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 \(\text{NO}_x\) (\(\text{NO} + \text{NO}_2\)) is hardly removed over the conventional three way catalysts (TWC) because of the presence of excess oxygen. With the increasing \(\text{NO}_x\) emission limit, it is urgent to develop effective catalytic after-treatment systems.\(^2,3\) To solve this problem, methodologies for \(\text{NO}_x\) storage and reduction (NSR) and selective catalytic reduction (SCR) of \(\text{NO}_x\) are being developed.\(^4,5\) Presently, the NSR technology is a preferred choice especially for light duty lean-burn engines.\(^6,7\)

Herein, we designed a new \(\text{NO}_x\) storage and reduction \(\text{CuO}/K_2\text{CO}_3/\text{MgAl}_2\text{O}_4\) catalyst operating within the high temperature region of 350–550 °C. Compared with the \(\text{Al}_2\text{O}_3\) supported catalyst with the same Cu and K loading, it exhibits superior \(\text{NO}_x\) storage and reduction performance. The \(\text{NO}_x\) reduction percentage (NRP) of the \(\text{CuO}/K_2\text{CO}_3/\text{MgAl}_2\text{O}_4\) 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 \(\text{CuO}/K_2\text{CO}_3/\text{MgAl}_2\text{O}_4\) catalyst, with the high \(\text{NO}_x\) oxidation and reduction ability above 400 °C. Potassium carbonates on the \(\text{CuO}/K_2\text{CO}_3/\text{MgAl}_2\text{O}_4\) 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 \(\text{CuO}/K_2\text{CO}_3/\text{MgAl}_2\text{O}_4\) catalyst can store \(\text{NO}_x\) to form nitrates, but only parts of them participate in \(\text{NO}_x\) storage on the \(\text{CuO}/K_2\text{CO}_3/\text{Al}_2\text{O}_3\) catalyst. The \(\text{MgAl}_2\text{O}_4\) support offers additional sites for \(\text{NO}_x\) adsorption, while the formed nitrate on it shows low thermal stability. So, \(\text{NO}_x\) is mainly stored on \(K_2\text{CO}_3\) at high temperatures, because \(\text{MgAl}_2\text{O}_4\) can enhance the thermal stability of the supported \(K_2\text{CO}_3\) on it. Our results show that the thermal stability of \(K_2\text{CO}_3\) directly determines the thermal stability of the formed nitrates. Accordingly, the \(\text{CuO}/K_2\text{CO}_3/\text{MgAl}_2\text{O}_4\) catalyst shows the high NSR activity because of the efficient redox ability of \(\text{CuO}\) and high thermal stability of \(K_2\text{CO}_3\) at high operating temperatures.

The process of NSR, also known as lean \(\text{NO}_x\) trap (LNT), is operated in alternative lean-burn/fuel-rich atmospheres, which mainly includes: \(\text{NO}_x\) is captured by alkalified earth components (e.g., barium and potassium) within a long lean-burn period (1–2 min); the trapped \(\text{NO}_x\) species is released and then reduced to harmless \(\text{N}_2\) by precious group metals (e.g., Pt and Rh) within a subsequent short fuel-rich period (3–20 s).\(^8,9\) High \(\text{NO}_x\) 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.\(^9,13\) 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.\(^10,12\) When the operating temperature exceeds 400 °C, the solid-phase reaction between BaO and Al\(_2\)O\(_3\) to form BaAl\(_2\)O\(_4\) will lower the surface area and reduce the \(\text{NO}_x\) storage sites.\(^18\) Pt sintering also hampers the reduction of \(\text{NO}_x\) 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 \(\text{NO}_x\) storage capacity.\(^18,21\) 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. 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, and Pt sintering can also be effectively inhibited. Additionally, the MgAl₂O₄ support can provide extra storage sites for NOₓ. 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 BaFeO₃₋ₓ, LaCoOₓ and La₁₋ₓSrₓCoO₃₋ₓ. The transition metal elements of manganese and copper were also studied as substitutes for platinum. It was reported that Cu/K₂Ti₂O₅ could be applied over a wide temperature range (200–600 °C) with the mutual transformation of different structures.

As for the storage material, it is generally admitted that potassium-based catalysts have higher ability to storage NOₓ at high temperatures (above 400 °C) than barium-based ones due to its stronger basicity and better mobility. Potassium is more suitable as the storage element for the high-temperature NSR catalyst.

Based on the above analysis, it is interesting to design a new NSR catalyst with CuO as the NOₓ oxidation and reduction center, potassium as the NOₓ storage element and MgAl₂O₄ as the support material. To the best of our knowledge, the reasonably designed CuO/K₂CO₃/MgAl₂O₄ catalyst herein has not been reported before.

In this study, we prepared the CuO/K₂CO₃/MgAl₂O₄ catalyst by successive impregnation method. The Al₂O₃-supported catalyst with the same Cu and K loading was also prepared for comparison. The NOₓ storage/reduction performance within 350–550 °C of the two catalysts was comparatively investigated. Then, we characterized the catalysts by the X-ray diffraction (XRD), X-ray absorption near-edge structures (XANES), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), Fourier-transforming infrared spectra (FT-IR), H₂ temperature-programmed reduction (H₂-TPR), temperature-programmed desorption of COₓ (COₓ-TPD) and temperature-programmed desorption of NOₓ (NOₓ-TPD). Through the results of the above characterizations, we investigated the states of K- and Cu-species in CuO/K₂CO₃/MgAl₂O₄ and CuO/K₂CO₃/Al₂O₃ catalysts. We also discussed the thermal stability of nitrate on the catalysts and revealed how the CuO/K₂CO₃/MgAl₂O₄ catalyst improved the NSR performance at high temperatures.

## 2. Experimental section

### 2.1. Support and catalyst preparation

#### 2.1.1. Support preparation. The MgAl₂O₄ support was prepared by co-precipitation method. A certain amount of Mg(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O was dissolved and mixed with vigorous stirring. The pH value of the aqueous solution was adjusted to 9.5 by addition of NH₃·H₂O. 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.

#### 2.1.2. Catalyst preparation. The CuO/K₂CO₃/MgAl₂O₄ catalyst was prepared by successive incipient wetness impregnation. The support was immersed into the solution of Cu(NO₃)₂·3H₂O, dried at 120 °C and then calcined at 600 °C for 4 h. Subsequently, K₂CO₃ 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/K₂CO₃/Al₂O₃ catalyst was also prepared by incipient wetness impregnation with the same process. The weight loadings of Cu and K were both 10%. The K₂CO₃/MgAl₂O₄, K₂CO₃/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 (Sₐ) 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 Kα 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. λ is the wavelength of the X-ray device. β is the full weight half maximum. θ is the Bragg’s angle.

XPS measurements were carried out by using a PHI-1600 ESCA spectrometer with Mg Kα (1253.6 eV) as radiation source. The base pressure in sample chamber was 5 × 10⁻⁸ 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.

H₂-TPR experiments were carried out on the TP-5079 TPDRO apparatus (Xian quan). The reduction gas is 8 vol% H₂/N₂ with a flow rate of 30 mL min⁻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⁻¹.
CO₂-TPD experiments derived from carbonate decomposition 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.

NO₂-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 NO₂ 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 NO₂ 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 C₃H₆, balanced by N₂). The NO₂ concentrations were monitored online by a chemiluminescence NO–NO₂–NO analyzer (Model 421-HL, 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 a N₂O modular gas analyzer (S710, SICK MAIHAK).

The isothermal NO₂ 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 NO₂ 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 NO₂ reduction percentage (NRP) was calculated according to the steady lean/rich cycle as the following formula:

\[
\text{NPR} = \frac{[\text{NO}_2]_{\text{inlet}} \times t_1 - \int [\text{NO}_2]_{\text{Outlet}} \, dt}{[\text{NO}_2]_{\text{inlet}} \times t_1} \times 100\%
\]

The NSC was taken after the NO₂ storage process prolonged 60 min and calculated as the following formula:

\[
\text{NSC} = \frac{[\text{NO}_2]_{\text{inlet}} \times V \times t_2}{N_0 \times m} \times \text{storage ratio} \times 10^{-6} \text{ mmol g}^{-1}
\]

The storage ratio was calculated as the following formula:

\[
\text{Storage ratio} = \frac{[\text{NO}_2]_{\text{inlet}} \times t_2 - \int [\text{NO}_2]_{\text{Outlet}} \, dt}{[\text{NO}_2]_{\text{inlet}} \times t_2}
\]

3. Results and discussion

3.1. NO₂ storage capacity measurement

NO₂ storage tests were carried out in the temperature range of 350–550 °C. The evolution of outlet NO₂ 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 NO₂ storage capacity of the CuO/K₂CO₃/MgAl₂O₄ catalyst varies with the increased reaction temperature. At 350 °C, the NO₂ trapping kinetics is too slow, inducing the low NSC. Fig. 1a shows that after introducing the feeding gas above 400 °C, a rapid NO₂ storage behavior occurs and the NO₂ signal diminishes sharply. Subsequently, the “lean trap” period is observed, namely the stage during which NO₂ is completely captured on the catalysts and no NO₂ is released. Then, the NO₂ 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 NO₂ storage under lean-burn conditions.

Meanwhile, the stored NO₂ gets thermally unstable. With the rising of the reaction temperature, the desorption rate of the released NO₂ from the catalysts is accelerated, as well as the equilibrium of the NO₂ storage process. The largest NSC uptake of the CuO/K₂CO₃/MgAl₂O₄ catalyst is obtained at 450 °C, which is the optimum
Table 1 NRP, NSC and NO to NO2 conversion of the catalysts

| Catalysts          | T (°C) | NRP (%) | NSC (mmol g⁻¹) | NO to NO2 conversion (%) |
|--------------------|--------|---------|----------------|--------------------------|
| CuO/K₂CO₃/MgAl₂O₄ | 350    | 75.6    | 1.09           | 24.1                     |
|                    | 400    | 97.7    | 1.31           | 32.8                     |
|                    | 450    | 99.9    | 1.56           | 34.0                     |
|                    | 500    | 99.0    | 1.48           | 24.3                     |
|                    | 550    | 94.7    | 1.42           | 19.6                     |
| CuO/K₂CO₃/Al₂O₃   | 350    | 23.6    | 0.80           | 14.1                     |
|                    | 400    | 80.8    | 0.88           | 33.3                     |
|                    | 450    | 78.6    | 0.57           | 32.7                     |
|                    | 500    | 71.6    | 0.49           | 23.8                     |
|                    | 550    | 37.5    | 0.38           | 18.9                     |

The NO₂ storage reaction. The “lean trap” period lasts for more than 20 min and the NSC value is 1.56 mmol g⁻¹ at 450 °C, which is comparable to or even better than the literature data.¹⁴ When the reaction temperature continues to increase, the NSC of the CuO/K₂CO₃/MgAl₂O₄ catalyst decreases slightly because a small amount of the trapped NO₂ 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.⁴³⁻⁵⁻⁸⁻¹⁸

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 NO₂ on the catalysts, the NO₂-TPD experiments were conducted after the saturated adsorption of NO₂ at 450 °C. Fig. 2 shows the NO₂-TPD profiles of the CuO/K₂CO₃/MgAl₂O₄, CuO/K₂CO₃/Al₂O₃ and CuO/MgAl₂O₄ catalysts. In the profile of the CuO/MgAl₂O₄, a single NO₂ 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 NO₂ adsorption. It is likely caused by the strong basicity of MgAl₂O₄. However, the MgAl₂O₄ support is not the main NO₂ 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 NO₂ desorption from the MgAl₂O₄ support as mentioned above. The latter peak appearing at 649 °C can be attributed to the desorption of the stored NO₂ species on K₂CO₃. The K₂CO₃ is identified as the main NO₂ 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 NO₂ storage ability at high temperatures.

The components of CuO and K₂CO₃ in the catalyst are designed to act as the NO₂ oxidation sites and storage sites, respectively. To clarify the roles of these two components, the stationary NO₂ storage tests were also performed over the K₂CO₃-free or CuO-free catalysts. In Fig. S1, the K₂CO₃-free catalyst of CuO/MgAl₂O₄ and CuO-free catalysts of K₂CO₃/Al₂O₃ and K₂CO₃/MgAl₂O₄ show the poor NO₂ adsorability. 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 NO₂ 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 NO oxidation ability of CuO plays a significant role in the NO₂ storage process, because NO₂ oxidized from NO is considered to be more easily captured than NO over NSR catalysts.³⁵⁻³⁸⁻³¹ The result above indicates that both the CuO and K₂CO₃ play the important roles in the NO₂ storage process.

3.2. NO₂ storage/reduction in the lean–rich cycles

The NO₂ 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 NO₂ is depicted
in Fig. 3. The NRP was calculated and summarized in Table 1. Fig. 3a shows the concentration of outlet NO\textsubscript{x} for the CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} catalyst during the lean–rich cycles. The NSR performance of the CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} catalyst behaves differently depending on the reaction temperatures. At 350 °C, the NRP of the catalyst is 75.6%. The escaping NO\textsubscript{2} increases with the prolonged operating period because the NO\textsubscript{2} can hardly be reduced. When the reaction temperature is above 400 °C, the NSR performance of the CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} catalyst improves greatly. As the profiles of the NO\textsubscript{2} concentration during the lean–rich cycles at 400–550 °C show, NO\textsubscript{2} in the feeding gas is captured completely in the lean period firstly; once switched to the rich period, the outlet NO\textsubscript{2} concentration is quite low, suggesting that most of the NO\textsubscript{2} can be reduced and nearly no NO\textsubscript{2} 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/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} catalyst can remain above 90% over a wide temperature range (400–550 °C). During the 20 lean–rich cycles, little N\textsubscript{2}O is produced as byproduct (Fig. S2†). The selectivity of 99.7% is obtained on the CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} catalyst at 450 °C. Fig. 3b shows the concentration of outlet NO\textsubscript{x} for the CuO/K\textsubscript{2}CO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} catalyst during the lean–rich cycles. The NO\textsubscript{2} reduction ability of the CuO/K\textsubscript{2}CO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} catalyst at 350 °C is only 23.6%. At 400 °C, the CuO/K\textsubscript{2}CO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} catalyst obtains the highest NRP (80.8%). As the reaction temperature continues to rise, the NRP decreases slightly. The mean crystallite size of CuO was calculated on the basis of the characteristic peaks of CuO (JCPDS 48-1548) with 2θ at 35.6°, 38.7° and 48.7° can be clearly identified on the CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} and CuO/K\textsubscript{2}CO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} catalysts. No characteristic peak of K-related species is detected on the pattern of the fresh CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} and CuO/K\textsubscript{2}CO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} catalysts as shown in Fig. 4a. 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/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} and CuO/K\textsubscript{2}CO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} 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 NO\textsubscript{x} storage at 450 °C. All of the diffraction peaks in Fig. 4a are well matched with spinel-type MgAl\textsubscript{2}O\textsubscript{4} phase (JCPDS 21-1152). It indicates that the MgAl\textsubscript{2}O\textsubscript{4} 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/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} and CuO/K\textsubscript{2}CO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} catalysts. No characteristic peak of K-related species is detected on the pattern of the fresh CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} and CuO/K\textsubscript{2}CO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} catalysts. The phase structure of the catalysts after NO\textsubscript{x} storage was also characterized as shown in Fig. 4d and e. After the NO\textsubscript{x} storage treatment at 450 °C, new diffraction peaks at 27.2°, 29.6° and 32.9° assigned to KNO\textsubscript{3} phase (JCPDS 32-0824) emerge in the XRD patterns of the CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} and CuO/K\textsubscript{2}CO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} catalysts. The transformation of carbonates to nitrates is revealed on the K-related storage sites. Stronger peaks of KNO\textsubscript{3}.

3.3. Structure of the catalysts

Fig. 3 shows the concentration of outlet NO\textsubscript{x} for the CuO/K\textsubscript{2}CO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} catalyst, the NSR performance of the CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} 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 NO\textsubscript{x} 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.

Fig. 3 NO\textsubscript{x} concentration curves during the lean/rich cycles over the (a) CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} and (b) CuO/K\textsubscript{2}CO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} 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. 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 K²⁺. 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. The weak peak locating at 289.7 eV is related to surface carbonate species. 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. 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. 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 again 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 NO₂ 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 NO₂ storage at 450 °C. The reference samples are Cu, CuO and CuO. Both of the two fresh catalysts show the similar shape and location of the adsorption edge to that of CuO.⁴⁴ 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 NO₂ 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.⁴⁹,⁵¹

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, only the uncovered CuO on the CuO/K₂CO₃/MgAl₂O₄ catalyst can be easy to contact to H₂ and results in 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.

Table 2  Spectra parameters obtained by XPS of the fresh catalysts

| Catalysts         | Cu 2p_3/2 (eV) | K 2p_3/2 (eV) | O 1s (eV) | Cu/K (atomic%) |
|-------------------|----------------|---------------|-----------|----------------|
| CuO/K₂CO₃/MgAl₂O₄ | 933.5          | 295.9         | 531.0     | 0.29           |
| CuO/K₂CO₃/Al₂O₃  | 933.8          | 296.1         | 531.1     | 0.24           |

Fig. 6  XANES spectra of Cu K-edge of the samples: (a) fresh CuO/K₂CO₃/MgAl₂O₄, (b) CuO/K₂CO₃/MgAl₂O₄ after NO₂ storage at 450 °C, (c) fresh CuO/K₂CO₃/Al₂O₃, (d) CuO/K₂CO₃/Al₂O₃ after NO₂ storage at 450 °C, (e) CuO, (f) Cu and (g) Cu₂O.
structure. Compared with the bulk K$_2$CO$_3$, the FT-IR spectra of K$_2$CO$_3$/Al$_2$O$_3$ catalysts shows an additional IR band at 1530 cm$^{-1}$, belonging to chelating bidentate carbonate. The bands at 695 cm$^{-1}$ and 518 cm$^{-1}$ are assignable to typical MgAl$_2$O$_4$ spinel structure. Compared with the bulk K$_2$CO$_3$, the FT-IR spectra of the loaded K$_2$CO$_3$ on the fresh CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ and CuO/K$_2$CO$_3$/Al$_2$O$_3$ catalysts shows an additional IR band at 1530 cm$^{-1}$, 1380 cm$^{-1}$ and 1110 cm$^{-1}$, belonging to chelating bidentate carbonate.

Thus, three kinds of K$_2$CO$_3$ species, including bridging bidentate carbonates (1652 cm$^{-1}$), free ionic carbonate CO$_3^{2-}$ (1410 cm$^{-1}$ and 1110 cm$^{-1}$) and chelating bidentate carbonates (1530 m$^{-1}$), co-exist on the fresh catalysts.

The IR spectra of the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ and CuO/K$_2$CO$_3$/Al$_2$O$_3$ catalysts after the NO$_2$ storage reaction at different temperatures were also collected to investigate the reactivity of the different types of K$_2$CO$_3$. Fig. 10a shows the IR spectra of the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst after the NO$_2$ storage reaction at different temperatures. As reported, both the ionic and bidentate nitrates presented on a series of K$_2$O/Al$_2$O$_3$ catalysts after NO$_2$ dosing. The most intense peak at 1380 cm$^{-1}$ can be identified as ionic nitrates after the NO$_2$ storage.

The intensity of this peak varies with the reaction temperature of CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst, the tendency of which is consistent with the NSC order. The intensity of this peak becomes strongest when the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst reacts at 450 °C. Differently from the fresh CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ 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/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst, suggesting most of carbonates on the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst participate in the NO$_2$ storage. Fig. 10b shows the IR spectra of the CuO/K$_2$CO$_3$/Al$_2$O$_3$ catalyst after the NO$_2$ 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 NO$_2$ storage process, suggesting that a part of the bridging bidentate carbonate and chelating bidentate carbonate in the CuO/K$_2$CO$_3$/Al$_2$O$_3$ catalyst can not completely store NO$_2$ at high temperatures. Comparing the IR spectra of the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ and CuO/K$_2$CO$_3$/Al$_2$O$_3$ catalysts after the NO$_2$ storage, there is more K$_2$CO$_3$ on CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ transformed to nitrate. It suggests that the MgAl$_2$O$_4$ can improve the NO$_2$ storage efficiency of K$_2$CO$_3$ at high operating temperatures. Additionally, after NO$_2$ storage at 450 °C, the two catalysts were heated in the N$_2$ flow at 450 °C for 10 min. The IR spectra of the two catalysts after NO$_2$-TPD are shown in Fig. 10a and b. For the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ 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/K$_2$CO$_3$/Al$_2$O$_3$ 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/K$_2$CO$_3$/MgAl$_2$O$_4$ 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 NO$_2$ storage reaction will limit their application at high operating temperatures. In Fig. 2, the thermal stability of the nitrates on the K sites of the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst is
highly compared with the CuO/K$_2$CO$_3$/Al$_2$O$_3$ 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.\textsuperscript{27} The charge density of Al$^{3+}$ and Mg$^{2+}$ is 4.8 $\times$ 10$^{-3}$ $\epsilon$ nm$^{-3}$ and 7.5 $\times$ 10$^{-4}$ $\epsilon$ nm$^{-3}$. Lower extent of polarization of Mg$^{2+}$ makes N=O bond less prone to breakage, and thus the nitrates on the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ show the higher thermal stability.

Additionally, in our study, the temperatures of NO$_x$ desorption correlate to the temperatures of K$_2$CO$_3$ decomposition as mentioned in Fig. 8. Thus, the thermal stability of nitrates is related to the thermal stability of K$_2$CO$_3$. In other word, the nitrates with high thermal stability may be transformed from the thermal stable K$_2$CO$_3$. As discussed in Fig. 10, there is more K$_2$CO$_3$ with high thermal stability on the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst than that on the CuO/K$_2$CO$_3$/Al$_2$O$_3$, and this part of K$_2$CO$_3$ is the main storage sites in the high-temperature NSR reaction. Thus, the trapped nitrate on the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst shows the high thermal stability.

Through the above discussion, the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst can store much more NO$_x$ than CuO/K$_2$CO$_3$/Al$_2$O$_3$ catalyst above 400 ℃, resulting from the former’s higher thermal stability of nitrates. The high thermal stability of nitrate is the main reason to induce the high NO$_x$ storage capacity of the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst at the high temperatures.

Therefore, with the high thermal stability of nitrates and the high redox capacity of CuO above 400 ℃, the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst exhibits the prominent NRP performance at high operating temperatures.

4. Conclusion

Herein, we report the high NSR activity of the newly designed CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst at high operating temperatures. As concerns of the NSR activity in successive 20 lean/rich cycles between 350–550 ℃, the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst performs more effectively and steadily on De-NO$_x$ in alternative lean/rich atmospheres than the Al$_2$O$_3$-supported catalyst. Especially, the NO$_2$ reduction efficiency of the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst achieves a maximum value of 99.9% with a large NO$_x$ uptake of 1.56 mmol g$^{-1}$ at 450 ℃. Meanwhile, a high N$_2$ selectivity of 99.7% was also obtained. The NRP of the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst maintains above 90% at 400–550 ℃. While the NRP of the CuO/K$_2$CO$_3$/Al$_2$O$_3$ catalyst decreases sharply with the increased reaction temperatures.

The states of CuO and K$_2$CO$_3$ species have an apparent difference on the MgAl$_2$O$_4$ and Al$_2$O$_3$ supported catalysts. After K loading, CuO is probably covered by K$_2$CO$_3$. There is still a part of the uncovered CuO on the MgAl$_2$O$_4$ supported catalyst, but none for the Al$_2$O$_3$ supported catalyst. This part of CuO is beneficial for the oxidation and reduction of NO$_x$ in alternative lean/rich cycles. CuO exhibits the high redox ability at the temperatures above 400 ℃. 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 K$_2$CO$_3$ on the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst can convert to nitrates, but only a part of them participates on the CuO/K$_2$CO$_3$/Al$_2$O$_3$ catalyst. Moreover, our results show that the thermal stability of nitrate is consistent with the thermal stability of K$_2$CO$_3$. The formed nitrates during the lean operation on the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst have the high thermal stability, because of the high thermal stability of K$_2$CO$_3$ supported on the catalyst. Accordingly, the CuO/K$_2$CO$_3$/MgAl$_2$O$_4$ catalyst exhibits a high NSR activity at high operating temperatures and is a promising high-temperature NSR catalyst.

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