Novel Multi-functional Mixed-Oxide Catalysts for Effective NO_x Capture, Decomposition, and Reduction**

By Jun Jie Yu, Xiao Ping Wang, Lan Dong Li, Zheng Ping Hao,* Zhi Ping Xu,*
and Gao Qing (Max) Lu

In this paper, novel multi-functional mixed-oxide catalysts have been rationally designed and developed for the effective abatement of NO_x. Ca_xCo_{3-x}Al hydrotalcite-like compounds (where $x = 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0$) are first synthesized by co-precipitation and calcined at 800 °C for 4 h in air to derive the mixed oxides. The resultant mixed oxides are generally of spinel phase, where the CaO phase is segregated when $x \geq 2.5$. It has subsequently been found that the derived oxides are catalytically multi-functional for NO_x decomposition, capture, and reduction. For example, the mixed Ca₂Co₁Al₁-oxide can decompose 55 % NO at 300 °C in 8 % oxygen, completely trap NO for 750 s, and capture 12.88 and 18.06 mg g⁻¹ NO within 30 and 60 min, respectively. The catalytic activities of the Ca₂Co₁Al₁-oxide catalyst have been further improved by incorporating La to form a quaternary catalyst Ca₂Co₁La_{0.1}Al_{0.9}-oxide. This catalyst significantly enhances the NO decomposition to 75 %, extends the complete trapping time to 1100 s, and captures more NO at 300 °C in 8 % O₂ (19.02 mg g⁻¹ NO within 60 min). The in-situ IR spectra of the catalysts with adsorbed NO indicates that the major nitrogen species formed on the catalysts are various kinds of nitrites and nitrates, which can be readily reduced by H₂ within 6 min at 350 °C. Therefore, the excellent catalytic activity of layered double hydroxide (LDH)-based mixed oxides for NO decomposition, storage, and reduction can be achieved by the elegant combination of normal transition metals.

1. Introduction

As a result of increasing global environmental concerns and energy conservation, new vehicle engines with improved fuel efficiency and high level of exhaust gas purification are urgently needed. A preferred option is lean-burn engines, which run under excess oxygen and have been one of the key technologies to improve fuel combustion efficiency. Lean-burn engines, especially diesel engines, can save about 30–35 % fuel consumption compared with similar gasoline engines working near the stoichiometric air to fuel mass ratio (i.e., rich-burn).^[1]

Rich-burn engines normally use three-way catalysts (TWCs), which can effectively oxidize CO and hydrocarbons, and decompose NO_x to N₂ and O₂ with little or no O₂ present in the exhaust gas. It is true that the employment of lean-burn engines favors the oxidation of CO and hydrocarbons, however, the excess O₂ inhibits the decomposition of NO_x, which leads to more NO_x emitted into the air. Therefore, catalysts that can effectively reduce NO_x in the presence of excess O₂ are now widely sought.

The NO_x storage/reduction (NSR) catalysts,^[2] which are used in engines that alternately operate under lean-burn and rich-burn conditions,^[3] seem to be a good option. Under lean-burn conditions, NO and NO₂ are oxidized and stored on the catalyst, and the stored NO_x is subsequently reduced by hydrocarbons and carbon monoxide when the engine is switched to rich-burn conditions.^[4] NSR catalysts normally consist of NO_x storage components based on alkali or alkaline earth metals (e.g., Ca, Sr, Ba, K, and Na) and a catalytic redox component such as noble metals Pt, Rh, and Pd, which are both dispersed on high surface area support materials (e.g., γ -Al₂O₃).^[1b,4a,5] Pt-Ba/Al₂O₃, as a model NSR catalyst, has been widely investigated in the past decade, and the catalytic performance has been enhanced by the introduction of transition metals, such as Fe, Ce, Cu, and Ni.^[1,4b,6] In addition, perovskites^[4b,7] and zeolites^[8] show a potential as alternative NSR catalysts. However, there is a fatal flaw in that the NSR catalysts are liable to be deactivated dramatically by SO₂ in the exhaust, even at trace amounts, because of the irreversible adsorption of SO₂ under both lean-burn and rich-burn conditions.^[6a,9] This, together with the high expense of noble metals, demands the further

[*] Prof. Z. P. Hao, J. J. Yu,
P. W. Wang, Dr. L. D. Li
Research Center for Eco-Environmental Sciences
Chinese Academy of Sciences
Beijing 100085 (P. R. China)
E-mail: zpinghao@rcees.ac.cn
Dr. Z. P. Xu, Prof. G. Q. Lu
ARC Centre for Functional Nanomaterials
Australian Institute for Bioengineering and
Nanotechnology and School of Engineering
The University of Queensland
Brisbane, QLD 4072 (Australia)
E-mail: gordonxu@uq.edu.au

[**] This work was financially supported by the National Basic Research Program of China (2004CB719500) and the Natural Science Foundation of China (20322201). The support from the ARC Centre for Functional Nanomaterials funded by the Australia Research Council under its Centre of Excellence Scheme is also appreciated.

search for cheap and SO₂-tolerant NSR catalysts with comparable or better performance for NSR.

Recently, a type of well-mixed and well-dispersed oxides derived from hydrotalcite-like compounds (HTlcs) have received considerable attention in the search for alternative NSR catalysts.^[10] HTlcs, also known as anionic clays or layered double hydroxides (LDHs), are widely used as adsorbents, ion exchangers, base catalysts, and as precursors of well-mixed oxides for various catalytic applications.^[11] HTlcs can be chemically expressed as a general formula: $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{II} represents any divalent metal cation, M^{III} any trivalent metal cation, and Aⁿ⁻ any anion.^[11] HTlcs can contain metal cations of more than two types, which provides a good platform for a rational design of NSR catalysts. Our recent studies^[12] show that Cu- and Co-containing calcined MgAl-HTlc catalysts perform well for NSR, and the improvement of NSR catalysts through substitution of M^{II} by Cu, Co, Ni, and Zn has been extensively studied.^[1b,10a,c,6c,12]

The current aim is to develop transition-metal, multi-functional, mixed-oxide catalysts that elegantly combine the catalytic capability of NO_x decomposition, storage, and reduction. First, Mg was replaced with Ca in hydrotalcite (Mg₃Al₂(OH)₈(CO₃)_{1/2}·2H₂O) to enhance the alkalinity for capturing/storing acidic NO_x. Attempts had been made to introduce Sr and Ba to enhance the catalyst alkalinity, but the NO_x storage capability was no longer enhanced. Secondly, Co was introduced into the matrix to provide basic redox sites because Co-oxide can actively decompose N₂O and NO.^[4a,13] It has also been found that mixed CoMgAl-oxide catalysts derived from HTlcs are good at capturing and decomposing NO_x.^[12b] Furthermore, La was imported into the HTlcs as the second redox sites, as La-

containing mixed oxides have been found to greatly enhance the activity to decompose and store NO_x.^[14] Well-designed CaCoAl-HTlcs can lead to a multi-functional mixed-oxide catalyst that can effectively and simultaneously decompose, capture, and reduce NO_x in the presence of excess O₂. For example, the catalyst Ca₂Co₁La_{0.1}Al_{0.9}-oxide can decompose 75 % NO and store 19.02 mg g⁻¹ NO (in 60 min) at 300 °C with 8 % O₂ in the stream, and can reduce the stored NO_x by H₂ within 6 min at 350 °C, with these three properties superior to or comparable with the best catalysts (to our knowledge) in both NO decomposition and NSR.^[15]

2. Results and Discussion

2.1. Physical Properties of Precursors and Mixed Oxide Catalysts

As-prepared CaCoAl-HTlcs (xCCA-HTs) are identified by their characteristic XRD patterns (Fig. 1A). In particular, when 0.0 ≤ x ≤ 2.0, the precursors Ca_xCo_{3-x}Al-HTlcs are of typical hydrotalcite (HT)-like phase with diffraction peaks at 2θ = ~11°, 23°, and 34°, which correspond to the basal planes of (003), (006), and (009) and indicates well-formed crystalline layered structures with a rhombohedral symmetry (3R).^[11] The in-plane X-ray diffractions from planes (110) and (113) can also be noted at ~60° and ~61° for these precursors. These characteristic diffractions suggest that Ca cations are well distributed in the HT phase. Only in the case of Ca₃Al-HTlc is the HT-like phase hardly observed, while some other phases, such as CaCO₃ (marked with ×), Ca(OH)₂ (marked with +), and

Figure 1. XRD patterns of A) xCCA-HTs samples and B) xCCAO catalysts where the HT phase is marked as 'H', CaCO₃ as 'X', Ca(OH)₂ as '+', Al(OH)₃ as '#', spinel as 'S', and CaO as ●.

Al(OH)₃ (marked with #) are predominant. The segregation of these phases instead of formation of a designed HT-like phase is presumably attributed to the greater insolubility of CaCO₃ and the incompatibility of the ionic size of Al and Ca (0.054 nm versus 0.100 nm).^[11b] In the case of Ca_{2.5}Co_{0.5}Al-HTlc, possibly because of the mediation of Co cations (0.065 nm), the HT-like phase co-exists with other phases.

Similarly, the mixed oxides Ca_xCo_{3-x}Al-oxide ($x \leq 2.0$, CCAO) derived by calcining at 800 °C for 4 h (Fig. 1B) are of typical spinel phase with diffraction peaks at ~31°, 36°, 39°, 45°, 55°, 59°, and 65°.^[16] This shows the complete transformation from HT-like compounds to oxides. It is obvious that the gradual replacement of Co with Ca in the HT structure does not lead to the gradual change in phase composition, which reveals that the cations are well dispersed in the spinel phase. However, for sample 3.0CCAO, i.e., Ca₃Al-oxide, the peaks at ~32°, 37°, 53°, 64°, and 67° are ascribed to the CaO phase (JCPDS 37-1497), possibly with amorphous Al₂O₃ as the filler. Sample 2.5CCAO mainly consists of a spinel phase, with a small amount of mixed CaO phase. For all tertiary mixed oxides ($0.5 \leq x \leq 2.5$), although they have the same spinel phase, the cation distribution and density are different, which presumably determines the activity for the NO decomposition, storage, and reduction, as addressed shortly.

In addition, such derived oxides have a spinel crystalline size of 15–23 nm and a CaO crystalline size of ~25 nm for the 3.0CCAO catalyst (Table 1), as estimated from the width of the most intense peak by using the Debye–Scherrer equation.^[17] Also listed in Table 1 are the Brunauer–Emmett–Teller

Table 1. Crystallite sizes, textual properties, and NO storage data of *x*CCAO.

Sample	Crystallite size [nm]	SSA [m ² g ⁻¹]	Pore size [nm]	Pore volume [cm ³ g ⁻¹]	Storage [a] [mg g ⁻¹]	
					100 °C	300 °C
0.0CCAO	21.2	22	23.7	0.13	2.28	2.18
0.5CCAO	23.0	29	35.2	0.25	2.40	2.75
1.0CCAO	18.9	58	18.7	0.27	4.21	6.43
1.5CCAO	18.8	59	17.8	0.26	3.06	8.54
2.0CCAO	18.8	72	15.8	0.29	4.46	12.88
2.5CCAO	~15 [b]	67	19.3	0.32	2.79	10.30
3.0CCAO	24.9	89	14.7	0.33	2.34	2.11

[a] The storage amount was deduced from the desorption from the catalyst that adsorbed NO at 300 °C for 30 min.

[b] The strongest peak is an overlapping peak of spinel and CaO, thus the peak width of spinel or CaO would be simply halved, to give a crystalline size of approx. 15 nm.

(BET) surface area, interparticle pore size, and pore volume of the oxides, which show that the oxides are slightly porous with a medium-scale surface area.

2.2. NO Adsorption on *x*CCAO Catalysts

The NO adsorption profiles of samples 0.0CCAO, 1.5CCAO, and 3.0CCAO at 100 and 300 °C in the presence of excess O₂

are presented in Figure 2. During the initial stage NO is completely adsorbed by the oxide catalysts as there is no NO_x detected in the outlet stream. The complete adsorption at 100 °C only lasts for 60–140 s for all catalysts, while the time is much longer at 300 °C. In particular, the complete adsorption on 1.5CCAO and 2.0CCAO lasts for over 600 s. Obviously, more NO is eliminated at 300 °C, which indicates that CaCoAl-oxide catalysts are much more suitable for high-temperature adsorption. After the complete adsorption stage at 100 °C, NO is continuously adsorbed over the next 100–1000 s since its concentration is gradually recovered to 780–800 ppm (Fig. 2A). Note that NO₂ in the downstream is detected at a very low concentration (~10 ppm, not shown here), which demonstrates limited conversion of NO to NO₂ at 100 °C in an O₂ rich environment.

At 300 °C, the NO adsorption behavior and the gas composition in the outlet stream after the initial complete adsorption are significantly different, as shown in Figures 2B–2D. Over catalyst 3.0CCAO (Ca₃Al-oxide), NO is continuously adsorbed and a small amount of NO₂ is generated (30 ppm, Fig. 2C). The total NO and NO₂ (NO_x) concentration after 900 s is equal to that of the supplied NO, which indicates no further adsorption or other reaction. On the other hand, over the 0.0CCAO (Co₃Al-oxide) catalyst, the NO concentration is only recovered to 410 ppm, but a considerable amount of NO₂ (320 ppm) in the downstream is constantly generated. The change in NO and NO₂ concentrations indicates the conversion of NO into NO₂ as they pass through the Co₃Al-oxide catalyst.^[12b] Furthermore, the total concentration of NO and NO₂ (NO_x) (730 ppm) is always lower than the feed NO (800 ppm), which suggests partial decomposition of NO to N₂ and N₂O, as addressed shortly in detail. In particular, for 1.5CCAO (Ca_{1.5}Co_{1.5}Al-oxide), the recovered NO concentration only reaches 320 ppm and NO₂ is generated at only 130 ppm, which demonstrates that 350 ppm NO is decomposed to N₂/N₂O. Therefore, the adsorption of NO in an O₂ and N₂ stream at 300 °C on Co-containing oxide catalysts is accompanied by two apparent reactions: oxidation of NO to NO₂ and decomposition of NO to N₂/N₂O.^[18]

2.3. NO_x Storage and Desorption

Figure 3 shows the desorption profiles of NO_x at 100–650 °C from catalysts 0.0-, 1.5- and 3.0CCAO that adsorbed NO at 100 or 300 °C. Basically, NO_x desorption from the catalyst with NO adsorption at 100 °C follows a two-step process in which NO is the predominant species, with a very limited amount of NO₂ (less than 10 ppm over 100–650 °C, not shown here). For example, non-Ca-containing catalyst 0.0CCAO (Co₃Al-oxide) exhibits two desorption bands at 262 and 350 °C, respectively (Fig. 3L). When more Ca is incorporated, such as in catalysts 1.5CCAO and 3.0CCAO, the desorption of NO_x occurs at higher temperatures, e.g., the lower-temperature desorption being at 290 and 421 °C and the higher-temperature one at 512 and 558 °C, respectively. The increase in desorption temperature of NO_x from Ca-containing catalysts is presumably a result of the stabilization effect of Ca on stored NO_x species.

Figure 2. NO adsorption on catalysts 0.0-, 1.5-, and 3.0CCAO at 100 (A) and 300 °C (B–D).

In the case of NO adsorption at 300 °C (Figs. 3M–3O), only the high-temperature desorption band occurs, which demonstrates that the lower-temperature desorption is responsible for the less stable nitrogen species formed at 100 °C. Meanwhile, a considerable amount of NO₂ is generated in all cases (Fig. 3N). Of particular note, catalyst 1.5CCAO desorbs much more NO_x than the other two catalysts (Fig. 3O).

The adsorbed NO_x species are reflected by the in-situ infrared spectra, and are mainly various nitrites and nitrates. For example, the pronounced peak (Fig. 4A) for catalyst 1.5CCAO (Ca_{1.5}Co_{1.5}Al-oxide) at 100 °C, initially located at 1331 cm⁻¹, which then shifts to 1219–1225 cm⁻¹, is attributed to bridging bidentate nitrite, together with another stronger peak at 1653–1665 cm⁻¹ assigned to the bridging bidentate nitrate. Some other weak peaks at 1473 and 1033 cm⁻¹ belong to the linear nitrite and monodentate nitrate, respectively.^[3a,5,19] These species (more nitrites and less nitrates) identified by IR spectroscopy are also reflected by the NO_x desorption profile in that more NO is desorbed from less stable nitrites at around 300 °C than from the stable nitrates at 400–500 °C (Fig. 3L). In the case of adsorption at 300 °C (Fig. 4B), it is noted that the initial peak at 1244–1250 cm⁻¹ assigned to the bridging bidentate nitrite shifts to 1306 cm⁻¹ as the strongest peak in the later adsorption stage. This strongest peak, accompanied by other peaks at 1021, 1058, and 1504 cm⁻¹, suggests that monodentate

nitrate is the major NO_x species in the later stage. In addition, linear nitrite (1461–1466 cm⁻¹)^[3a,5,19] and adsorbed N₂O₄ species (1733 cm⁻¹)^[20] are also observed. In brief, the major species are nitrites as well as nitrates in the case of 100 °C adsorption, while various nitrates are predominant during 300 °C adsorption for all catalysts.

The nitrite and nitrate NO_x species stored on the *x*CCAO catalysts as identified above indicate that the gaseous NO is oxidized to various NO₂⁻/NO₃⁻ on the catalyst surface, which are then spilt over to the basic sites to store. As described in the previous sections, NO is completely adsorbed during the initial stage either at 100 or 300 °C, and then the total NO_x concentration in the outlet stream is recovered to and kept at a constant level, which suggests that the adsorption/desorption reaches a steady state equilibrium. At 300 °C, in particular, a considerable amount of NO₂ (30–320 ppm) is generated in the outlet stream while the NO concentration (100–700 ppm) is much lower than the feed 800 ppm, which indicates an apparent conversion of NO into NO₂. This conversion is suggested to occur on the catalyst surface rather than in the gaseous phase. After NO is oxidized and stored as NO₂⁻/NO₃⁻, the NO₂⁻/NO₃⁻ can be catalytically decomposed to NO and NO₂ at this temperature (300 °C) since the desorption profiles reveal the generation of NO and NO₂ in a small amount at 300 °C (Figs. 3M–3O). Moreover, the total concentration of NO and

Figure 3. NO_x desorption profile on catalysts 0.0-, 1.5-, and 3.0 CCAO at 100 (L) and 300 °C (M–O).

NO₂ (NO_x) in the outlet stream over Co-containing catalysts (0.0 CCAO to 2.5 CCAO) is much lower than the supplied 800 ppm, which reveals the decomposition of NO_x to N₂, O₂, and N₂O, as detailed in the following. It seems that the adsorption/desorption and decomposition together reach a dynamic equilibrium after 20 min, as shown by the NO_x recovery profiles in Figure 2D.

The amount of NO adsorbed (stored) on the x CCAO catalysts at 100 and 300 °C for 30 min is estimated from the desorption profile and listed in Table 1. Note that the storage capacity of NO at 300 °C is higher than that at 100 °C on all tertiary catalysts x CCAO (0 < x < 3). Surprisingly, 2.0 CCAO and 2.5 CCAO show much higher NO storage capability at 300 °C.

2.4. Effect of La, Ba, and Sr Incorporation on NO Sorption

As the 2.0 CCAO catalyst shows higher activity for NO capture and decomposition at 300 °C and it has been found that replacement of Al with La significantly enhances the NO_x storage on the CoMg/Al-oxide catalyst,^[14] La was incorporated into 2.0 CCAO to derive a designed catalyst with a nominal composition of Ca₂Co₁/La_{0.1}Al_{0.9}-oxide (CCLAO). This catalyst has shown a great improvement in the NO storage and decomposition at 300 °C compared with catalyst 2.0 CCAO

(Ca₂Co₁/Al₁-oxide). In order to elucidate the processes of NO capture and decomposition on catalysts 2.0 CCAO and CCLAO, He was used as the carrier gas, and the outlet gases (NO, NO₂, N₂, and N₂O) were monitored by a chemiluminescence NO–NO₂–NO_x analyzer and a separate gas chromatograph. As shown in Figure 5A for the concentration change of these outlet nitrogen species over 2.0 CCAO during adsorption at 300 °C, NO is completely trapped and decomposed in the first 750 s, and only N₂ is detected. Between 750 and 2000 s, NO is continuously trapped and decomposed, while NO and NO₂ slowly increase to 280 and 80 ppm, respectively, which indicates that 55 % of the NO (440 ppm) decomposes to N₂. Concurrently, N₂ from NO decomposition appears from the beginning, but quickly reaches a constant concentration (200–210 ppm) after 900 s. Overall, the nitrogen equivalent derived by adding these three nitrogen species in the outlet, i.e., NO_x out = [NO] + [NO₂] + 2[N₂] (block triangle in Fig. 5A), is almost equal to the inlet NO (i.e., NO_x in, dashed line in Fig. 5A) after 2100 s. In comparison, the La-containing catalyst (CCLAO) extends the complete trapping time to 1100 s (longer than any reported catalyst) and decomposes approx. 75 % of the NO to N₂ (which is better than most oxide catalysts) (Fig. 5B).^[4a,21] An exception is that a small amount of N₂O is produced in the first 1200 s (Fig. 5B). The stoichiometric

Figure 4. In situ IR spectra of NO adsorption on the 1.5CCAO catalyst at A) 100 and B) 300 °C.

equivalence of nitrogen species between the inlet and outlet is better kept, which indicates that there is probably no other gaseous nitrogen species transferred from NO under the current conditions. In short, CCLAO and 2.0CCAO are very active in capturing NO and decomposing NO to N₂ at 300 °C.^[4a,12b]

Since N₂ is detected in an appreciable amount during the adsorption process, we suggest that N₂ will also be generated during the desorption process. As shown in Figure 6A, desorption from CCLAO over 200–650 °C in He indicates that an appreciable amount of N₂ is generated. A very similar desorption profile is observed for 2.0CCAO catalysts (Fig. 6B). Obviously, the N₂ that appears during desorption is generated by the direct decomposition of stored NO_x and/or by the decomposition path of just desorbed NO/NO₂ as during adsorption. So the total desorbed nitrogen equivalent, i.e., NO + NO₂ + 2N₂ in the desorbed stream is calculated to be 19.02 mg g⁻¹ for catalyst CCLAO and 18.06 mg g⁻¹ for 2.0CCAO after 60 min adsorption, which is regarded as the NO storage capability of the catalyst. The NO storage amount of all other catalysts is thus deduced from the corresponding desorption profiles in He and listed in Tables 1 and 2.

Furthermore, Ba and Sr were incorporated into CCLAO to give, namely, Ca_{1.5}Ba_{0.5}Co₁La_{0.1}Al_{0.9}-oxide (CBCLAO) and Ca_{1.5}Sr_{0.5}Co₁La_{0.1}Al_{0.9}-oxide (CSCLAO). These two catalysts show similar adsorption and desorption profiles. However, the

Table 2. NO_x storage amount of CCLAO, CBCLAO, CSCLAO, and 2CCAO.

Catalyst	Temp/Time [a] [°C/min]	Inlet gas composition	Storage amount [mg g ⁻¹]
CCLAO	300/60	800 ppm NO + 8% O ₂ in He	19.02
2CCAO	300/60	800 ppm NO + 8% O ₂ in He	18.06
2CCAO	300/30	800 ppm NO + 8% O ₂ in N ₂	12.88
CBCLAO	300/30	800 ppm NO + 8% O ₂ in N ₂	5.72
CSCLAO	300/30	800 ppm NO + 8% O ₂ in N ₂	6.51

[a] This means the adsorption temperature and time.

NO storage amount on CBCLAO and CSCLAO at 300 °C is much lower than catalysts 2.0CCAO and CCLAO (Table 2), which possibly reveals that the alkalinity of the oxide catalysts is not the only factor that determines the NO storage capability, or that Ba or Sr is not well incorporated into CCLAO because of the much larger ionic size.

2.5. Reduction of Adsorbed NO_x by H₂

The reduction experiments indicate that the stored nitrites/nitrates on CCLAO can be readily reduced by H₂ (1% in N₂) at 350 °C. As shown in Figure 7, the intensities of all IR bands that correspond to adsorbed NO_x species on the catalyst decrease significantly with time in H₂/N₂ at 350 °C. In particular, two peaks at 1268–1276 and 1555–1543 cm⁻¹ decrease very

Figure 5. Nitrogen species profiles in the outlet stream from catalysts 2CCAO (A) and CCLAO (B) in He during adsorption at 300 °C. Here the total NO_x inlet was 800 ppm as supplied and total NO_x outlet = [NO] + [NO₂] + 2[N₂O] + 2[N₂] that were measured in the outlet stream.

quickly in intensity, which shows that most nitrites/nitrates are reduced within 6 min. Such a performance in reducing the adsorbed NO_x is comparable with that of the noble metal catalyst Pt-Ba/γ-Al₂O₃.^[22]

2.6. Comparison with other Catalysts

The previous sections show that the two pre-optimized catalysts 2.0CCAO and CCLAO are three-fold functional. First, they have a high activity for the thermal decomposition of NO in the presence of O₂. For example, 2.0CCAO and CCLAO can directly decompose approx. 55 and 75 % of NO at 300 °C in the presence of 8 % O₂. This is a remarkable property that is even better than most oxide catalysts specially designed for NO decomposition.^[4a]

In terms of the storage capability, to the best of the author's knowledge, the catalysts reported here give the best performance of those reported to date. The NO storage amount over CCLAO and 2.0CCAO under similar conditions is higher than that of the best catalysts reported in the literature

Figure 6. Nitrogen species profiles desorbed from catalyst A) 2CCAO and B) CCLAO in He after NO adsorption at 300 °C for 1 h.

(Table 3).^[4a,13b,22,23] Our catalysts should prove even better when different evaluation methods are considered further. For example, the adsorption/dynamic method includes the amount of decomposed NO during the adsorption that is observed in our experiments, and thus gives a storage that is probably higher than the real value.^[22,23] To the contrary, our desorption method accounts for only four nitrogen species in the desorbed stream and thus gives a storage that is probably lower than the real value. Therefore, our rationally designed mixed oxides with normal transition metals are even superior to the noble-metal catalysts in storing NO under similar conditions (Table 3). Toops et al. reported that the NO storage on a Pt/K/Al₂O₃ catalyst is as high as 28.18 mg g⁻¹,^[24] yet their evaluation method (DRIFT) seemingly needs further validation.

3. Conclusions

The constant-pH co-precipitation method leads to Ca_xCo_{3-x}-Al-HTICs, except for $x = 3.0$. The corresponding mixed oxides

Table 3. Summary of NSR catalysts with notable performances.

Catalyst	Temp [°C] (Time)	NO _x (Bal. He or N ₂)	NO stored [mg g ⁻¹]	Method	Ref.
PtRh/Ba/washcoat	300 (saturation)	500 ppm NO + 7% O ₂	15.9	Adsorption	21b
Pt/Ba/Al ₂ O ₃	300 (~17 min)	1000 ppm NO + 3% O ₂	10.8	Adsorption	22
BaAl ₂ O ₄	80–350 (~100 min)	500 ppm NO + 500 ppm NO ₂ + 10% O ₂	15.6	Dynamic	23b
Ca ₂ CoAl-oxide	300 (60 min)	800 ppm NO + 8% O ₂	18.1	Desorption	This work
Ca ₂ CoLaAl-oxide	300 (60 min)	800 ppm NO + 8% O ₂	19.0	Desorption	This work
Pt/K/Al ₂ O ₃	250 (60 min)	300 ppm NO	23.9	DRIFT	24
	250 (saturation)	+12% O ₂	28.2		

Figure 7. In-situ FTIR spectra of adsorbed species on CCLAO at 350 °C in flowing H₂/N₂ (1 % H₂) after NO_x adsorption at 300 °C.

(xCCAOS), derived after calcination at 800 °C, were slightly porous with the surface area of 22–89 m² g⁻¹. The Co-containing mixed oxides catalytically decompose up to 55 % of NO at 300 °C in 8 % O₂ after NO adsorption reaches a steady state equilibrium (normally after 20–30 min), and some exhibit a higher NO storage capacity. For example, catalyst 2.0CCAO can store 4.46 mg g⁻¹ NO at 100 °C and 12.88 mg g⁻¹ NO at 300 °C within 30 min. The in situ IR spectra suggest that the major adsorbed species are various nitrites and nitrates. Further incorporation of La into the good catalyst 2.0CCAO

(Ca₂CoAl₁-oxide) gives a catalyst (Ca₂Co₁-La_{0.1}Al_{0.9}-oxide, CCLAO) that increases the NO decomposition from 55 to 75 %, extends the complete-trapping time from 750 to 1100 s, and increases the NO_x storage amount from 18.06 to 19.02 mg g⁻¹ in excess O₂ at 300 °C within 60 min. In addition, the stored NO_x (nitrites/nitrates) on the CCLAO catalyst can be readily reduced by H₂ at 350 °C within 6 min. Therefore, we can elegantly combine the normal transition metals into a novel multi-functional catalyst for NO abatement on the basis of HT-like materials.

4. Experimental

Various Ca_xCo_{3-x}Al HTLs with the (Ca²⁺ + Co²⁺)/Al³⁺ molar ratio fixed at 3.0 were prepared by a constant-pH coprecipitation method where *x* was set at 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 (denoted as xCCA-HT). Briefly, a mixed salt solution (100 mL) and a mixed basic solution (100 mL) were simultaneously added dropwise into 100 mL of doubly distilled water over 1 h at constant pH (10 ± 0.5) under vigorous mechanical stirring. The salt solution with a total metal concentration of 1.0 M contained suitable amounts of Ca(NO₃)₂·4H₂O (>99 %), Co(NO₃)₂·6H₂O (>99 %), Ba(NO₃)₂ (>99 %), Sr(NO₃)₂·6H₂O (>99 %), La(NO₃)₃·6H₂O (>99 %), and Al(NO₃)₃·9H₂O (>99 %). The basic solution contained NaOH (>96 %) and Na₂CO₃ (>99.8 %) with [OH⁻]/[CO₃²⁻] = 16 and [OH⁻]/[Al³⁺] = 8. Precipitates were aged in suspension at 60 °C for 4 h under stirring in the static air, and then filtered off and thoroughly washed with doubly distilled water. The cake was dried at 70 °C for 12 h and again at 120 °C overnight. Ca₂Co₁La_{0.1}Al_{0.9}-, Ca_{1.5}Ba_{0.5}Co₁La_{0.1}Al_{0.9}-, and Ca_{1.5}Sr_{0.5}Co₁La_{0.1}Al_{0.9}-HT (denoted as CCLA-HT, CBCLA-HT, and CSCLA-HT, respectively) were similarly prepared. The as-prepared HTLs were calcined at 800 °C for 4 h to derive the corresponding mixed oxide catalysts, referred as to xCCAO (*x* = 0.0–3.0), CCLAO, CBCLA, and CSCLA, respectively. The oxide catalysts were then crushed and sized using a 20–40 mesh, and kept in a desiccator.

The X-ray diffraction (XRD) patterns of HTLs and the derived mixed oxides were measured on a Rigaku powder diffractometer (D/MAX-RB) using Cu Kα radiation (λ = 0.15418 nm) in 2θ = 10–70° at a scanning rate of 4° per min. The surface area, the interparticle pore volume, and the pore size of the oxides were calculated from the typical N₂ adsorption/desorption isotherms at 77 K.

Thermal NO_x adsorption experiments were carried out in a quartz flow-reactor (ID = 8 mm and L = 600 mm) using 1.0 g of catalyst (20–40 mesh powder). The oxide catalyst was pre-treated in a gas flow of O₂-N₂ (8 % O₂ in volume) at 500 °C at a constant space velocity of ~30 000 h⁻¹ for 1 h, and then cooled to the experimental temperature (100 or 300 °C). When the target temperature was stabilized, 800 ppm of NO, 8 % O₂, and a balance of N₂ or He were introduced at a rate of 500 mL min⁻¹ (space velocity was ~30 000 h⁻¹) for the thermal NO_x adsorption. Concentrations of NO, NO₂, and NO_x in the outlet were monitored by a chemiluminescence NO-NO₂-NO_x analyzer (EC 9841, Ecotech Corporation). In the case of He as the carrier, a gas chromatograph was used to monitor N₂ and N₂O in the outlet stream.

After the adsorption, the flow gas was switched to pure N₂ or He (rate = 500 mL min⁻¹) to flush the oxide catalyst for 20 min at the absorption temperature. The oxide catalyst was then cooled to 100 °C if the adsorption temperature was 300 °C. The NO_x desorption was then conducted by heating the oxide from 100 to 650 °C at a ramp of 10 °C per min with N₂ or He flowing at a rate of 500 mL min⁻¹. Concentrations of NO, NO₂, N₂, and N₂O in the outlet were also monitored, and the adsorbed NO amount was thus calculated.

The in-situ FTIR spectra of NO_x sorption were recorded on a Bruker Tensor 27 spectrometer over 600–4000 cm⁻¹ after 128 scans at a resolu-

tion of 4 cm^{-1} . A self-supporting pellet ($\sim 50\text{ mg}$, $20\text{--}40\text{ mesh}$) was made from the oxide catalyst and used directly in the IR flow cell. The IR cell made of stainless steel with a KBr window was connected to a vacuum apparatus with a residual pressure below 10^{-4} Pa . A K-type thermocouple was placed in direct contact with the IR flow cell to detect the temperature. A Harric Series 999 temperature controller was used to control the experimental temperature. Prior to recording the IR spectrum, the catalyst sample was degassed for 1 h at 350°C . After cooling to 100 or 300°C under vacuum, a background spectrum of the treated sample was taken. A mixed gas stream (total flow 25 mL min^{-1}) that contained 800 ppm NO and $8\text{ \% O}_2$ in N_2 was then introduced for NO adsorption. Meanwhile, the IR spectra were sequentially recorded at time points of $1, 2, 5, 10, 20, 30, 60\text{ min}$. For reduction experiments, the oxide catalyst was further purged with pure N_2 for 30 min , and then the flow gas was switched to H_2/N_2 ($1\text{ \% H}_2$) at a rate of 25 mL min^{-1} with heating to 350°C , and the time-dependent in-situ IR spectra were recorded every 2 min .

Received: March 20, 2007

Revised: May 25, 2007

Published online: October 23, 2007

- [1] a) K. Yamazaki, N. Takahashi, H. Shinjoh, M. Sugiura, *Appl. Catal. B* **2004**, 53, 1. b) G. Centi, G. E. Arena, S. Perathoner, *J. Catal.* **2003**, 216, 443. c) V. T. Martyn, *Appl. Catal. B* **2007**, 70, 2. d) M. H. Ronald, J. F. Robert, *Appl. Catal. A* **2001**, 221, 443. e) N. B. David, C. T. Kathleen, *Curr. Opin. Solid State Mater. Sci.* **1999**, 4, 97.
- [2] a) S. Matsumoto, *Catal. Today* **1996**, 29, 43. b) H. Shinjoh, N. Takahashi, K. Yokota, M. Sugiura, *Appl. Catal. B* **1998**, 15, 189.
- [3] a) F. Prinetto, G. Ghiotti, I. Nova, L. Lietti, E. Tronconi, P. Forzatti, *J. Phys. Chem. B* **2001**, 105, 12732. b) L. Olsson, H. Persson, E. Fridell, M. Skoglundh, B. Andersson, *J. Phys. Chem. B* **2001**, 105, 6895.
- [4] a) F. Garin, *Appl. Catal. A* **2001**, 222, 183. b) S. Hodjati, K. Vaezzadeh, C. Petit, V. Pitchon, A. Kiennemann, *Appl. Catal. B* **2000**, 26, 5.
- [5] a) Y. Su, M. D. Amiridis, *Catal. Today* **2004**, 96, 31. b) W. Björn, F. Erik, *J. Mol. Catal. A* **2001**, 165, 249.
- [6] a) H. Y. Huang, R. Q. Long, R. T. Yang, *Energy & Fuels* **2001**, 15, 205. b) S. K. Karen, L. M. Rachel, P. H. Michael, *Catal. Today* **2004**, 96, 79. c) G. Fornasari, F. Trifirò, A. Vaccari, F. Prinetto, G. Ghiotti, G. Centi, *Catal. Today* **2002**, 75, 421.
- [7] a) S. Hodjati, C. Petit, V. Pitchon, A. Kiennemann, *Appl. Catal. B* **2001**, 30, 247. b) A. Sultana, D. D. Habermacher, C. E. A. Kirschhock, J. A. Martens, *Appl. Catal. B* **2004**, 48, 65.
- [8] a) J. Szanyi, J. H. Kwak, R. A. Moline, C. H. F. Peden, *Phys. Chem. Chem. Phys.* **2003**, 5, 4045. b) K. Takaaki, *Catal. Today* **2004**, 96, 171.
- [9] T. Nakatsuji, R. Yasukawa, K. Tabata, K. Ueda, M. Niwa, *Appl. Catal. B* **1999**, 21, 121.
- [10] a) G. Centi, G. Fornasari, C. Gobbi, M. Livi, F. Trifirò, A. Vaccari, *Catal. Today* **2002**, 73, 287. b) G. Fornasari, R. Glöckler, M. Livi, A. Vaccari, *Appl. Clay Sci.* **2005**, 29, 258. c) A. E. Palomares, J. M. Lopez-Nieto, F. J. Lazaro, A. Lopez, A. Corma, *Appl. Catal. B* **1999**, 20, 257.
- [11] a) F. Cavani, F. Triro, A. Vaccari, *Catal. Today* **1991**, 11, 173. b) P. S. Braterman, Z. P. Xu, F. Yarberry, in *Handbook of Layered Materials*, (Eds: S. M. Auerbach, K. A. Carrado, P. K. Dutta), Marcel Dekker, Inc.: New York, **2004**, p 373.
- [12] a) S. F. Kang, Z. Jiang, Z. P. Hao, *Acta Phys. Chim. Sini.* **2005**, 21, 278. b) J. J. Yu, Z. Jiang, L. Zhu, Z. P. Hao, Z. P. Xu, *J. Phys. Chem. B* **2006**, 110, 4291.
- [13] a) Z. P. Xu, H. C. Zeng, *J. Mater. Chem.* **1998**, 8, 2499. b) M. A. Gomez-garcia, V. Pitchon, A. Kiennemann, *Environ. Int.* **2005**, 31, 445.
- [14] J. J. Yu, Y. X. Tao, C. C. Liu, Z. P. Hao, Z. P. Xu, *Environ. Sci. Technol.* **2007**, 41, 1399.
- [15] a) S. Yu, K. S. Kabin, I. P. H. Michae, D. A. Michael, *Appl. Catal. B* **2007**, 71, 207. b) T. Naoki, Y. Kiyoshi, S. Hideo, S. Hirofumi, *Appl. Catal. B* **2007**, 70, 198. c) F. Basile, G. Fornasari, A. Gambatesa, M. Livi, A. Vaccari, *Catal. Today* **2007**, 119, 59. d) S. Tamás, H. K. Ja, H. K. Do, C. H. Jonathan, H. F. P. Charles, S. János, *J. Catal.* **2006**, 239, 51.
- [16] Z. P. Xu, H. C. Zeng, *J. Phys. Chem. B* **2000**, 104, 10206.
- [17] Z. P. Xu, G. Q. Lu, *Chem. Mater.* **2005**, 17, 1055.
- [18] Y. J. Li, J. N. Armor, *Appl. Catal.* **1991**, 76, L1.
- [19] Ch. Sedlmair, K. Seshan, A. Jentys, J. A. Lercher, *J. Catal.* **2003**, 214, 308.
- [20] I. Perdana, D. Creaser, O. Ohrman, J. Hedlund, *J. Catal.* **2005**, 234, 219.
- [21] a) W. S. Epling et al., *Catal. Today* **2004**, 96, 21. b) H. Mahzoul, J. F. Brilhac, P. Gilot, *Appl. Catal. B* **1999**, 20, 47.
- [22] L. Lietti, P. Forzatti, I. Nova, E. J. Tronconi, *J. Catal.* **2001**, 204, 175.
- [23] a) M. A. Gomez-garcia, V. Pitchon, A. Kiennemann, *Environ. Int.* **2005**, 31, 445. b) S. Hodjati, P. Bernhardt, C. Petit, V. Pitchon, A. Kiennemann, *Appl. Catal. B* **1998**, 19, 209.
- [24] T. J. Toops, D. B. Smith, W. S. Epling, J. E. Parks, W. P. Partridge, *Appl. Catal. B* **2005**, 58, 255.