Catalytic properties and characterization of Pd supported on hexaaluminate in high temperature combustion

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Abstract

The catalytic activities of palladium-supported $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$ (SLMA) and the effect of phase transformation of palladium on the catalytic activity after high temperature treatments were studied by XRD, TPD, temperature programmed reaction (TPRX) and temperature programmed reoxidation (TPRO). Also the interaction of palladium with $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$ at high temperature was studied by XPS. PdO formed on $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$ was dissociated to metallic Pd after calcination at $1000\,^\circ C$. TPD and TPRX study revealed that the surface oxygen of PdO cluster was the major source of oxygen to react with CH_4 in the absence of O_2. TPRO after TPRX experiments showed the reoxidation of catalysts was dependent on the calcination temperature. High temperature treatments caused the interaction of palladium and $Sr_{0.8}La_{0.2}MnAl_{11}O_{19}$ support resulting in the change of the oxidation state of palladium. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is well known that combustion catalyst can reduce the temperature of operation from 1500 to $1300\,^\circ C$ and suppress the NO_x formation [1,2]. There have been numerous studies on the application of high temperature oxidation catalyst in the gas-turbine power generation [3,4]. Some researchers [2,5,6] reported that hexaaluminate structure has the promising thermal stability and the high catalytic activity in the methane combustion reaction. Arai and coworkers [2] reported that this structure is highly resistant to sintering above $1300\,^\circ C$ because of the location of large cation in mirror plane.

The partial substitution of Mn for Al significantly promotes catalytic reaction. Therefore, SLMA is suitable for application for a back-end zone of the combustor catalyst. In order to possess the high catalytic activity to initiate the surface reaction at low temperature at inlet of combustor catalyst, palladium should be supported because of its high activity for the catalytic oxidation of methane at low temperature. Supported palladium catalyst show complex behaviors for the combustion of methane because of the formation and decomposition of palladium oxide [7–9]. Farrauto et al. [7] first reported the large hysteresis in methane combustion rate over a heating and cooling cycle and confirmed the lower rate of combustion by the metallic Pd. Sekizawa et al. [8] reported the study of Pd supported on SLMA using temperature programming methods. Their results show that the

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catalytic activity for methane combustion decreased as the transition from PdO to the metallic phase is completed. However, they did not examine the reactivity of oxygen evolved during the transition of Pd phase in parallel with temperature programming desorption experiments. McCarty [9] reported the kinetics of the catalytic combustion of methane of palladium supported on lanthanum hexaaluminate. They examined the specific combustion activity of catalyst using the TPR with dilute methane and oxygen. They reported the rate of combustion was dependent on the transition of palladium on the support. In our study, the temperature programmed reaction (TPRX) of methane and temperature programmed reoxidation (TPRO) after TPRX was conducted to study the reactivity of different forms of oxygen for the palladium supported on SLMA. Also, we examined the influence of calcination temperature on the chemical state of Pd on SLMA by XPS.

2. Experimental

2.1. Catalyst preparation

SLMA was prepared by hydrolysis of metal alkoxides [10]. Ten grams of aluminum isopropoxide (AIP, Aldrich Co., USA, 99.99%) and a stoichiometric amount of Sr metal (Aldrich Co., USA, 99%) were dissolved in 100 ml of isopropanol at 80 °C for 5 h under a N_2 atmosphere. Isopropanol was dehydrated with a molecular sieve before use. A stoichiometric amount of $Mn(NO_3)_2 \cdot 6H_2O$ (Waco Chemical, 99.8%) and $La(NO_3)_3 \cdot 6H_2O$ (Yakuri Pure Chemicals) was slowly added to the prepared solution as described above. The amount of water was fixed as the mole ratio of H_2O/M–OR of 10. This prepared gel was aged at 80 °C for 12 h, then dried at 60 °C. Dried gel was powdered at a size between 50 and 100 mesh, then calcined at 500 °C for 2 h.

Before impregnation of Pd on the SLMA, the SLMA was calcined at 1200 °C for 5 h in flowing air. Pd was deposited on the SLMA by impregnation of aqueous palladium(II) nitrate solution followed by drying. The loading of Pd metal was 1 wt.%. These samples were calcined at 600, 800, 1000, 1200 and 1400 °C for 5 h.

2.2. Surface area analysis and crystal structure analysis

The surface areas of SLMA calcined at 1200 °C and Pd/SLMA calcined at 600, 800, 1000, 1200 and 1400 °C were measured by BET method using N_2 adsorption. The measured surface area of SLMA was 13.0 m^2/g. After calcination at 600, 800, 1000 and 1200 °C for Pd/SLMA, similar surface areas with SLMA calcined at 1200 °C were measured within error range. The measured surface areas of SLMA calcined at 1200 °C and Pd/SLMA calcined at 1400 °C are 13.0 and 5.8 m^2/g, respectively. The crystal structures of the calcined samples were determined by X-ray diffraction (Regaku D/MAX-III) with Cu Kα radiation.

2.3. TPD of O_2

Before the TPD of O_2 was performed, 300 mg of Pd/SLMA was treated in a O_2 stream (50 cm^3/min) raising temperature to 800 °C (10 °C/min). Temperature was maintained at 800 °C for 1 h and cooled to room temperature. Helium was introduced to the reactor and the sample was heated at a 10 °C/min to 900 °C in a He stream (10 cm^3/min). Desorbed oxygen species in effluent gas was analyzed by mass spectrometer (VG Quardruples SX-300).

2.4. TPRX (temperature programmed reaction of methane) and TPRO (temperature programmed reduction of oxygen)

Methane TPRX was carried out in the quartz reactor in the absence of O_2. An amount of 300 mg of Pd/SLMA was heated in a O_2 stream (50 ml/min) raising temperature to 500 °C at constant rate followed by cooling to room temperature in a He stream. Samples were heated again at a 10 °C/min to 1000 °C in 50 cm^3/min of constant CH_4/He mixture (1/99 vol.%). Consumption of CH_4 and the production of CO and CO_2 were analyzed by mass spectrometer (VG Quardruples SX-300).

After TPRX experiment, the sample was cooled to room temperature and then helium was introduced. In a O_2 stream (20 cm^3/min), the sample was heated to 1000 °C at 10 °C/min. The consumption of O_2

and the production of CO were analyzed by mass spectrometer.

2.5. Surface analysis

XPS was performed with a SPECS LHS10 (Germany) spectrometer. An amount of 100 mg of samples was pelletized and mounted on the sample holder. The XPS spectra were recorded using Al Kα radiation and the normal operating pressure inside the analyzer chamber was below 5.0×10^{-9} Torr. The binding energy was referenced to the binding energy of C 1s of 284.5 eV.

3. Results and discussion

3.1. Crystal structure

The crystal structure of SLMA after calcination at 1200 °C is identical with that of $SrO \cdot 6Al_2O_3$ [11]. Fig. 1 shows the XRD spectra of Pd/SLMA calcined at various temperatures between 37° and 47°. The peak at $2\theta = 40.1°$ which was assigned to metallic Pd(1 1 1),

was observed after calcination above 1200 °C because of the formation of large metallic Pd particles.

3.2. TPD of O_2

The TPD of O_2 of Pd/SLMA was performed in order to investigate the evolution of O_2 during the phase transformation of Pd on SLMA support calcined at various temperatures. Each TPD spectra are shown in Fig. 2. For SLMA calcined at 1200 °C, a little desorption of oxygen was observed above 650 °C arising from the lattice oxygen generated by the addition of Mn in SLMA [8]. TPD spectrum of the Pd/SLMA calcined at 1400 °C (Fig. 2(b)) is similar to that of SLMA calcined at 1200 °C (Fig. 2(b)). It indicates that Pd calcined at 1400 °C dose not evolve oxygen. As the calcination temperature decreased, the relative amount of oxygen desorbed near 750 °C increased. For Pd/SLMA calcined at 800 °C, new desorption peak of oxygen was found above 800 °C. The desorption profile of Pd/SLMA calcined at 800 °C consists of mainly three parts (Fig. 2(e)). The first evolution of oxygen occurred below 700 °C seemed to arise from the desorption of oxygen chemisorbed on Pd or PdO
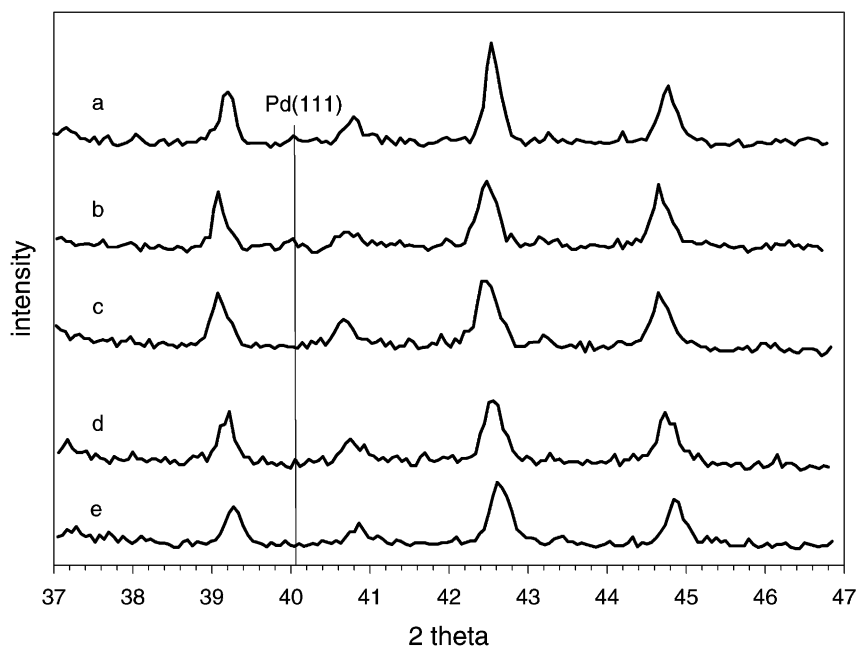

Fig. 1. XRD spectra of Pd/SLMA calcined at: (a) 1400 °C, (b) 1200 °C, (c) 1000 °C, (d) 800 °C and (e) 600 °C.
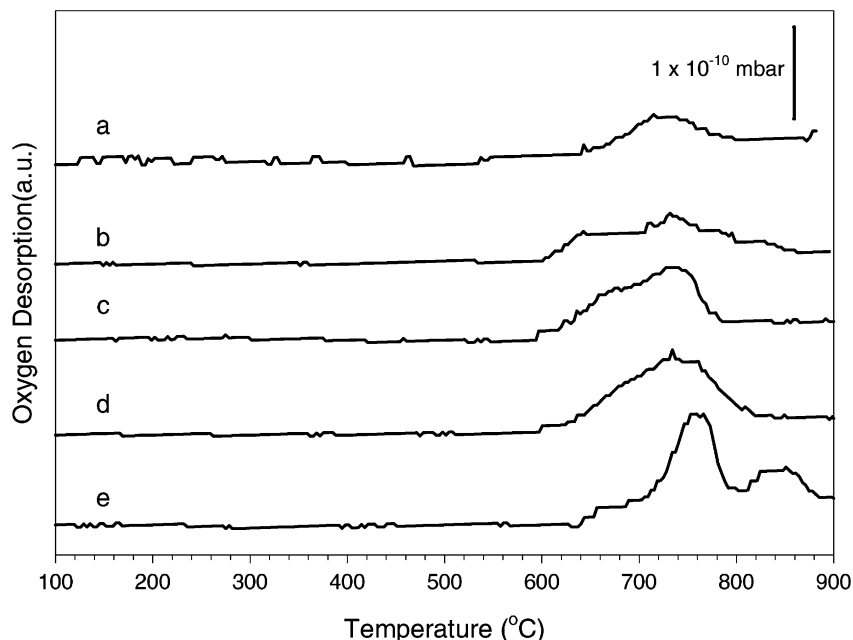
Fig. 2. TPD spectra of: (a) SLMA calcined at 1200 °C; Pd/SLMA calcined at (b) 1400 °C, (c) 1200 °C, (d) 1000 °C and (e) 800 °C.

clusters. The most significant evolution of oxygen was observed between 700 and 800 °C. In this temperature range the slight evolution of oxygen was also observed for SLMA (Fig. 2(a)) indicating that the predominant source of oxygen must be from the dissociation of PdO to metallic Pd. Hence, it can be suggested that this peak is arising from the desorption of oxygen of SLMA and palladium oxide clusters. Since the palladium oxide was decomposed and agglomerated to the large particles of metallic Pd as increasing the calcination temperature, the amount of oxygen evolved in this peak was decreased with increase of calcination temperatures as shown in Fig. 2(b)–(d). The third peak at 850 °C was observed only for Pd/SLMA calcined at 800 °C. This peak might be come from the dissociation of small cluster of PdO. The trend of TPD profiles of oxygen of Pd/SLMA can be explained by recycling mechanism between Pd and PdO proposed by Farrauto et al. [7]. The precursor Pd compound on SLMA was changed to metallic Pd during the calcination. On cooling process, the two different state of palladium oxide can be formed. One is PdO_x on Pd and the other is crystalline PdO. The former desorbed the oxygen between 740 and 770 °C and the latter above 800 °C.

Our results agree with recycling mechanism. However, when the calcination on the Pd/SLMA was done above 1000 °C, the desorption peak above 800 °C disappeared. This indicates that the small PdO crystalline did not form during cooling of large metallic Pd clusters supported on SLMA calcined above 1000 °C before TPD experiment. The intensities of other peaks also decreased with increase of calcination temperatures. Few results were reported on the effect of high temperature treatment of Pd/Al_2O_3 above 1000 °C. As increasing the calcinations temperature, it is expected that sintering are accelerated and then the size of particles of palladium becomes larger. Although the reconstruction which was proposed by Hicks et al. [12] and reoxidation of palladium particles occurred during the cooling after calcination, the reversible recycling of palladium and palladium oxide seems to be difficult because large palladium particles formed after high temperature calcination cannot converted to PdO crystallite during short period of cooling in the air. From the results of TPD of oxygen and XRD, the large cluster of metallic Pd was formed and the formation of crystalline PdO on SLMA was inhibited for Pd/SLMA calcined over 1000 °C because of the
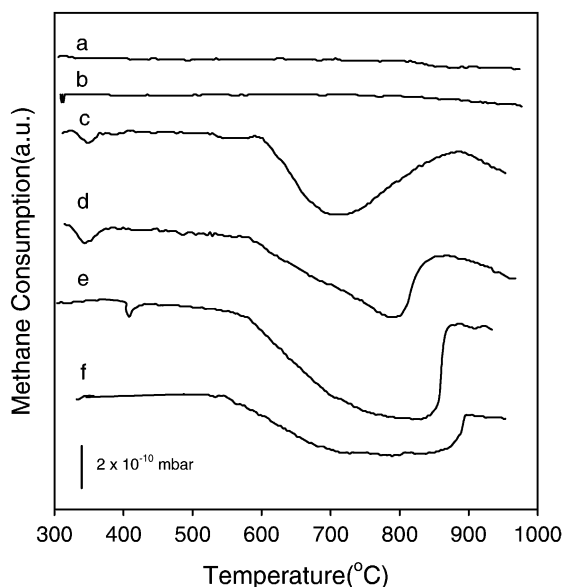
Fig. 3. TPRX spectra of methane of: (a) SLMA calcined at 1200 °C; Pd/SLMA calcined at (b) 1400 °C, (c) 1200 °C, (d) 1000 °C, (e) 800 °C and (f) 600 °C.

sintering of palladium particles to form the large Pd clusters.

3.3. TPRX and TPRO

In order to study the reactivity of surface oxygen with CH_4, TPRX was performed over SLMA and Pd/SLMA. Since gas mixture was composed of CH_4 and He without O_2, oxygen for reaction should be supplied from the surface oxygen of PdO and the lattice oxygen of SLMA. Fig. 3 shows the consumption profiles of methane for Pd/SLMA calcined at various temperatures during the TPRX of CH_4 with surface oxygen. For SLMA calcined at 1200 °C, methane was consumed over 800 °C indicating that very small amount of the lattice oxygen was activated to react with CH_4. For the Pd/SLMA calcined at 1400 °C, the profile of consumption of CH_4 was similar to that of SLMA, suggesting that large Pd metal particles calcined at 1400 °C did not play a role in CH_4 oxidation in the absence of O_2. For the Pd/SLMA calcined at 1200, 1000, 800 and 600 °C, little consumption of methane begun near 600 °C. The temperature to produce H_2O also was consistent with this temperature. The temperature to show maximum consumption of

methane and the width of temperature maintained the consumption of methane decreased as increasing the calcination temperature. This indicates that the oxygen species on PdO clusters was more reactive in the low temperature combustion of CH_4 than the lattice oxygen of SLMA.

Because the combustion of methane proceeded in the absence of O_2 coke species might be produced and deposited on Pd/SLMA. Grzybek and Baerns [13] reported that the reaction of methane with oxygen at the oxygen deficient condition produced coke. The deposition of carbon species such as carbonates on the support occurred. To study the characteristics of coke on Pd/SLMA, TPRO was performed for Pd/SLMA calcined at 600 and 1200 °C. Figs. 4 and 5 show the TPRO profiles of Pd/SLMA calcined at 600 and 1200 °C for the consumption of O_2 and the production of CO, respectively. For Pd/SLMA calcined at 600 °C, the sharp peak of O_2 consumption profile appeared at 580 °C. At the same temperature, the production of CO was also observed. In contrast with this result, constant consumption of oxygen between 800 and 1000 °C was observed for the Pd/SLMA calcined at 1200 °C. From this result, it can be suggested that the coke deposited on Pd/SLMA have at least two different species. The soft coke which was oxidized at 600 °C, was mainly formed on Pd/SLMA calcined at 600 °C after TPRX of CH_4, while hard coke which was oxidized above 800 °C was formed on Pd/SLMA calcined at 1200 °C. From the previous oxygen TPD study, we proposed that the calcination temperature affected the origin of oxygen desorbed. As calcination temperature increased, large palladium clusters supported on SLMA were converted to the Pd clusters having smaller area of PdO phases and the amount of oxygen evolved from palladium oxide phase supported on SLMA support decreased. The soft coke might be deposited on or near the surface of palladium oxide phase, which can be oxidized by O_2 at 600 °C, while hard coke on surface of SLMA support, which can be oxidized non-catalytically above 800 °C.

3.4. Surface analysis

The XPS spectra of the Pd 3d regions of Pd/SLMA calcined at various temperatures as shown in Fig. 6. Pd supported on SLMA not only decreased light off temperature but also promoted the activity. Three
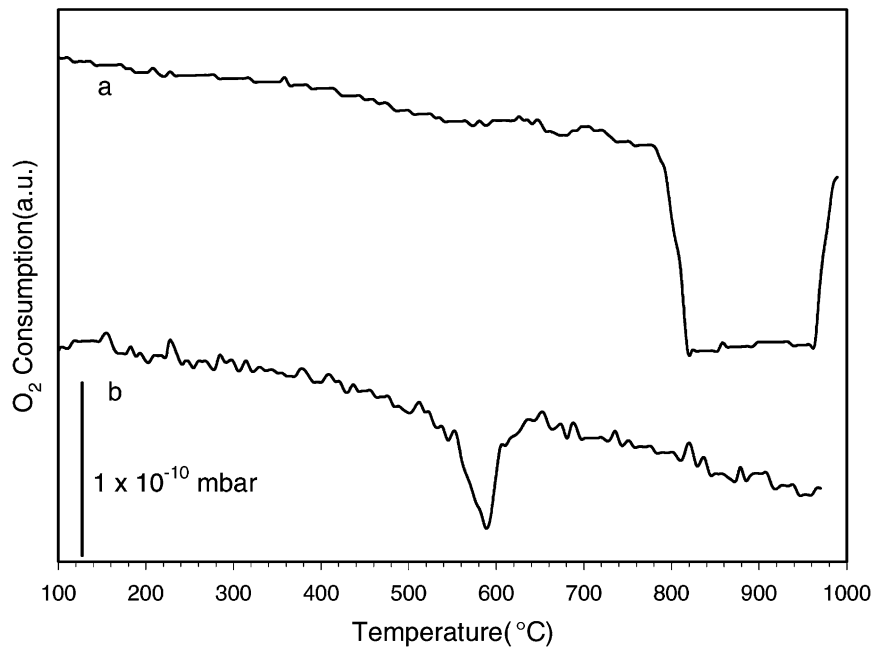
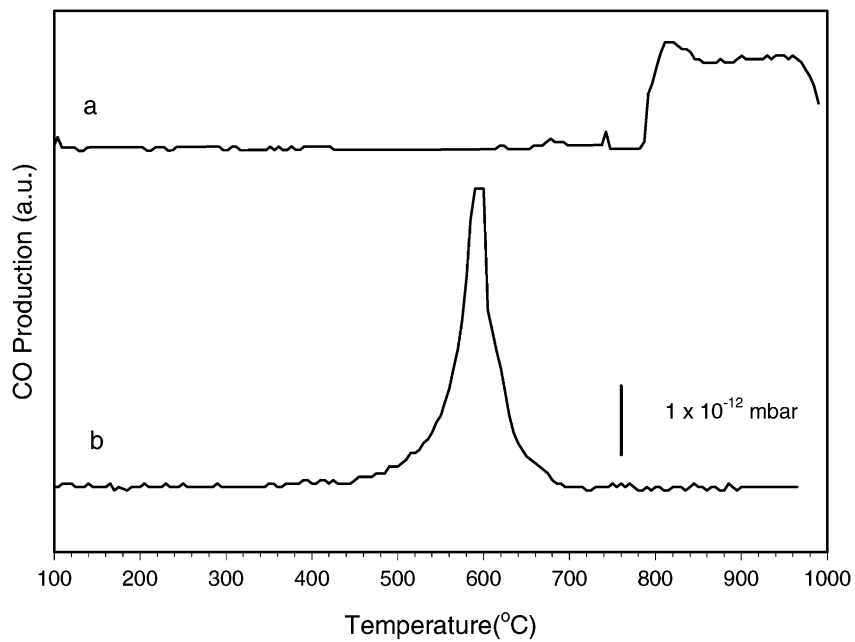Fig. 4. TPRO spectra of oxygen of Pd/SLMA calcined at (a) 1200 °C and (b) 600 °C.

Fig. 5. TPRO spectra of CO of Pd/SLMA calcined at (a) 1200 °C and (b) 600 °C.
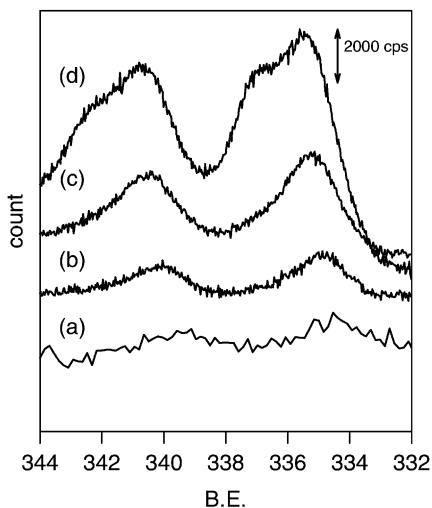
Fig. 6. XPS Pd 3d spectra of Pd/SLMA calcined at: (a) 1400 °C, (b) 1200 °C, (c) 1000 °C and (d) 800 °C.

species of oxygen on Pd clusters were indicated by the TPD of O_2 and TPRX experiments. After calcination at 800 °C on Pd/SLMA, the Pd showed two different chemical states. The intensity of Pd 3d peak was decreased with increase in the calcination temperatures. After calcination at 1400 °C, peak was not distinguishable. This result indicates that the dispersion of Pd on surface of SLMA was too low to be detected by XPS. A computer peak-fit of these envelopes of Pd 3d is shown in Figs. 7–9. The binding energy and surface composition calculated from the XPS spectra are summarized in Table 1. For the Pd/SLMA calcined at 800 and 1000 °C, Pd $3d_{5/2}$ peak was divided into two different peaks at 337.1 and 335.1 eV. The chemical state of Pd with binding energy at 337.1 and 335.1 eV can be assigned to PdO and metallic Pd, respectively. The calcination of Pd/SLMA at 1000 °C caused the peak intensity at 337.1 eV to decrease and the peak intensity at 335.1 eV to increase. However, the total
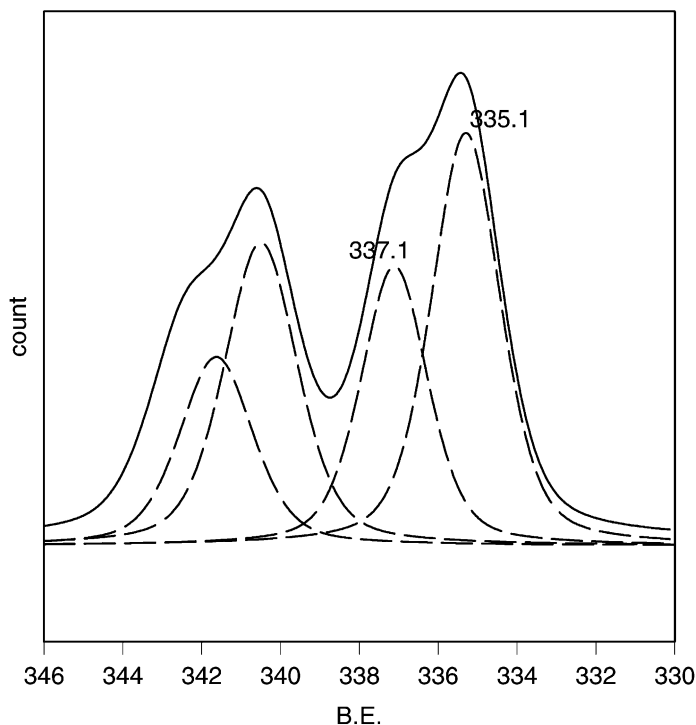

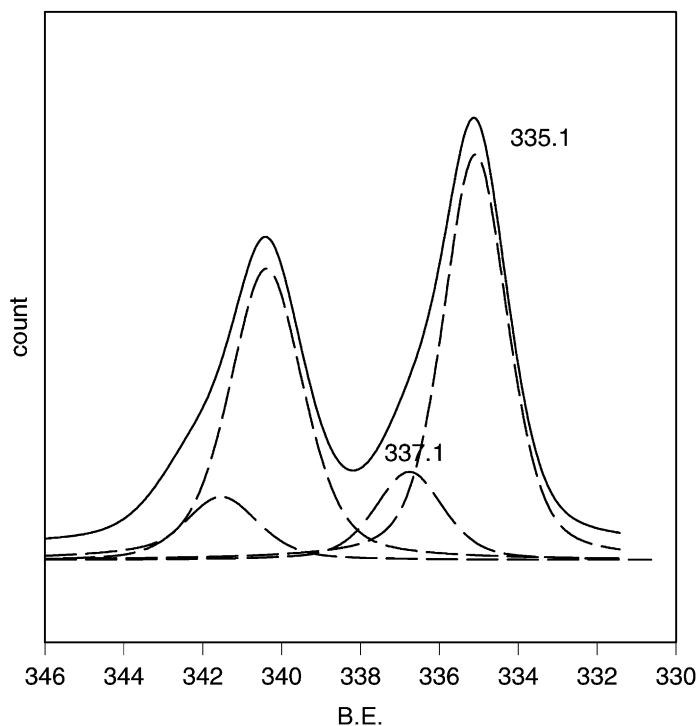Fig. 7. Deconvolution of Pd 3d peaks of Pd/SLMA calcined at 800 °C.

Fig. 8. Deconvolution of Pd 3d peaks of Pd/SLMA calcined at 1000 °C.

surface concentration of Pd^0 and PdO on SLMA, as shown in Table 1, was decreased drastically after calcination at 1000 °C. The atomic ratios of Pd/Al in PdO and Pd^0 species of Pd/SLMA calcined at 800 °C was 0.31 and 0.486, respectively. These ratios decreased to 0.041 and 0.197 after calcination at 1000 °C. The atomic ratio of Pd/Al of Pd^0 of Pd/SLMA calcined at 1000 °C was half of that of Pd calcined at 800 °C. This result can be explained by the dissociation of PdO and agglomeration to large metallic Pd clusters. For

Pd/SLMA calcined at 1200 °C as shown in Fig. 9, new peak was observed at 335.8 eV. The oxidation state of Pd at this binding energy was between metallic Pd and PdO. The Pd species with similar binding energy was reported by Otto and coworkers [15]. They suggest the Pd of binding energy at 335.8 eV assigned to the $Pd^{\delta+}$ arising from interaction with SLMA. The catalytic activity of Pd/SLMA calcined at 1200 °C decreased significant due to the suppression of formation of catalytically active PdO species.

Table 1
The comparison of Pd oxidation state of Pd/SLMA calcined at various temperatures

	Calcination temperature (°C)					
	800		1000		1200	
Binding energy (eV)	335.1	337.1	335.1	337.1	334.8	335.8
Species	Pd	PdO	Pd	PdO	Pd	$Pd^{\delta+}$
Concentration (Pd/Al)[a]	0.486	0.310	0.197	0.041	0.066	0.028

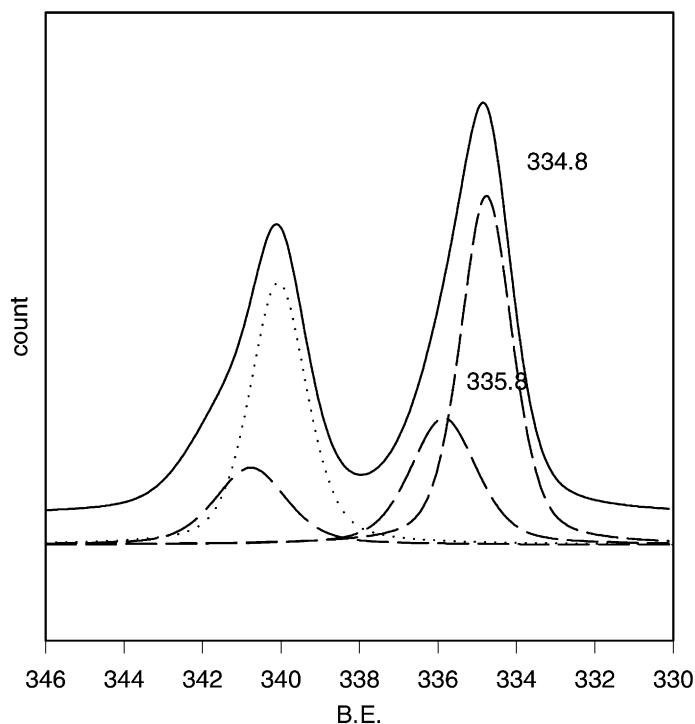[a] The concentration of Pd/Al was calculated from the XPS results using the sensitivity factor [14].

Fig. 9. Deconvolution of Pd 3d peaks of Pd/SLMA calcined at 1200 °C.

4. Conclusion

The growth of Pd metal on SLMA after calcination above 1000 °C was observed. The oxygen TPD showed the different kinds of PdO species on SLMA. As the increasing the calcination temperature, the formation of PdO crystalline was suppressed because of the formation of large Pd clusters. TPRX study indicated that the surface oxygen of PdO cluster was the major source of oxygen to react with CH_4 in the absence of O_2. TPRO study showed that the two kinds of coke were formed after TPRX. The coke decomposed at low temperature seemed to be deposited on Pd cluster, while the coke decomposed at high temperature deposited on SLMA support. XPS results showed that the relative amounts of PdO and Pd^0 on SLMA were affected by calcination temperature. XPS indicate the presence of $Pd^{\delta+}$ species arising from the strong interaction of Pd^0 and SLMA after calcination at 1200 °C.

Acknowledgements

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