



Effect of barium addition over palladium catalyst for CO–NO–O₂ reaction

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ABSTRACT

CO–NO–O₂ reaction over Pd supported on barium fixed alumina (Pd/Ba/Al) and ceria–zirconia mixed oxide (Pd/Ba/CZ) catalysts was investigated by XPS, TPR and in situ DRIFT during light-off under a stoichiometric condition. The activity of Pd supported on barium fixed alumina catalysts for CO oxidation as well as NO reduction was improved by increasing the amount of barium loading. In contrast, Ba addition decreased the activity of Pd on ceria–zirconia mixed oxide for CO oxidation, while it had little effect on NO reduction. Enhancement of CO oxidation on Pd/CZ is caused by the activated oxygen supplied from ceria–zirconia mixed oxide to Pd particles. The decrease of the activity for CO oxidation on Pd/Ba/CZ is derived from the reduced supply of the activated oxygen. On the other hand, NO reduction is independent of barium addition for CZ, indicating that the desorption and/or dissociation of NO is not affected by the activated oxygen supplied from CZ under stoichiometric CO–NO–O₂ reaction conditions.

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1. Introduction

Conventional three-way catalysts consist of noble metals, oxide supports such as alumina (Al) and ceria–zirconia mixed oxide (CZ), and some additives. It is well known that Rh possesses superior NO_x reduction activity, but its precious value and high cost demand minimum usage. As a replacement, palladium is very beneficial because of its higher activity for hydrocarbon oxidation and its relatively lower cost than other precious metals. However, palladium has a lower activity for NO reduction compared to rhodium. Then, in order to maximize the catalytic activity of palladium, alkaline earth metals such as barium have been added to some automotive catalysts in practical use [1]. Barium is generally known to play a supplemental role as NO_x absorber in NO_x storage–reduction (NSR) catalysts under lean operation conditions. Besides NO_x absorber in NSR, the effect of alkaline earth metals such as barium on alumina or alumina–ceria supported–palladium has been investigated in several papers; enhancement of thermal durability of alumina [2], suppression of hydrocarbon chemisorption on palladium [3,4] and increase of palladium dispersion [5–7] were reported in three-way catalysts operated under stoichiometric conditions.

On the other hand, understanding of the effect of barium on palladium supported on ceria–zirconia mixed oxide is not sufficiently established. The oxygen storage and release capacity of ceria–zirconia mixed oxide is technologically important for contributing an enlargement of the operating air/fuel ratio and leading

to the overall efficiency of three-way catalysts. The ceria–zirconia mixed oxide also plays a crucial role in enhancing the activity in reduction atmosphere by supplying more oxygen available for the oxidation processes. Furthermore, the oxygen vacancies associated with reduced ceria in the proximity of noble metal particles have been suggested as promoting sites for CO and NO reaction. Hence, the investigation of additive effect of barium on CZ is required for improving NO_x reduction on Pd catalyst.

In our previous work, it has been confirmed that Ba has the effect of improving the dispersion of palladium on alumina, while for palladium on ceria–zirconia mixed oxide it inhibits the supply of oxygen from CZ to palladium under CO–O₂ reaction condition [8]. In the reaction including NO as a reactant, NO predominantly adsorbs on Pd compared to CO [9] and further NO partially adsorbs as nitrite and/or nitrate on support materials such as alumina and ceria–zirconia [10,11]. Therefore, the desorption and/or dissociation of NO related species would affect to the catalytic activities. The purpose of this research is to clarify the effect of barium addition on the activity of the palladium catalysts supported on ceria–zirconia mixed oxide (Pd/Ba/CZ) for CO oxidation and NO reduction in comparison with that on alumina (Pd/Ba/Al) in the reaction of CO–NO–O₂. NO species during the reaction was especially characterized using TPR and in situ DRIFRS.

2. Experimental

Pd/Ba/Al and Pd/Ba/CZ were prepared by two-step incipient wetness impregnation. Commercially available γ -alumina (Al) (Sasol Ltd., SSA 160 m²/g) and ceria–zirconia mixed oxide (CZ) with cubic phase (Rhodia Co., Ltd., SSA 85 m²/g) were used. The molar

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Table 1
The list of each component loading for samples employed.

	Pd loading (wt.%)	Ba loading (wt.%)	SSA (m ² /g)	Pore volume (cm ³ /g)
Pd/Al	1.00	0	152	0.48
Pd/Ba(1)/Al	1.00	1.0	163	
Pd/Ba(5)/Al	0.99	5.5	150	
Pd/Ba(15)/Al	0.99	15.3	130	0.40
Pd/CZ	1.00	0	79	0.22
Pd/Ba(1)/CZ	1.02	0.94	80	
Pd/Ba(5)/CZ	1.06	4.0	78	
Pd/Ba(10)/CZ	1.03	9.5	70	0.18

ratio of CeO₂/ZrO₂ in CZ was adjusted to 1. Initially barium was impregnated on Al or CZ by aqueous solution of barium acetate. The Ba loaded oxides were dried at 150 °C for 2 h and calcined at 500 °C for 2 h in air. Subsequently, palladium was impregnated on these oxides by using aqueous solution of palladium nitrate and calcined at the same condition as the first step, resulting in Pd loading of 1 wt.%. Thus, Pd/Ba/Al catalysts with 0, 1, 5 and 15 wt.% Ba, and Pd/Ba/CZ catalysts with 0, 1, 5 and 10 wt.% Ba were prepared.

Specific surface areas (SSA) were determined by physisorption of N₂ at the liquid nitrogen temperature, using the BET equation. The samples were degassed in vacuum for at least 1 h at 200 °C prior to the adsorption measurements. Pore volumes were obtained from the desorption curve of the isotherm.

Catalytic activity using a stoichiometric mixture of 2.2% CO+0.2% NO+1.0% O₂ (He balance) was examined in a pyrex glass flow reactor system where a gas flow rate of 50 mL/min (SV = 6000 h⁻¹) and a linear heating rate of 10 °C/min from 50 °C to 400 °C were used. Prior to catalytic reaction, samples were calcined in situ under 10% O₂ (He balance) at 500 °C for 30 min and cooled in 10% O₂ gas and finally purged by He at 50 °C. Reactant gases were regulated with mass flow controllers and analyzed using a quadrupole mass spectrometer (QMS) on line.

DRIFTS analysis of adsorbed species on the catalysts under reaction conditions was carried out using a JASCO FTIR-610. A DRIFT cell was fitted with KBr windows and a heating cartridge for sample heating. Samples were pre-treated at 500 °C for 30 min in 10% O₂ (N₂ balance) and cooled to 30 °C. Then, each spectrum was measured every 20 °C with a heating rate of 10 °C/min up to 410 °C in a reaction mixture gas (5.0% CO + 0.45% NO + 2.3% O₂, N₂ balance).

XPS measurements were carried out by an Omicron EA125 spectrometer using the Mg K α radiation (1254.6 eV) at 150 W. The XPS system has a preparation chamber for samples in which in situ reduction and oxidation were fulfilled by the introduction (200 Pa) of hydrogen or oxygen to samples kept at 175 °C, respectively. All the data were referenced with C 1s binding energy fixed at 285.0 eV. The obtained peaks were deconvoluted with CasaXPS software, using a Shirley type background subtraction and symmetric Gaussian–Lorentzian line shapes.

3. Results and discussion

3.1. Catalyst characterization

Table 1 summarizes the catalyst properties; palladium and barium contents, specific surface area and pore volume. ICP analysis showed that all the samples included Pd close to 1 wt.%. The specified amount of barium supported on each material was determined by XRF. It was observed that the deposition of barium decreased the SSA and pore volume of alumina. The decrease of 14% in SSA from 152 m²/g for Pd/Al to 130 m²/g for Pd/Ba(15)/Al, corresponds to the addition of 15 wt.% barium. It indicates that the barium exists on the alumina surface without covering the pores of alumina because pore blockages should lead to a sharp drop in SSA. The decline of 17%

for pore volume also indicates that the pores are not covered with barium. Similar tendency was also revealed in Pd/CZ with barium. SSA of Pd/CZ and Pd/Ba(10)/CZ were 79 and 70 m²/g. The reduction of 11% is consistent with the barium content. It also indicates that the pores are not covered with barium for CZ.

3.2. Catalytic activity

Fig. 1a and b shows the QMS intensities of AMU28 (CO and N₂), AMU30 (NO), AMU32 (O₂), AMU44 (N₂O and CO₂) during light-off reaction over Pd/Al and Pd/Ba(15)/Al. On Pd/Al, CO oxidation and NO reduction simultaneously proceed in the CO–NO–O₂ mixture. The temperature (*T*₅₀) at which half of CO was converted to CO₂ was 219 °C, and similarly *T*₅₀ for NO and O₂ were observed at 218 °C and 220 °C, respectively. On Pd/Ba(15)/Al, CO oxidation and NO reduction occurred in the same manner as Pd/Al, although *T*₅₀ of CO and NO shifted to 179 °C and 185 °C, respectively (Fig. 1b). These results demonstrate the promoting effect of barium addition in consistent with the previous study showing the improvement of CO oxidation by barium [4]. It is to be noted that the increase of NO intensity was observed above 200 °C on Pd/Ba(15)/Al in Fig. 1b. It is reported that NO seems to be converted to N₂ and N₂O under lean conditions up to 200 °C but further increase in temperature would inhibit N₂O generation [8]. In the present study, AMU44 signals due to CO₂ and N₂O actually decreased in the same temperature range. Accordingly, the reactant gas is considered to be in a slightly lean condition although a stoichiometric mixture is introduced.

The activity of Pd supported on CZ supports for CO–NO–O₂ reaction is shown in Fig. 2a and b. Compared to the activity of alumina based catalysts, CO oxidation started already at 50 °C and CO was completely converted at 110 °C on barium free CZ supported Pd catalyst, which is in good agreement with the previous study [9]. This promoting effect of CZ is caused by the activation of oxygen supplied from CZ support [10]. After completion of CO–O₂ reaction, NO reduction seems to start through the reaction with residual

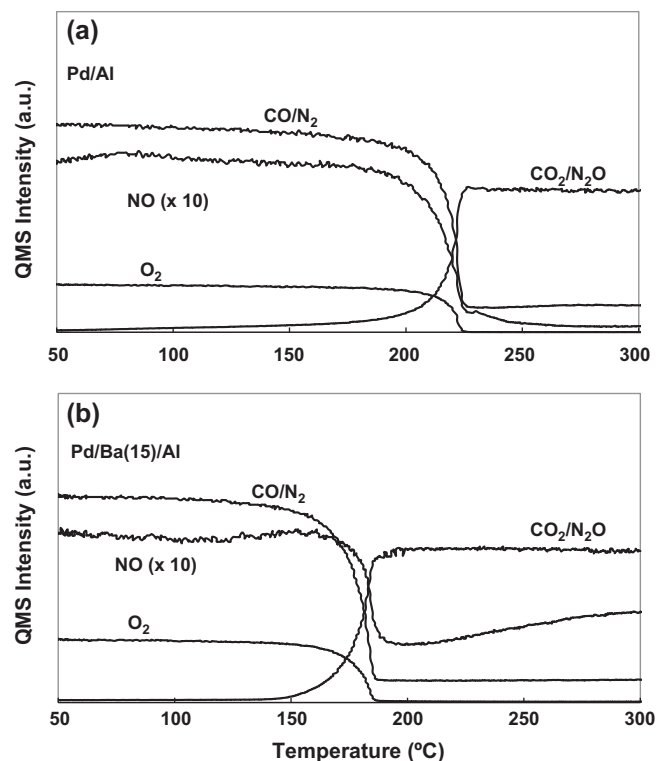


Fig. 1. QMS intensity profile of the effluent for the CO–NO–O₂ reaction over Pd/Al (a), Pd/Ba(15)/Al (b) catalysts.

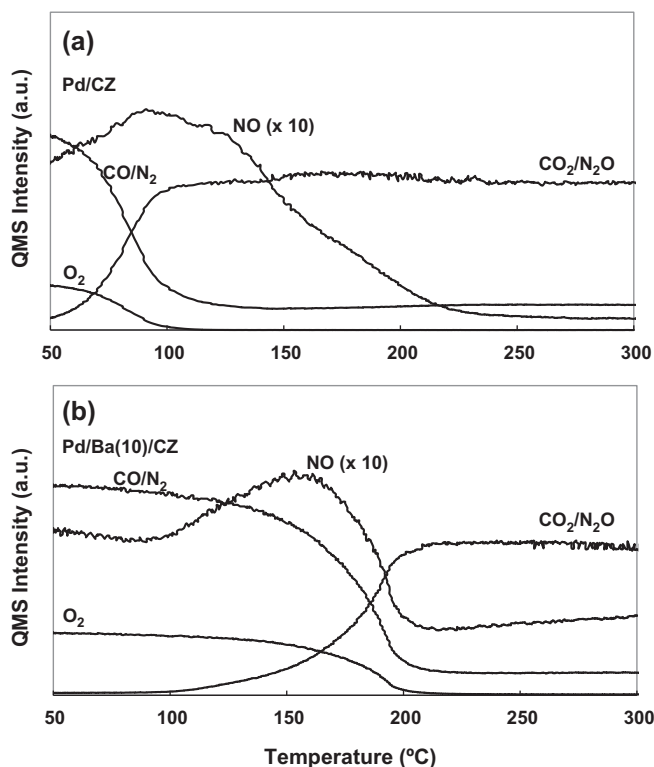


Fig. 2. QMS intensity profile of the effluent for the CO–NO–O₂ reaction over Pd/CZ (a), Pd/Ba(10)/CZ (b) catalysts.

CO. Just before the occurrence of NO reduction, NO desorption was observed at 90 °C on Pd/CZ. Similar NO desorption was reported for Rh deposited on CZ [11] as well as CZ support alone [11,12] where NO acts as ligand on the cationic Rh^{x+} species, or adsorbs strongly at defect sites presented on CZ support surface. Accordingly, it is supposed that molecular NO species adsorb over cationic Pd^{x+}, or nitrite and/or nitrate species are deposited over CZ surface, because NO desorption is absent from Pd/Ba(0, 15)/Al.

The presence of barium caused an apparent decrease of CO oxidation in the CZ supported system (Fig. 2b). T_{50} of CO conversion on the CZ catalyst with 10 wt.% Ba drastically shifted to a higher temperature. This indicates that barium prevents the contact between Pd–CZ and inhibits oxygen supply from CZ to Pd, resulting in the decrease of the activity of Pd/Ba/CZ for CO oxidation. In contrast, T_{50} of NO conversion was not noticeably different from that of Pd/CZ, and as a result NO reduction on Pd/Ba(10)/CZ started simultaneously with CO oxidation as observed on Pd/Ba(0, 15)/Al. It suggests that NO reduction is not influenced by the presence of oxygen from CZ. The QMS intensity of NO increased in a similar manner as Pd/CZ but the desorption peak from Pd/Ba(10)/CZ shifted to a higher temperature of 150 °C. The peak shift seems to be related to the change of the adsorption strength between NO and cationic Pd^{x+}, or between nitrite and/or nitrate and CZ surface due to Ba addition. Further investigation is needed for the origin of the different adsorption strength. The decrease of NO conversion above 200 °C on Pd/Ba(10)/CZ is also caused by the decrease of N₂O generation under a slightly lean condition as mentioned before.

The temperatures of T_{50} observed over Pd/Ba/Al and Pd/Ba/CZ in the CO–NO–O₂ reaction are summarized in Table 2. On Pd/Ba/Al system, T_{50} for CO conversion was constantly lowered from 219 °C to 179 °C in the order of Pd/Al, Pd/Ba(1)/Al, Pd/Ba(5)/Al and Pd/Ba(15)/Al. T_{50} of Pd/Ba(5)/Al was approximately the same as that of Pd/Ba(15)/Al, indicating the amount of 5 wt.% barium is enough to improve the activity under this condition. Similar tendency was

Table 2
50% isoconversion temperatures (T_{50} , °C) observed for Pd/Ba/Al and Pd/Ba/CZ catalysts in the CO–NO–O₂ reaction.

	T_{50} (CO conv.)	T_{50} (NO conv.)	T_{50} (O ₂ conv.)
Pd/Al	219	218	220
Pd/Ba(1)/Al	197	200	198
Pd/Ba(5)/Al	180	186	180
Pd/Ba(15)/Al	179	185	179
Pd/CZ	82	174	81
Pd/Ba(1)/CZ	87	197	85
Pd/Ba(5)/CZ	126	178	126
Pd/Ba(10)/CZ	179	198	180

confirmed for NO reduction as well. These results demonstrate the promoting effect of barium addition. Considering the behavior that CO oxidation and NO reduction start at the same temperature for each catalyst, it is most likely that a determining step controls commonly both reactions regardless of the present of Ba.

On Pd/Ba/CZ, T_{50} for CO oxidation drastically increased from 82 °C to 179 °C in the order of Pd/CZ, Pd/Ba(1)/CZ, Pd/Ba(5)/CZ and Pd/Ba(10)/CZ. Finally, the activity of Pd/Ba(10)/CZ resembles that of Pd/Ba(15)/Al. On the contrary, NO reduction was not affected by Ba addition, and all the catalysts showed approximately the same activity as that of Pd/Ba/Al. These results indicate that NO reduction is less influenced by support materials, in contrast to CO oxidation.

CO conversions based on the QMS intensities of CO during CO–O₂ and CO–NO–O₂ reactions on Pd/Ba(0, 15)/Al and Pd/Ba(0, 10)/CZ are compared in Fig. 3a and b. On Pd/Al, T_{50} of CO conversion varied from 185 °C to 218 °C by NO addition. Similarly, T_{50} of CO conversion shifted from 145 °C to 179 °C on Pd/Ba(15)/Al. It was, thus, clarified that the activity for CO oxidation is remarkably deteriorated by the presence of NO in the reaction gases irrespective of barium addition. It is most likely caused by NO adsorption on Pd surface, inhibiting CO adsorption and/or the dissociation of O₂ on palladium. Hence, the desorption and/or dissociation of NO adsorbed on Pd is considered to be the limiting step of CO–NO–O₂ reaction [10].

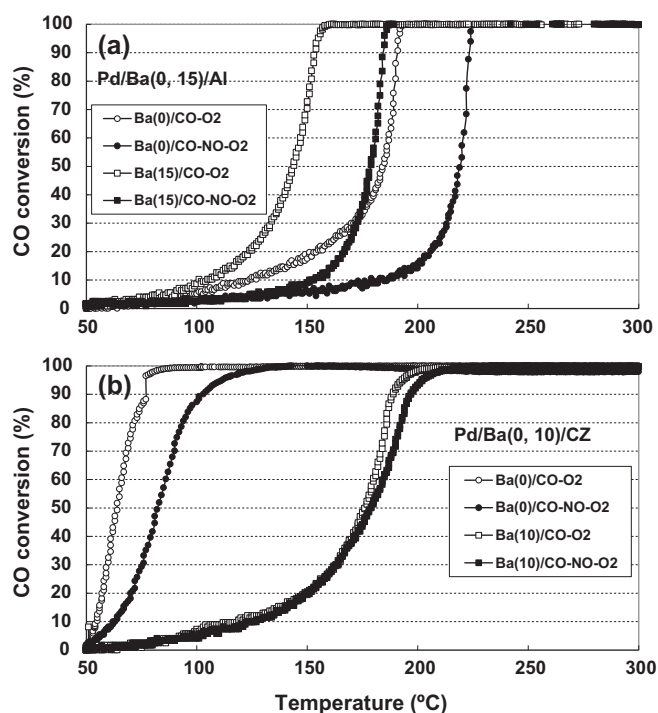


Fig. 3. CO conversion in CO–O₂ and CO–NO–O₂ reactions as a function of the amount of Ba loading for Pd/Ba(0, 15)/Al (a), Pd/Ba(0, 10)/CZ (b) catalysts.

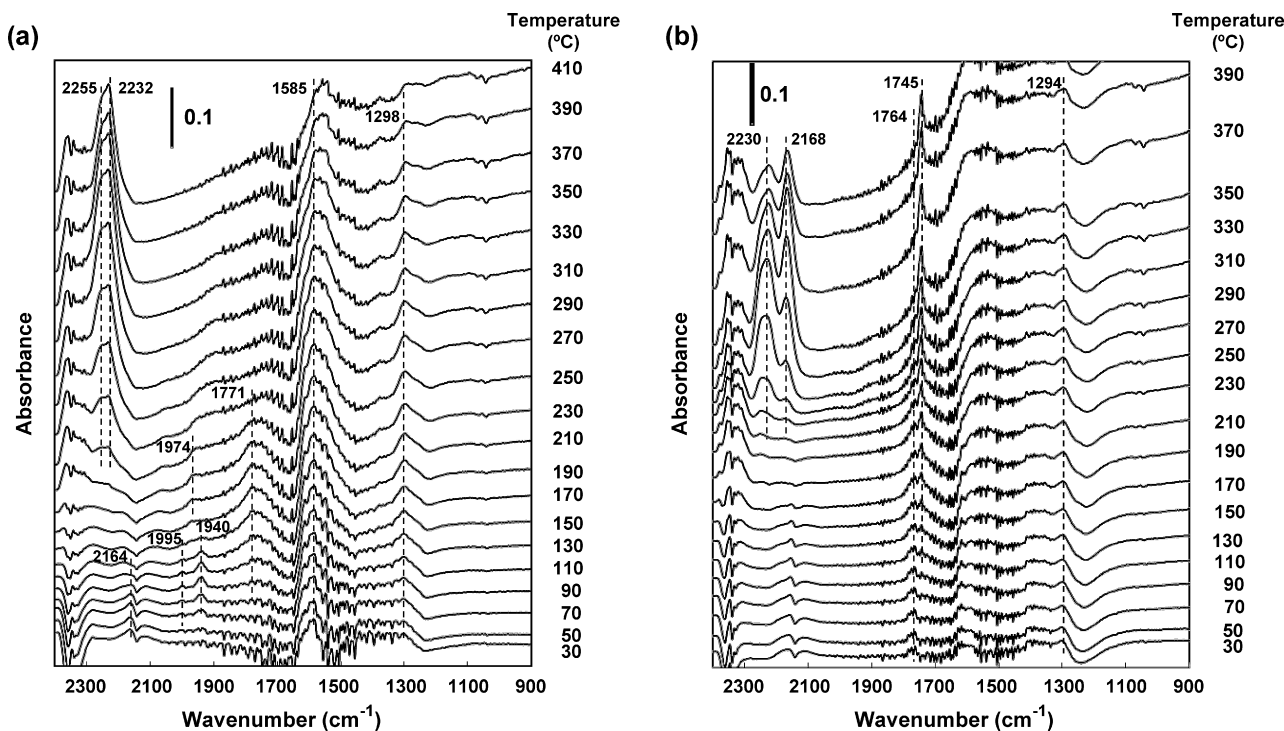


Fig. 4. DRIFT spectra for Pd/Al (a), Pd/Ba(15)/Al (b) in a temperature range of 30–410 °C under CO–NO–O₂ reaction conditions.

On the other hand, the activity of Pd/CZ for CO oxidation was slightly influenced by the addition of NO. T_{50} of CO conversion shifted from 65 °C to 82 °C by NO in the reaction gases, indicating that NO molecules prevent somehow the progress of CO oxidation. On the other hand, the activity of Pd/Ba(10)/CZ stayed almost constant irrespective of the presence of NO in contrast to the case of Pd/Ba/Al (Fig. 3a). NO actually gives little influence on CO oxidation over CZ based catalysts. Therefore, it is interpreted that the activation of oxygen supplied through O₂ dissociation is not significantly affected by NO, although barium certainly influences Pd–CZ interaction.

3.3. In situ DRIFTS

In order to elucidate the reaction mechanism, the adsorption states of each reactant on Pd/Al and Pd/CZ catalysts during the reaction were evaluated by using DRIFTS in a temperature range of 30–410 °C under a stoichiometric gas mixture of CO, NO and O₂. In the CO–O₂ reaction, on-top CO (2099 cm⁻¹) on Pd metal was observed even after O₂ pre-treatment, indicating that PdO is readily reduced by CO at 30 °C under NO free condition and CO adsorbs on metallic Pd sites [9]. However, in the spectra of DRIFT on Pd/Al as shown in Fig. 4a, an absorption band around 2164 cm⁻¹ corresponding to CO adsorbed on PdO overlapped to the absorption of CO gas at 30 °C, although absorption of NO gas was not observed due to its low concentration. Above 70 °C new peaks instead appeared at 1940 cm⁻¹ and 1995 cm⁻¹ which can be assigned as CO adsorbed on bridged sites of metallic Pd [13]. As for the adsorption of NO, an absorption band was detected at 1771 cm⁻¹ above 110 °C which is assignable to NO contacting with metallic Pd [13,14]. Upon increasing the temperature the peak intensity of bridged CO on Pd was lowered while that of NO on Pd was enhanced. Thus, NO predominantly adsorb on active sites of Pd and suppress the adsorption of CO [13]. When the temperature reached to 210 °C, the intensity of adsorbed NO gradually weakened and instead a peak at 1974 cm⁻¹ due to bridged CO appeared with the absorption of CO₂ in the gas phase. It corresponds well to the result of TPR (Fig. 1a) in which CO

oxidation and NO reduction started at the similar temperatures. Therefore, the desorption and/or dissociation of NO adsorbed on metallic Pd is a limiting step in this reaction. Above 250 °C, a peak was newly observed at 2255 cm⁻¹ with a shoulder at 2232 cm⁻¹ due to the vibration of Al–NCO of tetrahedral and octahedral Al³⁺ species, respectively [10]. It means that NCO species is formed via the reaction of dissociated NO and CO on palladium and spills over onto Al₂O₃ surface, because NCO species accumulated on alumina is stably present at higher temperatures as reported in the literature [13]. The vibrations of carbonate and nitrates on Al₂O₃ surface appeared in the 1200–1650 cm⁻¹ region. An unambiguous assignment of all the frequencies is not possible. However, the band at 1298 cm⁻¹ and 1585 cm⁻¹ could be assigned to bridging and/or chelating bidentate nitrate on Al₂O₃ based on the adsorption band reported for NO on Al₂O₃ surface [15].

On Pd/Ba(15)/Al, noticeable absorption bands related to CO on Pd were absent under the present condition (Fig. 4b), but a weak absorption band at 1764 cm⁻¹ assignable to NO adsorbed on metallic Pd developed from 90 °C, overlapping with that of Ba nitrate [15]. It indicates that CO on Pd desorbs more readily than that of Pd/Al. In agreement with the observation by XPS that the presence of Ba suppresses the growth of Pd particles [16], the surface of palladium particles is most likely covered by carbonates or nitrates detected in the 1200–1650 cm⁻¹ region due to the reaction of CO/NO and O₂ with barium. As a result, the reactivity could be improved by the desorption of CO and NO at relatively lower temperatures, leading to the evolution of CO₂ gas absorption at 190 °C. Above 210 °C a new band was observed at 1745 cm⁻¹ which could not be assigned in the present study, but it is related to the interaction of barium and CO because the same peak was also observed on Pd/Ba/CZ (Fig. 5b) as well as Ba/Al without Pd under CO–O₂ condition (not shown). In the temperature region higher than 230 °C, two bands at 2230 cm⁻¹ and 2168 cm⁻¹ were observed assignable to Al–NCO and Ba–NCO, respectively [17]. It is confirmed that the formation of isocyanate species on alumina and barium does not affect the reaction on the Pd/Ba/Al. The bands assignable to bridging and/or chelating bidentate nitrate on Pd/Ba/Al were detected immediately

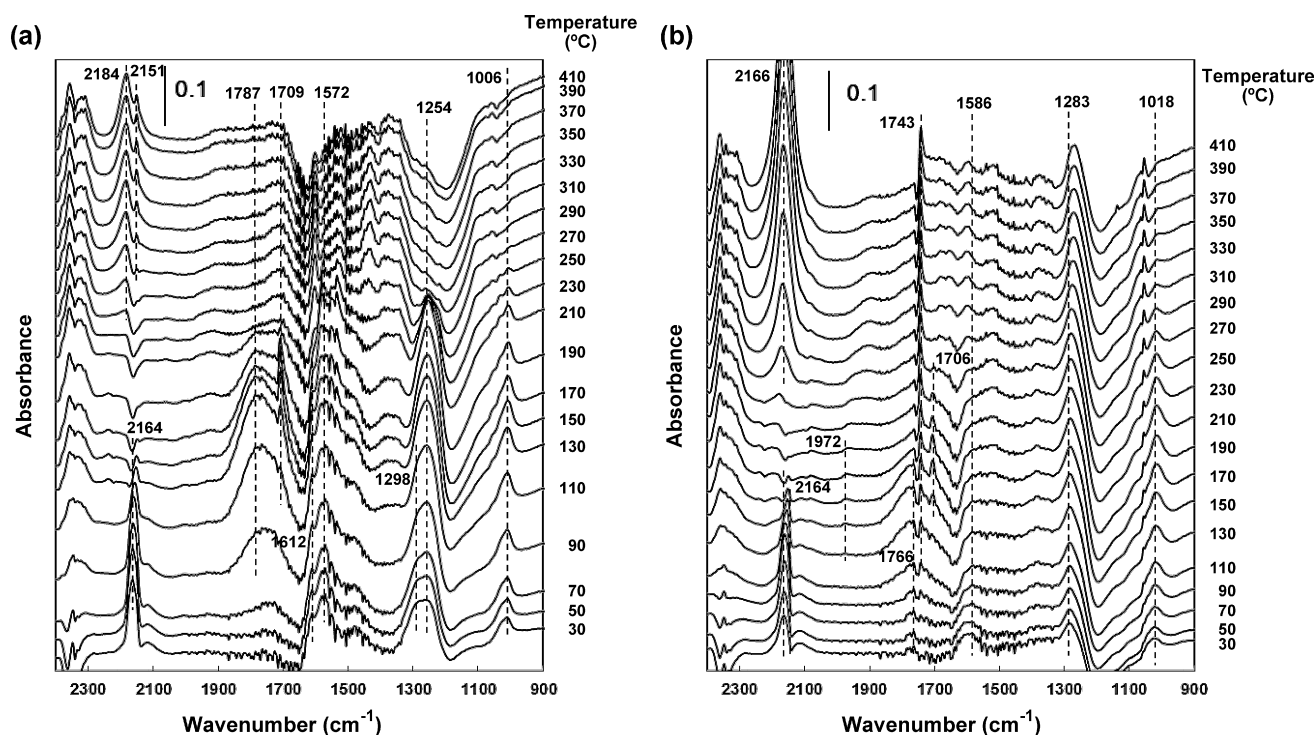


Fig. 5. DRIFT spectra for Pd/CZ (a), Pd/Ba(10)/CZ (b) in a temperature range of 30–410 °C under CO–NO–O₂ reaction conditions.

after the reaction at 1294 cm⁻¹ and around 1600 cm⁻¹ similar to Pd/Al [10].

Fig. 5a displays the intensive peak of on-top CO adsorbed on PdO at 2164 cm⁻¹ at 30 °C over Pd/CZ, where oxygen can be supplied from CZ support to Pd particles. The stability of CO on PdO is in agreement with the previous study [12]; the absorption peak of CO on Pd/ceria–zirconia/alumina disappeared at 150 °C. Concurrent with the decrease of CO on PdO, two large peaks assigned to Pd⁰–NO (1787 cm⁻¹) and Pd–NO^{δ-} (1709 cm⁻¹) [13,14,18] were observed above 90 °C. It seems that NO species adsorb on the metallic Pd sites reproduced by the reduction of PdO in the progress of CO oxidation reaction because there are no other peaks assigned to CO on Pd. This result corresponds to the result of TPR where O₂ is completely consumed at 110 °C as shown in Fig. 2a. The broad peak

at 1787 cm⁻¹ assignable to Pd⁰–NO was gradually enhanced until 130 °C and weakened with increasing temperature. This behavior is corresponding to the desorption of NO over 130 °C observed in TPR (Fig. 2a). On the other hand, Pd–NO^{δ-} at 1709 cm⁻¹ maintained its intensity over 150 °C and disappeared at 210 °C, namely T₁₀₀ of NO conversion in TPR. It indicates that the desorption of NO and/or the dissociation of NO^{δ-} on Pd is the limiting step for NO reduction in a similar manner as Pd/Al. This is consistent with a reaction mechanism proposed in the previous studies. Chuang et al. have proposed as the NO–CO reaction mechanism on Rh/Al that Rh–NO⁻ dissociates to form adsorbed nitrogen and oxygen, and adsorbed oxygen reacts with Rh⁺(CO)₂ to produce CO₂ [19]. Furthermore, it has been shown that Pd⁰–NO and Pd–CO are the active adsorbates involved in the NO–CO reaction on Pd/Al [13]. In the temperature region

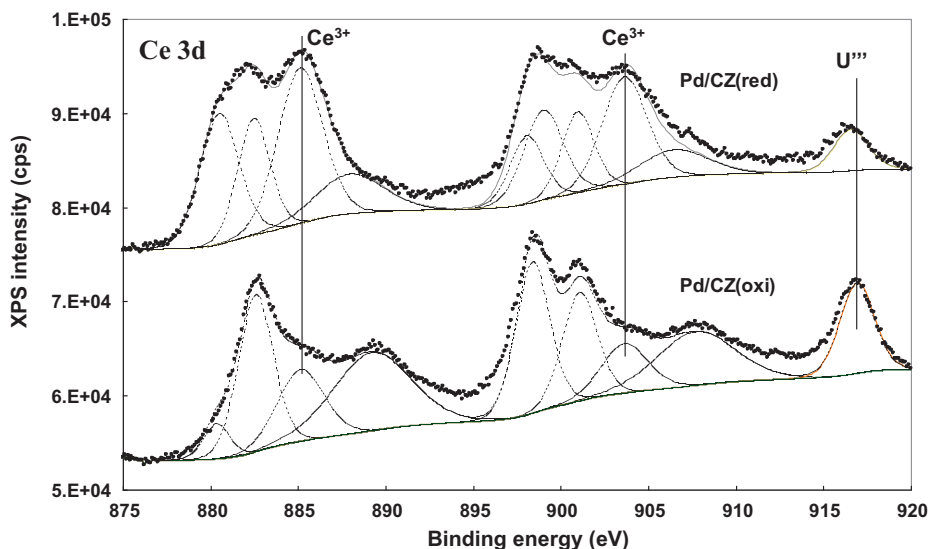


Fig. 6. The effect of reduction and oxidation treatment on Ce 3d lines for Pd/CZ.

higher than 250 °C, two bands at 2184 cm⁻¹ and 2151 cm⁻¹ were observed which can be assigned to CZ–NCO [20]. The appearance of two bands suggests the presence of two adsorption sites such as Ce⁴⁺ and Ce³⁺. The presence of Ce³⁺ is observed for Pd/CZ in Ce 3d XPS as shown in Fig. 6. The Ce 3d states at 885 eV and 904 eV B.E. due to Ce³⁺ increased together with the decrease of so-called U'' line at 917 eV B.E. characteristic to Ce⁴⁺ by reduction. Inversely, the Ce 3d states due to Ce³⁺ decreased by oxidation. However, it was revealed that a certain amount of Ce remained as Ce³⁺, which is nicely correlated with two bands assigned to CZ–NCO in the DRIFT (Fig. 5a). On CZ surface, bridged or chelated bidentate nitrates are observed as intensive absorption bands at 1572 cm⁻¹, 1254 cm⁻¹ and 1006 cm⁻¹ from 30 °C [21]. These nitrates species remained up to 210 °C, namely T₁₀₀ of NO conversion in TPR. However, the reduction of peak intensity at 1298 cm⁻¹ and 1612 cm⁻¹ below 110 °C seems to contribute to NO desorption in TPR, because there was no peak derived from molecular NO species on cationic Pd^{x+} [11].

On Pd/Ba(10)/CZ, PdO–CO (2164 cm⁻¹) was clearly identified at 30 °C as shown in Fig. 5b, which is different from the case of Pd/Ba/Al without any noticeable peaks assigned to PdO–CO. However, the peak of CO on PdO dropped its intensity to half of that on Pd/CZ (Fig. 5a) but remained until 190 °C. It indicates that to some extent oxygen supply from CZ support materials to Pd particles is inhibited by Ba addition. Above 150 °C, the peaks assigned to Pd⁰–NO and Pd–NO^{δ-} were observed at 1766 cm⁻¹ and 1706 cm⁻¹, respectively and bridged Pd–CO also appeared around 1972 cm⁻¹. These CO and NO bands depleted in a temperature range from 190 °C to 230 °C, corresponding to the simultaneous occurrence of CO oxidation and NO reduction at the same temperature as observed on Pd/Ba/Al. In consistent with the elimination of Pd–NO band, Ba–NCO species was detected (2166 cm⁻¹), providing evidence of NO dissociation. These results suggest that Ba has no effect on the desorption and/or dissociation of NO over palladium supported on CZ but inhibits oxygen supply from CZ to Pd particles. In the region of 1000–1650 cm⁻¹, several peaks assigned to nitrates on Pd/Ba/CZ were detected at 30 °C. However, these intensities were weakened compared with Pd/CZ because the CZ supports were partly covered with barium, and no noticeable variation is recognized for the nitrate species related to NO desorption in the range of 100–170 °C.

4. Conclusions

Effect of barium addition on Pd/Ba/Al and Pd/Ba/CZ systems was investigated by XPS, TPR and DRIFTS under CO–NO–O₂

stoichiometric condition. The improvement due to barium addition was clearly observed on Pd/Ba/Al, although negative effect was demonstrated on Pd/Ba/CZ. The activity of Pd/Ba/Al for CO oxidation as well as NO reduction was improved by increasing the amount of barium loading. In the DRIFT spectra, CO and NO species on Pd predominantly appeared with nitrates and carbonates on oxide supports. On both Pd/Al and Pd/Ba/Al, CO oxidation and NO reduction occurred simultaneously with the decrease of NO absorption bands on Pd. Thus, NO desorption and/or dissociation process is the rate-limiting step for both reactions regardless of the presence of barium on alumina. In Pd/Ba/CZ system, it was revealed that CO oxidation was enhanced by the activated oxygen supplied from CZ to Pd particles, which is inhibited by barium addition, resulting in the decrease of CO oxidation. In contrast, NO reduction was independent of barium addition, indicating that barium has no effect on the desorption and/or dissociation of NO over palladium supported on CZ.

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