Enhanced activity of CuO/K₂CO₃/MgAl₂O₄ catalyst for lean NOₓ storage and reduction at high temperatures†

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Herein, we designed a new NOₓ storage and reduction CuO/K₂CO₃/MgAl₂O₄ catalyst operating within the high temperature region of 350–550 °C. Compared with the Al₂O₃ supported catalyst with the same Cu and K loading, it exhibits superior NOₓ storage and reduction performance. The NOₓ reduction percentage (NRP) of the CuO/K₂CO₃/MgAl₂O₄ 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 N₂ selectivity of 99.7%. Uncovered CuO particles with better reducibility exist on the CuO/K₂CO₃/MgAl₂O₄ catalyst, with the high NOₓ oxidation and reduction ability above 400 °C. Potassium carbonates on the CuO/K₂CO₃/MgAl₂O₄ 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/K₂CO₃/MgAl₂O₄ catalyst can store NOₓ to form nitrates, but only parts of them participate in NOₓ storage on the CuO/K₂CO₃/MgAl₂O₄ catalyst. The MgAl₂O₄ support offers additional sites for NOₓ adsorption, while the formed nitrate on it shows low thermal stability. So, NOₓ is mainly stored on K₂CO₃ at high temperatures, because MgAl₂O₄ can enhance the thermal stability of the supported K₂CO₃ on it. Our results show that the thermal stability of K₂CO₃ directly determines the thermal stability of the formed nitrates. Accordingly, the CuO/ K₂CO₃/MgAl₂O₄ catalyst shows the high NSR activity because of the efficient redox ability of CuO and high thermal stability of K₂CO₃ at high operating temperatures.

The process of NSR, also known as lean NOₓ trap (LNT), is operated in alternative lean-burn/fuel-rich atmospheres, which mainly includes: NOₓ is captured by alkali/alkali earth components (e.g. barium and potassium) within a long lean-burn period (1–2 min); the trapped NOₓ species is released and then reduced to harmless N₂ by precious group metals (e.g. Pt and Rh) within a subsequent short fuel-rich period (3–20 s). High NOₓ removal efficiency has been achieved over the Pt/BaO/Al₂O₃ catalyst developed by the Toyota company within a narrow temperature window of 300–400 °C. 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/Al₂O₃ NSR catalyst significantly drops. When the operating temperature exceeds 400 °C, the solid-phase reaction between BaO and Al₂O₃ to form BaAl₅O₁₄ will lower the surface area and reduce the NOₓ storage sites. Pt sintering also hampers the reduction of NOₓ from cycle to cycle. 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 NOₓ storage capacity. 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, LaCoO₃, and Laₑ₋ₓSrₓCO₃O₄. The transition metal elements of manganese and copper were also studied as substitutes for platinum. It was reported that Cu/KₓTiO₂ 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 incipient wetness impregnation method. The Al₂O₃-supported catalyst was prepared 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-transferring infrared spectra (FT-IR), H₂ temperature-programmed reduction (H₂-TPR), temperature-programmed desorption of COₓ (CO₂-TPD) and temperature-programmed desorption of NOₓ (NO₂-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 (S_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 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:

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

where \( D \) is the crystallite size, \( K \) is a constant, \( \lambda \) is the wavelength of the X-ray device, \( \beta \) is the full width half maximum, and \( \theta \) 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.

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 C3H6, balanced by N2). The NOx concentrations were monitored online by a chemiluminescence NO-NO2-NOx analyzer (Model 42i-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 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:

\[
\text{NPR} = \frac{\int [\text{NO}_x]_{\text{inlet}} \times t_1 - \int [\text{NO}_x]_{\text{outlet}} \times dt}{[\text{NO}_x]_{\text{inlet}} \times t_1} \times 100\% 
\]

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

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

The storage ratio was calculated as the following formula:

\[
\text{Storage ratio} = \frac{[\text{NO}_x]_{\text{inlet}} \times t_2 - \int [\text{NO}_x]_{\text{outlet}} \times dt}{[\text{NO}_x]_{\text{inlet}} \times t_2}
\]

\([\text{NO}_x]\) and \([\text{NO}_2]\) is the concentration of NOx and NO2 in ppm unit, inlet and outlet refer to the inlet gas and the out gas, respectively. \(V\) is the flow rate of the inlet gas, \(N_0\) is 22.4 L mol⁻¹, \(m\) 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.

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. 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
The distinct difference of the NO\textsubscript{2} storage behavior at high temperature between 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 probably results from the different thermal stability of the formed nitrate during the NO\textsubscript{2} storage reaction. To investigate the thermal stability of the trapped NO\textsubscript{2} on the catalysts, the NO\textsubscript{2}-TPD experiments were conducted after the saturated adsorption of NO\textsubscript{2} at 450 °C. Fig. 2 shows the NO\textsubscript{2}-TPD profiles of the CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4}, CuO/K\textsubscript{2}CO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} and CuO/MgAl\textsubscript{2}O\textsubscript{4} catalysts. In the profile of the CuO/MgAl\textsubscript{2}O\textsubscript{4}, a single NO\textsubscript{2} desorption peak is observed at 365 °C, which is attributed to the decomposition of nitrates species formed on the MgAl\textsubscript{2}O\textsubscript{4} support, confirming that the support offers additional sites for NO\textsubscript{2} adsorption. It is likely caused by the strong basicity of MgAl\textsubscript{2}O\textsubscript{4}. However, the MgAl\textsubscript{2}O\textsubscript{4} support is not the main NO\textsubscript{2} 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/K\textsubscript{2}CO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} catalyst can be ascribed to the decomposition of KNO\textsubscript{3} on it. Two desorption peaks are clearly observed in the profile of the CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} catalyst. The first peak at 365 °C is assigned to the NO\textsubscript{2} desorption from the MgAl\textsubscript{2}O\textsubscript{4} support as mentioned above. The latter peak appearing at 649 °C can be attributed to the desorption of the stored NO\textsubscript{2} species on K\textsubscript{2}CO\textsubscript{3}. Thus, the K\textsubscript{2}CO\textsubscript{3} is identified as the main NO\textsubscript{2} storage sites according to the large desorption amount and high thermal stability. Meanwhile, a distinct difference in the decomposition temperatures of KNO\textsubscript{3} between the CuO/K\textsubscript{2}CO\textsubscript{3}/ Al\textsubscript{2}O\textsubscript{3} (481 °C) and CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} catalysts (649 °C) is observed, suggesting the higher thermal stability of the nitrates on the K sites of the CuO/K\textsubscript{2}CO\textsubscript{3}/MgAl\textsubscript{2}O\textsubscript{4} catalyst, which is the main reason of its higher NO\textsubscript{2} storage ability at high temperatures.

### Table 1

<table>
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<th>Catalysts</th>
<th>T (°C)</th>
<th>NRP (%)</th>
<th>NSC (mmol g\textsuperscript{-1})</th>
<th>NO to NO\textsubscript{2} conversion (%)</th>
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<td>1.48</td>
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<td>550</td>
<td>37.5</td>
<td>0.38</td>
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The NO\textsubscript{2} storage/reduction in the lean–rich cycles

The NO\textsubscript{2} 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 NO\textsubscript{2} is depicted...
in Fig. 3. The NRP was calculated and summarized in Table 1. Fig. 3a shows the concentration of outlet NO\(_x\) for the CuO/K\(_2\)CO\(_3\)/MgAl\(_2\)O\(_4\) catalyst during the lean–rich cycles. The NSR performance of the CuO/K\(_2\)CO\(_3\)/MgAl\(_2\)O\(_4\) catalyst behaves differently depending on the reaction temperatures. At 350 °C, the NRP of the catalyst is 75.6%. The escaping NO\(_x\) increases with the prolonged operating period because the NO\(_x\) can hardly be reduced. When the reaction temperature is above 400 °C, the NSR performance of the CuO/K\(_2\)CO\(_3\)/MgAl\(_2\)O\(_4\) catalyst improves greatly. As the profiles of the NO\(_x\) concentration during the lean–rich cycles at 400–550 °C show, NO\(_x\) in the feeding gas is captured completely in the lean period firstly; once switched to the rich period, the outlet NO\(_x\) concentration is quite low, suggesting that most of the NO\(_x\) can be reduced and nearly no NO\(_x\) 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\(_2\)CO\(_3\)/MgAl\(_2\)O\(_4\) catalyst can remain above 90% over a wide temperature range (400–550 °C). During the 20 lean–rich cycles, little N\(_2\)O is produced as byproduct (Fig. S2†). The selectivity of 99.7% is obtained on the CuO/K\(_2\)CO\(_3\)/MgAl\(_2\)O\(_4\) catalyst at 450 °C. Fig. 3b shows the concentration of outlet NO\(_x\) for the CuO/K\(_2\)CO\(_3\)/Al\(_2\)O\(_3\) catalyst during the lean–rich cycles. The NO\(_x\) reduction ability of the CuO/K\(_2\)CO\(_3\)/Al\(_2\)O\(_3\) catalyst at 350 °C is only 23.6%. At 400 °C, the CuO/K\(_2\)CO\(_3\)/Al\(_2\)O\(_3\) catalyst obtains the highest NRP (80.8%). As the profile of the NO\(_x\) concentration during the lean–rich cycles on the CuO/K\(_2\)CO\(_3\)/Al\(_2\)O\(_3\) 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 NO\(_x\) removal activity decreases from cycle to cycle. With further increasing the reaction temperature, the NRP of the CuO/K\(_2\)CO\(_3\)/Al\(_2\)O\(_3\) catalyst decreased gradually. At 550 °C, its NRP decreases sharply to 37.5%.

Compared with the CuO/K\(_2\)CO\(_3\)/Al\(_2\)O\(_3\) catalyst, the NSR performance of the CuO/K\(_2\)CO\(_3\)/MgAl\(_2\)O\(_4\) 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\(_x\) 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.

### 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 NO\(_x\) storage at 450 °C. All of the diffraction peaks in Fig. 4a are well matched with spinel-type MgAl\(_2\)O\(_4\) phase (JCPDS 21-1152). It indicates that the MgAl\(_2\)O\(_4\) 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\(_2\)CO\(_3\)/MgAl\(_2\)O\(_4\) and CuO/K\(_2\)CO\(_3\)/Al\(_2\)O\(_3\) catalysts. No characteristic peak of K-related species is detected on the pattern of the fresh CuO/K\(_2\)CO\(_3\)/Al\(_2\)O\(_3\) and CuO/K\(_2\)CO\(_3\)/Al\(_2\)O\(_3\) 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/K\(_2\)CO\(_3\)/MgAl\(_2\)O\(_4\) and CuO/K\(_2\)CO\(_3\)/Al\(_2\)O\(_3\) catalysts is 24.4 and 22.4 nm, respectively.

The phase structure of the catalysts after NO\(_x\) storage was also characterized as shown in Fig. 4d and e. After the NO\(_x\) storage treatment at 450 °C, new diffraction peaks at 27.2°, 29.6° and 32.9° assigned to KNO\(_3\) phase (JCPDS 32-0824) emerge in the XRD patterns of the CuO/K\(_2\)CO\(_3\)/MgAl\(_2\)O\(_4\) and CuO/K\(_2\)CO\(_3\)/Al\(_2\)O\(_3\) catalysts. The transformation of carbonates to nitrates is revealed on the K-related storage sites. Stronger peaks of KNO\(_3\)
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.⁴⁶–⁴⁸ No Cu-related species other than CuO is observed, suggesting the NOₓ oxidation and reduction center of the two catalysts is CuO. The above results are 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 centered 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.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 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.³⁰

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 reveal 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, Cu₂O and 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 Cu₂O 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.⁵⁰,⁴¹,⁵¹

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 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 the similar reducibility of CuO as the CuO/

Table 2  Spectra parameters obtained by XPS of the fresh catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Cu 2p₃/₂ (eV)</th>
<th>K 2p₃/₂ (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>531.0</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>

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 and 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.⁴ 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 regarding 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.

Fig. 6 XANES spectra of 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 K2CO3, the FT-IR spectra of K2CO3/Al2O3 catalysts shows an additional IR band at 1530 cm⁻¹. These 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. Thus, three kinds of K2CO3 species, including bridging bidentate carbonates (1652 cm⁻¹), free ionic carbonate CO3²⁻ (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/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. The most intense peak at 1380 cm⁻¹ can be identified as ionic nitrates after the NOx storage. 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, 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. 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.27 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 MgAl2O4 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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