Feature Article

NO_x decomposition, storage and reduction over novel mixed oxide catalysts derived from hydrotalcite-like compoundsJun Jie Yu^a, Jie Cheng^a, Chun Yan Ma^a, Hai Lin Wang^a, Lan Dong Li^a, Zheng Ping Hao^{a,*}, Zhi Ping Xu^{b,*}^a Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China^b Australian Research Council (ARC) Centre for Functional Nanomaterials, Australian Institute for Bioengineering and Nanotechnology and School of Engineering, The University of Queensland, Brisbane, QLD 4072, Australia

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ABSTRACT

Effective control and removal of nitrogen oxides (NO_x) emission from vehicles exhausts under lean-burn condition is one of the most important targets in scientific research of environmental protection. A comprehensive introduction of NO_x storage and reduction (NSR), the most promising lean-NO_x control technology, is given including the sum-up of NSR materials, catalytic activity and related reaction mechanisms. Emphasis is put on the novel multifunctional NSR catalysts, derived from hydrotalcite-like compounds, with characteristic of simultaneous NO_x storage–decomposition–reduction. Finally, future research directions in the area of lean-NO_x control based on mixed oxide catalysts derived from hydrotalcite-like materials is also proposed.

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1. Introduction

Nitrogen oxides (NO_x), generally refereed to NO and NO₂, are generated primarily from combustion processes in the power stations and various vehicles. The emission of NO_x into air are directly responsible to various environment problems, such as photochemical smog, formation of acid rain and resultant acidification of soils and waters, which has harmed some plants, animals and the human health [1]. For these reasons, NO_x emissions from the combustion processes are required to be severely controlled and regulated. Therefore, the abatement of NO_x emission, i.e. deNO_x, has attracted much attention and great efforts of worldwide researchers.

On the other hand, due to the limited resource of the raw oil in the world and more serious global warming, a fuel-efficient vehicle is more desirable. Most current gasoline-burning engines are run in a very narrow air to fuel ratio region near the stoichiometric value ($A/F = 14.7$, rich-burn) with little or no O₂ in the exhaust, but the lean-burn engines ($A/F = 20$ – 25) can more efficiently burn the fuel, saving 30–35% consumption and releasing less CO₂ [2,3]. However, under these conditions, the conventional three-way catalyst is no longer effective for NO_x abatement due to the oxidant environment. Therefore, NO_x removal from the lean-burn exhaust stream faces more challenges in the environmental sciences.

Current deNO_x technologies under the lean-burn conditions include direct catalytic decomposition of NO_x [4], catalytic NO_x stor-

age/reduction (NSR) [2], selective catalytic reduction (SCR) of NO_x with NH₃ and hydrocarbons (HCs) [5–7]. The SCR has been intensively investigated and a number of reviews have been published elsewhere [5–8], so this review paper will focus on the recent advances of the catalysts that are made of the normal transition metal oxides derived from hydrotalcite-like compounds (HTLcs) yet are effective in NO_x direct decomposition, and NO_x storage under lean-burn conditions. We finally present our comments on rational design of the active catalysts for such applications in terms of spatial structure and coordination of the active components in the nanometer scale as the concluding remarks.

2. Direct decomposition

Direct decomposition of NO_x to N₂ and O₂ is the simplest way to abate the NO_x emissions because no additional reactive agents are required and the operation is simple. The catalysts have been studied since 1970, however, the recent research advances in the material preparation and nanotechnology make direct decomposition prospective in NO_x abatement [4,9].

NO decomposition over various catalysts, such as single-crystal metals, oxides, oxide-supported metals, has been reviewed in detail by Garin [4], including the various decomposition mechanisms and kinetics. The reports suggested that oxide-supported Pd catalysts [10] and Cu-ZSM-5 [11] appeared as the potential catalysts which catalytically convert 50–95% NO in the temperature range of 400–700 °C. Very recently, Fe–Mn/H-beta catalysts were reported to effectively decompose NO_x in 300–400 °C in the presence of O₂ and CO₂ with the conversion of 25–45% [12]. It is worth mention-

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ing that BaMnO₃-based dopant perovskite oxides can efficiently convert NO to N₂, O₂ and NO₂, while the temperature required is high, usually 600–800 °C [13,14], and the decomposition is severely affected by the presence of CO₂, H₂O or O₂ [15,16]. There was only one paper reporting that a particular mixed oxide catalyst derived from CoNiAl-HTlc is very active for NO direct decomposition, with ca. 50% NO decomposition at 300 °C with the space velocity of 7000 h⁻¹ [17].

It is known that the decomposition is thermodynamically favorable at below 900 °C and the search for the catalysts for NO_x direct decomposition has been investigated for 40 years [4], there has been only a limited success. In our opinion, the major reason is the low selectivity of NO decomposition to N₂ and O₂. For example, during direct decomposition of NO to N₂ and O₂, NO₂ and N₂O are always the byproducts, and sometimes are the main components [4,13,14]. The second reason is the high decomposition temperature (600–900 °C) for high NO_x conversion (>80%), so that the practical application of the catalysts for the car exhaust treatment becomes impossible. The third factor is the low stability of catalysts in the catalytic activity under practical conditions. In general, the presence of water vapor, O₂ and CO₂ will reduce the activity to some to high degree [16]. More severely, the trace amount of SO₂ in the stream severely deactivates the catalytic activity. In this regard, the rational design of new types of active catalysts for NO_x direct decomposition has to take these factors into account.

3. NO_x storage/reduction technology

The NO_x storage/reduction method (NSR) developed by Toyota researchers is generally regarded as one of the leading technologies for the control of NO_x emission under lean-burn conditions [18–20]. The NO_x storage/reduction technology can be used in an engine that alternately operates under lean-burn and rich-burn conditions. Under lean-burn conditions, NO is oxidized and stored on the catalyst. When the engine is switched to the condition with a stoichiometric air-to-fuel ratio, i.e. the rich-burn condition, the stored NO_x are released and subsequently reduced by hydrocarbons (HCs) and CO. Therefore, NO_x storage/reduction (NSR) is a promising method to remove NO_x in the O₂-rich condition.

Pt/BaO/Al₂O₃ has been intensively investigated worldwide as a model system to catalytically store NO_x since the last decade, and the storage mechanism has been well understood. In principle, this model NO_x storage/reduction catalyst comprises three major components: a high surface area support material (e.g., γ-Al₂O₃), a NO_x storage component containing alkali or alkaline earth metals (e.g., Ca, Sr, Ba, K and Na), and noble metal (e.g., Pt, Rh, and Pd) as the catalytic redox component. Regarding the storage mechanism, as illustrated in Fig. 1a, NO is first oxidized to NO₂ over Pt particle surface under the lean-burn condition. The freshly formed

Fig. 1. Schematic of NO_x storage and reduction mechanism over Pt/Ba/Al₂O₃ under (a) lean-condition; (b) rich-condition [7].

NO₂ is either adsorbed on the Pt surface or released back into the gas phase. The gaseous NO₂ can be disproportionated into nitrate and gaseous NO over the 'BaO' surface, and stored in the form of nitrate. The adsorbed NO₂ can be further oxidized to nitrate (NO₃⁻) that can be then spilt over to the neighboring 'BaO' particle and stored in the form of nitrate. After switching to the rich-burn condition, the stored nitrate is decomposed to NO₂ that is reduced to N₂ by HCs, CO, and/or H₂ over noble metal particle surface (Fig. 1b), completing the removal of NO_x and resulting in regeneration of the catalyst.

In line with the understanding of NSR mechanism over Pt/BaO/Al₂O₃, a few similar systems have been also investigated as NSR catalysts. For example, as summarized in Table 1, Toops et al. examined the adsorption and oxidation of NO over Pt/K₂O/Al₂O₃ [21,22]. They reported that such a catalyst Pt(1.0 wt%)/K₂O(4.5 wt%)/Al₂O₃ can store up to 0.797 mmol (NO_x)/g at 250 °C within 1 h (300 ppm NO, 12% O₂ and bal. N₂). Yang et al. investigated the adsorption behaviors of NO on Pd/CaO/Al₂O₃, Pt/CaO/Al₂O₃ and Rh/CaO/Al₂O₃ with the storage amount of NO_x of 0.097 to 0.28 mmol/g at 300 °C within 7.5 min (1000 ppm NO, 7% O₂ and bal. He, Table 1) [23]. Vaccari et al. modified the storage component (BaO) into a composite (MgO–BaO) which shows a good

Table 1
Summary of NO_x storage catalysts that are known to have good performance.

Catalyst	Temp. (°C)/time	NO _x (bal. He or N ₂)	NO _x storage (mmol/g)	Evaluation method	Ref.
PtRh/Ba/washcoat	300 (saturation)	500 ppm NO + 7% O ₂	0.530	Adsorption	[51]
Pt/BaO/Al ₂ O ₃	300 (saturation)	1000 ppm NO + 3% O ₂	0.581	Adsorption	[52]
Pt/K ₂ O/Al ₂ O ₃	250 (60 min)	300 ppm NO + 12% O ₂	0.797	DRIFTS	[21]
Pt/K ₂ O/Al ₂ O ₃	250 (saturation)	300 ppm NO + 12% O ₂	0.936	DRIFTS	[21]
Rh/CaO/Al ₂ O ₃	300 (7.5 min)	1000 ppm NO + 3% O ₂	0.28	Adsorption	[23]
Rh/CaO/Al ₂ O ₃	300 (7.5 min)	1000 ppm NO + 3% O ₂	0.18	Adsorption	[23]
BaAl ₂ O ₄	80–350 (~70 min)	500 ppm NO + 500 ppm NO ₂ +	0.52	Dynamic	[53]
BaSnO ₃	100 (~70 min)	10% O ₂ + 5% CO ₂ + 5% H ₂ O	0.56	Dynamic	[29]
BaSnO ₃	300 (~70 min)		0.20	Dynamic	[29]
Ca ₂ CoAl-oxide	300 (60 min)	800 ppm NO + 8% O ₂	0.602	Desorption	This work
Ca ₂ CoLaAl-oxide	300 (60 min)	800 ppm NO + 8% O ₂	0.634	Desorption	This work
Ca ₂ CoAl-oxide	250 (60 min)	800 ppm NO + 8% O ₂	0.622	Desorption	This work
Ca ₂ CoLaAl-oxide	250 (60 min)	800 ppm NO + 8% O ₂	0.651	Desorption	This work

Fig. 2. Schematic representation of 3-dimensional structure of (A) brucite ($\text{Mg}(\text{OH})_2$) and (B) hydrotalcite ($[\text{Mg}_3\text{Al}(\text{OH})_8]^+(\text{CO}_3^{2-})_{0.5} \cdot 2\text{H}_2\text{O}$).

activity [24,25]. In addition, modification of the support (Al_2O_3) has been also reported to improve the NSR activity. For example, catalysts $\text{Pt}/\text{BaO}(\text{Al}_2\text{O}_3-\text{CeO}_2)$ and $\text{Pt}/\text{BaO}(\text{Al}_2\text{O}_3-\text{CeO}_2-\text{Fe}_2\text{O}_3)$ show a very high NO_x conversion in the storage/reduction cycle [26].

Meanwhile, a number of alkaline-earth based perovskites have also been examined for NO_2 storage from the lean exhaust gases [27]. In particular, BaSnO_3 can take up 0.20 mmol (NO_2)/g at 300 °C and 0.56 mmol (NO_2)/g at 100 °C, as listed in Table 1 [28,29]. The adsorption mainly involves the disproportionation of NO_2 into nitrate and NO where nitrate is stored as barium nitrate [30].

Although these storage/reduction catalysts seem to efficiently adsorb and reduce NO_x under lean- and rich-burn cycles in the absence of SO_2 , they possess a number of inherent disadvantages, such as small storage amount, narrow operating temperature window suitable for the storage, low thermal stability, easy deactivation, liable influence by other stream components and expensive noble metal. More severely, SO_2 generated in a trace amount in the exhaust often dramatically deactivates the activity of storage/reduction catalysts (more) [28], which demands the development of cheap and SO_2 tolerant storage/reduction catalysts with similar or better storage/reduction performance. More challengingly, such catalysts are enabled to catalyze direct decomposition of NO_x at temperature below 400 °C. In the recent pursuit of such catalysts, our group and a few other groups have found that mixed transition-metal oxides derived from hydrotalcite-like compounds (HTLcs) are the potential candidates that show some advantages over the traditional model catalyst $\text{Pt}/\text{BaO}/\text{Al}_2\text{O}_3$, and meet the requirements for the practical applications.

4. NO_x storage/reduction on catalysts derived from HTLcs

4.1. Features of hydrotalcite-like compounds

Hydrotalcite-like compounds (HTLcs), also known as anionic clays or layered double hydroxides (LDHs), are a big family of layered mixed hydroxides [31,32]. The layered structure of hydrotalcite ($\text{Mg}_3\text{Al}(\text{OH})_8(\text{CO}_3)_{0.5} \cdot 2\text{H}_2\text{O}$) is closely related to that of brucite, $\text{Mg}(\text{OH})_2$. In a brucite layer, each Mg^{2+} ion is octahedrally surrounded by six OH^- ions, and the different octahedra share edges to form an infinite two-dimensional layer. The brucite crystals are then formed when the 2-D layers are stacked one on the top of another via O–H...O hydrogen bonding between the adjacent layers (Fig. 2A). Partial replacement of Mg^{2+} ions by Al^{3+} gives the brucite-like layers a positive charge, which in hydrotalcite itself is balanced by carbonate anions, located in the interlayer region

(gallery) between the two brucite-like layers (Fig. 2B). This gallery also contains water molecules, hydrogen bonded to layer OH^- ions and/or to the interlayer anions. The electrostatic interactions and hydrogen bonds between the brucite-like layers and the gallery species hold the layers together, forming the three-dimensional structure, as shown in Fig. 2B [31].

Hydrotalcite-like compounds (HTLcs) normally adhere to a general formula: $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+}(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$, where M^{2+} represents any divalent metal cation, M^{3+} any trivalent metal cation and A^{n-} any anion. The only requirement for the cations is their ionic size. When the ionic size is less than 0.10–0.11 nm, then cation (divalent or trivalent) can be successfully incorporated into the brucite-like layers [31]. We can also incorporate more than two types of metal cations to obtain multi-component HTLcs. For example, Morpurgo et al. synthesized several multi-cations HTLcs, such as CuZnCoAlCr - and CuZnCoCr -HTLcs [33–35]. The only requirement is that the overall portion of trivalent cations (i.e. x value) should be kept in the range of 0.2 to 0.4. Very interestingly, some tetravalent cations, such as Zr^{4+} and Ti^{4+} , can also be incorporated into the brucite-like layer [31]. In addition, almost all types of anions, such as general inorganic and organic anions, polymeric anions, complex anions, polyoxometalates, and various biochemical anions, can be intercalated into the interlayer of HTLcs [31]. All of these features in the structure and composition provide a wide platform for a rational design of mixed oxide catalysts with variety of components so as to enable the derived mixed oxides to have the particular catalytic properties. In fact, HTLcs-derived mixed oxides have found a wide range of applications as adsorbents, ion exchangers, base catalysts for various catalytic syntheses [31].

Moreover, the cation distribution in the brucite-like layers could reach the ideal ordering after suitable post-treatment [31,36]. Ideally, the cations can be uniformly distributed in the brucite-like layers, forming so-called superlattices, two of which are shown in Fig. 3. The superlattice formation in the brucite-like layers enables us to finely tune the catalytic properties of HTLcs and derived mixed oxides by carefully selecting the combination of the catalytic metal elements. In the derived mixed oxides, the uniform cationic distribution could be kept when the calcination temperature is lower than 600 °C, or even 800 °C since the transformation from HTLcs to the mixed oxides follows a topotactic process [37–40]. Therefore, the derived mixed oxides could have higher surface area, good dispersion of the active components in space, and relatively higher hydrothermal stability, which are all good properties for the design of efficient NSR catalysts as either the catalyst supports or the direct catalysts.

To make full use of the advantages of HTLcs and the derived catalysts, we have carried out a series of investigations on developing the mixed oxide catalysts for NO_x direct decomposition,

Fig. 3. Hexagonal superlattices resulting from ideal cation ordering within a brucite-like layer in HTLcs with $M^{2+}:M^{3+} = 2:1$; (A), $a' = 2a \sin 60^\circ = a\sqrt{3}$ and $3:1$ (B), $a' = 2a$. Open circles stand for M^{2+} and shaded circles for M^{3+} .

Fig. 4. Schematic representation of HTLcs-derived catalysts for NO_x direct decomposition, storage and reduction.

storage and reduction based on the HTLcs materials by screening the effects of replacing Mg and Al in the brucite-like layers with various transition metals (M^{2+} and M^{3+}), as shown in Fig. 4 to present our strategy for NSR catalyst development. In particular, the three typical components required for an NO_x NSR catalyst could be all included in an HTLc-derived mixed oxide. For example, through substitution of Mg^{2+} with cations such as Ca^{2+} , Sr^{2+} , Ba^{2+} , Cu^{2+} , Co^{2+} , Ni^{2+} and Zn^{2+} and/or Al^{3+} with others such as Fe^{3+} , Mn^{3+} , Zr^{4+} , La^{3+} , or impregnation with noble metals, the mixed oxides can have the support component (such as ' Al_2O_3 '), the storage component (such as ' MgO ', ' CaO '), and the catalytic redox component (such as noble metal and/or transition metal oxide). It is worthy noting that some of the mixed oxides are simultaneously very active for NO_x direct decomposition and reduction of the stored NO_x .

4.2. NSR on catalysts with noble metal

Most reported NSR catalysts derived from HTLcs are noble-metal catalysts loaded on HTLcs. Hao et al. reported that Pt-loaded MgAl-mixed oxide can store NO_x via the oxidation of NO_x in the form of various nitrites and nitrates at 80 and 300°C [41]. Their further research shows that introducing a small amount of Cu to MgAl-HTlc to make Pt-loaded CuMgAl-oxide catalyst (5 wt% CuO in the oxide) increases NO oxidation rate and slightly improves the storage amount from 0.157 to 0.175 mmol (NO_x)/g at 350°C in a gas stream containing 560 ppm NO, 40 ppm NO_2 , 8% O_2 and bal. N_2 [41]. In addition, Lamb et al. loaded Pd (1.34 wt%) onto MgAl-oxide and the catalyst can take up 0.062 mmol (NO_x)/g in nitrate form at 300°C in a gas stream containing 500 ppm NO, 500 ppm N_2 , 5% O_2 and bal. He [42]. However, the storage amount of NO_x is far smaller than those reported elsewhere (Table 1).

In this field, the most mentionable research work has been reported by Vaccari et al. who made an intensive examination of MgAl-HTlc-based Pt and Pt–Cu catalysts for the storage and reduction of NO_x [43–45]. They first impregnated the calcined $\text{Mg}_2\text{Al-HTlc}$ with Pt or Cu salt solution to load 4 wt% Cu and/or 1 wt% Pt, and then tested the storage/reduction activity using a series of cyclic sequences of feed streams switching between the lean condition (120 s: 5% O_2 , 10.8% CO_2 , 954 ppm NO, bal. He) and the rich condition (6 s: 3.3% CO, 1.1% H_2 , 6000 ppm C_3H_6 , 5% O_2 , 10.8% CO_2 , 954 ppm NO, bal. He) with the space-velocity of $20,000\text{ h}^{-1}$. The activity was then given as mean conversion of NO_x during the 10 cycles, in comparison with that of the model catalyst Pt/BaO/ Al_2O_3 . They found that HTlc-based Pt and Pt–Cu catalysts can lead to 80–95% NO_x conversion at $200\text{--}300^\circ\text{C}$, comparable with the activity of the model catalyst Pt/BaO/ Al_2O_3 . More significantly, HTlc-based Pt–Cu catalyst, in comparison with Pt/BaO/ Al_2O_3 and HTlc-based Pt-catalyst, shows a higher resistance to SO_2 deactivation [44].

4.3. NSR on mixed oxide catalysts directly derived from HTLcs

In order to develop active non-noble-metal NSR catalysts based on HTLcs materials, we have investigated the influence of incorporating a number of transition metal cations (M^{2+} and M^{3+}) into the mixed oxides derived from the corresponding HTLcs precursors. For the divalent metal ions, Cu^{2+} and Co^{2+} are potentially the most active component for oxidation and decomposition of NO_x and N_2O [4,46]. Although Cu-doped zeolites are active for NO_x decomposition, the report from Vaccari's and our group to load Cu to HTLcs framework shows a limited enhancement on the NSR activity [41,43]. So we first focused on the examination of a series of Co-containing MgAl-HTLcs and the corresponding mixed oxide

catalysts. Our storage capacity tests of these $\text{Mg}_{3-x}\text{Co}_x\text{Al}$ -oxides in O_2 -rich gaseous stream show that Co incorporation into the MgAl-based catalysts enhances the storage amount of NO_x [47]. For example, MgCo_2Al - and $\text{Mg}_{0.5}\text{Co}_{2.5}\text{Al}$ -mixed oxides can store 0.15 mmol (NO_x)/g at 300 °C, almost two times that Mg_3Al -mixed oxide stores (0.08 mmol (NO_x)/g) (1300 ppm NO, 100 ppm NO_2 , 8% O_2 , bal. N_2). The introduction of Co into the mixed oxide significantly enhances the oxidation of NO to NO_2 , indicating the occurrence of NO oxidation in some way. In more particular, we noted that ca. 15 and 25% NO_x is directly decomposed to N_2 as well as N_2O over these two catalysts, respectively.

Consequently, we substituted half of Al^{3+} in $\text{Mg}_{0.5}\text{Co}_{2.5}\text{Al}$ -HTlc with Fe^{3+} , Mn^{3+} , Zr^{4+} , or La^{3+} and examined the effects of this substitution on the NO_x storage and decomposition over the corresponding mixed oxides [48]. The storage tests show that incorporating Fe^{3+} or Mn^{3+} into the mixed oxide does not enhance but decreases the NO_x storage, and incorporating Zr^{4+} slightly increases the storage capacity. Noticeably, $\text{Co}_{2.5}\text{Mg}_{0.5}\text{La}_{0.5}\text{Al}_{0.5}$ -mixed oxide catalyst exhibits a much higher storage capacity of NO in the O_2 and N_2 stream at 300 °C, with the storage amount up to 0.252 mmol (NO_x)/g (800 ppm NO, 8% O_2 , bal. N_2) for 30 min. We have also found that introduction of Zr^{3+} or La^{3+} brings about more direct decomposition of NO, i.e. ca. 50% NO is directly decomposed to N_2 as well as N_2O . In addition, the presence of CO_2 and H_2O is found to severely reduce the NO_x storage capacity by 50–70%, while not to affect the activity for the direct decomposition of NO.

After incorporation of Co^{2+} and/or La^{3+} was examined to enhance NO oxidation, NO direct decomposition and NO_x storage in the O_2 -rich stream, we then subsequently tried to increase the alkalinity of the system so as to store more NO_x in the form of nitrate. This is because ‘MgO’ as the storage component in an MgAl-HTlc-based NSR catalyst is a weaker base than BaO as the primary storage component in Pt/BaO/ Al_2O_3 system. To this end, we used Ca^{2+} instead of Mg^{2+} to reconstruct the Co-containing HTlcs-based framework since CaO is more basic than MgO. Therefore, a series of CaCoAl -mixed oxide catalysts were prepared by calcining the corresponding precursors $\text{Ca}_x\text{Co}_{3-x}\text{Al}$ -HTlcs [49,50]. The NO_x storage tests indicate that replacement of Mg with Ca leads the catalysts to have a much better performance. In particular, the best catalyst $\text{Ca}_2\text{Co}_1\text{Al}$ -oxide can store up to 0.429 mmol (NO_x)/g at 300 °C for 30 min, much higher than MgCoAl -oxide catalyst (0.15 mmol (NO_x)/g). It can also directly decompose 55% NO and gently catalyze the oxidation of NO to NO_2 at 300 °C in the same environment.

Further modification by incorporating La^{3+} to replace partial Al^{3+} in $\text{Ca}_2\text{Co}_1\text{Al}$ -HTlc enables the obtained catalyst ($\text{Ca}_2\text{Co}_1\text{La}_{0.1}\text{Al}_{0.9}$ -oxide) to have an even better performance both in NO direct decomposition and storage [50]. For example, the catalyst can store 0.634 mmol (NO_x)/g at 300 °C and 0.651 mmol (NO_x)/g at 250 °C (800 ppm NO, 8% O_2 , bal. N_2) within 60 min, close to or even better than the performance of most catalysts with/out noble metal reported elsewhere (Table 1), although our quantitative method does under-estimate the NO_x storage amount [49].

More significantly, the catalyst can directly decompose 75% NO to N_2 and N_2O at 300 °C in the same gas stream, much higher than that (50%) over CoNiAl -oxide previously reported [17]. As shown in Fig. 5, we monitored four nitrogen species (NO, NO_2 , N_2 and N_2O) and found that the outlet total nitrogen is almost equal to the inlet total nitrogen after 1200 s. Therefore, the amount of generated N_2 in the outlet stream indicates that 75% NO is directly decomposed to N_2 after 1200 s as there is no N_2O detected since then. The activity for NO direct decomposition is kept for 24 h (Fig. 6), and in our belief, can be kept for a much longer period of time. In comparison with Fe–Mn/H-beta [12] and BaMnO₃-based dopant

Fig. 5. Nitrogen species profiles in stream He at 300 °C. TN_{in} is the total nitrogen in the inlet He stream and $\text{TN}_{\text{out}} = [\text{NO}] + [\text{NO}_2] + 2[\text{N}_2\text{O}] + 2[\text{N}_2]$, i.e. the total nitrogen in the outlet He stream after passing catalyst $\text{Ca}_2\text{Co}_1\text{La}_{0.1}\text{Al}_{0.9}$ -oxide.

Fig. 6. NO_x adsorption profiles in the outlet stream over catalyst $\text{Ca}_2\text{Co}_1\text{La}_{0.1}\text{Al}_{0.9}$ -oxide at 300 °C for 24 h under conditions: 800 ppm NO, 8% O_2 , bal. He, space-velocity of 30000 h^{-1} .

perovskite oxides [28], the present HTlc-based catalyst shows a much higher activity and selectivity to N_2 and O_2 .

More interestingly, we found that the stored NO_x can be quickly reduced to N_2 and H_2O by H_2 . For example, when the inlet stream (800 ppm NO, 8% O_2 , bal. He) was switched to a reducing stream (1% H_2 in N_2), most stored NO_x on $\text{Ca}_2\text{Co}_1\text{La}_{0.1}\text{Al}_{0.9}$ -oxide was in situ reduced by H_2 at 350 °C within 4–6 min. Such a performance in reducing the adsorbed NO_x is comparable with that of noble metal catalyst Pt–Ba/ γ - Al_2O_3 [52].

However, furthermore modification of $\text{Ca}_2\text{Co}_1\text{La}_{0.1}\text{Al}_{0.9}$ -oxide by replacing some Ca^{2+} with more basic Ba^{2+} or Sr^{2+} to make $\text{Ca}_{1.5}\text{Ba}_{0.5}\text{Co}_1/\text{La}_{0.1}\text{Al}_{0.9}$ -oxide or $\text{Ca}_{1.5}\text{Ba}_{0.5}\text{Co}_1/\text{La}_{0.1}\text{Al}_{0.9}$ -oxide does not improve but affect the activity for NSR and direct decomposition of NO in O_2 -rich stream [49].

In summary, the multi-functional catalyst $\text{Ca}_2\text{Co}_1\text{La}_{0.1}\text{Al}_{0.9}$ -oxide shows excellent performances in simultaneous NO_x storage, decomposition, appearing as the potential candidate for the NO_x emission control under the O_2 -rich condition.

4.4. Mechanism of NSR and direct decomposition over Co-HTlcs-based catalysts

In terms of the reaction mechanism, NO_x direct decomposition and NO_x storage (i.e. oxidation of NO and storage in nitrate form) probably appear as the two aspects of the same set of reaction

pathways. To design more active catalysts for direct decomposition and storage of NO_x, it is necessary to get insight into the reaction mechanism which have been intensively investigated for catalyst Pt/BaO/Al₂O₃ [54,55]. The mechanisms of NO_x direct decomposition, NO_x storage on the HTLcs-based catalysts and desorption/reduction of the stored NO_x from the catalysts have been investigated via the in situ IR spectra [47]. Based on our observation data, we believe that NO_x is first oxidatively adsorbed on the catalytic site to form nitrite and nitrate since nitrite and nitrate are always first detected:

Even there is no O₂ present in the stream, the oxidative adsorption still spontaneously occurs. This is because the oxidative species Co³⁺–O^{2–} is present in a certain amount on the catalyst surface after calcination of the precursor HTLc, and more practically, the oxidative species Co³⁺–O^{2–} can be quickly recovered by oxidizing the Co²⁺–O^{2–} with the simultaneously generated O₂ from NO decomposition since CoO formed at 900–950 °C in air is automatically oxidized to Co₃O₄ in air when the temperature is decreased to 800–850 °C [46]. This process is supposed to be much different from the case over noble metal catalysts where NO_x are mainly adsorbed on the surface without valence state change if there is no O₂ present [4].

Following the oxidation adsorption on the active site, unstable nitrite is either oxidized to nitrate with O₂ present in the steam:

or decomposed via the following reactions:

In such a way, NO decomposes to N₂ and O₂ (Eqs. (1) and (5)). The other possible reaction is the disproportionation of NO₂ to nitrite and nitrate which may not involve any catalysis, i.e. Eq. (6) may also occur on the base site:

Note that nitrate associated with the active site sometimes is not stable enough at 300 °C, it either decomposes like the following reactions:

In such ways NO₂ decomposes to N₂ + O₂ (Eqs. (2) and (9)) and the conversion between NO and NO₂ (i.e. NO oxidation to NO₂ or NO₂ decomposition to NO and O₂). Nitrate associated with the active site may spill over to the neighboring basic site (CaO or MgO) and stored in more stable form of alkaline-earth nitrate (Ca–ONO₂ or Mg–ONO₂) (Figs. 1a and 7a). Therefore, the most abundant species of stored NO_x is nitrate associated with the base site at 300 °C.

Although there might be some other pathways, we suppose that Eqs. (1)–(9) are principally responsible for direct decomposition and storage of NO_x, where the valence switching between Co³⁺–O^{2–} and Co²⁺–O^{2–} assists the smooth completion of NO_x decomposition. The storage pathways are quite similar to those over the noble metal catalysts, i.e. nitrite route and disproportionation route [56]. However, catalytic NO_x decomposition could be fundamentally different. For our mixed oxide system, decomposition of nitrite (Eq. (5)) as well as nitrate (Eq. (9)) could be the

major route. However, NO decomposition over Pt, Rh or Pd metal catalyst undergoes dissociation of NO to adsorbed N and O and then two adsorbed N atoms or two adsorbed O atoms combine to generate N₂ or O₂ [4].

In addition, during the reduction, the stored NO_x, i.e. nitrate as well as nitrite, are supposed to spill over to the active site and then reduced by H₂ at 350 °C to N₂ and H₂O as follows (Figs. 1b and 7a):

It is worth mentioning that NO_x decomposition over LDH-based catalyst (Mg_{0.5}Co_{2.5}La_{0.5}Al_{0.5}-oxide) has not been affected by the presence of CO₂ and H₂O, but the NO_x storage capacity is significantly reduced [48]. This is probably attributed to different interactions of CO₂ and H₂O with the catalyst components. Since it is difficult for CO₂ and H₂O to interact with 'CoO' to form stable species, so NO_x decomposition occurring over 'CoO' site is not much affected. However, the storage site ('MgO') can react with CO₂ and H₂O and be occupied, so the storage site available for NO_x becomes fewer, reducing the NO_x storage amount.

4.5. Function of La in Co-HTLcs-based catalyst

Since the incorporation of small amount of La into CaCoLaO_x significantly brings about the increase in both NO_x direct decomposition and storage capacity, it is worth to understand the function of La in this system, in order for us to further design more active catalysts for this purpose. In summary of NO_x decomposition and storage over catalyst CaCoAlO_x, as schematically shown in Fig. 7a and like reported elsewhere [7], NO_x is first oxidized into nitrite/nitrate on the catalytic redox region (CoO_x). At 300 °C, the formed nitrite on CoO_x is not so stable, so it is either oxidized further to nitrate (Eq. (3)) or decomposed (Eqs. (4) and (5)). Under the current conditions, the formed nitrate is relatively stable and probably spilt over to the neighboring storage region (CaO) to be stored. In general, transition metal nitrate (e.g. Co-nitrate) is not stable as alkaline/alkaline-earth metal nitrate (e.g. Ca-nitrate), so the spillover of nitrate from transition metals to alkaline metals is thermodynamically favored, as schematically shown in Fig. 7b. Thus, the spillover undergoes a transition state (TS₁) and overcomes an activation energy (ΔE₁).

It is our suggestion that the stability of transition metal nitrate should not be too low and the stability of alkaline-earth metal nitrate should not be too high. If transition metal nitrate is too unstable, its residence time on the redox center is too short and nitrate may not have enough time to spill over to the storage site. Therefore, it would be better if the stability of transition metal nitrate can be enhanced to some extent. On the other hand, if alkaline-earth nitrate is very stable, the driving force for the spillover will be stronger, i.e. the spillover will be facilitated. However, it will be very difficult for the nitrate to transport back to the redox site to be reduced/decomposed during the subsequent process, as this has to overcome a much higher activation energy (ΔE₂, Fig. 7b). Therefore, it would be better if the stability of alkaline-earth metal nitrate can be decreased to some extent. Therefore, mitigating the stability gap between the transition metal nitrate and alkaline-earth metal nitrate would make the nitrate spillover back and forth more smoothly. In a particular Ca₂Co₁Al-oxide system, mediation of the stability of transition and alkaline-earth metal nitrate may be very helpful. Since introduction of La³⁺ into Ca₂Co₁Al-oxide significantly enhances the NSR activity and decomposition activity, we believe that 'LaO_{1.5}' acts as the mediator between 'CaO' and 'CoO'. 'LaO_{1.5}' may enhance the stability of CoO–NO_x but simultaneously decrease the stability of

Fig. 7. Schematic representation of NO_x oxidation, spillover, storage and reduction at the nanometer scale: (a) side view of NO_x spillover over CaCoAl-oxide and (b) the relative energy with the spillover process; (c) side view over CaCoAlLa-oxide and (d) the relative energy with the spillover process.

CaO-NO_x, and moreover, so that LaO_{1.5} may mediate the spillover of nitrate from 'CoO' to 'CaO' (storage) or from 'CaO' to 'CoO_x' (decomposition/reduction), as shown in Figs. 7c and 7d. Like a bridge, 'LaO_{1.5}' links the redox region and the storage region and makes the transport between them to more smoothly take place via lowering the activation energies although in more steps.

5. Concluding remarks

From the above presentation on the recent development of NSR catalysts based on HTICs materials, we may first conclude that a good catalyst needs a good combination of three components, particularly the catalytic redox component and the storage component. Beside the noble metals, most normal transition metal oxides can act as the catalytic redox active site that is responsible for NO_x oxidation. On the other hand, alkaline and alkaline-earth metal oxide can be used as the storage component. Our work reviewed above has just examined a few combinations of these two major components, and there are quite a lot of other combinations to be investigated. Thus we believe that there exist some other combinations that can lead to a higher activity for direct decomposition and NSR with higher resistance to deactivation of SO₂, H₂O and CO₂, etc.

From the point of view of the storage mechanism, a good combination has not only included the suitability in composition/ratio of the two components, but included the compatibility in the relative space, in order to enable the oxide catalysts with the maximum activity. As schematically shown in Fig. 7a, NO_x is oxidized into nitrite/nitrate on the catalytic redox region (CoO_x), and then

spilt over to the storage region (CaO). If the storage site is far away from the redox site, the spillover may not readily take place. In this connection, it is the best for the storage site to just locate nearby the catalytic redox site, which will require the fine control in the materials preparation at the nanometer scale.

It is acknowledged that the CaCoAlLa-oxide system, like Pt/BaO/Al₂O₃, does not have high resistance to SO₂ deactivation because of the presence of strong base-site. To avoid the SO₂ poisoning, we need to tradeoff between the storage capacity/decomposition activity and the resistance to SO₂ deactivation, which will be another story, reporting this tradeoff in our recent investigation.

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