



Influence of Co or Ce addition on the NO_x storage and sulfur-resistance performance of the lean-burn NO_x trap catalyst Pt/K/TiO₂-ZrO₂

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ABSTRACT

The Pt/K/TiO₂-ZrO₂ catalysts promoted by Co or Ce were prepared by successive impregnation or mechanically mixing method. The influence of Co or Ce addition on the NO_x storage and sulfur-resistance performance of the catalyst was investigated carefully. The techniques of XRD, FT-IR, *in-situ* DRIFTS, H₂-TPR and XPS were employed for catalyst characterization. The Co or Ce addition can greatly improve the NO_x storage capacity of Pt/K/TiO₂-ZrO₂ due to the enhanced oxidation ability and the release of more K sites. Ce addition induces higher K/Ti atomic ratio and larger NO_x storage capacity as compared with Co addition. After sulfation and regeneration, the promoted catalysts shows more or less decreased NSC than Pt/K/TiO₂-ZrO₂ due to the formation of more sulfates, especially for the Co-promoted catalysts, which possess better oxidation ability and facilitate the formation of large sulfates. The effect of Ce addition on Pt/K/TiO₂-ZrO₂ largely depends on the addition mode. The high oxidation ability and the high K/Ti ratio of the mechanically prepared Ce-promoted catalyst make it still possess considerable NO_x storage capacity (NSC) of 142 μmol/g after sulfation and regeneration. With the decrease of sulfur content in fuels, the Co- and Ce-promoted catalysts possessing large NO_x storage capacity, will be applicable to the purification of lean-burn NO_x.

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1. Introduction

Lean-burn NO_x trap (LNT) catalyst system is a great solution to increasing fuel economy, decreasing the emission of carbon oxides and hydrocarbons, and simultaneously removing poisonous NO_x, which could not be effectively reduced to N₂ over traditional three-way catalysts under lean-burn condition. The first generation of LNT catalyst was proposed by Toyota in the middle of 1990s [1,2]. It mainly consists of three major components: (1) noble metals, mainly Pt or Pt-Rh for NO_x oxidation and reduction; (2) alkali or alkaline oxides, mainly BaO for NO_x storage as nitrates due to its high NO_x storage capacity (NSC) and high rate for NO_x uptake; (3) Al₂O₃ support with a large specific surface area for providing a high dispersion of the other components. Under lean-burn conditions, the NO_x is oxidized and stored as nitrates in the basic storage components, such as Ba. When the engine is switched to a reducing atmosphere, the NO_x is released from the stored nitrates and reduced to N₂ by carbon monoxide and hydrocarbons.

The first generation of LNT catalysts has been put into market in Japan where the fuel contains ultra-low sulfur, however, it

cannot be extensively applied in many other countries due to the sulfur-resulted deactivation. SO₂ and NO_x, both as acidic gases, are competitive for the same adsorption sites, and sulfate is easier to form than nitrate due to its higher thermodynamic stability. During lean-burn period, sulfur oxides can poison not only the basic storage component but also the support [3–7]. In addition, under rich-burn condition, sulfur can also accumulate on the noble metal component, and then significantly decrease its oxidation ability [8,9]. Recently, a new LNT catalyst Pt/K/TiO₂-ZrO₂ defined as the third generation of LNT catalyst previously [10,11] has been put forward, using the binary oxides TiO₂-ZrO₂ as supports. The larger acidity of this kind of support can prevent SO₂ adsorption and promote SO₂ desorption, as a result, the new LNT catalysts show much better sulfur-resistance than the traditional Pt/Ba/Al₂O₃ catalysts. Besides, potassium is another element that has shown potential as a storage component with a significant benefit at higher temperatures since the K-based nitrate is more stable than the typical Ba nitrate [12]. Therefore, it is believed that the new generation LNT catalyst Pt/K/TiO₂-ZrO₂ is promising to be extensively used for the abatement of NO_x from lean-burn engines. As far as we know, for this catalytic system Pt/K/TiO₂-ZrO₂, only limited work has been performed up to now. Takahashi et al. [13] has studied the influence of TiO₂/ZrO₂ ratio on NO_x storage and sulfur-resistance of the LNT catalyst. It is shown that the optimal Ti/Zr atomic ratio is 4/6.

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Liu et al. [10] reported that the optimal calcination temperature of $\text{TiO}_2\text{-ZrO}_2$ support is 650°C in the view of both the NO_x storage capacity and the sulfur-resistance ability of the catalysts.

In addition to the newly proposed LNT catalysts with better sulfur-resistance as described above, in the past few years, much work has also been carried out on the modifying effect of transition metals on the conventional $\text{Pt/Ba/Al}_2\text{O}_3$ systems in order to increase their NO_x storage capacity and/or improve their sulfur-resistance ability [14–17]. Cobalt oxides, which possess high oxidation ability, can greatly increase the NO_x storage capacity when added to $\text{Pt/Ba/Al}_2\text{O}_3$ system. It is indicated that this increase in storage efficiency is associated with the strong oxidizing effect of Co_3O_4 , providing nitric oxide oxidation sites and contact area for NO_2 spillover to the Ba storage sites [14,15]. However, the literature about the effect of Co on the sulfur-resistance of the $\text{Pt/Ba/Al}_2\text{O}_3$ catalysts is very limited. Yamazaki et al. found that the addition of Co-compound to $\text{Pt/Ba/Al}_2\text{O}_3$ shows no effect on the NO_x conversion after the catalyst was sulfated and regenerated [17]. But the actual NO_x storage amount was not given in their experiment for the catalysts before and after sulfation-regeneration. So, the real function of Co, especially from the view of sulfur-resistance, is not totally made clear so far.

Ceria, as a widely used material in exhaust gas catalysis, has also been added into the LNT catalyst $\text{Pt/Ba/Al}_2\text{O}_3$ [18–22]. However, its effect reported in literature seems very controversial. Ji et al. [18,19] reported that the presence of ceria could improve NO_x storage capacity in the temperature range of $200\text{--}400^\circ\text{C}$ under both continuous lean and lean-rich cycling conditions. Besides, the regeneration behavior can also be influenced by Ce addition. It is found that NO_x stored in the ceria-containing catalyst was thermally less stable but more reactive to be reduced by both H_2 and CO. Rohr et al. [20] found that the addition of Ce cannot improve the sulfur-resistance of the $\text{Pt/Ba/Al}_2\text{O}_3$ catalyst due to the fact that the Ba is selectively poisoned by sulfur while ceria is not affected. However, by using CeO_2 instead of Al_2O_3 as the support, the Pt-BaO/CeO_2 sample exhibits slightly higher NO_x uptake compared with $\text{Pt-BaO}/\gamma\text{-Al}_2\text{O}_3$, and this ceria-based catalyst shows higher sulfur tolerance than the alumina-based one [21]. But Casapu et al. [22] indicated that Pt/Ba/CeO_2 exhibits inferior NO_x storage performance, particularly the reduction/regeneration activity compared with the Al_2O_3 supported catalyst. They proposed that the incomplete reduction of the stored NO_x -species in Pt/Ba/CeO_2 seems to be caused by a faster and more profound re-oxidation of Pt particles during the lean period.

As reviewed above, the addition of Co and Ce to the LNT catalyst $\text{Pt/Ba/Al}_2\text{O}_3$ has been widely investigated. However, up to now, no work is performed upon the influence of Co and Ce addition on the newly proposed LNT catalytic system $\text{Pt/K/TiO}_2\text{-ZrO}_2$ which possesses much better sulfur-resistance than $\text{Pt/Ba/Al}_2\text{O}_3$. Therefore, in the present work, the effect of Co or Ce addition on the storage capacity and sulfur-resistance behaviors of the third generation of LNT catalysts $\text{Pt/K/TiO}_2\text{-ZrO}_2$ is investigated carefully. Two different addition modes of Co or Ce were adopted during preparation in order to optimize the preparation method. The repeated H_2 -TPR was employed to characterize the sulfur desorption behaviors of all the catalysts containing Co or Ce. Their NO_x storage capacity and sulfur-resistance performance were correlated with their surface properties, oxidation ability and sulfur desorption behavior.

2. Experimental

2.1. Catalyst preparation

$\text{TiO}_2\text{-ZrO}_2$ binary oxide support with a molar ratio of 4:6 was prepared by co-precipitation in an aqueous solution containing tita-

nium tetrachloride and zirconium oxychloride. Aqueous ammonia was used as the precipitation reagent. The precipitate was kept at room temperature for 24 h, then filtered and washed with deionized water until no chloride ions were detected by AgNO_3 solution. After drying at 120°C for 24 h, the precipitate was calcined at 650°C for 5 h in air to obtain the final support $\text{TiO}_2\text{-ZrO}_2$, denoted as TZ.

The unmodified catalysts Pt/K/TZ was prepared by sequential impregnation. At first, the synthesized support TZ was impregnated with an aqueous solution of $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$, then dried at 120°C overnight and calcined at 250°C for 1 h in air to obtain the precursor, which was subsequently impregnated in an aqueous solution of CH_3COOK . After drying at 120°C overnight and calcination at 500°C for 2 h with the temperature ramp of $5^\circ\text{C}/\text{min}$, the final powder was pressed, crushed and sieved to 40–60 mesh. The weight loadings of metal Pt and CH_3COOK salt are 1 wt.% and 7 wt.%, respectively. In the case of Pt/K/Co/TZ and Pt/K/Ce/TZ catalysts, the process is similar to that for Pt/K/TZ but only with the impregnation of $\text{Co}(\text{NO}_3)_2$ or $\text{Ce}(\text{NO}_3)_3$ before the impregnation of Pt, giving the content of Co or Ce with 5 wt.%. The other two catalysts Pt/K/Co/TZ-mix and Pt/K/Ce/TZ-mix were prepared by mechanically mixing 10 wt.% Co/K/TZ or 10 wt.% Ce/K/TZ with the equal amounts of 2% Pt/K/TZ , giving the same contents of Pt, K, Co or Ce as those in the catalysts Pt/K/Co/TZ and Pt/K/Ce/TZ prepared by successive impregnation. All the reagents except $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$ used above are of analytical grade and purchased from The Third Chemical Reagents Factory of Tianjin. The noble metal precursor $\text{H}_2\text{PtCl}_6\cdot 6\text{H}_2\text{O}$ is also of analytical grade but supplied by Yingda Xigui Chemical Company of Tianjin. Before experiments, the samples were reduced from room temperature to 500°C with the ramp of $10^\circ\text{C}/\text{min}$ and held at 500°C for 1 h in a gas flow of 10 vol% H_2 in N_2 , as called fresh catalysts.

2.2. Catalyst characterization

XRD patterns were recorded on an X'pert Pro diffractometer (PANalytical Company) with a rotating anode using $\text{Co K}\alpha$ as radiation source ($\lambda = 0.1790\text{ nm}$) at 40 kV and 40 mA. The data of 2θ from 10° to 90° range were collected with the step size of 0.03° .

X-ray photoelectron spectroscopy (XPS) analysis was performed in a PHI-1600 ESCA SYSTEM spectrometer with $\text{Mg K}\alpha$ as X-ray source (1253.6 eV) under a residual pressure of 5×10^{-6} Pa. The error of the binding energy is ± 0.2 eV and the C 1s ($E_b = 284.6$ eV) of the contaminated carbon was used as a standard for binding energy calibration.

Temperature-programmed reduction (TPR) measurement was conducted on a TPDRO 1100 apparatus supplied by Thermo-Finnigan company. Before detection by the TCD, the gas was purified by a trap containing $\text{CaO} + \text{NaOH}$ materials in order to remove the H_2O and CO_2 . Each time, 30 mg of the sample was heated from room temperature to 900°C at a rate of $10^\circ\text{C}/\text{min}$. A mixture gas consisting of H_2 and N_2 with H_2 content of 5% (volume percentage) was used as reductant with a flow rate of 20 mL/min. For the repeated TPR cycles, the sample was reduced from room temperature to 500°C at a rate of $10^\circ\text{C}/\text{min}$ and held for 30 min, then the sample was reoxidized in 6% O_2/He flow at 500°C for 1 h to ensure the complete oxidation of sulfides to sulfates, after cooling to room temperature, the next TPR test of the sample was performed.

For FT-IR test, the sample with 1 mg diluted by vacuum-dried IR-grade KBr (weight ratio 1:100) was pressed into the disc, and then recorded in Nexus FT-IR spectrometer apparatus supplied by Thermo Nicolet Company, using 32 scans and a resolution of 4 cm^{-1} in the range of $4000\text{--}400\text{ cm}^{-1}$.

In-situ diffuse reflectance infrared spectroscopy (DRIFTS) measurement was performed on a Nicolet Nexus spectrometer equipped with a MCT detector cooled by liquid nitrogen, and an *in-situ* chamber allowing the sample heated up to 600°C . The NO_x

sorption experiments were carried out at different temperatures. The temperature was increased from 200 °C to 500 °C at 50 °C interval. The powder sample of 15 mg was firstly pretreated in pure helium at every temperature for 15 min and then the background spectrum was recorded using 32 scans and a resolution of 4 cm⁻¹. Subsequently, a mixture gas of 400 ppm NO + 5% O₂ balanced by N₂ was introduced to the sample cell, and the spectra were recorded at different exposure time up to 30 min. The flow rate of the mixture gas is 50 mL/min.

2.3. NO_x storage capacity (NSC) measurement, sulfur-aging and regeneration treatment

NSC measurements were carried out in a quartz-tubular continuous flow reactor (i.d. = 8 mm) containing 0.6 g of each catalyst (40–60 mesh). After the temperature reached 350 °C, a gas mixture of 400 ppm NO, 5% O₂ and the balance N₂ was introduced at a rate of 400 mL/min, corresponding to a space velocity of 40,000 h⁻¹. The concentrations of NO, NO₂, and total NO_x at the reactor outlet were monitored by an online Chemiluminescence NO-NO₂-NO_x Analyzer (Model 42i-HL, Thermo Scientific).

For sulfur-aging experiments, 400 mg catalyst was used, each exposed to a gas containing 200 ppm SO₂, 5% O₂, and the balance N₂ at 400 °C for 2 h, at a flow rate of 160 mL/min. The molar ratio of the total amount of SO₂ flowing through the catalyst bed to the amount of K in the catalyst is kept 0.55, ensuring that the deep sulfation could be achieved if all K is transformed into K₂SO₄. The regeneration of sulfur-aged catalysts was performed in a gas containing 10 vol% H₂ in N₂ at 500 °C for 60 min using 400 mg of the sulfur-aged catalyst.

3. Results and discussion

3.1. NO_x storage capacity (NSC) of the catalysts

Isothermal experiments of NO_x storage over all the fresh and regenerated samples were carried out at 350 °C, the results of which are shown in Fig. 1. The NO_x storage amounts, calculated by integrating the concentration curves of NO_x, are listed in Table 1. It can be seen that the addition of transition metal Co to Pt/K/TZ catalyst has remarkably increased its NO_x storage capacity. Depending on the two kinds of Co addition modes, namely the successive impregnation and mechanically mixing, the NSC of Pt/K/TZ could be increased by 31% and 44%, respectively. Compared with Co, Ce addition induces much larger increase in NSC. However, different from Co-containing catalysts, for Ce-promoted samples, successive impregnation shows better enhancement effect on NSC with an increased percentage up to 97%, larger than that (74%) for the sample prepared by mechanically mixing. After sulfation and regeneration, the NO_x storage capacities of all the samples are expectedly decreased to different extents. For the unmodified catalyst Pt/K/TZ, the NSC decreases very slightly, still keeping as high as 186 μmol/g. While for Co-promoted catalysts, sharp decrease in NSC is observed, regardless of the preparation methods. However, for Ce-promoted catalysts, the NSC seems to be more dependent on the prepara-

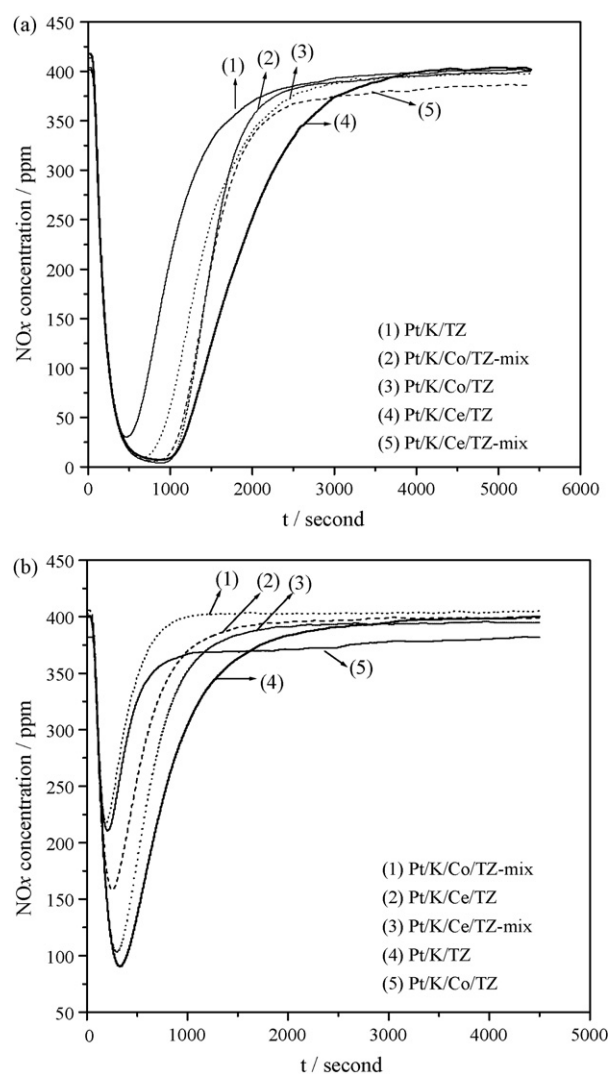


Fig. 1. NO_x storage curves over the catalysts at 350 °C: (a) fresh (b) regenerated. (Condition: the inlet gas contains 400 ppm NO and 5% O₂, balanced by N₂).

tion methods. The one prepared by successive impregnation shows a low NO_x storage capacity of 78 μmol/g while the mechanically mixed catalyst Pt/K/Ce/TZ-mix possesses a fairish NO_x storage capacity of 142 μmol/g.

According to literature [23], the NO_x storage performance is highly related to the ability of the catalysts for the oxidation of NO to NO₂. In this work, during NO_x storage over different catalysts, the concentrations of NO and NO₂ in the feed gas are almost the same and invariable, about 250 and 150 ppm, respectively. Therefore, the change in the concentrations of NO and NO₂ after NO_x storage saturation can reflect the ability of the catalysts for NO to NO₂ oxidation. As seen from Table 2, after storage saturation, the NO₂ concentrations over all the fresh catalysts promoted by Co or Ce are always

Table 1
NO_x storage capacities (NSC) and specific surface areas of the catalysts.

Sample	S _{BET} (m ² g ⁻¹)	NSC (μmol g ⁻¹)	
		Fresh sample	Regenerated sample
Pt/K/TZ	78	194	186
Pt/K/Co/TZ	76	255	65
Pt/K/Co/TZ-mix	65	280	46
Pt/K/Ce/TZ	59	382	78
Pt/K/Ce/TZ-mix	62	338	142

Table 2
Outlet concentrations of NO, NO₂ and NO_x after catalysts adsorption saturation.

Sample	Fresh (ppm)			Regenerated (ppm)		
	NO	NO ₂	NO _x	NO	NO ₂	NO _x
Pt/K/TZ	231	170	401	207	193	400
Pt/K/Co/TZ	132	266	398	207	175	382
Pt/K/Co/TZ-mix	191	209	400	240	165	405
Pt/K/Ce/TZ	205	197	402	217	182	399
Pt/K/Ce/TZ-mix	203	185	388	202	193	395

higher than that for the unmodified catalyst Pt/K/TZ, implying their higher oxidation ability, which is consistent with their larger NSC values. After sulfation and regeneration, the catalysts Pt/K/Co/TZ, Pt/K/Co/TZ-mix and Pt/K/Ce/TZ show lower oxidation ability, indicated by the lower NO₂ concentrations, as compared with the corresponding fresh catalysts. However, the other two regenerated catalysts Pt/K/TZ and Pt/K/Ce/TZ-mix show almost the same or a little better oxidation ability than the fresh ones, exhibiting much larger NSC than other three regenerated catalysts.

It should be noted that the oxidation ability of the catalysts is not the only factor to determine their NSC. The state and amount of the basic storage components will definitely affect the storage performance and NSC value of the catalysts. For the regenerated catalysts Pt/K/TZ and Pt/K/Ce/TZ-mix, although they show better oxidation ability, their NSC values are still lower than those for the fresh ones, which should be mainly caused by the sulfation of the storage component K, resulting in less K sites available to NO_x storage. In addition, the fresh catalyst Pt/K/Co/TZ shows much stronger oxidation ability than the fresh Pt/K/Ce/TZ in the light of the NO₂ concentrations in Table 2 while the NSC for the latter catalyst is much larger. Since no sulfation is performed, the dispersion and the amount of K sites available to NO_x storage in these two catalysts may be the key factors determining their NSC. It is ever reported that the solid-phase-reaction between TiO₂ and K species could result in the potassium deactivation of the LNT catalyst Pt/K/TiO₂-ZrO₂ [13]. So, in this work, it can be deduced that the Ce addition inhibits the solid-phase-reaction between K and TiO₂ to a greater extent than the Co addition. In a word, the oxidation ability, and the state and amount of K sites available to NO_x storage for the LNT catalysts should be the two main factors determining their NSC. Therefore, how the addition of Co or Ce affects the oxidation ability and the state and amount of K sites is necessary to make clear.

3.2. XRD results

XRD test was carried out in order to investigate the bulk structure of the catalysts. From the XRD patterns of the fresh samples shown in Fig. 2, it can be seen that ZrTiO₄ phase appears in all the samples. It is noted that the peak around $2\theta = 59.1^\circ$ should be contributed not only by ZrTiO₄ but also by tetragonal ZrO₂. According to the reference pattern of ZrTiO₄ phase (PCPDFWIN 74-1504), the

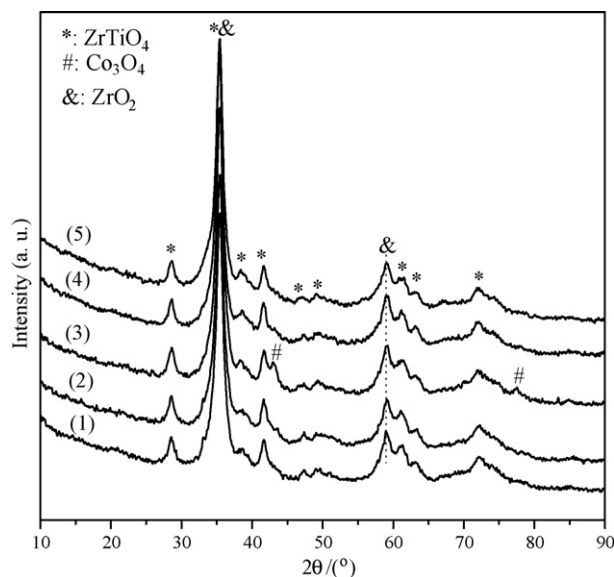


Fig. 2. XRD patterns of the fresh catalysts: (1) Pt/K/TZ (2) Pt/K/Co/TZ (3) Pt/K/Co/TZ-mix (4) Pt/K/Ce/TZ (5) Pt/K/Ce/TZ-mix

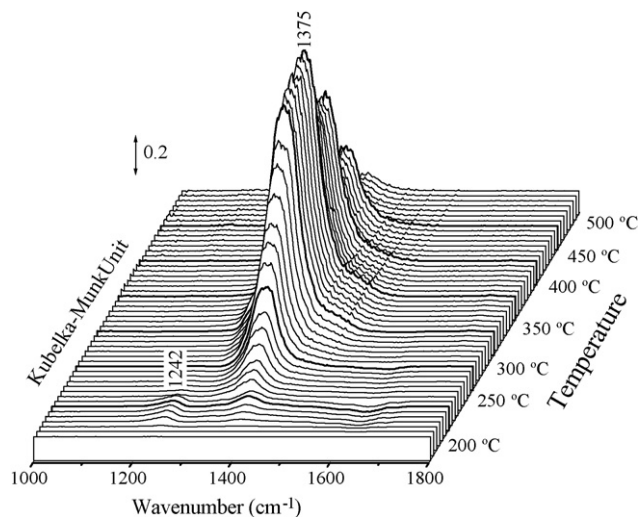


Fig. 3. In-situ DRIFTS spectra of Pt/K/TZ after exposure to 400 ppm NO and 5 vol% O₂ (balanced by N₂) for 30 min at different temperatures.

peak at $2\theta = 59.5^\circ$ should be weaker than those at $2\theta = 61.4^\circ$ and 63.6° , however, the peak around $2\theta = 59.1^\circ$ in Fig. 2 is stronger than the two mentioned peaks. Meanwhile, the first two strongest peaks of tetragonal ZrO₂ phase (PCPDFWIN 79-1769) appear at $2\theta = 35.2^\circ$ and 59.0° , respectively. Therefore, it is reasonable to assign the peak around $2\theta = 59.1^\circ$ to both the phases of ZrTiO₄ and ZrO₂. The strongest peak of ZrO₂ at $2\theta = 35.2^\circ$ should also be masked by the peak at $2\theta = 35.5^\circ$ of ZrTiO₄. This interpretation is consistent with the molar percentage of Ti to Zr in the samples (4/6), meaning that the molar percentage of Zr is larger than that of Ti. After calcination at 650 °C, most Zr oxide has reacted with Ti oxide to form ZrTiO₄, leaving excessive Zr component segregated into ZrO₂ crystallites.

With the addition of Co or Ce, no related oxides phases of Co or Ce can be detected by XRD except Pt/K/Co/TZ-mix, for which two small diffraction peaks corresponding to Co₃O₄ could be observed. All these results indicate that Ce oxides in Ce-containing catalysts and Co oxides in Pt/K/Co/TZ are in highly dispersed state. For the sample Pt/K/Co/TZ-mix, the cobalt phase shows lower dispersion than that in Pt/K/Co/TZ, since the same amount of cobalt was loaded on the half amount of TiO₂-ZrO₂ support during the preparation of Pt/K/Co/TZ-mix, as compared with Pt/K/Co/TZ prepared by successive impregnation.

3.3. In-situ DRIFTS of NO + O₂ co-adsorption on the catalysts

In order to figure out the NO_x storage pathways, in-situ DRIFTS experiment was carried out at different temperatures over all the samples. It is found that the spectra for all the five fresh samples are almost identical, so the DRIFTS spectra of NO + O₂ co-adsorption on the sample Pt/K/TZ were selected as a representative, as shown in Fig. 3. It can be seen that the spectra are obviously temperature-dependent. When the adsorption temperature is as low as 200 °C, there is an absorption band appearing at 1242 cm⁻¹, indicating the formation of a plenty of free nitrite ions [12]. With time increasing, a weak band at 1375 cm⁻¹ can be observed, suggesting the formation of a small quantity of free nitrate ions [12], which are converted from free nitrite ions in the presence of O₂. When the temperature is increased to 250 °C, the band at 1242 cm⁻¹ disappears totally while the peak associated with nitrates gets stronger. This means that the increased temperature favors the activation of oxygen species and the subsequent oxidation of nitrites to nitrates. From Fig. 3, it can be seen that the bands related to nitrates reach the maximum intensity when the adsorption temperature is increased to 350 °C. Further increase of temperature causes the decrease of

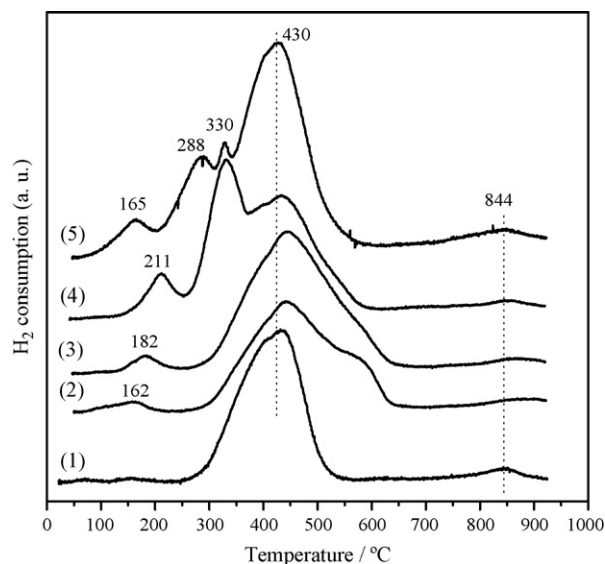


Fig. 4. H₂-TPR profiles of sulfur-aged catalysts: (1) Pt/K/TZ (2) Pt/K/Ce/TZ. (3) Pt/K/Ce/TZ-mix (4) Pt/K/Co/TZ-mix (5) Pt/K/Co/TZ

these bands, implying the decomposition of nitrates. In conclusion, the NO_x storage routes depend strongly on the temperature. At the temperature of 200 °C, NO_x storage should proceed via nitrite intermediates with partial nitrites converted to nitrates, while at the temperature above 250 °C, NO_x storage undergoes mainly via nitrate route. The optimal temperature for NO_x trapping as nitrates is around 350 °C.

3.4. Desulfation

H₂-TPR experiments were performed on sulfur-aged catalysts to investigate the sulfur desorption behavior, the results of which are presented in Fig. 4. For the catalyst Pt/K/TZ, the peak around 430 °C should be assigned to the reduction of sulfate, which is consistent with our previous study [10] and the reduction temperature is lower than that for Pt/Ba/A₂O₃ system [6,7]. Another small peak around 844 °C may be related to the reduction of TiO₂-ZrO₂ support since the surface Ti⁴⁺ can also be reduced to Ti³⁺ [24]. For all the promoted catalysts, the reduction behaviors become more complicated due to the metal oxides such as CoO, Co₃O₄ and CeO₂ can also be reduced. The small peaks below 220 °C for all the promoted catalysts should be ascribed to the reduction of Pt oxides, since the sulfation process was performed in oxygen-rich condition, making the re-oxidation of Pt possible. It is noted that for the Co-promoted catalysts, the peaks assigned to the reduction of Pt oxides are larger than those for Ce-promoted ones, implying the stronger oxidation ability of Co. The absence of this peak in catalyst Pt/K/TZ suggests that the re-oxidation of Pt during sulfation is difficult without Co or Ce. For the mechanically mixed catalyst Pt/K/Co/TZ-mix, the peak at 330 °C should be the reduction of Co₃O₄ since it has been detected by XRD for this sample (see Fig. 2), while for Pt/K/Co/TZ, the main reduction peak for cobalt oxides appears at 288 °C accompanied by a much weaker peak at 330 °C. The decrease of reduction temperature may be related to the smaller crystallites of cobalt oxides in Pt/K/Co/TZ, as well as the more efficient hydrogen spillover effect initiating by the reduced Pt [25,26]. For Ce-promoted catalysts, the main peaks around 430 °C become wider, extending to higher temperatures above 600 °C, as compared with the unmodified catalyst. It is reported that the reduction of surface CeO₂ often occurs at 437 °C [27]. Therefore, it is possible that the reduction of surface CeO₂ is included in the wide peaks assigned to sulfate reduction at 430 °C.

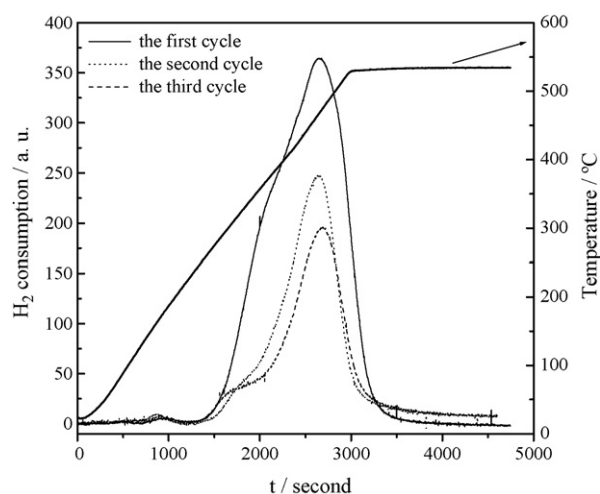


Fig. 5. Repeated H₂-TPR profiles of the sulfur-aged catalyst Pt/K/TZ. (Pretreatment: the sulfur-aged catalyst was reduced by 10 vol% H₂ in N₂ from room temperature to 500 °C at a rate of 10 °C/min and held for 30 min, followed by the reoxidation in 6% O₂/He flow at 500 °C for 1 h.)

From Fig. 4, it is found that the reduction temperatures for sulfates over all the sulfur-aged catalysts are almost the same, around 430 °C. Consequently, it is hard to distinguish the sulfur desorption behaviors among the different catalysts, so the repeated H₂-TPR tests were performed for all the five sulfur-aged catalysts to investigate the extent of desulfation. The sulfur-aged sample was reduced from room temperature to 500 °C at a rate of 10 °C/min and held for 30 min, and then the sample was reoxidized in 6% O₂/He flow at 500 °C for 1 h to ensure the complete oxidation of sulfides to sulfates, after cooling to room temperature, the next TPR test of the sample was performed. The results of the repeated H₂-TPR are shown in Figs. 5–7.

The profiles for the three reduction cycles of the unmodified catalyst Pt/K/TZ are shown in Fig. 5. It can be seen that the H₂ consumption becomes smaller and smaller with the increase of cycles. The difference of H₂ consumption between the two successive reduction cycles can reflect the extent of desulfation. In order to compare the desulfation extent among different catalysts, the ratios of H₂ consumption of the latter reduction cycles to the first cycle of each catalyst were calculated and shown in Table 3. For the first cycle this ratio is assumed to be 100%. As analyzed above, the reduction of Co and Ce related oxides is also included in the reduction process, so it is hard to quantitatively calculate the absolute H₂ consumption for the reduction of sulfates and Co or Ce oxides, respectively. Therefore, the ratios of H₂ consumption of the latter reduction cycles to the first cycle are used to reflect the extent of desulfation.

From Figs. 5–7 and Table 3, it can be seen that the H₂ consumption for both the unmodified and Ce-containing catalysts gradually decreases with the reduction cycles increasing. By comparing the ratios of H₂ consumption defined above, the desulfation of the catalyst Pt/K/TZ is the easiest, followed by Ce-containing catalysts. For

Table 3
The relative ratios of H₂ consumptions of cycle 2 or 3 to cycle 1.

Sample	Cycle 1 ^a (%)	Cycle 2 (%)	Cycle 3 (%)
Pt/K/TZ	100	54	46
Pt/K/Co/TZ	100	132	100
Pt/K/Co/TZ-mix	100	136	136
Pt/K/Ce/TZ	100	64	56
Pt/K/Ce/TZ-mix	100	59	52

^a It is assumed that the H₂ consumption for cycle 1 is always 100%.

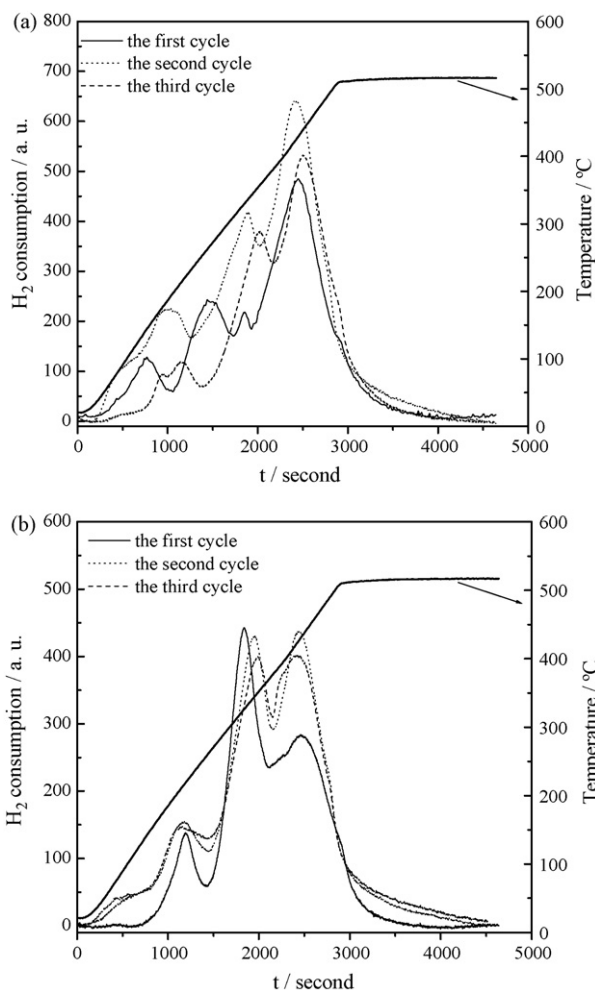


Fig. 6. Repeated H_2 -TPR profiles of the Co-containing sulfur-aged catalysts: (a) Pt/K/Co/TZ (b) Pt/K/Co/TZ-mix (pretreatment: the sulfur-aged catalyst was reduced by 10 vol% H_2 in N_2 from room temperature to $500^\circ C$ at a rate of $10^\circ C/min$ and held for 30 min, followed by the reoxidation in 6% O_2/He flow at $500^\circ C$ for 1 h.)

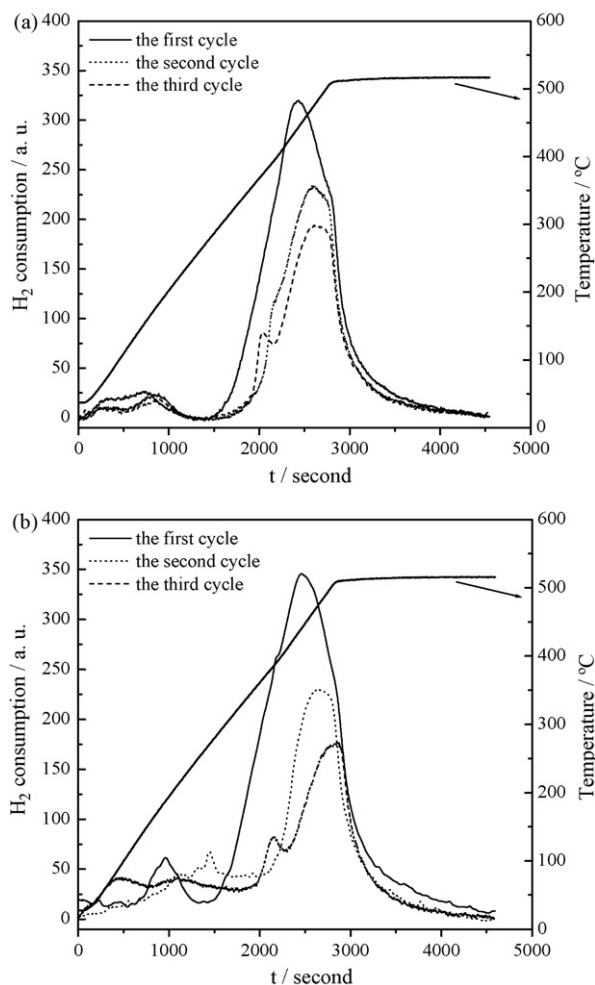


Fig. 7. Repeated H_2 -TPR profiles of the Ce-containing sulfur-aged catalysts: (a) Pt/K/Ce/TZ (b) Pt/K/Ce/TZ-mix (pretreatment: the sulfur-aged catalyst was reduced by 10 vol% H_2 in N_2 from room temperature to $500^\circ C$ at a rate of $10^\circ C/min$ and held for 30 min, followed by the reoxidation in 6% O_2/He flow at $500^\circ C$ for 1 h.)

the Co-containing catalyst, the reduction behavior is much more complicated due to the much larger reduction degree of Co oxides compared to Ce oxides. As seen from Fig. 6 and Table 3, the H_2 consumption of the second cycle is larger than that of the first cycle for the two Co-containing catalysts. As described in the experiments, between the first and second reduction process, the Co species in the catalysts were re-oxidized at $500^\circ C$, while before the first reduction cycle, the catalysts were sulfur-aged only at $400^\circ C$ in oxygen-rich condition. Therefore, it is reasonable that the second reduction process consumed more H_2 . Before the third reduction process, the oxidation condition is completely same with that before the second one, so the comparison of H_2 consumption between the third and second reduction cycle can reflect the desulfation extent. From Table 3, it can be seen that there is almost no difference between the third and the second reduction cycle for the catalysts Pt/K/Co/TZ-mix, however, the decreased H_2 consumption of the third reduction cycle can be observed for the catalyst Pt/K/Co/TZ. Therefore, it is thought that the sulfur desorption is more difficult over the mechanically mixed catalyst Pt/K/Co/TZ-mix than the one prepared by successive impregnation.

In order to compare the sulfur desorption extents among the five sulfur-aged catalysts, after reduction at $500^\circ C$, the catalysts were characterized by FT-IR technique, the results of which are shown in Fig. 8. The band at 1118 cm^{-1} clearly indicates the existence of residual sulfates [28]. The intensity of this band for the catalysts follows

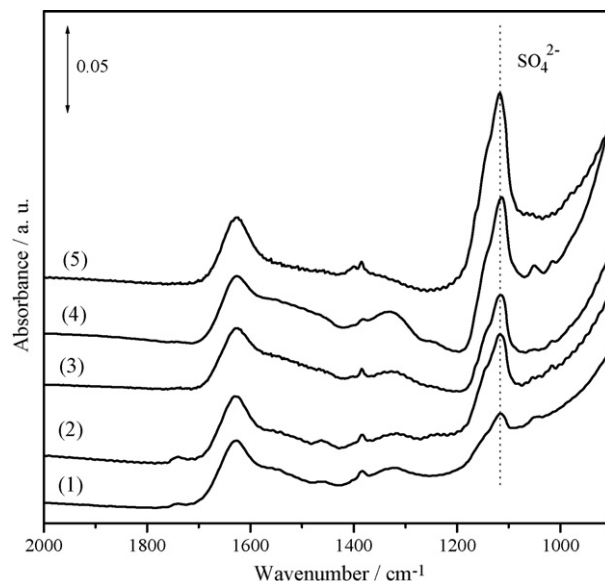


Fig. 8. FT-IR spectra of the regenerated catalysts: (1) Pt/K/TZ (2) Pt/K/Ce/TZ-mix. (3) Pt/K/Ce/TZ (4) Pt/K/Co/TZ (5) Pt/K/Co/TZ-mix

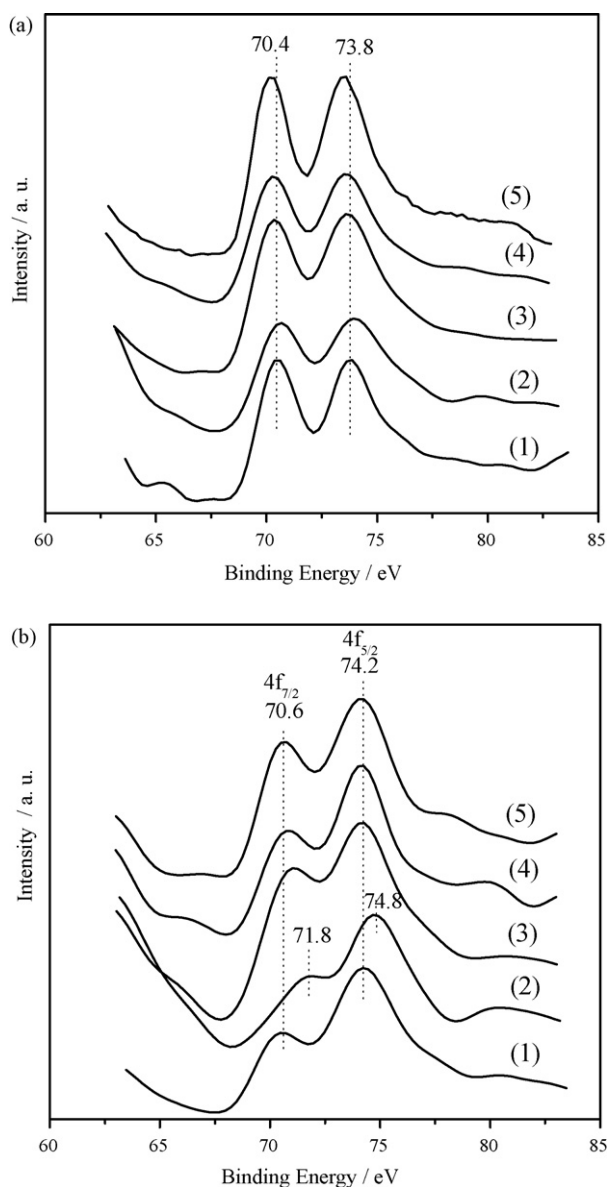


Fig. 9. The Pt XPS spectra of the fresh (a) and regenerated (b) catalysts: (1) Pt/K/TZ. (2) Pt/K/Co/TZ (3) Pt/K/Co/TZ-mix (4) Pt/K/Ce/TZ (5) Pt/K/Ce/TZ-mix

the order: Pt/K/Co/TZ-mix > Pt/K/Co/TZ > Pt/K/Ce/TZ ≥ Pt/K/Ce/TZ-mix > Pt/K/TZ. This sequence is also consistent with the desulfation extent observed from Figs. 5–7 and Table 3. All the results obtained from repeated TPR and FT-IR spectra show that the sulfur deposited on the catalysts promoted by Co or Ce is more difficult to remove than that on the unmodified catalyst Pt/K/TZ. The addition of Co or Ce to Pt/K/TZ, especially of Co, shows obvious disadvantage in sulfur-resistance, though they could improve the NSC of the catalyst remarkably.

3.5. XPS results

The XPS spectra of Pt4f for the fresh and regenerated catalysts are shown in Fig. 9. It can be seen that Pt in all the samples except the regenerated catalyst Pt/K/Co/TZ shows the Pt4f_{7/2} peak around 70.5 eV, which can be assigned to the reduced metallic Pt [29]. For the regenerated catalyst Pt/K/Co/TZ this peak shifts to a higher level of 71.8 eV, suggesting that some Pt still exists in oxidized state in this sample. Therefore, it can be concluded that the close contact of Pt and Co oxides may favor the formation of Pt oxides after sulfation

Table 4

The surface atomic ratio of K/Ti and surface S content of the catalysts.

Sample	Fresh	Regenerated	
	K/Ti	K/Ti	S (%)
Pt/K/TZ	0.53	0.59	0.1
Pt/K/Co/TZ	0.57	0.46	0.3
Pt/K/Co/TZ-mix	0.62	0.44	0.4
Pt/K/Ce/TZ	0.66	0.50	0.2
Pt/K/Ce/TZ-mix	0.64	0.53	0.2

and regeneration, which is due to the high oxygen mobility of the Co oxides.

It is proposed that one of the potassium deactivation of the LNT catalyst Pt/K/TiO₂-ZrO₂ is the solid-phase-reaction with the support, which is mainly caused by the reaction between TiO₂ and K species [13]. So, the atomic ratio of K/Ti is often utilized to evaluate the availability of K sites for NO_x storage. The K/Ti ratios of all the fresh and regenerated catalysts are listed in Table 4. For the fresh catalysts, the K/Ti ratios of Co or Ce promoted catalysts are larger than the unmodified one. The pre-impregnation of Co or Ce effectively inhibits the interaction between TiO₂-ZrO₂ support and K impregnated subsequently, as a result, more K sites are available to NO_x storage. However, the situation for the regenerated catalysts is totally reverse. As observed from Table 4, the K/Ti ratios for all the promoted catalysts are smaller than that for the unmodified catalyst Pt/K/TZ. This result should be related to the desulfation extent of the sulfur-aged catalyst. The surface deposit of sulfur and the formation of bulk or semi-bulk sulfate may have decreased the surface K content. This assumption could be well correlated with the desulfation performance of the catalysts, described in Section 3.4. In order to further confirm this point, the surface residual sulfur contents of the regenerated catalysts are also calculated from XPS test, as listed in Table 4. It is very obvious that more residual sulfur and lower K/Ti ratios were found for Co or Ce promoted catalysts, especially for Co-containing catalysts, as compared with the unmodified catalyst Pt/K/TZ.

3.6. Discussion on the effect of Co and Ce

As described in Section 3.1, the addition of Co or Ce has increased the NSC of Pt/K/TZ to different extents. The increase in oxidation ability of Co or Ce promoted catalysts seems an important factor to NO oxidation and further NO_x storage. To reveal the function of Co and Ce, the *in-situ* DRIFTS characterization on the co-adsorption of NO and O₂ on the sample K/TZ, Co/K/TZ and Ce/K/TZ was performed, the results of which are shown in Fig. 10. It can be seen that only nitrite species (1231 cm⁻¹) can be observed on the sample K/TZ due to the lack of oxidation component. When Ce is added, not only the nitrite species but also the nitrate species (1365 cm⁻¹) could be detected, indicating that Ce oxides can enhance the oxidation of NO to NO₂, and the further formation of nitrates. It should be noted that both the two bands at 1231 and 1365 cm⁻¹ are assigned to K associated species, no Ce associated nitrite or nitrate species are found over the Ce-containing sample, though Ce oxides itself can also store NO_x [30]. Therefore, it could be excluded that the improved NSC of Ce-promoted catalyst is contributed by the more storage sites related to Ce. When Co is added to K/TZ sample, only the much larger nitrate peak can be found except the negative peak due to carbonates decomposition, suggesting the better oxidation ability of Co oxides.

Apart from the improvement of oxidation ability, another function of Co or Ce addition is the effective inhibition of the interaction between K and TiO₂, increasing the surface K/Ti ratio and the NSC of the catalysts. The higher K/Ti ratio suggests more K sites available to NO_x storage. As indicated in Section 3.1, although the oxidation

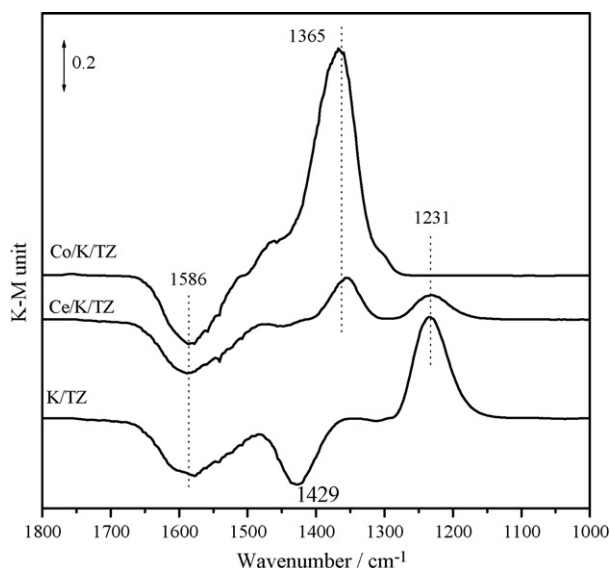


Fig. 10. *In-situ* DRIFTS spectra of NO + O₂ co-adsorption on K/TZ, Co/K/TZ or Ce/K/TZ catalysts. (Condition: the spectra were recorded at 350 °C after 30 min exposure to 400 ppm NO + 5 vol% O₂ + N₂.)

ability of Ce-promoted catalysts is lower than that of Co-promoted catalysts, the former possess larger NSC. From the XPS results, it is clear that the K/Ti ratios of the Ce-containing catalysts are larger than those of Co-containing catalysts, suggesting more K sites available to NO_x storage in Ce-containing catalysts. In a word, both Co and Ce addition has increased the NSC of Pt/K/TZ catalyst due to the improved oxidation ability and increased storage sites of K.

As for the sulfur-resistance, the effect of Co addition on LNT catalyst is seldom investigated, and that of Ce addition is very controversial in literature [20,21]. In the present work, it is found that the addition of Co or Ce could make the sulfur desorption more difficult. However, this negative effect largely depends on the kind of added metals and preparation methods. Co oxides, possessing better oxidation ability, may accelerate the formation of bulk sulfates, which are more difficult to reduce, as confirmed by repeated H₂-TPR. Luo et al. [31] indicated that sulfide species are formed after the reduction of Pt-Fe/Ba/Al₂O₃ LNT catalyst. However, in this work, the XPS spectra of S_{2p} (figure not shown) for all the regenerated catalysts show a main peak at 169.0 eV, which can be assigned to sulfate according to literature [21]. Therefore, it can be concluded that the larger bulk or semi-bulk sulfates formed during sulfation process with the help of the good oxidation ability of Co oxides are much more difficult to reduce and/or decompose compared to those formed over the unmodified catalyst Pt/K/TZ. On the other hand, the decreased oxidation ability of the Co-containing catalysts after sulfation and regeneration, should also account for the decreased NSC, especially for the catalyst Pt/K/Co/TZ. The interaction between Pt and Co oxides in the regenerated Co-containing catalysts favors the formation of Pt oxide as confirmed by XPS, decreasing the oxidation ability of the catalysts as well.

The effect of Ce addition on the sulfur-resistance performance of the LNT catalyst largely depends on the addition modes. In the catalyst Pt/K/Ce/TZ prepared by successive impregnation Pt and Ce contact and interact with each other more efficiently. Similar to the catalyst Pt/K/Co/TZ, the interaction between Pt and Ce also favors the SO₂ adsorption and sulfates formation, which are more difficult to reduce as confirmed by repeated H₂-TPR. For the mechanically mixed catalyst Pt/K/Ce/TZ-mix, the desulfation is easier because of the less efficient contact and interaction between Pt and Ce in this sample. Besides, the higher K/Ti ratio of the mechanical mixture Pt/K/Ce/TZ-mix ensures more K sites available to NO_x storage. Some

researchers [21] found that CeO₂ is in favor of sulfur-resistance for LNT catalysts while others did not think so [20]. This work shows that the Ce addition to Pt/K/TZ catalyst can greatly improve its NSC. However, the sulfur-resistance was decreased more or less, dependent on the addition mode of Ce. The mechanically mixed catalyst Pt/K/Ce/TZ-mix still possesses a considerable NSC of 142 μmol/g after sulfation and regeneration. In addition, the fresh catalyst Pt/K/Ce/TZ-mix shows much larger NSC of 338 μmol/g than the unmodified Pt/K/TZ. In the future with the decrease of sulfur content in fuels, the Ce- and Co-promoted catalysts, especially the mechanically mixed catalyst Pt/K/Ce/TZ-mix will be very promising for the practical purification of NO_x species from lean-burn engines.

4. Conclusions

- (1) The addition of Co or Ce to LNT catalyst Pt/K/TiO₂-ZrO₂ can greatly improve its NO_x storage capacity by improving the oxidation ability of the catalyst and increasing more K sites available to NO_x storage. At 350 °C the NO_x is stored only via K-associated nitrate intermediate. Compared with Co, Ce addition gives much higher surface K/Ti atomic ratio, and therefore bringing out much larger NSC. Preparation method also influences the K/Ti atomic ratio and NSC. The Ce-containing catalyst prepared by successive impregnation possesses higher K/Ti atomic ratio and higher NSC than the mechanically mixed one.
- (2) After sulfation and regeneration, the Co or Ce promoted catalysts, especially the Co promoted ones, show more or less decreased NSC than the unmodified catalyst Pt/K/TiO₂-ZrO₂ due to the more difficult desorption of the deposited sulfur. The Co-containing catalysts possess better oxidation ability than the Ce-containing ones, causing the formation of larger sulfates during sulfation, which are difficult to reduce by hydrogen during regeneration. Besides, the efficient Pt-Co contact favors the formation of Pt oxides after sulfation and regeneration, making the decrease of the oxidation ability and NSC of the catalyst.
- (3) The effect of Ce addition on the sulfur-resistance of Pt/K/TiO₂-ZrO₂ catalyst largely depends on the addition mode of Ce. Although Ce addition shows somewhat disadvantage in sulfur-resistance, the high oxidation ability and the high K/Ti ratio of the mechanically mixed catalyst Pt/K/Ce/TZ-mix make it still possess considerable NSC of 142 μmol/g. In the future with the decrease of sulfur content in fuels, the Co- and Ce-promoted catalysts possessing large NO_x storage capacity, will be promising candidates for lean-burn NO_x abatement.

Acknowledgements

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