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Effect of Co addition to Pt/Ba/Al₂O₃ system for NO_x storage and reduction

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ABSTRACT

A comparative study of Pt/Ba/Al₂O₃, Co/Ba/Al₂O₃, Pt/Co/Al₂O₃ and Pt/Co/Ba/Al₂O₃ was performed in regards to their NO_x storage capacities and NO oxidation abilities as a function of temperature. The nitrate stability and dynamic behaviors of NO_x storage reduction during lean/rich fuel cycles using hydrogen as a reductant were also investigated over these catalysts. It was found that Pt/Co/Ba/Al₂O₃ possessed the largest NO_x storage capacity within the temperature range of 200–350 °C. The existence of Co not only improved the oxidation of NO to NO₂ under lean conditions, but also enhanced the release and reduction of NO_x during the rich phase. The Pt and Co co-supported catalysts showed better NO_x storage reduction activity and higher N₂ selectivity than Pt supported Ba/Al₂O₃ catalysts within the tested temperature range. As for Pt/Co/Ba/Al₂O₃, high conversion was obtained at either a low reductant concentration with long duration time or a high reductant concentration with short duration time during the rich phase. *In situ* FTIR studies showed that NO_x adsorption over Co-containing catalysts takes "nitrite route" as an important pathway. The intimate contact of Co and Ba/Al could accelerate nitrite/nitrate formation and the synergistic effect of Pt and Co could accelerate NO_x reduction.

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1. Introduction

Due to its efficient fuel economy and low greenhouse gas CO_2 emissions, the lean-burn engine is considered as one of the promising candidates for meeting the world's growing energy crisis and contributing to the prevention of climate change [1]. However, its problem of exhaust abatement is yet to be resolved. Unlike gasoline engines, which operate on a stoichiometric air/fuel ratio, the lean-burn engine exhaust usually contains an excess of oxygen, which results in the well-accepted three-way catalysts failing to reduce NO_x [2]. Developing new catalysts has, therefore, attracted much attention around the world. Currently, several catalytic NO_x removal technologies, such as direct NO_x decomposition, selective catalytic reduction of NO_x using ammonia or hydrocarbons as reductants, and NO_x storage and reduction (NSR, also noted as lean NO_x traps, LNT) [3], are under research.

The NSR technology, first developed by Toyota in the 1990s [4], was designed for use on diesel or lean-burn gasoline engines. The applied operation is a cyclic mode with the lean fuel and rich fuel conditions alternating periodically. A typical NSR catalyst usually consists of noble metals, alkali, or alkaline earth metals and a high surface area support. A well known multi-component catalyst is the Pt/Ba/Al₂O₃ system, which functions according to several

sequential steps. Firstly, NO is oxidized to NO₂ over Pt sites and subsequently stored as nitrites and/or nitrates on the catalyst surface during lean operation. When the engine is switched to a short rich period, the nitrites/nitrates decompose and the released NO_x is then reduced by reducing agents such as H₂, CO, and HC on the surface of the precious metal. In this way, the catalyst is regenerated before going through another lean-rich cycle. This successive cycling operation can provide high NO_x removal efficiency [5,6].

Most of previous studies have focused on catalyst compositions and operating conditions that have a great impact on the performance of NO_x storage and reduction [7–13]. For Ba-containing catalysts, noble metal species and their dispersion can lead to different NO oxidation activity during the lean phase [8,14,15] thus directly influencing subsequent adsorption on Ba sites. Additionally, as a result of different preparation methods and reaction conditions, Ba can be present in the form of BaO, Ba(OH)₂, or BaCO₃, with NO_x adsorption ability showing a decreased order [9]. Furthermore, Ba sites located in proximity to Pt play an important role during the trap process. A spill-over mechanism has been proposed to explain the effective adsorption, which suggests that both oxygen and NO/NO₂ could easily migrate from a Pt site to a nearby Ba site, thus improving the adsorption efficiency [16,17]. Recent studies [18] have also demonstrated that the impregnation procedure of Pt or Ba influenced NSR performance, which is both interesting and effective in the optimization of catalyst preparation methods. In the present study, Pt addition after Ba impregnation was applied to facilitate comparison with previous research [8,16]. As referred to the catalytic performance of catalysts in reduction stage,

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the effects of different precious metals and reducing agents have been studied extensively by either *in situ* FTIR or by flow reactors [19–21]. Most recently, people place more emphases on the mechanism study of NO_x storage and reduction. Several kinetic models were developed to predict evolution of the effluent gases as well as surface species either in trapping processes or in lean/rich cycles [22–26]. Considering the complexities of catalyst components and multi-step reactions of this system, many aspects of Pt/Ba/Al₂O₃ still require improvement and clarification, including NO_x storage capacity, reduction efficiency, and low temperature performances.

Vijay et al. found that Co exhibits a similar ability as Pt to oxidize NO during the lean phase [27,28], which clarifies the application of easy obtain and low-cost transition metals. Park et al. further confirmed by XAFS measurement that the active phase of Co was as Co₃O₄ [29]. Both of these studies concentrated on the storage phase of the catalysts, however, the effect of Co in the rich phase is still unclear. Furthermore, temperature impact in the NSR process has not been clarified. Their work inspires us to give a thorough investigation on this meaningful system. In this paper, Pt/Ba/Al₂O₃ catalysts and Co-containing catalysts were carefully studied in regard to their storage ability, nitrate stability, and dynamic catalytic performance using H₂ as a reductant. Temperature impact, as well as reductant concentration and duration time, were also considered. Our aim was to further confirm the specific role of Co in both lean and rich phases during catalytic tests, and determine the appropriate operating conditions for this system.

2. Experimental

2.1. Catalysts preparation

The γ -Al₂O₃ supports were obtained by calcinations of commercial boehmite at 500 °C in air for 3 h. The Ba/Al₂O₃ catalysts were synthesized by an impregnation method. Firstly, the γ -Al₂O₃ support was impregnated in a Ba(CH₃COO)₂ solution. The samples were then dried at 120 °C for overnight and calcined at 500 °C for 3 h in air. The nominal Ba loading was 20 wt%. The Pt or Co was subsequently added to Ba/Al₂O₃ or γ -Al₂O₃ by the same impregnation method using PtCl₄ or Co(CH₃COO)₂ as precursors, respectively, followed by drying at 120 °C and calcining at 500 °C in air for 3 h. Nominal Pt and Co loading was 1 wt% and 5 wt%. The Pt/Co/Ba/Al₂O₃ and Pt/Co/Al₂O₃ catalysts were prepared by adding a calculated amount of PtCl₄ (1 wt% loading) solution into as-prepared Co/BaO/Al₂O₃ and Co/Al₂O₃ materials, respectively. All catalysts were sieved to 20–40 mesh before catalytic measurements.

2.2. Catalysts characterization

X-ray diffraction (XRD) patterns for all powder catalysts were collected (Bruker D8 Discover, 60 kV, 50 mA) with a scan speed of 4° /min at $10^{\circ} < 2\theta < 90^{\circ}$, the average crystal size of BaCO₃ was calculated according to the Scherrer equation.

Surface area and pore volume were determined by nitrogen adsorption–desorption isotherms at -196 °C over the whole range of relative pressures, using a Quantasorb-18 automatic instrument (Quanta Chrome Instrument Co.). Prior to the measurement, the catalysts were outgassed at 300 °C under vacuum for 4 h.

The dispersion of Pt was determined by a H_2-O_2 titration method using a homemade pulse flow system equipped with a computer-interfaced quadruple mass spectrometer (Hiden HPR 20). Prior to H_2-O_2 titration, 100 mg of the sample was reduced in 5 vol% H_2/Ar (40 cm³/min, 10 °C/min) at 450 °C for 1 h. The He gas (40 cm³/min) was then passed through the sample for 1 h. After cooling to room temperature in He, the O_2 adsorption experiment was conducted, followed by flushing with He and then the introduction of H₂ pulses ($1 \text{ cm}^3 \text{ of } 5 \text{ vol}\% \text{ H}_2/\text{Ar}$). The stoichiometries of H/Pt = 3 were assumed.

Diffuse-reflectance UV-vis spectra were recorded on a U-3010 (Hitachi) spectrometer with a standard diffuse reflectance unit under ambient conditions. The Ba/Al₂O₃ or γ -Al₂O₃ was used as a reference material. The testing range was 200–850 nm and the scan rate was 300 nm/min.

2.3. NO_x storage/release tests and cyclic activity measurements

The NO_x uptake experiments were carried out under lean fuel conditions as a function of temperature. Before each experiment, the catalysts (100 mg) were pretreated in 1% H₂/N₂ for 30 min at 450 °C, and then cooled to the desired temperature. A mixture of 500 ppm NO and 8% O₂ was used to simulate the lean fuel exhaust, using N₂ as a balance gas. All gases were carefully introduced by mass flow controllers with a total flow rate of 300 cm³/min. The outlet NO_x (NO + NO₂) concentration was monitored by a chemiluminescence detector (ECO Physics CLD 62). The reactor was also equipped with a bypass line to ensure inlet gas concentration.

A temperature-programmed desorption (TPD) procedure was used to study the NO_x release process under inert atmosphere. Prior to the experiment, all catalysts (100 mg) were pretreated in 1% H₂ at 450 °C for 30 min and then cooled to 300 °C under the same atmosphere. After that, 500 ppm NO and 8% O₂ were introduced and maintained for 2 h to ensure the catalysts were saturated. The samples were then purged and cooled to room temperature under flowing Ar and the temperature was increased to 900 °C at 10 °C/min subsequently. A mass spectrometer (Hiden HPR 20) was used for on-line monitoring of the signals of NO (*m/e* = 30), NO₂ (*m/e* = 46), and O₂ (*m/e* = 32) with an ionizing voltage of 70 eV.

The NSR cyclic measurements were conducted with 100 mg of the catalysts using a fixed-bed quartz reactor. The reactor was connected to a pneumatically actuated four-way valve, which provides a quick switching between the lean and rich atmospheres. Constant flows ($300 \text{ cm}^3/\text{min}$) of 500 ppm NO balanced with N₂ with either 8% O₂ or 0.5% H₂ were introduced alternately. The cycling experiments with a lean period of 67 s and a rich period of 33 s were performed between 200 °C and 400 °C. Nevertheless, H₂ concentration and duration time changed when required. The catalysts were exposed to 15 or 50 lean/rich cycles. The NO_x concentration was averaged over the cycles to give a mean conversion according to the following formula:

$$NO_x \text{ conversion} = \frac{NO_{x,in} - NO_{x,out}}{NO_{x,in}} \times 100\%$$

The outlet N₂O and NH₃ were analyzed using an FTIR spectrometer (Nicolet Nexus 6700) with a heated (120 °C), low volume multiple-path gas cell. The N₂ selectivity was calculated by the following formula:

$$N_2 \text{ selectivity} = \frac{NO_{x,in} - NO_{x,out} - NH_{3,out} - 2N_2O_{out}}{NO_{x,in} - NO_{x,out}} \times 100\%$$

2.4. In situ FTIR study of NO_x storage and reduction

In situ DRIFTS was performed on a Nexus 670 (Thermo Nicolet) FTIR spectrometer equipped with an *in situ* diffuse reflection chamber and a high-sensitivity MCT detector. The catalyst for the *in situ* DRIFTS studies was finely ground and placed in a ceramic crucible in the *in situ* chamber. Mass flow controllers and a sample temperature controller were used to simulate real reaction conditions, which were identical to the catalytic activity tests. Prior to recording each DRIFTS spectrum, the catalyst was pretreated in 1%



Fig. 1. XRD patterns of Pt, Co and Pt–Co-supported catalysts: (a) $Pt/Co/Al_2O_3$, (b) Ba/Al_2O_3 , (c) $Pt/Ba/Al_2O_3$, (d) $Co/Ba/Al_2O_3$, and (e) $Pt/Co/Ba/Al_2O_3$.

H₂ at 450 °C for 30 min and then cooled to 300 °C under N₂ flowing in order to acquire a reference spectrum. A gas mixture of 500 ppm NO and 8% O₂ was then introduced, and a series of NO_x adsorption spectra over time were obtained. After adsorption for 30 min, 0.5% H₂ was used to conduct the reduction procedure. All spectra reported here were collected at a resolution of 4 cm^{-1} for 100 scans.

3. Results and discussion

3.1. Structural properties

The X-ray diffraction patterns of Pt/Co/Al₂O₃, Ba/Al₂O₃, Pt/Ba/Al₂O₃, Co/Ba/Al₂O₃ and Pt/Co/Ba/Al₂O₃ are shown in Fig. 1. Results demonstrate that Pt/Co/Al₂O₃ had three distinct peaks, identified as Al₂O₃ (JCPDS No. 10-425) and CoAl₂O₄ (JCPDS No. 44-0160) phase. The main phase of Ba/Al₂O₃ was Al₂O₃ support, while a small peak at 24° was the characteristic of BaCO₃ diffraction (JCPDS No. 44-1487). When Pt or Co was incorporated into Ba/Al₂O₃, the peaks indexed to BaCO₃ become more distinct due to the addition of drying and calcination steps during the preparation process, and both orthorhombic and monoclinic phases were detected [30]. The sharp peaks of BaCO₃ in these reflections indicate good crystallization and the estimated crystal sizes are listed in Table 1. In Co/Ba-containing samples, a wide and weak peak at 36.8° was detected, which is characteristic of a Co₃O₄ phase (JCPDS No. 74-2120). The low intensity of the peak indicates high dispersion of cobalt in the matrix. Although using the same Co content, the XRD patterns of Co/Ba-containing catalysts obtained here are quite different from what Vijay et al. reported, which is a possible reflection of different preparation methods and precursors applied [27]

The surface areas, pore volume, and average pore radius of the catalysts are listed in Table 1. Pure γ -Al₂O₃ had the largest surface area and pore volume. Although surface area decreased as a result of sequential impregnation and calcinations, it was still relatively high (larger than 200 m²/g) for all prepared catalysts.

The UV–vis spectra obtained to further investigate the nature of Co are represented in Fig. 2. Results show that Co/Ba/Al₂O₃ and Pt/Co/Ba/Al₂O₃ demonstrated the same features, with two broad peaks at 380 and 650 nm, while Pt/Co/Al₂O₃ exhibited three peaks centered at 540 nm, 580 nm, and 625 nm. According to the literature [31], the spectrum of Co₃O₄ is characterized by broad bands at 380 nm and 670 nm, and the three peaks at 540 nm, 580 nm, and



Fig. 2. UV-vis spectra of Co-containing catalysts: (a) $Co/Ba/Al_2O_3$, (b) $Pt/Co/Ba/Al_2O_3$, and (c) $Pt/Co/Al_2O_3$.

625 nm are related to the presence of tetrahedral coordination Co^{2+} in CoAl₂O₄. The band at 650 nm might, therefore, be a combination of the 670 nm peak of Co₃O₄ and the 625 nm peak of Co²⁺. In this case, Co species in Co/Ba/Al₂O₃ and Pt/Co/Ba/Al₂O₃ were mainly present in the form of Co₃O₄ clusters, with a small portion entering Al₂O₃ by forming CoAl₂O₄, while the Co species in Pt/Co/Al₂O₃ was attributed to CoAl₂O₄. These results are in line with the XRD characterization (Fig. 1).

3.2. NO_x storage performances at different temperatures

Fig. 3a–d shows the NO_x breakthrough curves *versus* time of Pt/Ba/Al₂O₃, Co/Ba/Al₂O₃, Pt/Co/Ba/Al₂O₃, and Pt/Co/Al₂O₃ at different temperatures. As soon as the lean feed was switched from the bypass loop to the catalysts, NO_x concentration in the outlet dropped sharply from 500 ppm to 0 ppm, followed by a complete uptake process. The complete absorption time varied from thirty seconds to several hundred seconds with different catalyst compositions and temperatures. With increased time, outlet NO_x concentration gradually increased and a saturation state was achieved slowly by the end of 4000 s. The NO_x evolution profiles obtained here are similar to previously reported on Pt/Ba/Al₂O₃ [32].

The area between the inlet feed and the breakthrough curves represents the trapped amount of NO_x , with the calculated NO_x storage capacities (NSC) summarized in Table 2. As Muncrief et al. [33] have stressed, storage time and saturation level have an influence on maximum NO_x storage versus temperatures and all NSC data presented here were calculated during the initial 4000 s after switching from the bypass loop. As shown in Table 2, NSC increased as temperature increased. The maximum NSC was obtained at 300 °C for Pt/Ba/Al₂O₃, Co/Ba/Al₂O₃, and Pt/Co/Ba/Al₂O₃. Further temperature increases led to a decrease in amounts of trapped NO_x , which was attributed to the instability of nitrates at elevated temperatures. It was clear that Co/Ba/Al₂O₃ and Pt/Co/Ba/Al₂O₃ showed much larger NSC than Pt/Ba/Al₂O₃ at all temperatures tested. The combination of Pt and Co greatly improved the low temperature (200-250 °C) storage performance, about 1.5 times that of samples only containing either Pt or Co. The maximum NSC, with a value of 882.5 μmol g⁻¹, was obtained at 300 °C. However, when the temperature was increased to 400 °C, the trapped amounts decreased by 23% compared with the maximum value, but it was still 1.4 times as large as Pt/Ba/Al₂O₃. After increasing the temperature to 450 °C, however, the Pt-Co combination advantage disappeared and gave

Table 1 Physical properties of catalysts.

Catalysts	Surface areas (m ² /g)	Pore volume (cm ³ /g)	Average pore radius (nm)	BaCO ₃ particle size (by XRD, nm)	Pt dispersion (by H ₂ -O ₂ titration, %)
Al ₂ O ₃	270.3	0.87	12.8	-	-
Ba/Al ₂ O ₃	208.7	0.67	12.9	28.2	-
Pt/Co/Al ₂ O ₃	223.0	0.73	13.0	-	27
Pt/Ba/Al ₂ O ₃	217.7	0.65	12.0	31.4	25
Co/Ba/Al ₂ O ₃	220.1	0.70	11.8	33.3	-
Pt/Co/Ba/Al ₂ O ₃	208.4	0.66	12.7	33.5	30



Fig. 3. Outlet NO_x concentration as a function of time and temperature under lean condition: (a) Pt/Ba/Al₂O₃, (b) Co/Ba/Al₂O₃, (c) Pt/Co/Ba/Al₂O₃, and (d) Pt/Co/Al₂O₃. Lean gas composition: 500 ppm NO, 8% O₂, N₂ balanced.

the same trapped amounts of NO_x as Pt/Ba/Al₂O₃. It was because the equilibrium limitation dominates at such high temperatures and the formed Ba(NO₃)₂ are easy to decompose. Unlike Ba-containing catalysts, the NSC of Pt/Co/Al₂O₃ decreased as a function of temperature, with the maximum value of 261.9 μ mol g⁻¹ obtained at 200 °C. The adsorption ability of Pt/Co/Al₂O₃ was mostly related to Al₂O₃. The trend of NSC *versus* temperature was also consistent with previous research, which suggests that Al₂O₃ can adsorb significant amounts of NO_x below 300 °C [34]. It is true that Co could also provide some storage capacity, however, its contribution was quite small compared to the major storage component of Ba and Al₂O₃ supporter due to its low content and weak basicity. To provide evidence, we tested the NSC of pure cobalt oxide obtained by calcining Co(CH₃COO)₂ at 500 °C for 3 h (the same Co introducing method as described in Section 2.1). The 5% Co oxides possessed

limited storage capacity by calculation, lower than 4μ mol g⁻¹ at each temperature tested. As a result, storage capacity was mostly relevant to Ba or Al species in all the prepared catalysts.

Although many factors can influence the trapping process, the oxidation of NO to NO_2 is regarded as a key step since NO_2 more effectively traps than NO [35,36]. In typical studies, platinum plays an important role in NO oxidation. Fig. 4 compares the conversions of NO to NO_2 over Pt and/or Co-supported catalysts at the end of the storage process, where the NO_2/NO_x ratio reached a steady state. On the Pt/Ba/Al₂O₃ catalyst, NO conversion increased with increasing temperature from 200 °C to 400 °C, but NO_2 yield decreased with a further temperature increase to 450 °C. In regard to 5% Co containing catalysts, Co/Ba/Al₂O₃, Pt/Co/Ba/Al₂O₃, and Pt/Co/Al₂O₃ showed much higher NO conversion than 1% Pt containing Pt/Ba/Al₂O₃ above 200 °C. Specifically, Co/Ba/Al₂O₃ gave the

Table 2

NO_x storage capacities (NSC) tested at different temperatures.

Catalysts	200 ° C	250°C	300 ° C	350 °C	400 °C	450 °C
Pt/Ba/Al	451.9	550.3	582.3	553.7	482.3	453.7
Co/Ba/Al	505.9	623.5	846.7	762.4	743.2	469.9
Pt/Co/Ba/Al	708.2	852.9	882.5	850.1	681.4	458.4
Pt/Co/Al	261.9	183.7	174.7	153.2	119.9	16.6

Unit: μ mol NO g(cat)⁻¹.



Fig. 4. The outlet NO_2/NO_x ratio at the end of 4000s NO_x adsorption over $Pt/Ba/Al_2O_3$, $Co/Ba/Al_2O_3$, $Pt/Co/Ba/Al_2O_3$ and $Pt/Co/Al_2O_3$.

highest NO₂ yield at 300 °C with a NO to NO₂ conversion of 77%, which was twice that of Pt/Ba/Al₂O₃. Nevertheless, Pt/Co/Ba/Al₂O₃ showed a 60% conversion of NO at the same temperature, and the maximum NO conversion temperature shifted to 350 °C with a value of 68%. This unexpected feature may correlate with catalyst structure and thus induced dynamic equilibrium between surface species and gaseous NO₂. Further increases in the temperature also led to a decrease in NO₂ yield. The Pt/Co/Al₂O₃ catalyst exhibited a similar NO oxidation trend to Pt/Co/Ba/Al₂O₃. For comparison, the NO oxidation ability of pure Co oxides was also depicted. The maximum NO conversion of 81% was obtained at 300 °C, indicating pure Co oxides exhibited an excellent NO oxidation ability. All these NO oxidation profiles support the fact that the NO oxidation process is a kinetic limitation at low temperatures but an equilibrium limitation at higher temperatures.

For Pt or/and Co-supported catalysts, the NO oxidation ability is quite dependent on catalyst compositions, especially the state of active sites of Pt and Co. Previous studies have found that the dispersion and state of Pt had an influence on the reaction of $NO + 1/2O_2 \rightarrow NO_2$. Olsson and Fridell [37] demonstrated that high dispersion of platinum may lead to low NO conversion due to the easy oxidation of small Pt particles, and that Pt is prone to forming an oxide on Ba/Al₂O₃ compared with Al₂O₃ support. Bhatia et al. [38] further confirmed an inhibitory effect of NO₂ and O2 on the NO oxidation reaction. The highly oxidizing nature of these gases could accelerate the formation of Pt oxides, resulting in the loss of activity. These may explain the relatively low NO conversion on Pt supported Ba/Al₂O₃. In regards to 5% Co incorporated catalysts (Co/Ba/Al₂O₃, Pt/Co/Ba/Al₂O₃, and Pt/Co/Al₂O₃), the promising NO oxidation features had a direct connection to the nature of Co species. As previously discussed in Section 3.1, Co was in the form of CoAl₂O₄ in the Pt/Co/Al₂O₃ catalyst and a mixture of $Co_3O_4/CoAl_2O_4$ in the Co/Ba/Al_2O_3 catalyst. Both of these Co oxides can promote NO₂ formation due to their good redox property, and may therefore improve the storage ability of Co-containing catalysts. It seems that Co oxides could accelerate NO oxidation independent of the state of Pt. Although the inhibition effect may still be present over Pt supported catalysts due to the unavoidable Pt oxides formation under a lean atmosphere, the addition of 5% Co could compensate or even improve NO oxidation to NO2. Furthermore, we should noticed that the NO_2/NO_x ratio presented in Fig. 4 just represents a steady gas/solid equilibrium between NO₂ and the $BaO/Ba(NO_3)_2$ phase and is not completely consistent with the storage capacities listed in Table 2. This result indicates that



Fig. 5. NO_x (m/e = 30 signal intensity) evolution during Ar-TPD-MS experiments.

other factors also influence the storage process. For example, the proximity of an oxidative component (Pt or Co) to trapping sites (Ba or Al) can influence NO and O_2 spill-over and the temperature has an impact on the diffusion rates of adsorbed NO_x species into the bulk of the catalysts.

In relation to the storage mechanism, formed NO₂ on Pt/Co sites can be either transferred to nearby Ba/Al sites via a spill-over pathway or released and reabsorbed at Ba/Al sites distant from Pt/Co [6]. A disproportion reaction has been proposed with NO₂ adsorption, in which $3 \mod NO_2$ are consumed to form $2 \mod Ba(NO_3)_2$, simultaneously with the release of 1 mol NO. This reaction route is widely used to explain the adsorption mechanism on Pt/Ba/Al₂O₃. However, Nova et al. [12] proposed another mechanism to explain adsorption called the "nitrite route", in which NO can be directly absorbed on the surface by forming nitrites that are subsequently oxidized to nitrates by O₂. This "nitrites route" may also play a significant role in NO_x uptake on both Co and/or Pt containing catalysts, and detailed progress will be discussed later by FTIR experiments. As a consequence, the promotion effects of Co are not only concerned with its high NO oxidizing ability towards NO₂, but also related to the intimate contact of Co with Ba and Al. This provides more active sites and a larger interface contact area between Co and Ba/Al than Pt/Ba/Al₂O₃ for the activation of NO/O₂ and spill-over of NO/NO₂, thus directly accelerating nitrites/nitrates formation. The synergistic effect of Pt and Co improved NO_x storage efficiency by extending the usage of Ba and Al sites on the surface of the catalysts.

3.3. NO_x-TPD experiments

The thermal stabilities of NO_x stored on Pt/Ba/Al₂O₃, Co/Ba/Al₂O₃, Pt/Co/Ba/Al₂O₃, and Pt/Co/Al₂O₃ were compared by NO-TPD experiments. As seen in Fig. 5, most stored NO_x was desorbed within the temperature range of 300–550 °C. The results are in good accordance with previous reports on Pt/Ba/Al₂O₃ [39]. In addition, oxygen desorption peaks were observed over the same temperature range. It has been reported that the nitrate desorption may follow the equation: Ba(NO₃)₂ \rightarrow BaO+2NO₂+1/2O₂ [40]. However, the signal of NO₂ (m/e = 46) in our experiment was very weak and the main desorption feature was NO (m/e = 30) and O₂ (m/e = 32). This is because NO₂ was easily dissociated to an NO ionization fragment under our MS conditions.

Obviously, the four catalysts showed different NO_x releasing amount and different maximum NO_x desorption temperatures



Fig. 6. Evolutions of NO_x concentrations under cyclic lean-rich condition at different temperatures. Left side: Pt/Ba/Al₂O₃, right side: Pt/Co/Ba/Al₂O₃. Lean (67 s): 500 ppm NO, 8% O₂, N₂ balanced; rich (33 s): 500 ppm NO, 0.5% H₂, N₂ balanced.

(Fig. 5). Specifically, Pt/Co/Ba/Al₂O₃ showed the largest desorption amount of NO_x, followed by Co/Ba/Al₂O₃, then Pt/Ba/Al₂O₃, and finally Pt/Co/Al₂O₃. This sequence was in agreement with the NO_x storage amounts at 300 °C (Table 2). In addition, Pt/Ba/Al₂O₃ catalysts gave a maximum NO_x desorption peak around 468 °C, while for Co/Ba/Al₂O₃ and Pt/Co/Al₂O₃ NO desorption shifted to lower temperatures and gave a maximum desorption around 400 °C. Two apparent peaks centered at 400 °C and 470 °C were observed for Pt/Co/Ba/Al₂O₃, which seemed to be a combinatorial contribution of Pt/Ba/Al₂O₃ and Co/Ba/Al₂O₃. It should be pointed out that, the desorption peak centered at 400 °C only appeared in the Co-containing samples of Pt/Co/Al₂O₃, Co/Ba/Al₂O₃ and Pt/Co/Ba/Al₂O₃, indicating that this peak is closely related to the presence of Co. Generally, there are two possibilities contributing to this situation: Co species, serves as the adsorption sites for NO_x storage; the intimate contact of Co with NO_x storage components (Ba and/or Al) enhances the storage of NO_x at low temperatures. Considering that the contribution of Co species (5% Co) to NO_x storage is marginal, it is reasonable to conclude that the NO desorption centered at 400 °C over Pt/Co/Ba/Al₂O₃ could be ascribed to decomposition of Ba and/or Al nitrates in intimate contact with Co. Even though Pt/Co/Al₂O₃ and Co/Ba/Al₂O₃ possess the same Co loading of 5%, the latter shows much stronger peak at 400 °C than the former, clearly confirming that Ba also plays a crucial role in NO_x storage at low temperatures. The NO peak at 470 °C could be attributed to the decomposition of Ba nitrate species, which were far from Co but in proximity with Pt or isolated (far from Co and Pt), neither could be eliminated. Consequently, Co addition can decrease the thermal stability of nitrates associated with Ba or Al due to the specific interaction of Co/Al and Co/Ba, which may have a great impact on regeneration performances of NSR.

3.4. Dynamic NO_x storage and reduction performances

High NO_x removal efficiency is not only concerned with its storage capacity in the lean phase, but also related to effective reduction of trapped NO_x during the regeneration phase. Of the most common reducing agents used in NSR system, H₂ is more reductive than CO and C_3H_6 , especially at low temperatures [20,41]. Herein, H₂ was selected as the reductant in our current study. NO_x storage and reduction performances were investigated comparatively under cyclic conditions within a temperature range of 200–400 °C using Pt/Ba/Al₂O₃ and Pt/Co/Ba/Al₂O₃ catalysts. Firstly, the experiments were performed with a lean period of 67 s and a rich period of 33 s. For the latter duration, 0.5% H₂ was applied in an amount abundant enough to reduce the introduced NO_x . The NO_x entering during the lean cycle was 7.5 µmol, and the reduction process was assumed to occur as per the following equation: $Ba(NO_3)_2 + 5H_2 \rightarrow N_2 + BaO + 5H_2O$. Supposing all NO_x was trapped as Ba(NO₃)₂, 18.7 µmol H₂ was needed to completely reduce the NO_x introduced in the lean phase. However, NO_x also existed in the feed gas during the rich phase, and the reduction process was $2NO + 2H_2 \rightarrow N_2 + 2H_2O$. As a result, another 3.7 µmol H₂ was required to completely reduce NO in the rich gas phase. In this experiment, 0.5% H₂ (36.8 µmol H₂) was introduced to the catalyst during a 33 s regeneration period, which was about 1.6 times the calculated amounts required to reduce all introduced NO_x.

The evolution of NO_x in the outlet feed of the initial 15 lean/rich cycles of Pt/Ba/Al₂O₃ and Pt/Co/Ba/Al₂O₃ at different temperatures are depicted in Fig. 6. Just as this kind of catalysts supposed to function, NO_x was effectively trapped under lean conditions with very low NO_x emission. When the feed gas was switched to a rich condition, a sharp NO_x spike occurred and then decreased quickly to a low level. This distinct peak during cycle transition has been commonly observed by earlier publications and is thought to be caused by the different initial rate between the nitrate decom-



Fig. 7. NO_x conversion of Pt/Ba/Al₂O₃, Pt/Co/Al₂O₃ and Pt/Co/Ba/Al₂O₃ under cyclic lean-rich condition at different temperatures. Lean (67 s): 500 ppm NO, 8% O₂, N₂ balanced; rich (33 s): 500 ppm NO, 0.5% H₂, N₂ balanced.

position and the NO_x reduction [42,43]. With different catalysts and temperatures, however, the NO_x evolution features were quite different. For Pt/Ba/Al₂O₃, the highest spikes occurred during the transition at 200 °C. With increasing temperatures, the transition spikes gradually decreased and gave the lowest NO_x spikes between 300 °C and 350 °C (<10 ppm), which indicated that NO_x removal performance reached a maximum at this temperature range. Although the performance of NO_x removal at 400 °C showed minor deterioration, it was still better than that at 200 °C. The Pt/Co/Ba/Al₂O₃ catalysts showed much better NO_x removal performances than the Pt/Ba/Al₂O₃ catalysts at all tested temperatures under the same experimental conditions. It was easy to see that the transition spikes were greatly reduced, especially at 300-350 °C (lower than 2 ppm). It seemed that the NO_x release and reduction rates reached a balance at such a situation and nearly 100% conversion of NO_x was obtained. The averaged fifteen-cycle NO_x conversions over Pt/Ba/Al₂O₃ and Pt/Co/Ba/Al₂O₃ are compared in Fig. 7. Due to the relatively short lean duration time and the use of the most effective reductant, the removal efficiencies were all extremely high, with more than 90% of NO_x conversion obtained for both Pt/Ba/Al₂O₃ and Pt/Co/Ba/Al₂O₃. However, Co addition may improve low temperature NO_x conversion of the catalysts, and may, to some extent, compensate the activity loss due to Pt oxide formation. The experiments were also conducted with 50 cycles, and similar conversions were obtained to 15 cycles, presenting good reproducibility. We also tested the catalytic NO_x removal performance over the Pt/Co/Al₂O₃ catalyst under this operation mode (67 s/33 s). Since this catalyst possessed quite small NO_x storage capacity, the overall NO_x conversions were less than 25% under the temperature range of 200–400 °C (Fig. 7).

The reduction products were simultaneously detected over these catalysts. Since N₂ was not measured directly, the evolution of NH₃ and N₂O in the outlet was measured to predict N₂ selectivity. In this operation mode, little NH₃ and N₂O (<2 ppm) were formed above 300 °C for Pt/Ba/Al₂O₃ and Pt/Co/Ba/Al₂O₃. However, significant amounts of NH₃ and N₂O were formed at 200 °C (Fig. 8). The formation of NH₃ and N₂O at this temperature decreased the N₂ selectivity to 86% for Pt/Co/Ba/Al₂O₃ and to 77% for Pt/Ba/Al₂O₃. It is obvious that N₂ selectivity was higher when Co was present in the catalysts due to less N₂O formation and more NO_x trapping.

During the steady state under rich condition (500 ppm NO + 0.5% H₂), Pt-containing catalysts could catalyzed H₂ to completely reduce gaseous NO_x at temperatures as low as 200 °C (NH₃ was the only product). The effect of Co species under the same atmosphere,



Fig. 8. N₂ selectivity of Pt/Ba/Al₂O₃ and Pt/Co/Ba/Al₂O₃ under cyclic lean-rich condition at 200 °C. Lean (67 s): 500 ppm NO, 8% O₂, N₂ balanced; rich (33 s): 500 ppm NO, 0.5% H₂, N₂ balanced.

however, was not so clear. To identify the specific role of Co species during the rich phase, the removal efficiency of NO_x by Co/Ba/Al₂O₃ under rich conditions (500 ppm NO+0.5% H₂) was tested. Steady state NO_x conversions are shown in Fig. 9. As temperature increased from 200 °C to 400 °C, the rich NO_x conversion of Co/Ba/Al₂O₃ improved from 8% to 99%. The major reduction products were composed of a mixture of N₂ and NH₃, with little N₂O detected. Detailed NO_x reduction selectivity to N₂ is also depicted in Fig. 9. Although it was less effective than Pt in catalyzing the reduction of NO_x at low temperatures, Co species had significant catalytic reduction



Fig. 9. Steady state NO_x conversion and N₂ selectivity of Co/Ba/Al₂O₃ under rich phase (500 ppm NO + 0.5% H₂).



Fig. 10. Evolutions of NO_x concentrations under cyclic lean-rich condition at different temperatures on Co/Ba/Al₂O₃. Lean (67 s): 500 ppm NO, 8% O₂, N₂ balanced; rich (33 s): 500 ppm NO, 0.5% H₂, N₂ balanced.

ability above 250 °C. The cyclic performances of NO_x storage and reduction were also tested over Co/Ba/Al₂O₃. The outlet NO_x features at 200 °C, 300 °C, and 400 °C are depicted in Fig. 10. It can be seen that Co/Ba/Al₂O₃ exhibited excellent storage ability, as previously stated in Section 3.2, but also showed limited reduction ability here. At 200 °C, NO_x was completely trapped on the catalysts during the first cycle but was not fully released or reduced at such low temperature. The NO_x removal performances of subsequent cycles were affected and a deactivation was observed as cycles continued. As a result, the average NO_x conversion was only 5% at 200 °C. The main reduction by-product was N₂O at this temperature, resulting in a N₂ selectivity of 71%. The NO_x removal performance at 300 °C increased to 31% due to the increased thermal instability of stored NO_x and the catalytic reduction ability of Co/Ba/Al₂O₃. In this case, the NO_x storage sites were completely regenerated (by NO_x release or reduction) during the preceding cycles, leading to full adsorption of NO_x during the subsequent cycles. The reduction products consisted of a mixture of N₂, N₂O, and NH₃, which gave a N₂ selectivity of 80%. The regeneration effect was even more significant with increasing temperature, and the cyclic NO_x removal efficiency improved to 45% with a N₂ selectivity of 83% at 400 °C. Apparently, NO_x conversion under cyclic conditions was lower than under steady rich conditions. This could be attributed to the large amount of released NO_x/O_2 to be reduced with a relatively short duration time of the reductant. The important role of Co in the reduction process can also be speculated on by the NO_x evolution of Pt/Co/Ba/Al₂O₃ (Fig. 6). Specifically stated, Pt/Co/Ba/Al₂O₃ showed higher nitrate instability, as evidenced in the TPD experiment, but exhibited lower NO_x spikes during lean/rich transitions compared with Pt/Ba/Al₂O₃. This phenomenon indicates that Co species also participated in the NO_x catalytic reduction process. As a result, the combination of Pt and Co not only greatly enhanced the amounts of NO_x storage during the lean phase, but also improved the reduction efficiency during the rich phase.

Compared with a practical operation mode of a few seconds, the reduction time used above (33s) was much longer. We reduced the reduction time to 6s, which is closer to actual conditions. As 0.5% H₂ was insufficient to reduce all introduced NO_x, 1.5% H₂ was instead used. With 1.5% H_2 (20 $\mu mol) used during the rich$ period, introduced NO_x (8.4 μ mol) was assumed to be completely converted to N_2 . As shown in Fig. 11, the outlet NO_x concentrations under cyclic lean fuel (67s) and rich fuel (6s) conditions for Pt/Co/Ba/Al₂O₃ at different temperatures with fifty cycles were calculated. At 200 $^{\circ}$ C, the average NO_x conversion was 70%. When the temperature increased to $300 \,^{\circ}$ C, the average NO_x conversion increased to 90%. This improvement could be attributed to the enhancement of efficiencies during both the storage and reduction stages, which was evidenced by less NO_x breakthrough during the lean period and lower NO_x spikes during the transitions. Increasing the temperature to 400 °C led to a decreased conversion of only 60% as NO_x evolution gradually reached a steady state after the initial five cycles. In this steady state, NO_x was not completely stored or reduced in the repeated cycle. Even though the regeneration efficiency was high at such temperatures, the deteriorated trapping efficiency led to poor NO_x conversion. As previously stated, introduced H_2 were calculated to completely reduce NO_x both in lean and rich phases. However, the residual oxygen on the surface and in the gas phase may also consume part of the reductant. In such case, 1.5% H₂ can only partially regenerate the storage sites during the 6s duration, leading to decreased trapping amounts in the subsequent cycles.

We extended the reduction time to 13 s using $1.5\% \text{ H}_2$ and maintained the lean phase at 67 s. The total introduced reductant was about twice the amount needed to completely reduce NO_x. The outlet NO_x evolution of fifty cycles is depicted in Fig. 12. Compared with the outlet NO_x features in Fig. 11, it can be observed that both the NO_x breakthrough during the lean stage and the transition spikes during the rich stage were greatly reduced at all tested temperatures. Correspondingly, the average NO_x conversions were improved to 82%, 96%, and 90% at 200 °C, 300 °C, and 400 °C, respectively. We also noted that small amounts of NH₃ and N₂O were formed at 200 °C (specific graph not shown here), and the N₂ selectivity was calculated to be 90%. Both NH_3 (<2 ppm) and N₂O (<2 ppm) were hardly detected above 300 °C, resulting in a high production of N₂. These results indicate that the introduced reductant at such operation mode (67 s lean/13 s rich) could regenerate the trapping sites more efficiently and a higher N₂ selectivity was obtained comparing to 67 s/6 s mode. Therefore, according to the experiments above, satisfied NO_x conversion could be achieved



Fig. 11. Evolutions of NO_x concentrations under cyclic lean-rich condition at different temperatures of Pt/Co/Ba/Al₂O₃. Lean (67 s): 500 ppm NO, 8% O₂, N₂ balanced; rich (6 s): 500 ppm NO, 1.5% H₂, N₂ balanced.

by either a low concentration of reductant with a relatively long regeneration time or by a high concentration of reductant with a relatively short regeneration time, which is similar to results obtained by Breen et al. [44].

As confirmed by previous studies and our experiments, the efficiencies of storage and regeneration determine the overall NO_x removal performance of Pt or Co based catalysts. During lean periods, NO oxidation ability and trap site locations affect NO_x trapping



Fig. 12. Evolutions of NO_x concentrations under cyclic lean-rich condition at different temperatures of $Pt/Co/Ba/Al_2O_3$. Lean (67 s): 500 ppm NO, 8% O_2 , N_2 balanced; rich (13 s): 500 ppm NO, 1.5% H_2 , N_2 balanced.

performance. If the trap sites are not basic enough or not easily accessible, NO_x may not be trapped effectively, leading to a NO_x breakthrough before the end of the lean stage, and a deterioration in the storage efficiency. During the rich period, the stability of nitrates, the proximity of stored NO_x to active sties, the type and concentration of the reductant, and the rich phase duration time can induce different NO_x reduction efficiency. This study aimed, therefore, to optimize catalyst composition and operation conditions. Typical Pt/Ba/Al₂O₃ catalysts were optimized by adding Co. Both the transient cyclic results (Figs. 6 and 10) and steady state experiments (Fig. 9) confirmed the positive effect of Co. Not only

does Co addition increase NO oxidation and storage ability at the lean phase, it also has a specific interaction with trapping sites and accelerates the release of NO_x , thereby providing additional active sites for the NO_x catalytic reduction process.

Operation conditions optimization is another purpose of our experiments. For Pt/Co/Ba/Al₂O₃ catalysts, high NO_x conversion was obtained with either a 67 s/33 s (0.5% H₂) mode or with a $67 \text{ s}/13 \text{ s} (1.5\% \text{ H}_2)$ mode. In regard to a specific operating mode, temperature and regeneration efficiency determined whole NO_v removal activities. It was observed that the outlet NO_x gradually slipped when using a 6 s reduction interval with 1.5% H₂, owing to poor regeneration efficiency. Furthermore, residual oxygen either in the gas feed or on the catalyst surface may also have an added to consumption of the reductant. Therefore, supplying excess reductant is essential for the reduction of NO_x/O_2 , which both presented in the rich gas flow and emitted from trapping sites. It is worth noting, however, that supplying an excess reductant of H₂ may also increase the risk of NH₃ production due to a high H/N ratio, which ultimately reduces the selectivity to N2. Recent studies have found that NH₃ is an important intermediate at the reduction stage [44,45]. Although we detected a significant amount of NH₃ at low temperatures, its role needs further study and the emitted amount should be reasonably controlled when using H₂ as a reductant.

3.5. NO_x storage and reduction mechanism studied by in situ DRIFTS

Species evolution during the NO_x storage and reduction process with different exposure time at 300 °C is shown in Fig. 13. After exposing the Pt/Ba/Al₂O₃ catalyst to a NO/O₂/N₂ mixture for 2 min at 300 °C, an obvious band at 1230 cm⁻¹ and a small band at 1315 cm⁻¹ were observed (Fig. 13a). These bands were assigned to bridged nitrite species on Al or on Ba sites [10,33]. By increasing exposure time, the band at $1230 \,\mathrm{cm}^{-1}$ gradually decreased and was overlapped by a new band at 1245 cm⁻¹. Meanwhile a band centered at 1548 cm⁻¹ increased. These two new bands were assigned to monodentate nitrates associated with Al [46]. At 30 min of adsorption (Fig. 13a), the bands between 1250 cm⁻¹ and 1450 cm⁻¹ became dominant on the spectrum and were difficult to assign due to the overlapping of nitrites and nitrates bands from both BaO and Al_2O_3 . Tentatively, the bands at 1338 cm⁻¹ and 1400 cm⁻¹ may be attributed to the presence of monodentate nitrates over Ba sites [10], and the band centered at 1315 cm⁻¹ may be a combination of bridged nitrites and bidentate nitrates associated on Al [10,34,47]. When the gas feed was switched to the rich conditions (Fig. 13b), surface nitrates/nitrites species decreased immediately, indicating a high reduction efficiency. By observing that the bands at 1548 cm⁻¹ and 1315 cm⁻¹ diminished more rapidly than the bands at 1338 cm^{-1} and 1400 cm^{-1} , it is easy to infer that the reduction of nitrates/nitrites on the Al sites were easier than on the Ba sites. These results are in accordance with previous reports that nitrites and nitrates formed on BaO are more stable than those formed on Al_2O_3 [10]. As the reduction process continued, most of the adsorbed NO_x species were removed after 10 min of reduction.

The DRIFT spectra of NO_x storage and reduction process on the Co/Ba/Al₂O₃ catalyst are shown in Fig. 13c and d. Bridged bidentate nitrites on Al or Ba (1230 cm⁻¹ and 1301 cm⁻¹) were formed as soon as the catalyst was exposed to NO and O₂ for 1 min, and nitrites at 1230 cm⁻¹ and 1540 cm⁻¹) after 3 min exposure. The most distinct bands between 1250 cm^{-1} and 1450 cm^{-1} may be a combination of monodentate nitrates on Ba (1338 cm⁻¹ and 1411 cm⁻¹) and bridged nitrites or bidentate nitrates on Al (1301 cm⁻¹) [10,34]. In addition, the band at 1540 cm^{-1} shifted towards higher wave num-



Fig. 13. In situ FTIR studies of storage (a, c, e) and reduction (b, d, f) process for Pt/Ba/Al₂O₃, Co/Ba/Al₂O₃ and Pt/Co/Ba/Al₂O₃.

bers (1558 cm^{-1}) due to the increasing coverage of nitrates [34]. When exposing Co/Ba/Al₂O₃ to a reducing atmosphere (Fig. 13d), the bands at 1250 cm^{-1} , 1301 cm^{-1} , and 1558 cm^{-1} gradually decreased, while the bands at 1332 cm^{-1} and 1405 cm^{-1} were less affected. These results indicate that Co species can catalytically reduce the surface nitrates/nitrites associated on Al, which corroborated the activity test in Figs. 9 and 10.

The same experiments were carried out on $Pt/Co/Ba/Al_2O_3$, and corresponding DRIFT spectra are illustrated in Fig. 13e and f. The NO_x storage process on $Pt/Co/Ba/Al_2O_3$ was similar to that on Co/Ba/Al_2O_3. However, $Pt/Co/Ba/Al_2O_3$ showed a great improvement in the reduction process. The IR bands of adsorbed nitrites/nitrates decreased quickly as soon as the reductant was introduced. Similar to the reduction process on Pt/Ba/Al₂O₃, bands at 1305 cm⁻¹ and 1558 cm⁻¹ decreased faster than bands at 1411 cm⁻¹ and 1338 cm⁻¹ due to the instability of nitrates on Al. It seems reduction efficiency on Pt/Co/Ba/Al₂O₃ was more effective than on Pt/Ba/Al₂O₃ as few nitrates remained after 5 min reduction. These findings were consistent with the transient experiment results in Section 3.4. Notably, both Pt and Co-containing catalysts take nitrites as intermediates, and the final adsorption species may be a combination of nitrites and nitrates. During the rich phase,

nitrites/nitrates were reduced readily when Pt was present on the catalysts, and the reduction effect was more predominant when Co was added.

As confirmed in Fig. 4, Co-containing catalysts presented high production of NO₂ during the gas phase, thus NO₂ could be directly stored as nitrates on the surface according to the widely accepted reaction of $BaO + 3NO_2 \rightarrow Ba(NO_3)_2 + NO$. Although it was difficult to observe NO release because a mixture of NO/O2 was used as the NO_x source, an adsorption process following this pathway could not be ruled out. The direct proof obtained by the FTIR study did, however, provide another important pathway for trapping. Firstly, nitrites were formed, possibly by the NO oxidation by surface adoxygen. As time continued, more gas oxygen could be adsorbed and participate in the oxidation such that nitrites were transformed gradually to nitrates. These processes are in accordance with data observed by the FTIR on Pt/Ba/Al₂O₃ [12]. It should be stressed that Co plays an outstanding role in the catalysts. As Co is finely dispersed on the catalysts, H₂ pretreatment may produce more oxygen vacancy around Co. Under lean conditions, O₂ was prone to absorb and dissociate on such sites. Atomic oxygen subsequently migrated to adsorbed NO or the nearby Ba phase. This process improved the gas NO₂/NO ratio and sped up nitrite formation and oxidation. According to the in situ DRIFTS experiments, Co addition accelerated nitrites/nitrates formation on both the Ba and Al sites during the initial storage stage, which plays an important role during the relatively short storage period in cyclic operating conditions. Additionally, the synergistic effect of Pt and Co can catalyze H₂ to reduce the surface nitrites/nitrates and provide a higher NO_x removal activity than the Pt/Ba/Al₂O₃ catalyst.

4. Conclusions

On the basis of the comparative studies of Pt and/or Cosupported catalysts, we confirmed the unique performance of Co species. The improved lean/rich cyclic NO_x removal performance on Pt/Co/Ba/Al₂O₃ was a comprehensive consequence of improved storage and reduction ability. The addition of Co led to high NO oxidation ability, as well as decreased thermal stability of nitrite/nitrate species, which may be ascribed to the specific interaction of Co with the storage sites. High NO_x conversion was obtained with a low concentration reductant and longer duration time or with a high concentration reductant and shorter duration time during the rich phase. Study of the mechanisms study demonstrated that Co-containing catalysts take the "nitrite route" as an important pathway during NO_x storage. Not only dose Co addition accelerates nitrites/nitrates formation on Ba sites, but it also improves NO_x adsorption on Al sites. The intimate contact of Co with Ba/Al provides more active sites for NO adsorption, oxidation and desorption, and the synergistic effect of Pt and Co can accelerate NO_x reduction.

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