Catalysis Science & Technology

Accepted Manuscript

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ARTICLE

DRIFTS study of the role of alkaline earths in promoting the catalytic activity of HC and NO_x conversion over Pd-only three-way catalyst

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Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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To reveal the role of alkaline earths modification in promoting the catalytic activity of HC and NO_x conversion, the catalytic activity tests and DRIFT experiments at different reaction conditions were performed. The introduction of alkaline earths promotes the catalytic activities of both HC and NO_x elimination under stoichiometric NO_x-CO-HC-O_2 condition, especially for Pd/CZBa, whereas inhibits the CO oxidation. In addition, the operation window of NO_x conversion is also widened obviously as a result of enhanced NO_x storage ability. DRIFTS results demonstrate that the modification with alkaline earths improves the formation rate of nitrites and nitrates due to enhanced electron transfer and oxygen mobility, as well as the dissociation of NO species on the active metal, which increases the storage ability and reduction performance of NO_x. On the other hand, the doping of alkaline earths could weaken the inhibiting effect arising from strongly bonded HC species on NO adsorption and dissociation due to the promoted catalytic activity of HC deep oxidation, which promotes the reaction of CO and NO_x at low temperature.

1. Introduction

Three-way catalysts (TWCs), up to now, is the most satisfactory and efficient solution to control and suppress automobile exhaust emission by converting basic air pollutants like CO, HC and NO_x to their inactive products CO_2, N_2 and H_2O[1]. In recent years, Pd supported on various CeO_2-ZrO_2 mixed oxides has been studied for exhaust catalysis with great interest because of low cost and high activity[2-4]. However, the evolution towards more strict standards in gasoline exhaust emission, requiring decrease of cold-start emissions (especially HC and NO_x). Therefore, considerable efforts have focused on improving the NO_x and HC elimination activities of Pd-only three-way catalysts by structural modification with electropositive promoters, such as rare earths, transition earths and alkaline earths[5-8].

More attention has been paid to the alkalis and alkaline earths addition recently, considering higher basicity or electron-donating ability of them compared with the rare earths and transition earths[9-11]. As reported in previous literatures[12, 13], barium has been added to the Ce-based or Al_2O_3-based supports as a NO_x absorber in NO_x storage-reduction (NSR) catalysts under lean operation conditions. Recently we have also found that the doped alkaline earth metal could enter into the CeO_2 lattice and lead to the formation of more homogenous solid solution with higher surface area and smaller crystallite size. The corresponding Pd-only three-way catalysts, especially Ba modified catalyst, presenting obviously improved catalytic activity of HC and NO_x conversions as well as thermal aging resistance[14]. Nevertheless, knowledge of the configuration of the active metals and reactivity of adsorbates on the catalyst surface is the key factor to developing a fundamental understanding of the reaction mechanism[15]. The most widely used technique for determining the structure of adsorbates on supported metal catalysts is in situ DRIFT spectroscopy[16-19]. As evidenced by previous work, interaction of the reaction mixture with the surface of the catalysts at high temperature leads to the formation of more isocyanate species which are considered as one of the reactive intermediates in the reaction of NO and CO[20-23]. They considered that the high activity of the catalyst can be attributed to more isocyanate species formed on the catalyst surface. The formation process of isocyanate species involves the dissociation of adsorbed NO on active metal sites and thus the NCO band intensity can be used as fingerprint of NO dissociation. Furthermore, the NO dissociation and consequently de-NO_x performance could be enhanced by structural modification. For instance, M. Konsolakis and I. V. Yentekakis[5] found that the introduction of Na would result in a progressive red shift of N-O stretching frequency associated with NO adsorbed on the active metal sites. This red-shift is attributed to the weakening of the N-O bond induced by Na promotion. Regarding to the reaction mechanisms of the active intermidiate species[24], it is generally accepted that the adsorbed NO might dissociate and react with CO to produce N^* followed by the subsequent reaction with CO_{ads} or CO_g to form NCO species. Recently, it was found that the key step in the reaction between NO and CO is the flip of a cyanide group from metal sites to the Al_2O_3 support, followed by the subsequent formation of NCO species on Al_2O_3 support[25]. Hence, the catalytic performance of the catalysts can be well interpreted on the basis of the formation and consumption of the active intermediates.

To gain further insight into the role of alkaline earths in promoting the catalytic activity of HC and NO_x conversions, the impact of alkaline earths promoters on the nature and reactivity of surface species formed over $Pd/Ce_{0.67}Zr_{0.33}O_2$ catalysts as well as the configuration of noble metal species dispersed on $Ce_{0.67}Zr_{0.33}O_2$ support were investigated using in situ DRIFTS, CO chemisorption, UV-HR Raman, XPS and NO_x-TPD-MS. On the other hand, the catalytic activities under stoichiometric NO_x-HC-CO-O_2, NO_x-CO-O_2 and NO_x-HC-O_2 reaction conditions have also been examined.

2. Experimental

2.1. Synthesis of Catalyst

$Ce_{0.67}Zr_{0.33}O_2$ (designated as CZ) and alkaline earths modified supports $Ce_{0.67}Zr_{0.33}M_xO_{2+x}$ (designated as CZM) with 3 wt.% dopant were prepared by a co-precipitation and supercritical drying method[8]. The corresponding supported Pd-only catalysts with Pd content of 1.0 wt. % were prepared by conventional wet impregnation method with an aqueous H_2PdCl_4 as metal precursor[7]. The catalysts were calcined at 600 ^{o}C in air for 4 h and designated as Pd/CZ, Pd/CZMg, Pd/CZCa, Pd/CZSr and Pd/CZBa, respectively.

2.2. Catalytic performance studies

Catalytic tests corresponding to reaction mixture at the stoichiometric point (0.745 % O_2-0.067 % C_3H_6-0.033 % C_3H_8-0.75 % CO-0.1 % NO-0.03 % NO_2 with balance Ar at a GHSV of 43, 000 h^{-1}) were carried out with a fixed-bed continuous flow reactor, and the concentrations of CO, NO, NO_2 and total HC (C_3H_6 and C_3H_8) were quantified by an on-line Bruker EQ55 FTIR spectrometer. In order to investigate the competing reaction of HC (C_3H_6, C_3H_8) and CO, the NO_x-CO-O_2 and NO_x-HC-O_2 reactions were also performed at the stoichiometric point (0.295 % O_2-0.75 % CO-0.1 % NO-0.03 % NO_2 and 0.5565 % O_2-0.067 % C_3H_6-0.033 % C_3H_8-0.1 % NO-0.03 % NO_2 with balance Ar at a GHSV of 43, 000 h^{-1}).

λ is defined as $(2\nu O_2 + \nu NO + 2\nu NO_2) / (\nu CO + 9\nu C_3H_6 + 10\nu C_3H_8)$ (ν means concentration in volume percent unit), λ=1.0 is at stoichiometry. Under lean combustion, the NO_x operation window was measured when the λ is up to 1.1 from 1.0 by a Hiden QIC-20 mass detector working in electron impact (EI) mode at 70 eV.

2.3. Dispersion of Pd

Dispersity of Pd species was calculated on the basis of CO chemisorption using CHEMBET-3000 (Quantachrome Co.). The catalyst (0.2 g) was reduced by purified H_2 at 400 ^{o}C for 1 h, then purged at 400 ^{o}C by He for 0.5 h and cooled down to 30 ^{o}C. CO was pulsed into the sample bed every 5 min until no consumption of CO could be detected.

2.4. In situ DRIFTS measurements

DRIFT spectra were collected using a Nicolet 6700 FTIR with a MCT detector and an IR cell that allowed in situ sample treatment. All spectra were obtained with resolution of 4 cm^{-1} and accumulation of 32 scans. Before each DRIFT experiment, the samples were in situ pre-treated for 0.5 h in Ar (10 ml/min) stream at 450 ^{o}C. Subsequently, the system was cooled down to 30 ^{o}C and the background spectra were recorded prior to the introduction of reacting gases. Three different types of DRIFT experiments were performed: (1) CO adsorption experiments were performed in the DRIFTS reactor at 30 ^{o}C with a flow of 0.75 % CO, and balance Ar. The catalyst was first reduced by purified H_2 at 350 ^{o}C for 0.5 h and then purged by Ar for 0.5 h. After cooling to 30 ^{o}C, a background spectrum was taken in Ar, and then the CO adsorption experiment was performed for 0.5 h. (2) NO_x adsorption experiments were performed at 30 ^{o}C with a flow of NO_x (0.1 % NO-0.03 % NO_2, Ar balance) for 0.5 h, and consequently the gas of O_2 was introduced into the DRIFTS reactor. The time-course spectra of NO_x adsorption were recorded. (3) DRIFTS reaction experiments were also conducted under three different conditions (stoichiometric NO_x-CO-HC-O_2, NO_x-CO-O_2 and NO_x-HC-O_2), and spectra were recorded as a function of temperature at the interval of 50-400 ^{o}C. The simulated gas concentration and space velocity are same to the corresponding catalytic activity test.

3. Results and discussion

3.1. Catalytic performance under NO_x-HC-CO-O_2 reaction condition

The results of light-off temperature ($T_{50\%}$) and full-conversion temperature ($T_{90\%}$) for CO, HC, NO and NO_2 conversion under stoichiometric NO_x-HC-CO-O_2 reaction condition are presented in Fig. 1. It can be seen that the introduction of alkaline earths obviously promotes the catalytic conversions of both HC and NO_x, the $T_{50\%}$ and $T_{90\%}$ clearly decrease with the doping of alkaline earths. It is worthwhile to note that the catalytic activities of HC, NO and NO_2 conversions over the catalysts are in the order of Pd/CZBa > Pd/CZSr > Pd/CZCa > Pd/CZMg > Pd/CZ. However, the appearance of alkaline earths shows an inhibiting effect on CO elimination since the $T_{50\%}$ and $T_{90\%}$ of CO increase over all the modified catalysts. The sequence of the catalytic activity of CO oxidation over the catalysts is Pd/CZ > Pd/CZBa > Pd/CZSr > Pd/CZCa > Pd/CZMg.

From Fig. 1C, it can be seen that the catalysts show high selectivity of NO_x to N_2O formation at lower temperature than $T_{50\%}$ of NO_x. However, the N_2O selectivity is reduced by the modification with alkaline earths, and which sharply decreases at lower temperature (190 °C) compared with that of Pd/CZ (230 °C). The results indicate that N_2O is the dominating N-containing product during the cold start process, and the doping of alkaline earths obviously increases the selectivity of NO_x to N_2 formation under this reaction condition. Moreover, compared with other catalysts, Pd/CZBa catalyst exhibits the lowest selectivity of N_2O, indicating that the introduction of Ba obviously promotes the reduction performance of NO_x.

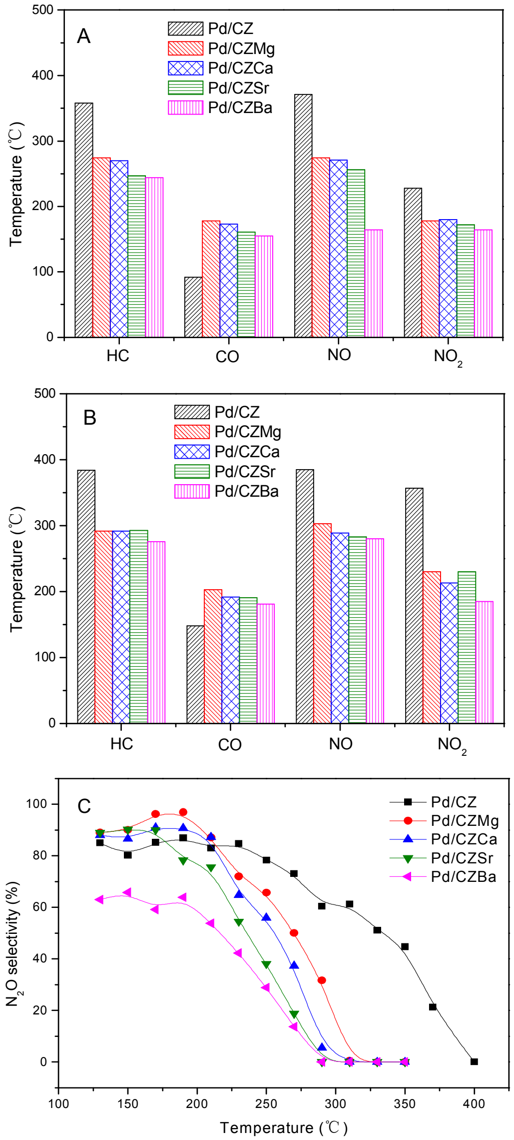

Fig. 1. Light-off temperature (A: $T_{50\%}$) and full-conversion temperature (B: $T_{90\%}$) of HC, CO and NO_x and the selectivity of N_2O formation (C) over the catalysts.

In this work, the NO_x concentration was monitored when the λ is up to 1.1 from 1.0 in order to evaluate the influence of alkaline earths modification on the width of the NO_x operation window. As presented in Fig. 2, it takes more time for NO_x concentration to reach the equilibrium value and there are smaller amounts of NO_x produced over the alkaline earths doped catalysts when the reaction switched from stoichiometric to lean-burn condition (λ=1.1). This result indicates that the modification with alkaline earths, especially Ba, Sr and Ca, obviously promotes the catalytic activity of NO_x reduction under lean combustion condition and widens the operation window of NO_x conversion. The width of the NO_x operation window over the catalysts is as follows: Pd/CZBa, Pd/CZSr, Pd/CZCa > Pd/CZMg > Pd/CZ. The basic reason is that the introduction of alkaline earths obviously improves the NO_x storage ability of the catalysts, especially Pd/CZBa, as revealed by NO_x-TPD-MS results that the desorption quantity of NO_x over the doped catalysts is much larger than that of Pd/CZ (see Fig. S1in ESI).

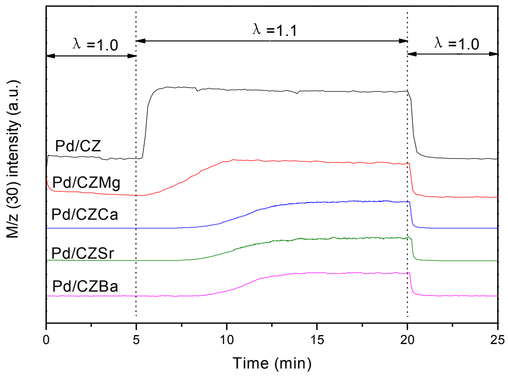

Fig. 2. The operation window of NO_x over the indicated catalysts.

3.2. Catalytic performance under NO_x-CO-O_2 and NO_x-HC-O_2 reaction conditions

To reveal the role of alkaline earths in promoting the catalytic activity of HC and NO_x conversion, the catalytic activity tests under stoichiometric NO_x-CO-O_2 and NO_x-HC-O_2 conditions have been carried out. Pd/CZBa catalyst which presents the best catalytic activities of HC and NO_x conversions has been chosen as the representative, and the corresponding catalytic activity of Pd/CZBa was compared with that of Pd/CZ catalyst.

Fig. 3A shows $T_{50\%}$ and $T_{90\%}$ of NO, NO_2 and CO over the indicated catalysts under stoichiometric NO_x+CO+O_2 condition. $T_{50\%}$ and $T_{90\%}$ of the target pollutants over the Ba modified catalyst are higher than that of Pd/CZ, indicating that the Pd/CZ catalyst presents higher catalytic activities of CO oxidation and NO_x reduction than that of Pd/CZBa under stoichiometric NO_x+CO+O_2 condition. Compared with the catalytic activity of the pollutants obtained under stoichiometric NO_x-CO-HC-O_2 condition, it can be seen that the presence of HC has no obvious influence on the oxidation activity of CO, while obviously decreases the catalytic activity of NO_x reduction over Pd/CZ. This result suggests that the fierce competition exists between CO-O_2 and CO-NO_x reactions, and the presence of HC inhibits the CO-NO_x reaction, especially over Pd/CZ. However, the doping of Ba could weaken this inhibiting effect caused by the presence of HC under NO_x-CO-HC-O_2 condition, especially at low reaction temperature.

As shown in Fig. 3B, under stoichiometric NO_x-HC-O_2 condition, $T_{50\%}$ and $T_{90\%}$ of NO_x conversion over the catalysts are lower than that of HC conversion, indicating that HC more easily reacts with NO_x than O_2. Meanwhile, Pd/CZBa catalyst shows little higher catalytic activities of HC and NO_x conversions than the non-doped Pd/CZ. Nevertheless, the catalytic activities of HC and NO_x conversions obviously increase over Pd/CZ and decrease over Pd/CZBa compared with that under stoichiometric NO_x-HC-CO-O_2 condition. These results mean that the doping of Ba has no obvious promoting effect on the NO_x-HC and HC-O_2 reactions under NO_x-HC-O_2 condition. However, the modification with Ba promotes the reaction of CO with NO_x under NO_x-HC-CO-O_2 condition, due to the presence of competing reactions of CO with O_2 and NO_x, and thus also promotes the reaction of HC with O_2.

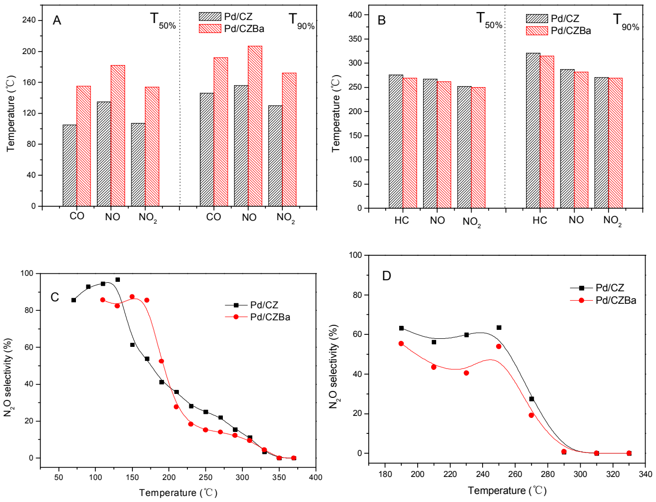

Fig. 3. Light-off temperature ($T_{50\%}$) and full-conversion temperature ($T_{90\%}$) of CO, HC, and NO_x conversions and the selectivity of N_2O formation over the Pd/CZ and Pd/CZBa under NO_x-CO-O_2 (A, C) and NO_x-HC-O_2 (B, D) reaction condition.

From Figs. 3C and D, it can be seen that the selectivity of N_2O formation are decreased by the modification with Ba under these two reaction conditions, suggesting that pronounced beneficial effects on N_2-seletivity are achieved over Ba-promoted catalyst, which is consistent with the results obtained under NO_x-HC-CO-O_2 condition. As is well-known, the nature and configuration of PdO_x species dispersed on the supports and the nature of adsorbates on supported metal catalysts have a great effect on catalytic performance. In order to obtain the related information, several characterization techniques have been carried out below.

3.3. DRIFTS spectra of CO adsorption

The DRIFTS spectra of CO adsorbed at 30 °C are exhibited in Fig. 4. Three intense IR bands at 2088, 1965 and 1914 cm^{-1} can be observed. The band at 2088 cm^{-1} corresponds to linear CO chemisorbed on metallic Pd sites, whereas the other two bands at 1965 and 1914 cm^{-1} are related to carbonyls species chemisorbed on the bridging and hollow sites of metallic Pd particles, respectively[26-28]. The relative intensities of these bands are much higher over Pd/CZ than the alkaline earths doped catalysts, suggesting that there are more carbonyls absorbed on active sites for Pd/CZ catalyst, in accordance with the dispersity of Pd species. Pd/CZ exhibits the highest dispersion and the sequence is Pd/CZ (40.7 %) > Pd/CZBa (10.3 %) > Pd/CZSr (9.6 %), Pd/CZCa (9.5 %) > Pd/CZMg (6.1 %). The introduction of alkaline earths increases the specific surface area of the supports (as reported in our previous work[14]) but decreases the dispersion of active metals. One possible reason is that the modification with alkaline earths possibly changes the surface property of the supports. It could be due to the improved basicity of the alkaline earth modified support[29]. Hence, H^+ rather than $PdCl_4^{2-}$, was preferentially adsorbed on the modified support. On the other hand, the electron-donating ability of alkaline earth would increase electronegativity of the supports, which also goes against the adsorption of $PdCl_4^{2-}$ species with negative charge.

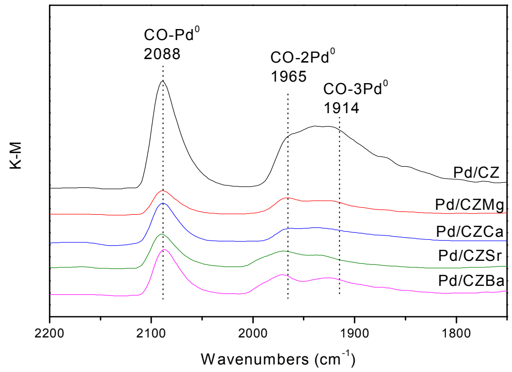

Fig. 4. DRIFTS spectra of CO adsorption over the indicated catalysts.

Martínez-Arias[16] pointed out that the small structural differences between the PdO particles formed for each catalysts are not reflected in strong kinetic changes for the CO-O_2 reaction, according to the structurally insensitive character of this reaction over the supported Pd catalyst. The main differences between them are essentially related to the different numbers of active centers present in each case. Therefore, Pd/CZ catalyst with higher dispersity of Pd exhibits the better oxidation activity of CO as a result of much more active sites on the catalyst surface. Nevertheless, for the reduction reaction of NO, NO dissociation is essential[30] and most favoured over the larger Pd particles[16], and which may be the rate-determining step under the employed conditions. Thus the catalytic activities of NO_x reduction by CO and HC could be promoted by the introduction of alkaline earths.

3.4. Time-resolved DRIFTS spectra of NO_x adsorption

To gain insight into the NO_x storage processes occurring at the catalytic solid-gas interface and the influence of alkaline earths doping, the adsorption behaviour of NO_x over Pd/CZ and Pd/CZBa catalysts at 30 °C is displayed in Fig. 5. According to the literature[31, 32], the intense bands in the range of 1700 cm^{-1}-900 cm^{-1} can be attributed to nitrite/nitrate species adsorbed on supports. From Fig. 5, it can be seen that the intensity of the band at 1180 cm^{-1} assigned to bidentate nitrite species gradually increases as a function of time when the catalysts were exposed to NO_x/Ar gas. The formation of nitrite species is mainly via electron transfer from a reduced Ce^{3+} center to a NO_2 molecule to give bonded NO_2^- entity, and the Ce^{3+} is oxidized simultaneously to Ce^{4+} cation with one O healing the vacancy[33]:

$$NO_2 + Ce^{3+} - \square \rightarrow Ce^{4+} = O_2N^-$$

Here, Ce^{3+}-□ represents an oxygen vacancy linked to Ce^{3+}. As presented by the above equations, the oxygen vacancy as the adsorption sites of NO_x plays an important role in nitrites formation. Considering the strong oxidizing properties of ceria-based materials, it is possible that NO^- species exist as transient species in the electron and oxygen transfer processes involved in the formation of nitrites from NO[34]. The nitrite species cannot be further oxidized, due to the absence of activated O^* species.

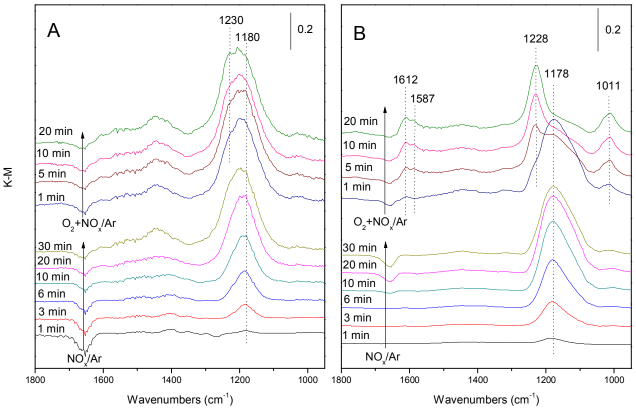

Fig. 5. Time-resolved DRIFT adsorption spectra of NO_x over Pd/CZ (A) and Pd/CZBa (B) under NO_x/Ar and O_2+NO_x/Ar flow gas.

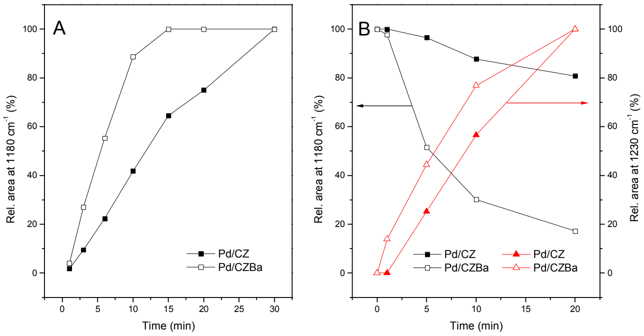

Fig. 6. The evolution of nitrites and nitrates with time measured as relative area of bands at 1180 and 1230 cm^{-1} under NO_x/Ar (A) and O_2+NO_x/Ar (B) flow gas.

However, after stoichiometric O_2 is added into the NO_x/Ar flow, the intensity of bands at around 1612, 1587, 1230 and 1011 cm^{-1} obviously increases along with the gradual weakening of the band related to nitrites, especially over Pd/CZBa. The corresponding species are attributed to nitrates in a variety of structures/configurations ranging from bridged bidentate (1620-1600, 1225-1170 and 1030-1000 cm^{-1}) to chelating bidentate (1585-1545, 1265-1225 and 1040-1010 cm^{-1}) nitrate species[10]. This phenomenon shows that nitrites species adsorbed on supports are oxidized to nitrates with the introduction of oxygen, because of the O_2 molecule can be adsorbed following electron transfer by one-electron or two-electron surface defects as activated O^* species (superoxide O_2^- or peroxide O_2^{2-})[33].

The most intense bands related to nitrites and nitrates lies at 1180 and 1230 cm^{-1}, respectively. We therefore consider these two bands as a measure for the rate of nitrites and nitrates formation. Fig. 6 presents the evolution of these two species expressed by the relative area of the band at 1180 and 1230 cm^{-1} as a function of time. It can be seen that the formation rates of nitrite and nitrate species are obviously increased by the addition of Ba, which is favourable to the storage and elimination of NO_x. As the formation of nitrites/nitrates occurs mainly via electron or oxygen transfer, the above results indicate that the modification with alkaline earths promotes the electron transfer and oxygen mobility probably due to the increased oxygen vacancies and Ce^{3+} concentration as revealed by the UV Raman (see Fig. S2 in ESI) and XPS results (see Table S1 in ESI).

3. 5. In situ reaction

3. 5. 1. In situ DRIFTS studies of NOx-HC-CO-O2 reaction system

Fig. 7 depicts IR spectra of adsorbed species over Pd/CZ and Pd/CZBa catalysts under stoichiometric NO_x-CO-HC-O_2. Bands at 2930 and 2852 cm^{-1} in the high frequency region are associated with -CH stretching vibrations[35]. The intensities of these bands are weakened by the presence of Ba, indicating that the introduction of Ba inhibits the adsorption of hydrocarbon and corresponding fragments on the catalyst surface and facilitates the transformation of -HC species to other intermediates (e.g. carbonyls and carboxylates). Bands in the range of 2200-2000 cm^{-1} can be attributed to CO and intermediate species (NCO and CN) adsorbed on active metal sites[22]. Band at 2167 cm^{-1} observed below 210 °C corresponds to Pd^{2+}-CO-adsorbed species, indicating that Pd species are mainly in its oxidized form under lower temperature condition. The band related to Pd^{2+}-CO species decreases in the intensity and shifts to lower wavenumber with increasing reaction temperature. This phenomena results from the decreased dipole-dipole coupling between CO chemisorbed molecules with decreasing coverage as well as progressive reduction of Pd sites, which would act to decrease the C-O bond order and thus lowering the C-O stretching vibration frequency[22]. Bands at 2142 (CO-$Pd^{\delta+}$), 2120 (CO-Pd^+) and 2097 cm^{-1} (CO-Pd^0) assigned to carbonyl species chemisorbed on Pd sites are observed when the temperature rises up to 230 °C[28, 36, 37]. According to the results of the catalytic activity test (Figs. 1A and B), the oxidation reactions of HC reactants are significantly promoted at this temperature, which means that the carbonyl species arise from the partial oxidation of HC. This observation is also confirmed in NO_x-HC-O_2 reaction system below. However, compared with Pd/CZ catalyst, the intensity of bands related to carbonyl species adsorbed on Pd^0/Pd^+ sites over Pd/CZBa is obviously decreased, indicating that the doping of

Ba promotes the deep oxidation activity of HC reactants, resulting in less carbonyls formation.

When the reaction temperature is further increased above 310 °C, new bands at 2172 and 2146 cm^{-1} assigned to isocyanate (NCO) and cyanide (CN) species adsorbed on metallic Pd sites[21, 38] can be observed, and which attains their maximum intensity at 400 °C. It is generally accepted that the formation of NCO and CN species requires NO dissociation to produce adsorbed N atoms, accompanied by the bonding with CO and C atoms on metal active sites, respectively[25, 39]. Thus the intensity of the bands related to intermediate species is usually regarded as a useful fingerprint to monitor the NO dissociation process, and the formation of NCO and CN species is an important path for NO reduction[5, 24]. Important to note that the introduction of Ba promotes the formation of these intermediate species, demonstrating that the introduction of Ba promotes NO dissociation on active metal, and thus Pd/CZBa catalyst presents higher reduction activity of NO.

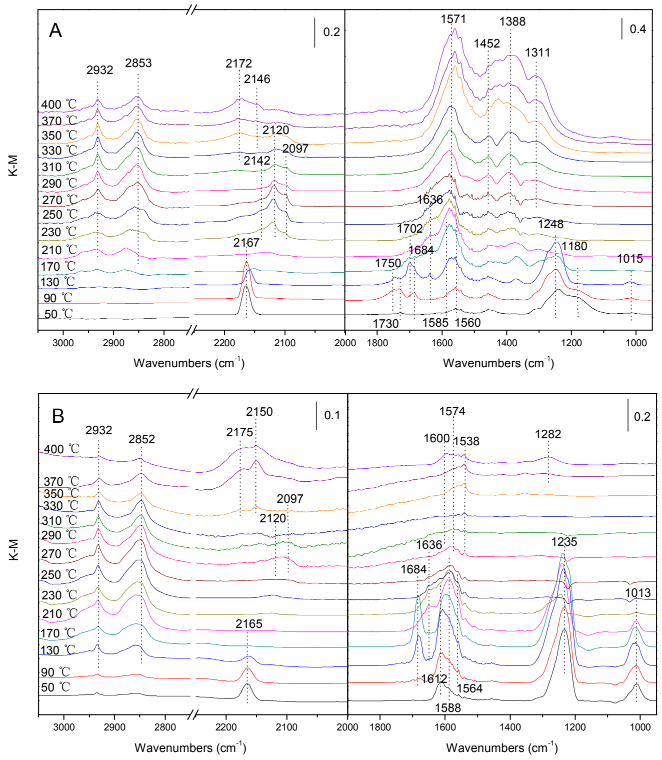

Fig. 7. In situ DRIFTS spectra over Pd/CZ (A) and Pd/CZBa (B) catalysts under stoichiometric NO_x-CO-HC-O_2.

Moreover, bands in the region of 1800-1650 cm^{-1} can be attributed to NO species adsorbed on metallic Pd sites[34, 38, 40]. Three bands at 1750, 1730 and 1702 cm^{-1} assigned to linear Pd-N=O adsorbed on Pd(112), (111) and (110) facets as well as the band at 1684 cm^{-1} associated with bent Pd-N=$O^{\delta-}$ could be observed over Pd/CZ at lower temperature, while only Pd-N=$O^{\delta-}$ band with stronger intensity appears over Pd/CZBa. Changes in the strength of the metal-NO bond is usually related to the electron-withdrawing effect of oxygen atoms from the dissociation of NO and activation of O_2. The oxygen atoms accumulated around Pd would further lower the extent of electron-back-donation into the molecular anti-bonding π^* of NO [40], and thus Pd-N=$O^{\delta-}$ species can be observed. However, only Pd-N=$O^{\delta-}$ species are observed over Pd/CZBa catalyst, which may be related to increased electron density of Pd species due to the outstanding electron-donating ability of Ba and promoted oxygen mobility. It is worth noting that these adsorbed nitroxyl species are produced before carbonyl species adsorbed on Pd^0/Pd^+ sites appear, indicating that the electron-rich sites, such as Pd^0, prefer to interact with the electron-accepting NO molecules rather than CO at lower temperature.

N_2O is formed by the reaction of N^* and NO_{ads}, and N_2 is formed by the recombination of two N^*. While two reaction mechanisms have been proposed for the N^* formations[32]. The first mechanism involes a direct bimolecular reaction between NO and CO to form N^* and CO_2. While the second one involves the unimolecular dissociative adsorption of NO to form N^* and O^*, followed by a rapid removal of O^* by CO to form CO_2. The dissociation adsorption of NO species on Pd sites is strongly structure-sensitive and requires higher temperatures[41]. Compared with neutral Pd-N=O species, the negatively charged Pd-N=$O^{\delta-}$ are dissociated more easily and would lead more probably to the production of N^* at lower temperature[42]. Simultaneously, an increased coverage of N^* on catalyst surface promotes the N_2 formation[43]. It suggests that the presence of alkaline earths would obviously promotes the dissociation of NO species on the active metal, especially for the bimolecular reaction between NO and CO at lower temperature, which is in accordance with the test results of catalytic activity and N_2O selectivity displayed in Fig. 1.

In addition, bands in the range of 1650-950 cm^{-1} can be attributed to nitrite, nitrate and carboxylate species adsorbed on the supports[22]. The bands (1612, 1588, 1560, 1235 and 1010 cm^{-1}) related to nitrate species in a variety of structures or configurations can be observed at lower temperatures, and the band (1180 cm^{-1}) assigned to nitrite species is only observed over Pd/CZ, indicating that the introduction of Ba promotes the oxidation of nitrites to nitrates, which is consistent with the adsorption behaviour of NO_x displayed in Fig. 5. However, it is worth noting that the bands related to carbonates (1571, 1452 and 1311 cm^{-1}), bicarbonate (1636 and 1388 cm^{-1}) and formate species (1600 cm^{-1}) appear when the temperature was raised up to 250 °C[5, 28] and the intensity of these bands obviously increases with temperature increasing, especially for Pd/CZ. It suggests that the presence of Ba could weaken the adsorption of carboxylate species on catalyst surface due to the promoted catalytic activity of HC deep oxidation, and prevents the poisoning caused by strongly bonded carboxylates.

3. 5. 2. In situ DRIFTS studies of NO_x-CO-O_2 reaction system

Fig. 8 depicts IR spectra of adsorbed species over Pd/CZ and Pd/CZBa catalysts under stoichiometric NO_x-CO-O_2 condition from 50 to 400 °C. It can be seen that just bands associated with CO species adsorbed on Pd^{2+} sites and NCO/CN species adsorbed on Pd^0 sites appear in the range of 2200-2000 cm^{-1}. However, compared with Fig. 7, the intensity of these bands is obviously increased. Furthermore, the bands at 2172 and 2150 cm^{-1} associated with NCO/CN species attains maximum in the intensity at lower temperature, especially over Pd/CZ. In addition, the intensities of the bands in the region of 1800-1650 cm^{-1} associated with NO species adsorbed on metallic Pd sites obviously increase over Pd/CZ. These results demonstrate that the adsorption and dissociation of NO species occur more easily on the active metal over Pd/CZ than Pd/CZBa under NO_x-CO-O_2 condition. The romoval of adsorbed oxygen as a rate-deterining step has been proposed for the NO-CO reaction on Pd catalysts[15], while the adsorbed oxygen could be quickly consumed by CO under NO_x-CO-O_2 condition at lower temperature. Therefore, the catalytic activity of NO_x reduction is obviously promoted, especially for Pd/CZ, which is in accordance with the result of the catalytic activity test (Fig. 3A).

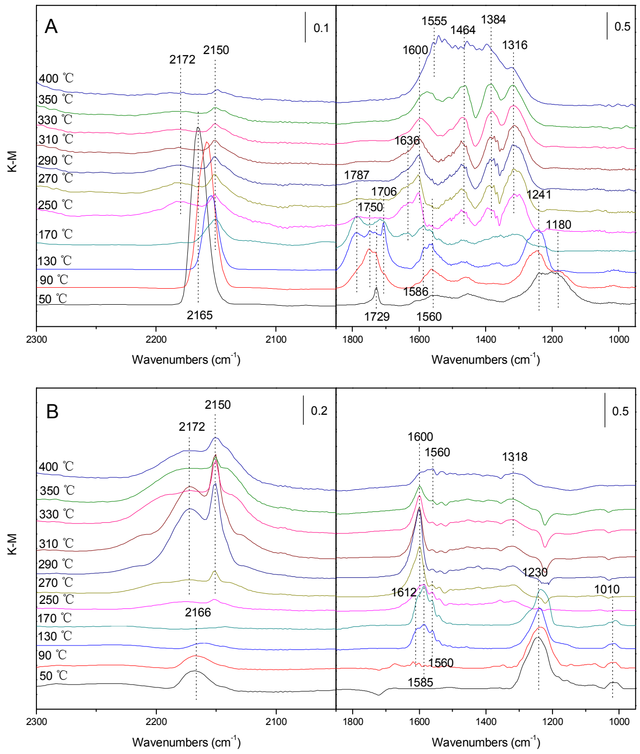

Fig. 8. In situ DRIFTS spectra over Pd/CZ (A) and Pd/CZBa (B) catalysts under stoichiometric NO_x-CO-O_2 condition.

3. 5. 3. In situ DRIFTS studies of NO_x-HC-O_2 reaction system

Fig. 9 depicts IR spectra of adsorbed species over Pd/CZ and Pd/CZBa catalysts under stoichiometric NO_x-HC-O_2 condition. Comparing Figs. 9 and 7, there was no obvious difference about the bands associated with -CH stretching vibrations. However, the intense bands at 2167 (CO-Pd^{2+}), 2142 (CO-$Pd^{\delta+}$), 2120 (CO-Pd^{+}) and 2097 cm^{-1} (CO-Pd^{0}) assigned to adsorbed carbonyls derived from the partial oxidation of HC[44] are observed, especially over Pd/CZ at above 230 °C, whereas only CO-Pd^{+} and CO-Pd^{0} species appear over Pd/CZBa. This result again demonstrates that the modification with Ba promotes the deep oxidation of HC. Moreover, it is obvious that the intensity of the bands at 2176 and 2150 cm^{-1} assigned to isocyanate and cyanide species significantly decreases compared with Figs. 7 and 8, especially over Pd/CZ catalyst. It is likely to be because the chemisorbed carbonyls on the active metal inhibit NO adsorption and dissociation under NO_x-HC-O_2 condition, which seriously decreases the reduction activity of NO_x, especially over Pd/CZBa, resulting that catalytic activity of NO_x conversion is obviously lower than that under NO_x-HC-CO-O_2 condition.

For Pd/CZ, in contrast to the spectra of NO_x-HC-CO-O_2 and NO_x-CO-O_2 reaction, the bands related to nitrosyl species in the region of 1800-1700 cm^{-1} could not be seen over both the catalysts. However, the peak at 1686 cm^{-1} with high intensity could be observed under NO_x-HC-O_2 and NO_x-HC-CO-O_2 reactions. These results indicate that the oxidation state (electron density) of Pd depends on the reaction environment[15]. The negatively charged NO species, that dissociate more easily compared with neutrally and positively charged NO species[42], would lead more probably to the production of nitrogen. Hence, the catalysts present higher N_2 selectivity under NO_x-HC-O_2 condition.

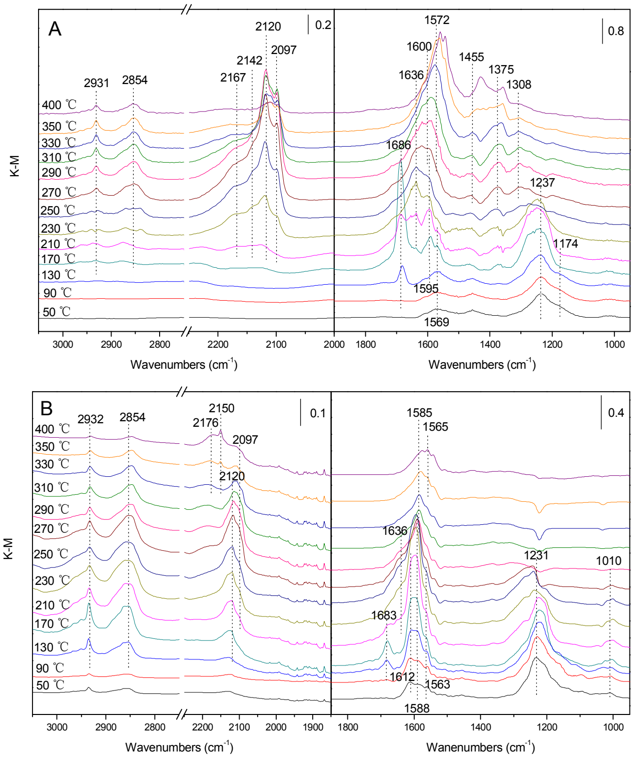

Fig. 9. In situ DRIFTS spectra over Pd/CZ (A) and Pd/CZBa (B) catalysts under stoichiometric NO_x-HC-O_2 reaction condition.

Conclusions

The introduction of alkaline earth obviously improves the catalytic activity of both HC and NO_x conversion as well as the selectivity of NO_x to N_2 formation, whereas shows an inhibiting effect on CO elimination under stoichiometric NO_x-CO-HC-O_2 condition. The fierce competition exists between CO-O_2 and

CO-NO$_x$ reactions, and the presence of HC inhibits the CO-NO$_x$ reaction, especially over Pd/CZ. However, the doping of Ba could weaken this inhibiting effect caused by the presence of HC, especially at low reaction temperature. In addition, widened operation window as a result of enhanced NO$_x$ storage ability were achieved with the promoted catalysts. The doped alkaline earth could enter into the CeO$_2$ lattice and facilitate the formation of oxygen vacancies along with the reduction of Ce^{4+} to Ce^{3+}. Hence, the modification with Ba improves the NO$_x$ storage efficiency due to the enhanced electron transfer and oxygen mobility.

Pd/CZ catalyst with higher dispersion of Pd exhibits the better oxidation activity of CO as a result of much more active sites on the catalyst surface, according to the structurally insensitive character of the CO-O$_2$ reaction. The modification with Ba inhibits the strong adsorption of hydrocarbon and corresponding fragments and facilitates the deep oxidation of HC species. On the other hand, the introduction of Ba promotes NO dissociation on active metal and thus there are more active intermediate species (NCO and CN) formed over Pd/CZBa catalyst, which may be related to increased electron density of Pd species due to the outstanding electron-donating ability of Ba.

Acknowledgements

We gratefully acknowledge the financial supports from the Ministry of Science and Technology of the People`s Republic of China (No.: 2011AA03A406) and Zhejiang Leading Team of Science and Technology Innovation (No.: 2009R50020).

Notes and references

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† Electronic Supplementary Information (ESI) available: Details of NO$_x$-TPD-MS, UV Raman and XPS measurements and their results are provided. See DOI: 10.1039/b000000x/

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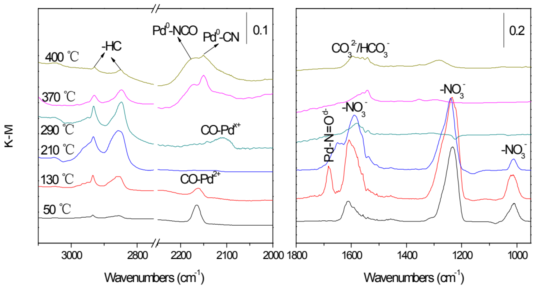

The modification with alkaline earths, especially Ba, promotes NO$_x$ storage efficiency and NO dissociation, as well as the deep oxidation of HC. Thus doped catalysts present improved catalytic activity.