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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}

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

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Herein, we designed a new NO_x 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 NO_x storage and reduction performance. The NO_x 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/ 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/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 NO_x to form nitrates, but only parts of them participate in NO_x storage on the CuO/K₂CO₃/Al₂O₃ catalyst. The MgAl₂O₄ 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_2CO_3 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 NO_r 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).48 High NO_x 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.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/Al₂O₃ NSR catalyst significantly drops.16,17 When the operating temperature exceeds 400 °C, the solid-phase reaction between BaO and Al₂O₃ to form BaAl₂O₄ will lower the surface area and reduce the NO_x storage sites.¹⁸ Pt sintering also hampers the reduction of NO_r 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_r storage capacity.^{18,21} Thus, it is urgent to develop a NSR catalyst with good high-temperature performance.

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It was reported that mixing an alkaline earth metal oxide with Al_2O_3 could enhance the basicity of the support and also improve the thermal stability of the trapped nitrates.¹⁶ 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,^{16,18} and Pt sintering can also be effectively inhibited.¹⁷ Additionally, the MgAl₂O₄ support can provide extra storage sites for NO_x.²² 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 $BaFeO_{3-x}$, $LaCoO_3$ and $La_{1-x}Sr_xCOO_3$.^{23–28} The transition metal elements of manganese and copper were also studied as substitutes for platinum.^{29,30} It was reported that $Cu/K_2Ti_2O_5$ could be applied over a wide temperature range (200–600 °C) with the mutual transformation of different structures.³¹

As for the storage material, it is generally admitted that potassium-based catalysts have higher ability to storage NO_x at high temperatures (above 400 °C) than barium-based ones due to its stronger basicity and better mobility.³² Potassium is more suitable as the storage element for the high-temperature NSR catalyst.¹⁷

Based on the above analysis, it is interesting to design a new NSR catalyst with CuO as the NO_x oxidation and reduction center, potassium as the NO_x storage element and $MgAl_2O_4$ 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 NO_x 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), temperatureprogrammed desorption of CO₂ (CO₂-TPD) and temperatureprogrammed desorption of NO_x (NO_x -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 $MgAl_2O_4$ support was prepared by co-precipitation method. A certain amount of $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ was dissolved and mixed

with vigorous stirring. The pH value of the aqueous solution was adjusted to 9.5 by addition of $NH_3 \cdot H_2O$. 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 K α 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 K α (1253.6 eV) as radiation source. The base pressure in sample chamber was 5 \times 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.

 H_2 -TPR experiments were carried out on the TP-5079 TPDRO apparatus (Xian quan). The reduction gas is 8 vol% H_2/N_2 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.

 $\rm CO_2$ -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.

 NO_x -TPD test was conducted in a quartz-tubular continuous flow reactor (i.d. = 4 mm). The samples were heated in pure N_2 (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 NO_x in the lean gas (400 ppm of NO, 5% O_2 , balanced by N_2) 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 NO_x 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 NO_x concentrations were monitored online by a chemiluminescence NO–NO₂–NO_x 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 NO_x 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 NO_x 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 NO_x reduction percentage (NRP) was calculated according to the steady lean/rich cycle as the following formula:

$$NPR = \frac{[NO_x]_{inlet} \times t_1 - \int [NO_x]_{outlet} dt}{[NO_x]_{inlet} \times t_1} \times 100\%$$

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

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

The storage ratio was calculated as the following formula:

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

 $[NO_x]$ and $[NO_2]$ is the concentration of NO_x and NO_2 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 NO_x to the introduced one.³³

Results and discussion

3.1. NO_x storage capacity measurement

 NO_x storage tests were carried out in the temperature range of 350–550 °C. The evolution of outlet NO_r 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 NO_x storage capacity of the CuO/K₂CO₃/MgAl₂O₄ catalyst varies with the increased reaction temperature. At 350 $^{\circ}$ C, the NO_x trapping kinetics is too slow, inducing the low NSC. Fig. 1a shows that after introducing the feeding gas above 400 °C, a rapid NO_x storage behavior occurs and the NO_x signal diminishes sharply. Subsequently, the "lean trap" period is observed, namely the stage during which NO_x is completely captured on the catalysts and no NO_x is released. Then, the NO_x 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 NO_x storage under lean-burn conditions.^{34,35} Meanwhile, the stored NO_x gets thermally unstable. With the rising of the reaction temperature, the desorption rate of the released NO_x from the catalysts is accelerated, as well as the equilibrium of the NO_x storage process. The largest NSC uptake of the CuO/K₂CO₃/MgAl₂O₄ catalyst is obtained at 450 °C, which is the optimum



Fig. 1 Isothermal NO_x storage curves of the (a) CuO/K₂CO₃/MgAl₂O₄ and (b) CuO/K₂CO₃/Al₂O₃ catalysts at the different temperatures.

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

Catalysts	T (°C)	NRP (%)	NSC (mmol g^{-1})	NO to NO ₂ conversion (%)
CuO/K2CO3/MgAl2O4	350	75.6	1.09	24.1
2 0 0 2 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/K ₂ CO ₃ /Al ₂ O ₃	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

temperature for the NO_x 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.^{17,36} When the reaction temperature continues to increase, the NSC of the CuO/K₂CO₃/MgAl₂O₄ catalyst decreases slightly because a small amount of the trapped NO_x decomposes at high temperatures. Fig. 1b shows the NO_x 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 NO_x 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/Al₂O₄ 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/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.^{5,37,38}

The distinct difference of the NO_x 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 NO_x storage reaction. To investigate the thermal stability of the trapped NO_x on the catalysts, the NO_x-TPD experiments were conducted after the saturated adsorption of NO_x at 450 °C. Fig. 2 shows the NO_x-TPD profiles of the CuO/K₂CO₃/MgAl₂O₄, CuO/K₂CO₃/Al₂O₃ and CuO/MgAl₂O₄ catalysts. In the profile of the CuO/MgAl₂O₄, a single NO_x 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 NO_x adsorption. It is likely caused by the strong basicity of MgAl₂O₄. However, the MgAl₂O₄ support is not the main NO_r 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_2CO_3/Al_2O_3 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 NO_x desorption from the MgAl₂O₄ support as mentioned above. The latter peak appearing at 649 °C can be attributed to the desorption of the stored NO_r species on K_2CO_3 . Thus, the K_2CO_3 is identified as the main NO_r 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 NO_x storage ability at high temperatures.

The components of CuO and K₂CO₃ in the catalyst are designed to act as the NO_x oxidation sites and storage sites, respectively. To clarify the roles of these two components, the stationary NO_x 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 $K_2CO_3/MgAl_2O_4$ show the poor NO_r adsorbability. The NSC of the CuO/MgAl₂O₄ sample is only 0.11 mmol g^{-1} , because of the absence of K_2CO_3 , suggesting that K_2CO_3 is the main NO_r 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 NO_x storage process, because NO2 oxidized from NO is considered to be more easily captured than NO over NSR catalysts.4,8,39 The result above indicates that both the CuO and K₂CO₃ play the important roles in the NO_x storage process.

3.2. NO_x storage/reduction in the lean-rich cycles

The NO_x 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_x is depicted



Fig. 2 NO_x-TPD profiles of the catalysts.

in Fig. 3. The NRP was calculated and summarized in Table 1. Fig. 3a shows the concentration of outlet NO_r 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 NO_r increases with the prolonged operating period because the NO_r 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 NO_x concentration during the leanrich 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 deceases 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 NO_x for the CuO/K₂CO₃/Al₂O₃ catalyst during the lean-rich cycles. The NO_x 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 NO_x concentration during the lean-rich cycles on the $CuO/K_2CO_3/$ 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 NO_x 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 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 $^{\circ}$ 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.⁴⁰ 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 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 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 NO_x concentration curves during the lean/rich cycles over the (a) CuO/K₂CO₃/MgAl₂O₄ and (b) CuO/K₂CO₃/Al₂O₃ catalysts.



Fig. 4 XRD patterns of the catalysts: (a) fresh MgAl₂O₄, (b) fresh CuO/K₂CO₃/MgAl₂O₄, (c) fresh CuO/K₂CO₃/Al₂O₃, (d) CuO/K₂CO₃/MgAl₂O₄ after NO_x storage at 450 °C and (e) CuO/K₂CO₃/Al₂O₃ after NO_x storage at 450 °C.

are observed in the XRD pattern of the CuO/K₂CO₃/MgAl₂O₄ catalyst than those of the CuO/K₂CO₃/Al₂O₃ catalyst, implying that more NO_x was trapped on the CuO/K₂CO₃/MgAl₂O₄ catalyst. It is in good agreement with the results of NSC. Additionally, after the NO_x 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.^{29,41}

We measured the specific surface areas of the catalysts by N_2 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 K₂CO₃.⁴²

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 2p_{3/2}) and 952.9 eV (Cu 2p_{1/2}) with a satellite shakeup at around 942.3 eV.⁴³⁻⁴⁶ No Cu-related species other than CuO is observed, suggesting the NO_x 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 $2p_{3/2}$) accompanied by a less intense peak at about 293.0 eV (K $2p_{1/2}$) 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



Fig. 5 XPS spectra of the fresh catalysts: (a) Cu 2p, (b) K 2p and C 1s and (c) O 1s.

precursor on the catalysts has decomposed into K_2O and CO_2 during the calcination at 600 °C. However, the K_2O is easy to react with CO_2 and form K_2CO_3 again when the samples are exposed in air. So, the detected K_2CO_3 by the XPS measurement probably results from the reaction of K_2O with CO_2 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 NO_x 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 NO_x 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 NO_x 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.^{29,41,51}

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 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 the similar reducibility of CuO as the CuO/

Table 2 Spectra parameters obtained by XPS of the fresh catalysts							
Catalysts	Cu 2p _{3/2}	K 2p _{3/2}	O 1s	Cu/K			
	(eV)	(eV)	(eV)	(atomic%)			
CuO/K ₂ CO ₃ /MgAl ₂ O ₄	933.5	295.9	531.0	0.29			
CuO/K ₂ CO ₃ /Al ₂ O ₃	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 NO_x storage at 450 °C, (c) fresh CuO/K₂CO₃/Al₂O₃, (d) CuO/K₂CO₃/Al₂O₃ after NO_x storage at 450 °C, (e) CuO, (f) Cu and (g) Cu₂O.

 $MgAl_2O_4$ catalyst. The K_2CO_3 loading on the catalysts may cover the CuO, which can hinder the diffusion of H_2 to CuO. Based on the H_2 -TPR result, some of the uncovered CuO by K_2CO_3 exists on the CuO/ $K_2CO_3/MgAl_2O_4$ catalyst, while the CuO on the CuO/ K_2CO_3/Al_2O_3 catalyst is totally covered. Thus, the CuO/ $K_2CO_3/MgAl_2O_4$ catalyst shows a better NSR performance than the CuO/ K_2CO_3/Al_2O_3 catalyst.

Additionally, the released CO_2 *via* the decomposition of K_2CO_3 during the TPR process can dilute the feed gas and generate pseudo H_2 consumption peaks. The high temperature peaks at 724 °C and 763 °C can be assigned to the decomposition of bulk-like K_2CO_3 .

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.⁴¹ The reaction occurs as the following expression: $K_2CO_3 \rightarrow K_2O + CO_2$. 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.

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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 K_2CO_3 on the fresh CuO/ $K_2CO_3/MgAl_2O_4$ and CuO/ K₂CO₃/Al₂O₃ catalysts shows an additional IR band at 1530 cm⁻¹, belonging to chelating bidentate carbonates.⁵² Thus, three kinds of K₂CO₃ species, including bridging bidentate carbonates (1652 cm⁻¹),⁵³ free ionic carbonate CO₃^{2–} (1410 cm⁻¹ and 1110 cm⁻¹)⁵² and chelating bidentate carbonates (1530 m^{-1}), co-exist on the fresh catalysts.

The IR spectra of the CuO/K2CO3/MgAl2O4 and CuO/K2CO3/ Al_2O_3 catalysts after the NO_x 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 NO_x storage reaction at different temperatures. As reported, both the ionic and bidentate nitrates presented on a series of K2O/Al2O3 catalysts after NO2 dosing.54 The most intense peak at 1380 cm⁻¹ can be identified as ionic nitrates after the NO_x storage.⁵²

640 °C

840 °C

900

724 ° C

767 ° C

240 ° (

264 ° C

238 ° C

32

326 376 ° C

300

400 500

T/°C

Fig. 7 H₂-TPR profiles of the samples: (a) CuO/MgAl₂O₄, (b) CuO/

K₂CO₃/MgAl₂O₄, (c) CuO/Al₂O₃, (d) CuO/K₂CO₃/Al₂O₃, (e) CuO and (f)

600 700 800 900



3.6. Thermal stability of the stored nitrates

The low thermal stability of the nitrate formed on NSR catalysts in the NO_x storage reaction will limit their application at high operating temperatures.¹⁶ In Fig. 2, the thermal stability of the nitrates on the K sites of the CuO/K2CO3/MgAl2O4 catalyst is



CuO/K,CO,/MgAl,O

CuO/K2CO3/Al2O

304 °C

Fig. 8 CO₂-TPD profiles of the fresh catalysts.



Fig. 9 FT-IR spectra of the samples: (a) CuO/K₂CO₃/Al₂O₃, (b) CuO/ K₂CO₃/MgAl₂O₄, (c) pure K₂CO₃ and (d) MgAl₂O₄.

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H, consumption / a.u.

MgAl₂O₄

(b)

(d)

(f)

100 200



Fig. 10 FT-IR spectra of the (a) CuO/K₂CO₃/MgAl₂O₄ and (b) CuO/K₂CO₃/Al₂O₃ catalysts: (1) fresh catalyst, and the catalyst after NO_x storage reaction at (2) 350 °C, (3) 400 °C, (4) 450 °C, (5) 500 °C and (6) 550 °C, and (7) the catalyst (4) heated at 450 °C in N₂ flow for 10 min.

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.¹⁷ 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 NO_x desorption correlate to the temperatures of K_2CO_3 decomposition as mentioned in Fig. 8. Thus, the thermal stability of nitrates is related to the thermal stability of K_2CO_3 . In other word, the nitrates with high thermal stability may be transformed from the thermal stable K_2CO_3 . As discussed in Fig. 10, there is more K_2CO_3 with high thermal stability on the CuO/ K_2CO_3 /MgAl₂O₄ catalyst than that on the CuO/ K_2CO_3 /Al₂O₃, and this part of K_2CO_3 is the main storage sites in the high-temperature NSR reaction. Thus, the trapped nitrate on the CuO/ K_2CO_3 /MgAl₂O₄ catalyst shows the high thermal stability.

Through the above discussion, the CuO/K₂CO₃/MgAl₂O₄ catalyst can store much more NO_x 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 NO_x 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 $^{\circ}$ 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-NO_x in alternative lean/rich atmospheres than the Al₂O₃-supported catalyst. Especially, the NO_x reduction efficiency of the CuO/K₂CO₃/MgAl₂O₄ catalyst achieves a maximum value of 99.9% with a large NO_x 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 NO_x in alterative 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 hightemperature NSR catalyst.

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