Enhanced activity of CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst for lean NO$_x$ storage and reduction at high temperatures$^\dagger$

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Herein, we designed a new NO$_x$ storage and reduction CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst operating within the high temperature region of 350–550 °C. Compared with the Al$_2$O$_3$ supported catalyst with the same Cu and K loading, it exhibits superior NO$_x$ storage and reduction performance. The NO$_x$ reduction percentage (NRP) of the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst remains above 90% over a wide temperature range (400–550 °C), and reaches the highest NRP of 99.9% at 450 °C with the N$_2$ selectivity of 99.7%. Uncovered CuO particles with better reducibility exist on the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst, with the high NO$_x$ oxidation and reduction ability above 400 °C. Potassium carbonates on the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst mainly exist in three forms, including free ionic carbonate, bridging bidentate carbonate and chelating bidentate carbonate. Under lean-burn conditions, most of carbonates on the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst can store NO$_x$ to form nitrates, but only parts of them participate in NO$_x$ storage on the CuO/K$_2$CO$_3$/Al$_2$O$_3$ catalyst. The MgAl$_2$O$_4$ support offers additional sites for NO$_x$ adsorption, while the formed nitrate on it shows low thermal stability. So, NO$_x$ is mainly stored on K$_2$CO$_3$ at high temperatures, because MgAl$_2$O$_4$ can enhance the thermal stability of the supported K$_2$CO$_3$ on it. Our results show that the thermal stability of K$_2$CO$_3$ directly determines the thermal stability of the formed nitrates. Accordingly, the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst shows the high NSR activity because of the efficient redox ability of CuO and high thermal stability of K$_2$CO$_3$ at high operating temperatures.

1. Introduction

Modern lean-burn engines usually operate at a high air/fuel ratio, which results in a high fuel utilization efficiency.$^1$ Unfortunately, the emitted NO$_x$ (NO and NO$_2$) is hardly removed over the conventional three way catalysts (TWC) because of the presence of excess oxygen. With the increasing NO$_x$ emission limit, it is urgent to develop effective catalytic after-treatment systems.$^{2,3}$ To solve this problem, methodologies for NO$_x$ storage and reduction (NSR) and selective catalytic reduction (SCR) of NO$_x$ are being developed.$^{4,5}$ Presently, the NSR technology is a preferred choice especially for light duty lean-burn engines.$^{6,7}$

The process of NSR, also known as lean NO$_x$ trap (LNT), is operated in alternative lean-burn/fuel-rich atmospheres, which mainly includes: NO$_x$ is captured by alkali/alkali earth components ($e.g.$ barium and potassium) within a long lean-burn period (1–2 min); the trapped NO$_x$ species is released and then reduced to harmless N$_2$ by precious group metals ($e.g.$ Pt and Rh) within a subsequent short fuel-rich period (3–20 s).$^{4,8}$ High NO$_x$ removal efficiency has been achieved over the Pt/BaO/Al$_2$O$_3$ catalyst developed by the Toyota company within a narrow temperature window of 300–400 °C.$^{9–15}$ However, some newly developed lean-burn gasoline engine technologies, such as gasoline direct injection (GDI), are required to operate at higher temperatures than normal. Under this condition, the activity of the traditional Pt/BaO/Al$_2$O$_3$ NSR catalyst significantly drops.$^{16,17}$ When the operating temperature exceeds 400 °C, the solid-phase reaction between BaO and Al$_2$O$_3$ to form BaAlO$_4$ will lower the surface area and reduce the NO$_x$ storage sites.$^{18}$ Pt sintering also hampers the reduction of NO$_x$ from cycle to cycle.$^{19,20}$ Furthermore, the low thermal stability of barium nitrates declines its application at high operating temperatures, which is believed to be the essential factor to limit the NO$_x$ storage capacity.$^{19,21}$ Thus, it is urgent to develop a NSR catalyst with good high-temperature performance.
It was reported that mixing an alkaline earth metal oxide with Al2O3 could enhance the basicity of the support and also improve the thermal stability of the trapped nitrates.\textsuperscript{10} MgAl2O4, as one of these mixed oxides, has been employed as support of high-temperature NSR catalysts. Through supported on MgAl2O4, the stability of nitrate species is strongly improved whether on potassium sites or barium sites,\textsuperscript{16,18} and Pt sintering can also be effectively inhibited.\textsuperscript{23} Additionally, the MgAl2O4 support can provide extra storage sites for NOx.\textsuperscript{24} Hence, we chose MgAl2O4 as the support of NSR catalysts operated at high temperatures.

Additionally, to lower the price of NSR catalysts, it is valuable to substitute Pt with non-noble metal components. In the previous study, the perovskite-type oxides were used in replacement of platinum-based catalyst, such as BaFeO\textsubscript{3−x}, LaCoO\textsubscript{3} and La\textsubscript{1−x}Sr\textsubscript{x}CoO\textsubscript{3}.\textsuperscript{25−28} The transition metal elements of manganese and copper were also studied as substitutes for platinum.\textsuperscript{29,30} It was reported that Cu/K\textsubscript{2}Ti\textsubscript{2}O\textsubscript{5} could be applied over a wide temperature range (200−600 °C) with the mutual transformation of different structures.\textsuperscript{31}

As for the storage material, it is generally admitted that potassium-based catalysts have higher ability to storage NO\textsubscript{x} at high temperatures (above 400 °C) than barium-based ones due to its stronger basicity and better mobility.\textsuperscript{32} Potassium is more suitable as the storage element for the high-temperature NSR catalyst.\textsuperscript{33}

Based on the above analysis, it is interesting to design a new NSR catalyst with CuO as the NO\textsubscript{x} oxidation and reduction center, potassium as the NO\textsubscript{x} storage element and MgAl2O4 as the support material. To the best of our knowledge, the reasonably designed CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl2O4 catalyst herein has not been reported before.

In this study, we prepared the CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl2O4 catalyst by successive impregnation method. The Al\textsubscript{2}O\textsubscript{3}-supported catalysts were prepared by co-precipitation method. A certain amount of Mg(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O and Al(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O was dissolved and mixed with vigorous stirring. The pH value of the aqueous solution was adjusted to 9.5 by addition of NH\textsubscript{3}·H\textsubscript{2}O. The mixture was aged at 65 °C for 12 h and then filtrated. The obtained solid was dried at 120 °C for 12 h and then calcined at 800 °C for 5 h. The commercial γ-Al2O3 support (Tianjin Chemical Research & Design Institute) was pre-treated at 600 °C before using.

### 2.1. Catalyst preparation

The CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl2O4 catalyst was prepared by successive incipient wetness impregnation. The support was immersed into the solution of Cu(NO\textsubscript{3})\textsubscript{2}·3H\textsubscript{2}O, dried at 120 °C and then calcined at 600 °C for 4 h. Subsequently, K\textsubscript{2}CO\textsubscript{3} was loaded on the above powder by incipient wetness impregnation. The final sample was obtained after calcination at 600 °C for 2 h. The weight loadings of Cu and K were both 10%.

For comparison, the CuO/K\textsubscript{2}CO\textsubscript{3}/Al2O3 catalyst was also prepared by incipient wetness impregnation with the same process. The weight loadings of Cu and K were both 10%. The K\textsubscript{2}CO\textsubscript{3}/MgAl2O4, K\textsubscript{2}CO\textsubscript{3}/Al2O3, CuO/MgAl2O4 and CuO/Al2O3 samples were prepared with the same method. The weight loadings of Cu or K was also 10%.

### 2.2. Catalyst characterization

The measurement of the specific surface area (S\textsubscript{BET}) was carried out at −196 °C on a Quantachrome QuadraSorb SI instrument. Before measurements, the samples were degassed in vacuum at 300 °C for 3 h to remove the adsorbed species.

XRD analysis was conducted on an X’pert Pro rotatory diffractometer (PANalytical Company, Cu K\textalpha{} radiation λ = 0.15418 nm) operating at 40 mA and 40 kV. The diffraction data were collected in the 10 to 90° range at a step size of 0.02°. The crystallite sizes of CuO were calculated by using Scherrer equation:

\[
D = \frac{K \lambda}{\beta \cos \theta}
\]

D is the crystallite size. K is a constant. \(\lambda\) is the wavelength of the X-ray device. \(\beta\) is the full width half maximum. \(\theta\) is the Bragg’s angle.

XPS measurements were carried out by using a PHI-1600 ESCA spectrometer with Mg K\textalpha{} (1253.6 eV) as radiation source. The base pressure in sample chamber was 5 × 10\textsuperscript{−8} Pa. The binding energy (BE) peak of C 1s at 284.6 eV was employed to be standard to calibrate the recorded spectra.

The tests of XANES were performed on the 14 W1 beamline of Shanghai Synchrotron Radiation Facility. Tests were operated at 250 mA and 3.5 GeV. A Si (1 1 1) double-crystal monochromator was employed to monochromatize X-ray. A copper foil was used for energy calibration.

The morphologies of the catalysts were observed by SEM (S-4800, Hitachi). Before the SEM test, the samples were coated on a thin Pt layer to improve the electrical conductivity.

H\textsubscript{2}-TPR experiments were carried out on the TP-5079 TPDRO apparatus (Xian quan). The reduction gas is 8 vol% H\textsubscript{2}/N\textsubscript{2} with a flow rate of 30 mL min\textsuperscript{−1}. The weight of sample used for test is 30 mg. The sample was heated from room temperature (RT) to 900 °C, and the heating rate is 10 °C min\textsuperscript{−1}.
CO₂-TPD experiments derived from carbonate decomposition tests were carried out on a Thermo-Finnigan TPDRO 1100. The samples were heated in highly pure helium gas (20 mL min⁻¹) from RT to 900 °C. The heating rate was 10 °C min⁻¹.

NOₓ-TPD test was conducted in a quartz-tubular continuous flow reactor (i.d. = 4 mm). The samples were heated in pure N₂ (400 mL min⁻¹) from 50 °C to 750 °C and the temperature ramp is 5 °C min⁻¹. Before the measurements, the samples were saturated with NOₓ in the lean gas (400 ppm of NO, 5% O₂, balanced by N₂) at 450 °C.

The Fourier-transforming infrared spectroscopy (FT-IR) experiment was performed on a Thermo Nicolet Nexus spectrometer. The fresh sample and KBr were mixed with a weight ratio of 1 : 100, and pressed into a pellet. The spectra based on 32 scans were collected in 400–4000 cm⁻¹ with resolution of 4 cm⁻¹. The spectra were recorded in air at RT.

2.3. Activity tests

The isothermal NOₓ storage and reduction experiments of catalysts were carried out in a quartz-tubular continuous flow reactor (i.d. = 4 mm) using 240 mg of the fresh catalysts (40–60 mesh) from 350 to 550 °C with an increment of 50 °C. It was measured by 20 lean/rich (L/R) cycles (L/R = 50/10 s; lean gas 400 ppm of NO, 5% O₂, balanced by N₂; rich gas 1000 ppm C₂H₂, balanced by N₂). The NOₓ concentrations were monitored online by a chemiluminescence NO–NO₂–N₂O analyzer (Model 42i-3HL, Thermo Scientific). The total gas flow rate was 400 mL min⁻¹, corresponding to a weight hourly space velocity of 100 000 mL g⁻¹ h⁻¹. Meanwhile, the concentration of the byproduct N₂O was monitored online by an N₂O modular gas analyzer (S710, SICK MAIHAK).

The isothermal NOₓ storage experiments of the catalysts were carried out in the lean atmosphere (400 ppm of NO, 5% O₂, balanced by N₂) in the same reactor as above mentioned. The NOₓ concentrations were also monitored by the same analyzer. The total gas flow rate was 400 mL min⁻¹, corresponding to a weight hourly space velocity of 100 000 mL g⁻¹ h⁻¹.

The NOₓ reduction percentage (NRP) was calculated according to the steady lean/rich cycle as the following formula:

\[
NPR = \left( \frac{\left[ NO_x \right]_{\text{inlet}} \times t_1 - \int \left[ NO_x \right]_{\text{outlet}} \, dt}{\left[ NO_x \right]_{\text{inlet}} \times t_1} \right) \times 100\%
\]

The NSC was taken after the NOₓ storage process prolonged 60 min and calculated as the following formula:

\[
\text{NSC} = \left( \frac{\left[ NO_x \right]_{\text{inlet}} \times V \times t_2}{N_0 \times m} \right) \times \text{storage ratio} \times 10^{-6} \text{ mmol g}^{-1}
\]

The storage ratio was calculated as the following formula:

\[
\text{Storage ratio} = \left( \frac{\left[ NO_x \right]_{\text{inlet}} \times t_2 - \int \left[ NO_x \right]_{\text{outlet}} \, dt}{\left[ NO_x \right]_{\text{inlet}} \times t_2} \right)
\]

[m] is the weight of the sample, \( t_1 \) is the lean period in one L/R cycle, \( t_2 \) is 60 min, storage radio is the percentage of the stored NOₓ to the introduced one.\(^ {33} \)

3. Results and discussion

3.1. NOₓ storage capacity measurement

NOₓ storage tests were carried out in the temperature range of 350–550 °C. The evolution of outlet NOₓ is depicted in Fig. 1. The NSC was calculated and summarized in Table 1. Fig. 1a shows the NSC profiles of the CuO/K₂CO₃/MgAl₂O₄ catalyst at the different temperatures. The NOₓ storage capacity of the CuO/K₂CO₃/MgAl₂O₄ catalyst varies with the increased reaction temperature. At 350 °C, the NOₓ trapping kinetics is too slow, inducing the low NSC. Fig. 1a shows that after introducing the feeding gas above 400 °C, a rapid NOₓ storage behavior occurs and the NOₓ signal diminishes sharply. Subsequently, the “lean trap” period is observed, namely the stage during which NOₓ is completely captured on the catalysts and no NOₓ is released. Then, the NOₓ concentration gradually recovers to the inlet level until saturation. Probably, CuO is activated above 400 °C for NO oxidation to generate NO₂, which is beneficial to NOₓ storage under lean-burn conditions.\(^ {34,35} \) Meanwhile, the stored NOₓ gets thermally unstable. With the rising of the reaction temperature, the desorption rate of the released NOₓ from the catalysts is accelerated, as well as the equilibrium of the NOₓ storage process. The largest NSC uptake of the CuO/K₂CO₃/MgAl₂O₄ catalyst is obtained at 450 °C, which is the optimum
To investigate the thermal stability of the trapped NO storage sites, the NO to NO2 conversion of the catalysts was measured, and the results were calculated and summarized in Table 1. The NO to NO2 conversion of the two catalysts are very similar at low temperatures. The NO to NO2 conversion of the CuO/K2CO3/MgAl2O4 catalyst decreases slightly because a small amount of the trapped NO decomposes at high temperatures. The NO to NO2 conversion of the CuO/K2CO3/Al2O3 catalyst increases with temperature, reaching a maximum at 450 °C, which is comparable to or even better than the literature data.\cite{17,36,51} When the reaction temperature continues to increase, the NO to NO2 conversion of the CuO/K2CO3/MgAl2O4 catalyst decreases slightly because a small amount of the trapped NO decomposes at high temperatures. Fig. 1b shows the NO2 concentration profiles on the CuO/K2CO3/Al2O3 catalyst at the different temperatures. Similarly, the CuO/K2CO3/Al2O3 catalyst also presents a volcano-type tendency of NSC values in the temperature range of 350–550 °C. Maximum storage capacity is achieved at 400 °C on CuO/K2CO3/Al2O3 and the NSC value is 0.88 mmol g\(^{-1}\). Differently from the CuO/K2CO3/MgAl2O4 catalyst, the CuO/K2CO3/Al2O3 catalyst nearly presents no “lean trap” period in the NO2 storage profiles. Additionally, the CuO/K2CO3/MgAl2O4 catalyst achieves maximum NSC value at 450 °C, which is 50 °C higher than that of the CuO/K2CO3/Al2O3 catalyst. With further increasing the reaction temperature above 400 °C, the NSC value of the CuO/K2CO3/Al2O3 catalyst decreases seriously, whereas, the CuO/K2CO3/MgAl2O4 catalyst can maintain the large NSC values, making it suitable for the NSR reaction at high temperatures. The NO to NO2 conversion of the CuO/K2CO3/MgAl2O4 and CuO/K2CO3/Al2O3 catalysts was also measured, and the results were calculated and summarized in Table 1. The NO to NO2 conversions of the two catalysts are very similar because the oxidation of NO to NO2 is thermodynamically limited at high temperatures.\cite{5,17,18}

The distinct difference of the NO2 storage behavior at high temperature between the CuO/K2CO3/MgAl2O4 and CuO/K2CO3/Al2O3 catalysts probably results from the different thermal stability of the formed nitrate during the NO2 storage reaction. To investigate the thermal stability of the trapped NOx on the catalysts, the NOx-TPD experiments were conducted after the saturated adsorption of NOx at 450 °C. Fig. 2 shows the NOx-TPD profiles of the CuO/K2CO3/MgAl2O4, CuO/K2CO3/Al2O3 and CuO/MgAl2O4 catalysts. In the profile of the CuO/MgAl2O4, a single NOx desorption peak is observed at 365 °C, which is attributed to the decomposition of nitrates species formed on the MgAl2O4 support, confirming that the support offers additional sites for NOx adsorption. It is likely caused by the strong basicity of MgAl2O4. However, the MgAl2O4 support is not the main NOx storage sites at the high temperatures as indicated by its small desorption amount and poor thermal stability. The desorption peak located at 481 °C in the profile of the CuO/K2CO3/Al2O3 catalyst can be ascribed to the decomposition of KNO3 on it. Two desorption peaks are clearly observed in the profile of the CuO/K2CO3/MgAl2O4 catalyst. The first peak at 365 °C is assigned to the NOx desorption from the MgAl2O4 support as mentioned above. The latter peak appearing at 649 °C can be attributed to the desorption of the stored NOx species on K2CO3. Thus, the K2CO3 is identified as the main NOx storage sites according to the large desorption amount and high thermal stability. Meanwhile, a distinct difference in the decomposition temperatures of KNO3 between the CuO/K2CO3/Al2O3 (481 °C) and CuO/K2CO3/MgAl2O4 catalysts (649 °C) is observed, suggesting the higher thermal stability of the nitrates on the K sites of the CuO/K2CO3/MgAl2O4 catalyst, which is the main reason of its higher NOx storage ability at high temperatures. The components of CuO and K2CO3 in the catalyst are designed to act as the NOx oxidation sites and storage sites, respectively. To clarify the roles of these two components, the stationary NOx storage tests were also performed over the K2CO3-free or CuO-free catalysts. In Fig. S1,\textsuperscript{4} the K2CO3-free catalyst of CuO/MgAl2O4 and CuO-free catalysts of K2CO3/Al2O3 and K2CO3/MgAl2O4 show the poor NOx adsorbability. The NSC of the CuO/MgAl2O4 sample is only 0.11 mmol g\(^{-1}\), because of the absence of K2CO3, suggesting that K2CO3 is the main NOx storage sites. The NSC values of the K2CO3/Al2O3 and K2CO3/MgAl2O4 catalysts are 0.43 mmol g\(^{-1}\) and 0.60 mmol g\(^{-1}\), respectively. The decline in the NSC values suggests that the NOx oxidation ability of CuO plays a significant role in the NOx storage process, because NOx oxidized from NO is considered to be more easily captured than NO over NSR catalysts.\cite{3,18,39} The result above indicates that both the CuO and K2CO3 play the important roles in the NOx storage process.

### Table 1  NRP, NSC and NO to NO2 conversion of the catalysts

<table>
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<tr>
<th>Catalysts</th>
<th>T (°C)</th>
<th>NRP (%)</th>
<th>NSC (mmol g(^{-1}))</th>
<th>NO to NO2 conversion (%)</th>
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<td>CuO/K2CO3/MgAl2O4</td>
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3.2. NOx storage/reduction in the lean–rich cycles

The NOx storage and reduction tests in the periodical lean/rich cyclic atmospheres (50 s/10 s) were carried out in the temperature range of 350–550 °C. The evolution of outlet NOx is depicted...
in Fig. 3. The NRP was calculated and summarized in Table 1. Fig. 3a shows the concentration of outlet NOx for the CuO/K2CO3/MgAl2O4 catalyst during the lean–rich cycles. The NSR performance of the CuO/K2CO3/MgAl2O4 catalyst behaves differently depending on the reaction temperatures. At 350 °C, the NRP of the catalyst is 75.6%. The escaping NOx increases with the prolonged operating period because the NOx can hardly be reduced. When the reaction temperature is above 400 °C, the NSR performance of the CuO/K2CO3/MgAl2O4 catalyst improves greatly. As the profiles of the NOx concentration during the lean–rich cycles at 400–550 °C show, NOx in the feeding gas is captured completely in the lean period firstly; once switched to the rich period, the outlet NOx concentration is quite low, suggesting that most of the NOx can be reduced and nearly no NOx escapes. At 450 °C, the highest NRP of 99.9% is achieved. As the temperature continues to rise, the NRP decreases slightly. The NRP of CuO/K2CO3/MgAl2O4 catalyst can remain above 90% over a wide temperature range (400–550 °C). During the 20 lean–rich cycles, little N2O is produced as byproduct (Fig. S2†). The selectivity of 99.7% is obtained on the CuO/K2CO3/MgAl2O4 catalyst at 450 °C. Fig. 3b shows the concentration of outlet NOx for the CuO/K2CO3/Al2O3 catalyst during the lean–rich cycles. The NOx reduction ability of the CuO/K2CO3/Al2O3 catalyst at 350 °C is only 23.6%. At 400 °C, the CuO/K2CO3/Al2O3 catalyst obtains the highest NRP (80.8%). As the profile of the NOx concentration during the lean–rich cycles on the CuO/K2CO3/ Al2O3 catalyst at 400 °C shows, the catalyst exhibits outstanding NSR performance at the beginning, however, with the prolonged operating time, the storage sites can not be fully regenerated and the NOx removal activity decreases from cycle to cycle. With further increasing the reaction temperature, the NRP of the CuO/K2CO3/Al2O3 catalyst decreased gradually. At 550 °C, its NRP decreases sharply to 37.5%.

Compared with the CuO/K2CO3/Al2O3 catalyst, the NSR performance of the CuO/K2CO3/MgAl2O4 catalyst is consistently more effective and steady in the successive 20 cycles in the whole high-temperature region. Additionally, the NRP results show that the NOx reduction efficiency is poor at 350 °C for both catalysts. It indicates that CuO is only active above 400 °C, which coincides with the NSC results.

3.3. Structure of the catalysts

XRD is employed to investigate the structure of the catalysts. Fig. 4 shows the XRD patterns of the fresh catalysts and the catalysts after NOx storage at 450 °C. All of the diffraction peaks in Fig. 4a are well matched with spinel-type MgAl2O4 phase (JCPDS 21-1152). It indicates that the MgAl2O4 support is successfully synthesized after calcination at 800 °C with no other phase detected. Crystallized CuO phase (JCPDS 48-1548) with 2θ at 35.6°, 38.7° and 48.7° can be clearly identified on the CuO/K2CO3/MgAl2O4 and CuO/K2CO3/Al2O3 catalysts. No characteristic peak of K-related species is detected on the pattern of the fresh CuO/K2CO3/MgAl2O4 and CuO/K2CO3/Al2O3 catalysts in Fig. 4b and c, suggesting that the K-related species may be highly dispersed or in amorphous state. Additionally, the mean crystallite size of CuO was calculated on the basis of the XRD data by using Scherrer equation. The mean crystallite size of CuO on the fresh CuO/K2CO3/MgAl2O4 and CuO/K2CO3/Al2O3 catalysts is 24.4 and 22.4 nm, respectively.

The phase structure of the catalysts after NOx storage was also characterized as shown in Fig. 4d and e. After the NOx storage treatment at 450 °C, new diffraction peaks at 27.2°, 29.6° and 32.9° assigned to KNO3 phase (JCPDS 32-0824) emerge in the XRD patterns of the CuO/K2CO3/MgAl2O4 and CuO/K2CO3/Al2O3 catalysts. The transformation of carbonates to nitrates is revealed on the K-related storage sites. Stronger peaks of KNO3

![Fig. 3](https://example.com/fig3.png) NOx concentration curves during the lean/rich cycles over the (a) CuO/K2CO3/MgAl2O4 and (b) CuO/K2CO3/Al2O3 catalysts.
are observed in the XRD pattern of the CuO/K₂CO₃/MgAl₂O₄ catalyst than those of the CuO/K₂CO₃/Al₂O₃ catalyst, implying that more NOₓ was trapped on the CuO/K₂CO₃/MgAl₂O₄ catalyst. It is in good agreement with the results of NSC. Additionally, after the NOₓ storage, the crystallite size of CuO on the two catalysts is 25.0 and 24.6 nm, respectively, which is similar to the fresh catalysts. Probably, the CuO phase is the active site in the NSR reaction.

We measured the specific surface areas of the catalysts by N₂ physisorption. The MgAl₂O₄ support has a specific surface area of 100.2 m² g⁻¹, lower than the commercial-Al₂O₃ support (179.8 m² g⁻¹). After loading the same amount of Cu and K, the surface areas of the CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts drop to 60.5 and 109.8 m² g⁻¹, respectively. Combined with the NRP and NSC results, the CuO/K₂CO₃/MgAl₂O₄ catalyst owns the higher NSR activity in spite of the smaller specific surface area compared with the CuO/K₂CO₃/Al₂O₃ catalyst, suggesting that the specific surface area is not the key factor to determine the catalytic activity of the catalysts.

Fig. S3† shows the SEM image of the fresh CuO/K₂CO₃/MgAl₂O₄ catalyst to determine its morphology. The SEM image clearly indicates that the catalyst possesses dense lamellar and needle-like structure, which may be attributed to MgAl₂O₄ and K₂CO₃.

### 3.4. Chemical states of Cu- and K-species

To investigate the chemical states of the Cu- and K-species on the surface of the CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts, the XPS characterization was carried out, as shown in Fig. 5. Fig. 5a displays the XPS spectra in the Cu 2p region of the fresh CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts. For the two catalysts, the Cu 2p spectra are both composed of two typical peaks of Cu²⁺ at about 933.5 eV (Cu 2p₃/₂) and 952.9 eV (Cu 2p₁/₂) with a satellite shakeup at around 942.3 eV.¹⁻⁴ No Cu-related species other than CuO is observed, suggesting the NOₓ oxidation and reduction center of the two catalysts is CuO. The above result is in agreement with the XRD result in Fig. 4.

Fig. 5b shows the XPS spectra in the C 1s and K 2p region of the fresh CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts. An apparent peak centering at about 296.1 eV (K 2p₃/₂) accompanied by a less intense peak at about 293.0 eV (K 2p₁/₂) can be assigned to K⁺. Contamination carbon was taken as a reference at 284.6 eV. The C 1s peaks in the region of 278–287 eV are ascribed to the impurities or adventitious in the fresh catalysts.⁴⁷ The weak peak locating at 289.7 eV is related to surface carbonate species.⁴⁸ In Fig. 5c, the catalysts present a single asymmetric peak of O 1s at about 531.1 eV. It was reported that the C 1s and O 1s peaks of pure K₂CO₃ were at 288.1 eV and 531.1 eV.⁴⁷ Therefore, the C 1s at 289.7 eV and O 1s at 531.1 eV may be assigned to K₂CO₃ on the surface of the catalysts.⁴⁹ In the preparation process of the catalysts, a part of the K₂CO₃...
precursor on the catalysts has decomposed into K₂O and CO₂ during the calcination at 600 °C. However, the K₂O is easy to react with CO₂ and form K₂CO₃ when the samples are exposed in air. So, the detected K₂CO₃ by the XPS measurement probably results from the reaction of K₂O with CO₂ in air.⁵⁰

The binding energies and elemental compositions from the XPS data are given in Table 2. The surface atomic ratios of Cu/K of the fresh CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts are much lower than their theoretical composition (Cu/K = 0.62). It indicates that the K₂CO₃ may partially cover the CuO phase on the surface of the catalysts. The surface Cu/K atomic ratio of the CuO/K₂CO₃/MgAl₂O₄ catalyst is 0.29, larger than that of the CuO/K₂CO₃/Al₂O₃ catalyst (0.24). As we discussed in Fig. S1, the NO₃ storage process will be substantially hindered without the aid of CuO. The higher surface Cu/K ratio of the MgAl₂O₄-supported catalyst reveals that there is more CuO existing and uncovered on the surface of CuO/K₂CO₃/MgAl₂O₄ catalyst, which can improve the accessibility of the active CuO sites, and then enhance the catalytic activity.

To further identify the chemical state of Cu species, Fig. 6 shows the XANES spectra of Cu K-edge of the fresh CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts and the catalysts after NO₃ storage at 450 °C. The reference samples are Cu, CuO and CuO/CuO. Both of the two fresh catalysts show the similar shape and location of the adsorption edge to that of CuO.⁴¹ There is no Cu and CuO detected on the two catalysts. Therefore, the Cu species on the CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts is in the form of CuO. After NO₃ storage, the Cu K-edge of the spent catalysts are also the same as that for the fresh ones, suggesting that little change has taken place for the Cu species before and after reaction. It coincides with the XRD results in Fig. 4. Therefore, CuO is the active component of the CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts.⁴⁰⁴¹

The H₂-TPR experiment was conducted to elucidate the reducibility of the fresh catalysts, as shown in Fig. 7. No reduction reaction happens in the profile of the inert MgAl₂O₄ support. For contrast, pure CuO shows a H₂ consumption peak at 350 °C. CuO particles on the MgAl₂O₄ support and Al₂O₃ support can be reduced at much lower temperature of 240 °C and 238 °C, respectively. After 10% K loading on the CuO/MgAl₂O₄ sample, the main reduction peak shifts to 327 °C, which is close to the unsupported bulk CuO. Notably, a weak reduction peak at 264 °C is observed, which is assignable to the uncovered CuO on the CuO/K₂CO₃/MgAl₂O₄ catalyst. While after 10% K loading on the CuO/Al₂O₃ sample, the reduction of CuO occurs at above 300 °C. Herein, the only uncovered CuO on the CuO/K₂CO₃/MgAl₂O₄ catalyst can be easy to contact to H₂ and results in the similar reducibility of CuO as the CuO/MgAl₂O₄ catalyst. The K₂CO₃ loading on the catalysts may cover the CuO, which can hinder the diffusion of H₂ to CuO. Based on the H₂-TPR result, some of the uncovered CuO by K₂CO₃ exists on the CuO/K₂CO₃/MgAl₂O₄ catalyst, while the CuO on the CuO/K₂CO₃/Al₂O₃ catalyst is totally covered. Thus, the CuO/K₂CO₃/MgAl₂O₄ catalyst shows a better NSR performance than the CuO/K₂CO₃/Al₂O₃ catalyst.

Additionally, the released CO₂ via the decomposition of K₂CO₃ during the TPR process can dilute the feed gas and generate pseudo H₂ consumption peaks. The high temperature peaks at 724 °C and 763 °C can be assigned to the decomposition of bulk-like K₂CO₃.

### 3.5. Property of the supported potassium carbonates on the catalysts

To further investigate the thermal decomposition of K₂CO₃ species, the CO₂-TPD experiments of the fresh CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts were implemented, and the evolution profiles of CO₂ are presented in Fig. 8. As reported in the literature, two kinds of K₂CO₃ with different thermal stability can be distinguished as a function of decomposition temperature.⁴⁴ The reaction occurs as the following expression: K₂CO₃ → K₂O + CO₂. For the CuO/K₂CO₃/MgAl₂O₄ catalyst, the desorption of CO₂ at 304–640 °C is regard to the decomposition of unstable surface K₂CO₃ on the catalyst. The second desorption stage within 640–840 °C can be attributed to bulk/bulk-like K₂CO₃ species with the high thermal stability. For the CuO/K₂CO₃/Al₂O₃ catalyst, the desorption of CO₂ initiates at 245 °C. The unstable surface K₂CO₃ decomposes from 245 to 763 °C, and the bulk/bulk-like K₂CO₃ decomposes from 763 to 840 °C. By the integration of the CO₂-TPD curves area, we find that the CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts have similar amount of CO₂ desorption, suggesting that the amount of the desorbed K₂CO₃ is similar on the two catalysts. However, the amount of bulk/bulk-like K₂CO₃ on the CuO/K₂CO₃/MgAl₂O₄ catalyst is much larger than that on the CuO/K₂CO₃/Al₂O₃ catalyst, suggesting the higher thermal stability of the K₂CO₃ on the CuO/K₂CO₃/MgAl₂O₄ catalyst.

To further identify the chemical state of Cu species, Fig. 6 shows the XANES spectra of Cu K-edge of the fresh CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts and the catalysts after NO₃ storage at 450 °C. The reference samples are Cu, CuO and CuO/CuO. Both of the two fresh catalysts show the similar shape and location of the adsorption edge to that of CuO.⁴¹ There is no Cu and CuO detected on the two catalysts. Therefore, the Cu species on the CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts is in the form of CuO. After NO₃ storage, the Cu K-edge of the spent catalysts are also the same as that for the fresh ones, suggesting that little change has taken place for the Cu species before and after reaction. It coincides with the XRD results in Fig. 4. Therefore, CuO is the active component of the CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts.⁴⁰⁴¹

### Table 2 Spectra parameters obtained by XPS of the fresh catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Cu 2pₓ/₂ (eV)</th>
<th>K 2pₓ/₂ (eV)</th>
<th>O 1s (eV)</th>
<th>Cu/K (atomic%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO/K₂CO₃/MgAl₂O₄</td>
<td>933.5</td>
<td>295.9</td>
<td>531.1</td>
<td>0.29</td>
</tr>
<tr>
<td>CuO/K₂CO₃/Al₂O₃</td>
<td>933.8</td>
<td>296.1</td>
<td>531.1</td>
<td>0.24</td>
</tr>
</tbody>
</table>
In order to explicit the nature of K₂CO₃ species, the FT-IR technique was carried out for the fresh CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts, as well as the references of the bulk K₂CO₃ and MgAl₂O₄. Fig. 9 shows their FT-IR spectra. The characteristic peaks of the reference bulk K₂CO₃ appear at 1652 cm⁻¹, 1427 cm⁻¹, 1386 cm⁻¹ and 1110 cm⁻¹. The bands at 695 cm⁻¹ and 518 cm⁻¹ are assignable to typical MgAl₂O₄ spinel structure. Compared with the bulk K₂CO₃, the FT-IR spectra of the loaded K₂CO₃ on the fresh CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts shows an additional IR band at 1530 cm⁻¹, belonging to chelating bidentate carbonates.³² Thus, three kinds of K₂CO₃ species, including bridging bidentate carbonates (1652 cm⁻¹),³³ free ionic carbonate CO₃²⁻ (1410 cm⁻¹ and 1110 cm⁻¹)³² and chelating bidentate carbonates (1530 m⁻¹), co-exist on the fresh catalysts.

The IR spectra of the CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts after the NOₓ storage reaction at different temperatures were also collected to investigate to the reactivity of the different types of K₂CO₃. Fig. 10a(2–6) shows the IR spectra of the CuO/K₂CO₃/MgAl₂O₄ catalyst after the NOₓ storage reaction at different temperatures. As reported, both the ionic and bidentate nitrates presented on a series of K₂O/Al₂O₃ catalysts after NOₓ dosing.³⁴ The most intense peak at 1380 cm⁻¹ can be identified as ionic nitrates after the NOₓ storage.³²

The intensity of this peak varies with the reaction temperature of CuO/K₂CO₃/MgAl₂O₄ catalyst, the tendency of which is consistent with the NSC order. The intensity of this peak becomes strongest when the CuO/K₂CO₃/MgAl₂O₄ catalyst reacts at 450 °C. Differently from the fresh CuO/K₂CO₃/MgAl₂O₄ catalyst in Fig. 9, the IR bands of bridging bidentate carbonate and chelating bidentate carbonate almost disappear leaving a tiny amount of carbonate residue on the CuO/K₂CO₃/MgAl₂O₄ catalyst, suggesting most of carbonates on the CuO/K₂CO₃/MgAl₂O₄ catalyst participate in the NOₓ storage. Fig. 10b(2–6) shows the IR spectra of the CuO/K₂CO₃/Al₂O₃ catalyst after the NOₓ storage reaction at different temperatures. The peak at 1380 cm⁻¹ attributed to ionic nitrates can also be detected. However, the peaks at 1652 cm⁻¹ and 1530 cm⁻¹ do not completely disappear after the NOₓ storage process, suggesting that a part of the bridging bidentate carbonate and chelating bidentate carbonate in the CuO/K₂CO₃/Al₂O₃ catalyst can not completely store NOₓ at high temperatures. Comparing the IR spectra of the CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts after the NOₓ storage, there is more K₂CO₃ on CuO/K₂CO₃/MgAl₂O₄ transformed to nitrate. It suggests that the MgAl₂O₄ can improve the NOₓ storage efficiency of K₂CO₃ at high operating temperatures. Additionally, after NOₓ storage at 450 °C, the two catalysts were heated in the N₂ flow at 450 °C for 10 min. The IR spectra of the two catalysts after NOₓ-TPD are shown in Fig. 10a(7) and b(7). For the CuO/K₂CO₃/MgAl₂O₄ catalyst, the intensity of the peak at 1380 cm⁻¹ in Fig. 10a(7) has little change compared with Fig. 10a(4). For the CuO/K₂CO₃/Al₂O₃ catalyst, a distinct decrease of peak at 1380 cm⁻¹ in Fig. 10b(7) is observed compared with Fig. 10b(4). The different behaviors at 1380 cm⁻¹ on the two catalysts reveal that the nitrates on the CuO/K₂CO₃/MgAl₂O₄ catalyst exhibit higher thermal stability.

3.6. Thermal stability of the stored nitrates

The low thermal stability of the nitrate formed on NSR catalysts in the NOₓ storage reaction will limit their application at high operating temperatures.³⁰ In Fig. 2, the thermal stability of the nitrates on the K sites of the CuO/K₂CO₃/MgAl₂O₄ catalyst is
higher compared with the CuO/K₂CO₃/Al₂O₃ catalyst. Based on the previous report, the strength of N-O bond in nitrate is sensitive to the metal cations exposed from the support because of electronic polarization. The charge density of Al³⁺ and Mg²⁺ is 4.8 × 10⁻³ e nm⁻³ and 7.5 × 10⁻⁴ e nm⁻³. Lower extent of polarization of Mg²⁺ makes N-O bond less prone to breakage, and thus the nitrates on the CuO/K₂CO₃/MgAl₂O₄ show the higher thermal stability.

Additionally, in our study, the temperatures of NOx desorption correlate to the temperatures of K₂CO₃ decomposition as mentioned in Fig. 8. Thus, the thermal stability of nitrates is related to the thermal stability of K₂CO₃. In other word, the nitrates with high thermal stability may be transformed from the thermal stable K₂CO₃. As discussed in Fig. 10, there is more K₂CO₃ with high thermal stability on the CuO/K₂CO₃/MgAl₂O₄ catalyst than that on the CuO/K₂CO₃/Al₂O₃, and this part of K₂CO₃ is the main storage sites in the high-temperature NSR reaction. Thus, the trapped nitrate on the CuO/K₂CO₃/MgAl₂O₄ catalyst shows the high thermal stability.

Through the above discussion, the CuO/K₂CO₃/MgAl₂O₄ catalyst can store much more NOx than CuO/K₂CO₃/Al₂O₃ catalyst above 400 °C, resulting from the former’s higher thermal stability of nitrates. The high thermal stability of nitrate is the main reason to induce the high NOx storage capacity of the CuO/K₂CO₃/MgAl₂O₄ catalyst at the high temperatures.

Therefore, with the high thermal stability of nitrates and the high redox capacity of CuO above 400 °C, the CuO/K₂CO₃/MgAl₂O₄ catalyst exhibits the prominent NRP performance at high operating temperatures.

4. Conclusion

Herein, we report the high NSR activity of the newly designed CuO/K₂CO₃/MgAl₂O₄ catalyst at high operating temperatures. As concerns of the NSR activity in successive 20 lean/rich cycles between 350–550 °C, the CuO/K₂CO₃/MgAl₂O₄ catalyst performs more effectively and steadily on De-NOx in alternative lean/rich atmospheres than the Al₂O₃-supported catalyst. Especially, the NO₂ reduction efficiency of the CuO/K₂CO₃/MgAl₂O₄ catalyst achieves a maximum value of 99.9% with a large NOx uptake of 1.56 mmol g⁻¹ at 450 °C. Meanwhile, a high N₂ selectivity of 99.7% was also obtained. The NRP of the CuO/K₂CO₃/MgAl₂O₄ catalyst maintains above 90% at 400–550 °C. While the NRP of the CuO/K₂CO₃/Al₂O₃ catalyst decreases sharply with the increased reaction temperatures.

The states of CuO and K₂CO₃ species have an apparent difference on the MgAl₂O₄ and Al₂O₃ supported catalysts. After K loading, CuO is probably covered by K₂CO₃. There is still a part of the uncovered CuO on the MgAl₂O₃ supported catalyst, but none for the Al₂O₃ supported catalyst. This part of CuO is beneficial for the oxidation and reduction of NOx in alternative lean/rich cycles. CuO exhibits the high redox ability at the temperatures above 400 °C. Based on the FT-IR results, the carbonates on the two catalysts can be classified into three types: free ionic carbonate, bridging bidentate carbonate and chelating bidentate carbonate. Most of the K₂CO₃ on the CuO/K₂CO₃/MgAl₂O₄ catalyst can convert to nitrates, but only a part of them participates on the CuO/K₂CO₃/Al₂O₃ catalyst. Moreover, our results show that the thermal stability of nitrate is consistent with the thermal stability of K₂CO₃. The formed nitrates during the lean operation on the CuO/K₂CO₃/MgAl₂O₄ catalyst have the high thermal stability, because of the high thermal stability of K₂CO₃ supported on the catalyst. Accordingly, the CuO/K₂CO₃/MgAl₂O₄ catalyst exhibits a high NSR activity at high operating temperatures and is a promising high-temperature NSR catalyst.

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