Novel NO Trapping Catalysts Derived from Co–Mg/X–Al (X = Fe, Mn, Zr, La) Hydrotalcite-like Compounds

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Co2+5Mg0.5/Al1.0 and Co2+5Mg0.5/X2.5Al0.5 hydrotalcite-like compounds (where X = Fe, Mn, Zr, La) were synthesized from a constant-pH coprecipitation. The derived oxides from hydrotalcites upon calcination at 800 °C for 4 h in static air are mainly of spinel phase, with a surface area of 14.2–23.8 m2/g, where new phase ZrO2 and La2O3 are segregated in Zr- and La-containing oxides, respectively. Incorporation of the fourth element has assisted the reduction of transition-metal cations in the oxide catalysts, which may lead to the enhancement of the NO storage capacity in O2 at 100 °C for all catalysts. However, at 300 °C, only Zr- and La-containing catalysts improve the NO storage performance. Substantially, La-containing catalyst excels over other catalysts in NO storage capability both at 100 and 300 °C. More remarkably, the NO storage at 300 °C (7.56 mg/g) is much higher than that at 100 °C (4.69 mg/g). NO adsorption/desorption routes have been proposed to explain the NO storage, the NO-to-NO2 conversion, and the reduction (decomposition) of NO to N2O/N2 in O3 on the catalysts. In addition, the negative influences of CO2 or H2O on the NO storage/reduction have been further revealed in this research.

Introduction

Most gasoline-burning engines are run in a very narrow air to fuel range near the stoichiometric value (A/F = 14.7, richburn) with little or no O2 in the exhaust. However, the lean-burn engines (A/F = 20–25) are much more preferred as the fuel in the engines can be more efficiently burned so as to save 30–35% consumption (1) and release less CO2. Although three-way catalytic (TWC) converters can effectively remove NOx, CO, and hydrocarbon simultaneously under the rich-burn conditions to meet the legislation for NOx, particulate, hydrocarbons, and CO emission in the exhaust (2), the current TWC technology has not necessarily led to the decrease of gas pollutants under the lean-burn conditions in the presence of excess O2 since TWC catalysts are designed to operate in little or no O2 presence. Therefore, development of new catalysts so as to effectively remove NOx, hydrocarbons, and CO for both rich-burn and lean-burn engines becomes an urgent task for material scientists.

Currently, NOx reduction is conducted through exhaust gas recirculation (EGR), selective catalytic reduction (SCR) (3), direct decomposition of NO with Co/zeolite catalysts (4), and NOx storage/reduction (NSR) (5). Among these NOx reduction technologies, NSR catalytic treatment shows a higher potential (6) as NSR catalysts have been successfully used in stationary-power and natural-gas turbine posttreatment for several years (7). In general, the NOx storage/reduction technology (NSR) is applied to 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 rich-burn conditions, NOx is released and subsequently reduced by hydrocarbons and carbon monoxide. A typical NOx storage/reduction catalyst is composed of a storage component (such as oxide/hydroxide of Ca, Sr, Ba, K, or Na), a catalytic redox component (e.g., Pt, Rh, and Pd) (1, 8), and a porous support (such as high surface area γ-Al2O3). Abundant research studies are focused on the model storage/reduction catalyst Pt–Ba/Al2O3 and its modification (8–11). However, these catalysts are liable to be deactivated dramatically by a trace of SO2 in the exhaust because of the irreversible adsorption of SO2 under both lean-burn and rich-burn conditions, which, together with the high expenses of noble metals, demands the development of cheap and SO2 tolerant NSR catalysts with similar or better performance. Perovskites (12, 13) and zeolites (14) are the starring candidates that show a potential while a new type of well-mixed oxide catalysts derived from hydrotalcite-like compounds (HTlcs) receives considerable attention in the recent search of alternative NSR catalysts (1, 10, 11).

HTlcs are known as anionic clays or layered double hydroxides (LDHs) and are widely used as adsorbents, ion exchangers, base catalysts, and precursors of mixed oxides for various catalytic applications (15). HTlcs can be chemically expressed in a general chemical formula [MII1–xMIIIx(OH)2]n−(A−x)2+–x·mH2O, where MII represents any divalent metal cation, MIII any trivalent metal cation, and A− an anion (inorganic or organic) (15). As HTlcs can contain metal cations more than two types with various ratios, a limitless number of mixed oxides can be derived from the precursor HTlcs. For example, the three typical components required for a NOx NSR catalyst could be all designed in an HT1 compound. Our recent studies (16, 17) have shown that Cu-containing and Co-containing calcined MgAl-HTlcs catalysts perform well for NOx storage/reduction. In contrast, with much research on the improvement of NSR catalysts through substitution of MIII (Mg2+) by cations such as Cu, Co, Ni, and Zn (1, 10, 11, 16, 17), modifying the catalysts by replacement of MIV (Al3+) with others seems to draw less attention. In this regard, we designed and prepared a series of CoMgXAl-mixed oxide catalysts [X = Fe(III), Mn(III), Zr(IV), La(III)] from the corresponding HTlcs precursors and investigated the catalytic performance in NO storage in excess O2, CO2, and H2O in the current research.

Experimental Section

Materials Preparation. Four Co2+5Mg0.5/X2.5Al0.5 HTlcs (see Supporting Information, Table 1S) were prepared with a constant-pH coprecipitation method where X represents Fe, Mn, Zr, and La and is denoted as CMX-HT. For comparison, Co2+5Mg0.5/Al1.0-HT (CMA-HT), a good precursor for NOx storage in our previous study (17), was prepared similarly. In brief, a mixed salt solution (100 mL) and a mixed basic
solution (100 mL) were simultaneously added dropwise into 100 mL doubly distilled water within 1 h at constant pH (10 ± 0.5) under vigorous mechanical stirring. The mixed salt solution contains a total cation concentration of 1.0 M from Mg(NO₃)₂·6H₂O (Yili), Co(NO₃)₂·6H₂O (jinke), Al(NO₃)₃·9H₂O (Yili), Fe(NO₃)₃·9H₂O (Beihua), Mn(NO₃)₂·5H₂O (Beihua), and La(NO₃)₃·6H₂O (jinke) with the designed molar ratio. The basic solution consists of NaOH (Beihua) and Na₂CO₃ (Beihua) with [OH⁻] = 2.0 M and [OH⁻/][CO₃²⁻] = 16. Precipitates were aged in suspension at 60 °C for 4 h with stirring in the static air and then filtered and thoroughly washed with doubly distilled water. The cake was dried at 70 °C for 12 h and again at 120 °C overnight. These HTlcs were calcined at 800 °C for 4 h to derive CoMg/XAl mixed oxide catalysts (denoted as CMXAO and CMAO, X = Fe, Mn, Zr, La). The oxide catalysts were then crushed and sized in 20–40 mesh for sorption experiments and kept in a desiccator to avoid reconstruction of the hydrotalcite-like structure.

Materials Characterization. The X-ray diffraction (XRD) patterns of Co₀.₅Mg₀.₅/X₀.₅Al₀.₅-HTs (CMXAOs) and the derived mixed oxides (CMXAOs) were measured on a Rigaku powder diffractometer (D/MAX-RB) using Cu Kα radiation (λ = 0.15418 nm) in the 2θ range of 10–70° at a scanning rate of 4°/min. The textural properties of the derived oxides (CMXAOs) were analyzed by N₂ adsorption/desorption at −196 °C, using a Quantachrome NOVA-1200. The specific surface area was calculated with the BET equation, and pore volume and pore size distribution were obtained with the BJH method from the adsorption isotherm. In addition, TGA/DSC analysis of CMXAO-HTs, TPR analysis of CMXAOs, and the in-situ IR monitoring on CMLAO were conducted accordingly, which can be referred to in the Supporting Information and in ref 17.

NO Adsorption/Desorption. Thermal NO adsorption experiments were carried out in a quartz flow-reactor (ID = 8 mm and L = 600 mm) using 1.00 g of CMXAO catalyst (20–40 mesh powder). Oxide catalyst was pretreated in O₂−N₂ (8% O₂) at 500 °C at a constant flow rate of 500 mL/min for 1 h and then was cooled down to the experimental temperature (100 or 300 °C). When the temperature was stabilized at 100 or 300 °C, 800 ppm NO, 8% O₂, and balanced N₂ were introduced at 500 mL/min for 30 min for the thermal NO adsorption. During the adsorption, concentrations of NO, NO₂, and N₂ in the outlet stream were monitored by a chemiluminescence NO−NO₂−NOx analyzer (EC 9841, Ecotech Corporation). The influence of H₂O or CO₂ on NO sorption on catalyst CMLAO was further investigated by introducing 8% H₂O or 8% CO₂ into the stream of 800 ppm NO, 8% O₂, and the balance being N₂ in the tests.

After the thermal NO adsorption, the flowing gas was switched to pure N₂ at the same flowing rate (500 mL/min) to flush the catalyst for 20 min to remove the weakly absorbed species at the adsorption temperature. The catalyst was cooled to 100 °C if the adsorption temperature was 300 °C. Temperature-programmed desorption (TPD) was then conducted by heating the sample from 100 to 650 °C at a ramp of 10 °C/min with N₂ flowing at 500 mL/min. Concentrations of NO, NO₂, and NOₓ in the outlet stream were monitored.

Results and Discussion

Effect of the Fourth Element on HTc and Derived Oxides. As shown in Figure 1A, the hydrotalcite-like phase can be identified with the XRD patterns. All the compounds show the typical diffraction peaks at 2θ = ~11°, 23°, and 34°, attributed to the (003), (006), and (009) crystal planes in the layered structure with a rhombohedral symmetry (3R) (15). The in-plane X-ray diffractions from plane (110) and (113) can also be noted at ~60° and ~61° for all HTlcs. These characteristic diffractions suggest that the fourth metal cations are well distributed in the hydrotalcite-like phase. The diffraction patterns of samples CMFA- and CMMA-HT are similar to that of Co₀.₅Mg₀.₅Al-HT (CMA-HT), indicating that the introduction of Fe(III) and Mn(III) does not affect the crystallinity. However, the diffraction peaks of samples CMZA- and CMLA-HT are much weaker, showing the

### Table 1. Crystallite Sizes, Textural Properties, and NO Adsorption Data of CMXAOs

<table>
<thead>
<tr>
<th>Samples</th>
<th>Spinel size (nm)</th>
<th>SSA* (m²/g)</th>
<th>Pore size (nm)</th>
<th>Pore volume (cm³/g)</th>
<th>100 °C (mg/g)</th>
<th>300 °C (mg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMAO</td>
<td>14.8</td>
<td>21.6</td>
<td>24.8</td>
<td>0.13</td>
<td>2.08</td>
<td>2.36</td>
</tr>
<tr>
<td>CMFAO</td>
<td>15.6</td>
<td>23.8</td>
<td>12.5</td>
<td>0.07</td>
<td>2.36</td>
<td>1.23</td>
</tr>
<tr>
<td>CMMAO</td>
<td>17.6</td>
<td>16.9</td>
<td>11.1</td>
<td>0.05</td>
<td>3.73</td>
<td>0.46</td>
</tr>
<tr>
<td>CMLAO</td>
<td>11.2</td>
<td>23.5</td>
<td>18.6</td>
<td>0.12</td>
<td>4.13</td>
<td>2.74</td>
</tr>
<tr>
<td>CMZAO</td>
<td>11.7</td>
<td>14.2</td>
<td>32.0</td>
<td>0.11</td>
<td>4.69</td>
<td>7.56</td>
</tr>
</tbody>
</table>

* SSA means specific surface area.
deterioration of the hydrotalcite-like phase by introducing Zr(IV) and La(III). For CMLA-HT, the ionic radius of La(III)
deterioration of the hydrotalcite-like phase by introducing
second one by 20°C. For oxide CMZAO, a new phase (ZrO2, marked with #
phase and no crystalline Mg oxide phase is detected (Figure 1B).
the introduction of Al with Fe, Mn, Zr, or
La causes slightly different oxide phase composition, which
could influence the activity for NO storage, conversion,
and decomposition, as addressed shortly. Such derived oxides
have a spinel crystalline size of 11–18 nm (Table 1), as
estimated from the strongest (311) peak width, by using
Debye–Schererrer equation (20). Inclusion of Fe(II) and Mn-
(III) increases the spinel size from 14.8 nm to 15.6 and 17.6
nm while segregation of ZrO2 and La2O3 decreases it to 11.2
and 11.7 nm, respectively. The BET surface area, pore size,
and pore volume of the oxides (Table 1) show that the oxides
are slightly porous with a medium-scale surface area.
The HTIcs normally undergo two thermal decomposition
processes to transform to the mixed oxides (see Supporting
Information, Figure 1S): dehydration in 100–200 °C, that is,
the release of interlayer and adsorbed water molecules, and
dehydroxylation of interlayer hydroxyl groups, decomposition
of interlayer carbonate and nitrate anions, and collapse of
the layered structure in 200–400 °C (17, 19). Interestingly,
the introduction of Fe(III), Mn(III), Zr(IV), and La(III)
facilitates both the decomposition stages to some degree
because of the lower thermal stability of the hydroxides [Fe-
(OH)3, Mn(OH)3, Zr(OH)4, and La(OH)3] and the weak
interaction with H2O in respect to that of Al(OH)3.

The reduction of catalysts CMXAO by H2, like catalyst
CMXAO (Co0.5Mg0.5Al-oxide) (17), undergoes two major
reduction processes: the Cu0 to Cu+ reduction (150–600 °C)
and the Co3 to Co+ reduction (>600 °C) in spinel matrices
(see Supporting Information, Figure 2S) (17, 21). The two-
stage reduction is consistent with reports by Sexton et al.
(22) and by Lin and Chen (23) in the similar temperature
range. The incorporation of the fourth element has facilitated
both the reduction processes. For all oxide catalysts, the first
reduction peak moves down at least by 70–100 °C and the
second one by 20–50 °C without much changing in the
contour. Presumably, the replacement of Al with Fe, Mn, Zr,
or La weakens the stabilization effect of Al+3 cations on the
reducibility of cobalt cations in the oxide (21). Moreover,
Fe(III), Mn(III), and Zr(IV) can also join the H2 reduction
process (24), such as from M–O–M to M••••M, to generate
micropores in the matrix that allow H2 to easily access the
neighboring reducible cations. Particularly for CMFAO,
the second peak moves down by up to 200 °C because of easier
reduction of Fe than Co (24).

NO Adsorption/Desorption on Oxide Catalysts. The
adsorption progress of NO on catalysts CMXAOs at 100 and
300 °C in the presence of O2 is presented in Figure 2. NO
was completely trapped in the initial period (60–300 s) for all
catalysts at 100 °C (Figure 2A). NO was continuously trapped
in the next 600–900 s since NO concentration was gradually
recovered to 720–780 ppm (Figure 2A). The fourth element
 delays the recovery of NO concentration, that is, increases
the storage of NO, with Zr and La enhancing more significan-
tly. NO2 in the downstream was found at a very low
concentration (~10 ppm, not shown here), demonstrating
very limited conversion of NO to NO2 at 100 °C in O2. The
total concentration of NO and NO2 (NOx) was 720–790 ppm,
10–80 ppm less than 800 ppm of NO supplied, probably
attributed to the catalytic decomposition of NO to N2O/N2,
like in the case of catalyst Cu–ZSM-5 (25).
The NO adsorption behaviors at 300 °C and the gas
composition in the outlet stream are significantly different
(Figure 2B and 2C). The complete trapping of NO lasted for
a longer time (80–450 s) for all oxide catalysts. Noticeably,
a considerable amount of NO2 (170–200 ppm, Figure 2C)
was generated while NO concentration was only recovered
to 150–450 ppm, much lower than 800 ppm supplied. The
total concentration of NO and NO2 (NOx) was only 300–650
ppm, indicating that 150–500 ppm NO was seemingly
transformed to other nitrogen species, most probably N2,
and N2O. Therefore, the adsorption of NO in O2 and N2 stream
at 300 °C is additionally accompanied by two apparent
reactions: oxidizing NO to NO2 and decomposing NO to N2
as in the report by Li and Armor that Cu–ZSM-5 catalyst
dispersproportionates NO to N2O and NO2 (26).

Figure 3 shows desorption progresses of NOx from CMXAO
catalysts upon heating from 100 to 650 °C that previously
adsorbed NO at 100 or 300 °C. Obviously, NOx desorption
follows a two-step process in the case of NO adsorption at
100 °C, the lower-temperature one occurring at 180–200 °C.
while the higher-temperature one occurring at 275–445 °C (Figure 3A). The predominant species is NO, with NO₂ concentration being less than 30 ppm in all cases (not shown here). Significantly, the substitution of Al by Fe, Mn, Zr, or La increases the temperature of the second process from 275 to 350–445 °C (Figure 3A) and also intensifies both desorption bands, that is, increases the NO adsorption amount at 100 °C (Table 1).

In the case of NO adsorption at 300 °C (Figure 3B and 3C), only the higher-temperature desorption band appears, so the lower-temperature desorption is responsible for the less stable nitrogen species formed at 100 °C. Also, a considerable amount of NO₂ is desorbed at 250–500 °C from all catalysts (Figure 3C).

In particular, catalyst CMLAO has broader and more intense desorption bands while catalyst CMMAO has the weakest bands both at 100 and 300 °C, with the NO desorption band from CMLAO saturated with NO at 300 °C significantly broader and more intense (Figure 3B). It is surprising to note that the NO adsorption amount by CMLAO at 300 °C (7.56 mg/g) is much higher than that at 100 °C (4.69 mg/g). Such excellent performance in NO storage could be resulted from the well-balanced tradeoff in the three active storing components in this catalyst.

**NO Sorption Mechanism in O₂.** During NO adsorption on catalysts CMXAO, various forms of nitrates and nitrites are generated (17). In our belief, the main route leading to the formation of these nitrates and nitrites in the initial period at 100 and 300 °C is (8, 9)

\[
4\text{NO} + \text{O}_2 + 2\text{O}^{2-} \rightarrow 4\text{NO}_2^{-} \quad (1)
\]

The formed NO₂⁻ can be further transferred to various nitrates (8, 9), for example, via further oxidation (2) and disproportionation (3):

\[
4\text{NO}_2^{-} + 2\text{O}_2 \rightarrow 4\text{NO}_3^{-} \quad (2)
\]

\[
3\text{NO}_2^{-} \rightarrow 2\text{NO} + \text{NO}_3^{-} + \text{O}_2^{-} \quad (3)
\]

Simultaneously, some possible routes undergo on the catalyst surface:

\[
8\text{NO} + 4\text{O}_2 \rightarrow 3\text{N}_2\text{O}_2^{-} + 2\text{NO}_3^{-} \quad (4)
\]

\[
2\text{NO} + \text{O}_2 + \text{O}^{2-} \rightarrow \text{NO}_2^{-} + \text{NO}_3^{-} \quad (5)
\]

Reaction 4 is the other disproportionation that can take place at 100−400 °C (9). The transition metals, particularly La(III), in CMXAO catalysts are expected to assist all the reactions to form nitrites and nitrates. These nitrites and nitrates are supposed to spill over to the sites with higher basicity, such as those associated with Mg and Al. As these reactions are going on, the available sites with higher basicity are all occupied, so that the freshly formed nitrites and nitrates are temporarily stored on the sites with less basicity, such as those associated with the transition metal, so they are less thermally stable and liable to desorb, which leads to an apparent steady state in the outlet gas composition. For example, the least stable nitrites first undergo desorption during NO adsorption at 100 °C (9):

\[
4\text{NO}_2^{-} \rightarrow 4\text{NO} + \text{O}_2 + 2\text{O}^{2-} \quad (6)
\]

\[
2\text{NO}_2^{-} \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2^{-} \quad (7)
\]

Since NO₂ in the outlet stream was detected at only 5–10 ppm at 100 °C for all catalysts, disproportionation (7) should be very limited. However, at 300 °C, most nitrites, stable or less stable, could join desorption, like eqs 6 and 7, together with decomposition of some nitrates concurrently:

\[
4\text{NO}_3^{-} \rightarrow 4\text{NO}_2 + \text{O}_2 + 2\text{O}^{2-} \quad (8)
\]

In the outlet stream, NO₂ was monitored at 150–200 ppm that presumably comes from eqs 7 and 8 as well as the following catalytic surface reaction:

\[
2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \quad (9)
\]

Moreover, as mentioned previously for NO adsorption at 300 °C, 150–500 ppm NO₃ (NO + NO₂) is converted to other forms of nitrogen species, most possibly N₂O and N₂ (27) via the following consecutive decomposition reactions:

\[
\text{N}_2\text{O}_2^{-} \rightarrow \text{N}_2\text{O}_2^{-} + \text{O}^{2-} \quad (10)
\]

As reported (9, 26), the two transient species N₂O₂⁻ and

\[
2\text{N}_2\text{O}_2^{-} \rightarrow 2\text{N}_2 + \text{O}_2 \quad (11)
\]

N₂O₂⁻ decompose at 200–400 °C, so eqs 10 and 11 could account for NO decomposition at 300 °C. In our opinion, the transition metals in presence catalyze the formation of hyponitrite [N₂O₂²⁻] at 300 °C:

\[
2\text{M}^{2+} + 2\text{NO} \rightarrow \text{M}_2^{3+} - (\text{N}_2\text{O}_2^{-})_{\text{[s]}} \quad (12)
\]
where the metal species $M^{2+}$ could be transiently formed from $M^{3+}$ via the oxidation of NO (17), as observed in H$_2$ reduction. As a result, more NO directly decomposes to N$_2$ during the adsorption at 300 °C, which is also pursued for NO$_x$ storage/reduction catalysts.

**Effects of H$_2$O and CO$_2$ on NO Adsorption/Desorption.**

Since H$_2$O and CO$_2$ are inevitable under real operating conditions, their impact on NO$_x$ storage/reduction needs to be clarified. Catalyst CMLAO ($Co_{2.5}Mg_{0.5}La_{0.5}Al_{0.5}$-oxide) was chosen for this test as it shows the best performance in NO$_x$ storage. The resultant profiles of NO adsorption in O$_2$, CO$_2$, and H$_2$O on this catalyst are shown in Figure 4.

In general, both CO$_2$ and H$_2$O show the negative impact on NO adsorption. First, the existence of CO$_2$ or H$_2$O shortens the time for complete trapping NO$_x$ from 210 to 100–170 s at 100 °C and from 450 to 200–300 s at 300 °C, respectively (Figure 4A and 4D). Second, the recovery to the steady-state concentration (i.e., 750 ppm at 100 °C and 300–350 ppm at 300 °C) is much quicker in the presence of CO$_2$ or H$_2$O (Figure 4A and 4D). Individually, the negative impact of H$_2$O seems greater than that of CO$_2$ on NO adsorption at 100 and 300 °C while their influence is not additive (Figure 4A and 4D) (28). Particularly, CO$_2$ assists NO-to-NO$_2$ conversion but H$_2$O inhibits it during the later stage of NO adsorption at 300 °C (Figure 4C). Accordingly, CO$_2$ inhibits the NO recovery while H$_2$O assists it (Figure 4B). In addition, NO$_2$ is only at 5–10 ppm in the outlet stream at 100 °C while 100–300 ppm NO$_2$ is converted from NO at 300 °C (Figure 4C). These observations on the CO$_2$/H$_2$O influences are consistent with the previous report on Pt/Ba/Al$_2$O$_3$ (28).

As for NO$_x$ desorption from catalyst CMLAO, the presence of CO$_2$ or H$_2$O in the stream seems not to affect the desorption patterns (see Supporting Information Figure 3S) but decreases the desorption amount, that is, the storage amount, by 50–70% on CMLAO at 100 and 300 °C (see Supporting Information Table 2S). The similar desorption behaviors suggest that CO$_2$ and H$_2$O mainly inhibit the sorption reactions to a great extent during NO adsorption.

The negative impacts of CO$_2$ on NO adsorption could be understood in terms of the NO adsorption processes. The evolution of in-situ IR spectra of CMLAO (see Supporting Information Figure 4S) indicates that at 100 °C, various nitrites are formed at the beginning and most are kept unchanged until 60 min, with little amount being further oxidized to nitrate. At 300 °C, both nitrites and nitrate are generated at the beginning while the amount of nitrates becomes more and more over time. The formation and storage of these nitrites and nitrates are severely influenced by the presence of CO$_2$. First of all, CO$_2$ competes to occupy the basic sites of the catalyst, such as those O$^{2-}$ associated with Mg, Al, and transition-metal cations. As a result, the basic sites available for storing the various nitrites and nitrates thus become fewer, and thus the NO storage on the catalyst becomes less. Second, CO$_2$ seems to assist the conversion of NO to NO$_2$ at 300 °C (Figure 4C). Since some basic sites (more possibly with stronger basicity, such as those associated with Mg and Al) are occupied by CO$_2$, and the formed carbonate is more thermally stable (28), formation and storage of NO$_2$ via eqs 2–5 can only take place on some sites with weaker basicity (associated with transition-metal, etc.). These nitrites are less thermally stable and are easily decomposed via eqs 7 and 8, which seem to convert more NO to NO$_2$ catalytically at 300 °C.

The water effect could be understood in terms of the hydration of Mg and Al oxide. The hydration affects the formation of Mg and Al nitrates/nitrites (28) and, moreover, affects the adsorption process. Since the hydration presumably causes the volume expansion and blocks some micropores, the accessible surface area for NO adsorption is decreased to some extent. Therefore, the formation/storage reactions are limited to some degree. The hydration may also involve the transition metals, which may further limit some catalytic adsorption reactions.

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**Supporting Information Available**

Nominal composition and lattice parameters of the mixed oxides, the NO adsorption amount of CMLAO under various atmosphere, DSC, and TPR profiles of the mixed oxides, NO$_x$ desorption profile of CMLAO under various conditions as well as in-situ IR spectral evolution of CMLAO.
Literature Cited


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