measurement were varied with the energy regions as follows: 15, 2, 0.5 and 15 eV for the region of 11.2–11.55, 11.55–11.56, 11.56–11.577 and 11.577–12.0 keV, respectively. The measurement time for each record was typically 5 s: It cost 4 min for the measurement of the white line region (11.55–11.577 keV), and 9.5 min for the measurement of one spectrum.

The background subtraction and normalization were performed by using a modified Victoreen equation with a constant correction term [32]. The white line area intensity of the normalized Pt L_{III}-edge XANES spectrum was evaluated by a curve-fitting analysis [6,30,33] using a set of a Gaussian and an arctangent function.

Temperature programmed desorption of oxygen was performed on a TPD instrument (Bel Japan, Inc.). Prior to the measurement, the sample was sequentially treated in H_2 (67 kPa), in vacuo and in O_2 (67 kPa) at selected temperature (473, 673 or 823 K) for 30 min each, followed by cooling down to room temperature and evacuation. Then, under monitoring O_2 desorbed from the sample by a mass spectrometer (ANELVA, AQA-100R), the temperature of the sample bed was elevated at a constant rate in a flow of He.

3. Results

Fig. 2 shows the Pt L_{III}-edge XANES spectra of the 2% Pt catalysts in a steady oxidation state at 473 and 823 K together with the spectra of the PtO_2 and Pt foil samples as the references. The PtO_2

Table 1
Properties of catalysts.

Catalyst	Support			Pt catalyst		
		Surface area[a] ($m^2\ g^{-1}$)	Acid strength[a] (H_o)	Pt loading (wt%)	Pt(s)/Pt[b] (%)	Pt particle size[c] (nm)
2%Pt/Al_2O_3	Al_2O_3[d]	183	3.3	2.0	62	1.8
5%Pt/Al_2O_3	Al_2O_3[d]	183	3.3	5.0	31	3.7
2%Pt/MgO	MgO[d]	138	22.3	2.0	63	1.8
5%Pt/MgO	MgO[d]	138	22.3	5.0	30	3.8

[a] Reported previously [7].
[b] Estimated by CO adsorption method.
[c] Calculated from the CO/Pt value by using the following equation: particle size (nm) = 113.5/(Pt(s)/Pt (%)).
[d] Reference catalysts of Catalysis Society of Japan, JRC-ALO-4 for Al_2O_3 and JRC-MGO-1 for MgO [28,29].

sample exhibited the largest absorption band (i.e., white line) at 11.567 keV among the samples (Fig. 2f), while the Pt foil showed a very small white line (Fig. 2a). The white line intensities for the supported catalysts were varied with the support material and the oxidation temperature between those for the PtO_2 and Pt foil samples (Fig. 2b–e). The white line was larger for the 2%Pt/MgO sample, especially at higher oxidation temperature. Since the white line of the Pt L_{III}-edge XANES spectrum is assignable to the electron transition mainly to $5d_{3/2}$ and $5d_{5/2}$ orbitals, the white line intensity is expected to be an informative indication for the oxidation state of platinum. Thus, above-mentioned result indicates that the oxidation state of Pt is higher on the MgO support than that on the Al_2O_3 support, which agrees well with the results of previous studies [3,4,7,9,10]. Another interesting feature is that the effect of the oxidation temperature also depended on the support. For the MgO support, the white line intensity increased with the oxidation temperature, while for the Al_2O_3 support, the intensity seemed to be independent of the oxidation temperature.

The oxidation state of the supported Pt was then quantified by using the previously reported correlation between the oxidation state and the white line intensity [30]. First, the white line intensity was evaluated from the XANES spectrum: A simple curve-fitting analysis was carried out by using a set of a Gaussian and an arctangent functions, and the white line intensity was expressed by the area intensity of the Gauss function. Then, the oxidation state of Pt, defined as the atomic ratio of oxygen to platinum (O/Pt), was calculated from the linear correlation to the white line intensity.

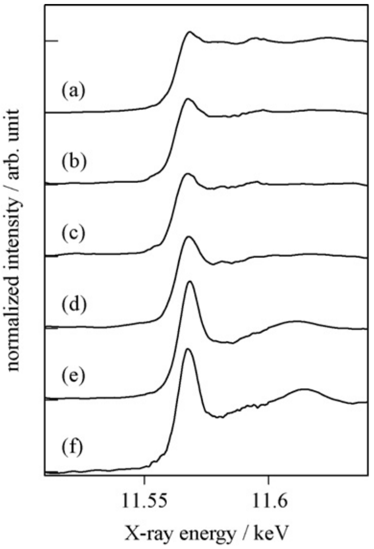

Fig. 2. Pt L_{III}-edge normalized XANES of the 2% Pt catalysts in the steady oxidation state at 473 K or 823 K in 5% O_2/He and those of the references: (a) the Pt foil, (b) the 2%Pt/Al_2O_3 sample at 473 K, (c) the 2%Pt/Al_2O_3 sample at 823 K, (d) the 2%Pt/MgO sample at 473 K, (e) the 2%Pt/MgO sample at 823 K, and (f) the PtO_2 sample.

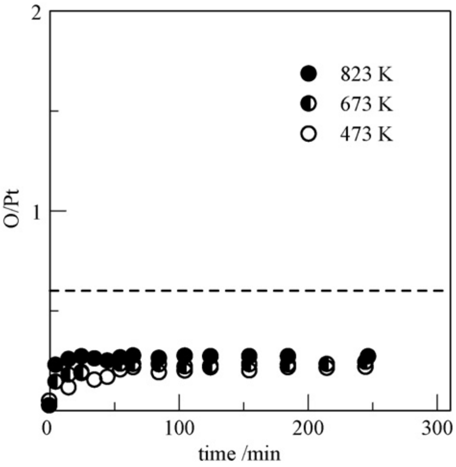

Fig. 3. Time course of the oxidation of the 2%Pt/Al_2O_3 sample in 5% O_2/He at selected temperature. The horizontal broken line represents the Pt(s)/Pt ratio for the sample.

Figs. 3 and 4 show the change in the oxidation state of the 2% Pt catalysts in the time course of the oxidation in 5% O_2 in He at 473, 673 and 823 K. In the case of the 2%Pt/Al_2O_3 sample shown in Fig. 3, the oxidation state of Pt, the O/Pt ratio, attained a steady state quickly. It is noted that the value at the steady state were almost the same at any temperature examined (473–823 K) and further oxidation did not occur at any temperature. The value at the steady state was about a half of the Pt(s)/Pt ratio for the 2%Pt/Al_2O_3 sample, suggesting the formation of the surface oxide such as $Pt(s)_2O$. This means the bulk oxidation of the supported Pt particles was inhibited as expected. On the other hand, in the

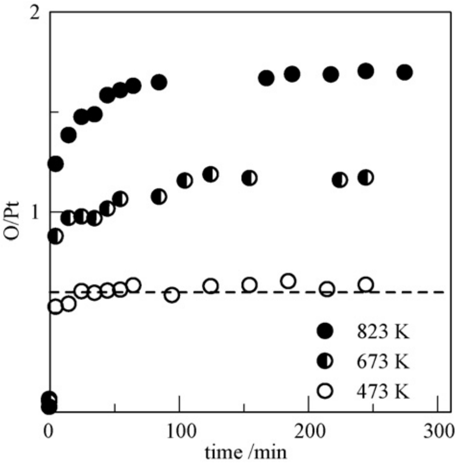

Fig. 4. Time course of the oxidation of the 2%Pt/MgO sample in 5% O_2/He at selected temperature. The horizontal broken line represents the Pt(s)/Pt ratio for the sample.

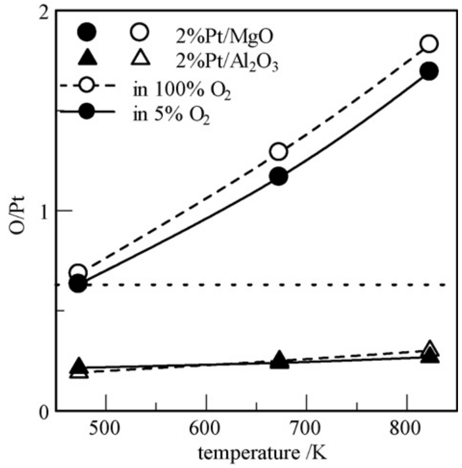

Fig. 5. Effect of the oxidation temperature on the oxidation state at the steady state of the 2%Pt/MgO and 2%Pt/Al_2O_3 samples in 5% O_2/He and 100% O_2. The horizontal broken line represents the Pt(s)/Pt ratio of the 2%Pt/MgO sample. For the 2%Pt/Al_2O_3 sample, see Table 1.

case of the 2%Pt/MgO sample shown in Fig. 4, the O/Pt ratio initially increased very rapidly in the same way as that on the 2%Pt/Al_2O_3 sample shown in Fig. 3, but it attained higher oxidation state. It was close to the Pt(s)/Pt ratio of the 2%Pt/MgO sample at 473 K while it exceeded the Pt(s)/Pt ratio at higher temperatures. Although the O/Pt ratio did not increase further at 473 K, the initial rapid oxidation was followed by the gradual oxidation at higher temperatures. The final oxidation state at 823 K corresponded to the formation of bulk oxide close to PtO_2. These results were also obtained in the flow of 100% O_2 (not shown).

Fig. 5 summarizes the effect of the oxidation temperature on the oxidation state at the steady state of the 2% Pt catalysts in 5% and 100% O_2. As shown, the O_2 concentration in gas phase did not give a significant effect on the O/Pt ratio at the steady state although the time for achieving the steady state was rather short in 100% O_2 (not shown). In both 5% and 100% O_2, the O/Pt ratio at the steady state for the Pt/MgO sample corresponded to the Pt(s)/Pt ratio at 473 K and increased with the oxidation temperature, but the O/Pt ratio for the Pt/Al_2O_3 sample was almost constant around the half of the Pt(s)/Pt ratio at any temperatures. The results on the 5% Pt catalysts were shown in Fig. 6 together with the data for the 2% Pt catalysts. These results showed that the oxidation states of the 5% Pt catalysts were similar to those on the 2% Pt catalysts, except that the O/Pt ratio on the Pt/Al_2O_3 sample was close to the Pt(s)/Pt ratio at high temperature.

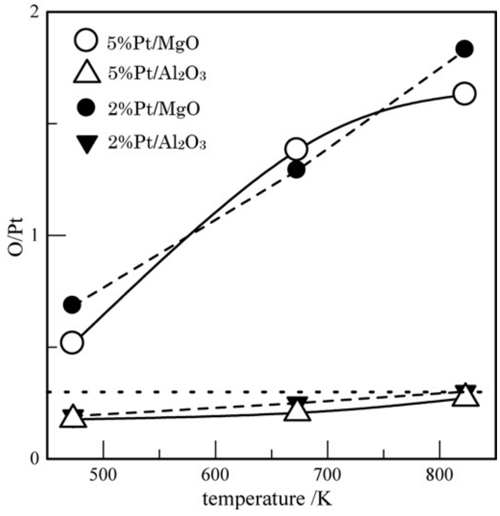

Fig. 6. Effect of the oxidation temperature on the oxidation state at the steady state of the 5%Pt/MgO, 5%Pt/Al_2O_3 2%Pt/MgO and 2%Pt/Al_2O_3 samples in 100% O_2. The horizontal broken line represents the Pt(s)/Pt ratio of the 5%Pt/MgO sample. For other samples, see Table 1.

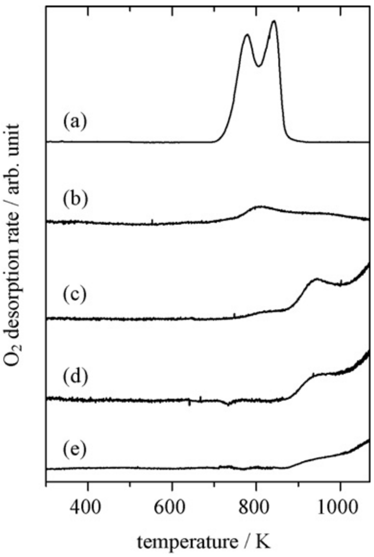

Fig. 7. O_2-TPD profiles of (a) the bulk PtO_2, (b) the 2%Pt/Al_2O_3 sample oxidized at 823 K, and the 2%Pt/MgO sample oxidized at (c) 823 K, (d) 673 K and (e) 473 K. The heating rate was 5 K/min. Before the measurement, the sample was oxidized in 5% O_2/He for 30 min at each temperature.

Fig. 7 shows the O_2-TPD profiles of the 2% Pt catalysts and the PtO_2 sample. The PtO_2 exhibited two sequential desorption peaks around 800 K, which corresponded the decomposition temperature of PtO_2 to Pt and O_2. As for the catalyst samples, the oxygen desorption peak started at higher temperature than those of the PtO_2 sample. This means that the oxidized platinum species was stabilized on these oxide supports [10]. Especially on the MgO support, the decomposition temperature was clearly higher than the others, which means the oxidized platinum species was well stabilized on the MgO support as reported [7,10,21]. Another interesting feature of the Pt/MgO samples is that two desorption peaks were observed at ca. 950 K and at/above 1075 K on the 2%Pt/MgO samples. In the case of the 5%Pt/MgO catalysts shown in Fig. 8, the low temperature peak seemed to shift to lower temperature, as the pretreatment temperature was lowered.

4. Discussion

The oxidation state of the Pt/Al_2O_3 catalysts in the present study, shown in Figs. 5 and 6, corresponded to the formation of the surface oxide with a stoichiometry of $Pt(s)_2O$ to Pt(s)O, which agreed with the above-mentioned general consensus that only the surface layer of Pt particle was oxidized by dioxygen [24,26,27]. In the present cases on the Al_2O_3 support, the O/Pt(s) ratio was less than unity. On the other hand, the O/Pt(s) ratio of the Pt/MgO catalysts was much higher than that of the Pt/Al_2O_3 catalysts, especially at higher temperature, as shown in Figs. 5 and 6. This result was quite different from the above-mentioned consensus. We previously reported that the high oxidation state of Pt was obtained when Pt was supported by the basic oxides [7,9,10]. In the present study, the oxidation state of Pt was quantitatively determined by using each in situ XANES spectrum: The oxidation state of whole Pt on the Pt/MgO catalyst with a dispersion of 63% was close to tetravalent at high temperature, corresponding to the formation of bulk PtO_2. The stabilization of such highly oxidized Pt on the MgO support can be explained by

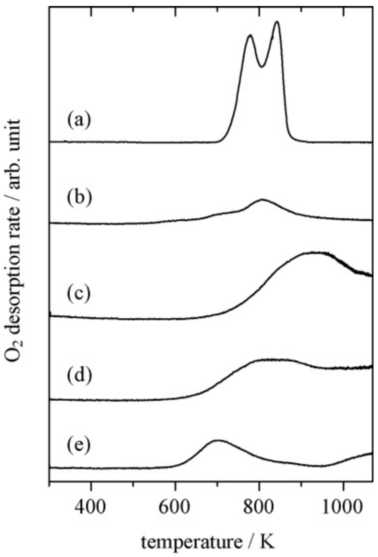

Fig. 8. O_2-TPD profiles of (a) the bulk PtO_2, (b) the 5%Pt/Al_2O_3 sample oxidized at 823 K, and the 5%Pt/MgO samples oxidized at (c) 823 K, (d) 673 K and (e) 473 K. The heating rate was 10 K/min. Before the measurement, the sample was oxidized in 5% O_2/He for 30 min at each temperature. The profile of the PtO_2 sample was measured at the heating rate of 5 K/min.

previously proposed mechanism [10] that the electrophobic materials promote the oxidation of platinum through the stabilization of *platinum oxo-anion species* such as $PtO_x^{\delta-}$ by the surface electrophobic property of the support in a similar way to the formation of mixed oxides containing precious metal, or platinates, such as Mg_2PtO_4 [34] and Sr_3MgPtO_6 [35] with tetravalent Pt.

One might suspect it is improbable that such atomically dispersed mixed oxides can be formed on the 5%Pt/MgO catalyst, because the dispersion of the catalyst was only 30% corresponding to the particle diameter of ca. 4 nm. Adamiec et al. reported that oxygen treatment at 823 K increased the dispersion of Pt on basic supports (0.5–5%Pt/MgO as well as 0.5–1%Pt/Al_2O_3) [36]. Asakura et al. reported that Pt clusters on 1%Pt/MgO were transformed to atomically dispersed Pt species by oxidation with O_2 at 623 K [21]. Recently, Tanabe et al. proposed on the basis of quantitative curve-fitting analysis of the EXAFS spectra of 1%Pt/MgO oxidized at 1073 K that Pt agglomerates redispersed at the atomic level with the formation of an Mg_2PtO_4-like compound on the MgO surface [37]. In Mg_2PtO_4 spinel, Pt is located at 6-oxygen coordinated octahedral sites as tetravalent cation. These would explain the high oxidation state of Pt supported on the MgO support even with low dispersion: Pt particles redispersed and reacted with MgO to form atomically dispersed platinates, which would be tetravalent octahedral Pt cation surrounded by 6-oxygen, under the effect of the electrophobic Mg cations.

In the TPD spectra of the 2%Pt/MgO sample shown in Fig. 7, two desorption peaks were observed at ca. 950 K and at/above 1075 K. The high temperature peak should be assignable to the Pt species with the strongest interaction with the MgO support, that is, to the atomically dispersed platinates mentioned above. In this case, the average particle size was estimated to be as small as ca. 2 nm. Thus, the particle could redisperse and react with the surface of MgO to form platinates.

In the case of the 5%Pt/MgO catalysts shown in Fig. 8, the increase in desorption peak temperature at high oxidation temperature should be attributed to the enhanced interaction with the MgO support, i.e., to the redispersion of Pt species. However, as the oxidation temperature was lowered, the low temperature peak seemed to shift to lower temperature, suggesting only weak interaction with MgO. In this catalyst, the average particle size before the oxidation treatment was estimated to be ca. 4 nm. This implies that the redispersion and reaction with the surface would be rather difficult at lower temperature, which seems consistent with the literature: the low treatment temperature would not promote redispersion [36]. Thus, the Pt species corresponding to the low temperature peak should be transitional state with moderate dispersion and moderate interaction with the MgO support, such as platinum oxide cluster anions, $(PtO_x)_n{}^{y-}$, as previously proposed in Pd catalysts [13], though further study is necessary for the full understanding of this species.

5. Conclusion

Stabilizing effect of basic support on the oxidized Pt was demonstrated by using in situ laboratory XANES and O_2-TPD. In the case of the Al_2O_3 support, the oxidation state of Pt after O_2 treatment corresponded to the formation of the surface oxide, where the O/Pt(s) ratio was less than unity, calculated from the oxidation state quantitatively measured by in situ XANES. In contrast, after O_2 treatment Pt was highly oxidized on the MgO support. The O/Pt(total) ratio exceeded unity at the oxidation temperature of 673 K and was close to two at 873 K: The latter indicated that almost whole Pt atoms were oxidized to form tetravalent cations. O_2-TPD from oxidized Pt/MgO gave two desorption peaks attributed to the platinate anion species with different dispersions from one another. From these results, it is proposed that Pt particles would be redispersed and stabilized on basic support through the formation of *atomically dispersed platinate anions*, which would be octahedral tetravalent Pt cations coordinated by some oxygen anions, after the oxidation at high oxidation temperature and *Pt oxide cluster anions*, $(PtO_x)_n{}^{y-}$, where x would be less than two, at lower oxidation temperature.

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