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# Enhanced activity of CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst for lean NO<sub>x</sub> storage and reduction at high temperatures†

Yaoyao Liu,<sup>a</sup> Lihong Guo,<sup>ab</sup> Dongyue Zhao,<sup>a</sup> Xingang Li,<sup>ID</sup> <sup>\*a</sup> Zhongnan Gao,<sup>a</sup> Tong Ding,<sup>\*a</sup> Ye Tian<sup>a</sup> and Zheng Jiang<sup>c</sup>

Herein, we designed a new NO<sub>x</sub> storage and reduction CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst operating within the high temperature region of 350–550 °C. Compared with the Al<sub>2</sub>O<sub>3</sub> supported catalyst with the same Cu and K loading, it exhibits superior NO<sub>x</sub> storage and reduction performance. The NO<sub>x</sub> reduction percentage (NRP) of the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> 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<sub>2</sub> selectivity of 99.7%. Uncovered CuO particles with better reducibility exist on the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst, with the high NO<sub>x</sub> oxidation and reduction ability above 400 °C. Potassium carbonates on the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst mainly exist in three forms, including free ionic carbonate, bridging bidentate carbonate and chelating bidentate carbonate. Under lean-burn conditions, most of carbonates on the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst can store NO<sub>x</sub> to form nitrates, but only parts of them participate in NO<sub>x</sub> storage on the CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. The MgAl<sub>2</sub>O<sub>4</sub> support offers additional sites for NO<sub>x</sub> adsorption, while the formed nitrate on it shows low thermal stability. So, NO<sub>x</sub> is mainly stored on K<sub>2</sub>CO<sub>3</sub> at high temperatures, because MgAl<sub>2</sub>O<sub>4</sub> can enhance the thermal stability of the supported K<sub>2</sub>CO<sub>3</sub> on it. Our results show that the thermal stability of K<sub>2</sub>CO<sub>3</sub> directly determines the thermal stability of the formed nitrates. Accordingly, the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst shows the high NSR activity because of the efficient redox ability of CuO and high thermal stability of K<sub>2</sub>CO<sub>3</sub> at high operating temperatures.

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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.<sup>1</sup> Unfortunately, the emitted NO<sub>x</sub> (NO and NO<sub>2</sub>) is hardly removed over the conventional three way catalysts (TWC) because of the presence of excess oxygen. With the increasing NO<sub>x</sub> emission limit, it is urgent to develop effective catalytic after-treatment systems.<sup>2,3</sup> To solve this problem, methodologies for NO<sub>x</sub> storage and reduction (NSR) and selective catalytic reduction (SCR) of NO<sub>x</sub> are being developed.<sup>4,5</sup> Presently, the NSR technology is a preferred choice especially for light duty lean-burn engines.<sup>6,7</sup>

The process of NSR, also known as lean NO<sub>x</sub> trap (LNT), is operated in alternative lean-burn/fuel-rich atmospheres, which mainly includes: NO<sub>x</sub> is captured by alkali/alkali earth components (*e.g.* barium and potassium) within a long lean-burn period (1–2 min); the trapped NO<sub>x</sub> species is released and then reduced to harmless N<sub>2</sub> by precious group metals (*e.g.* Pt and Rh) within a subsequent short fuel-rich period (3–20 s).<sup>4,8</sup> High NO<sub>x</sub> removal efficiency has been achieved over the Pt/BaO/Al<sub>2</sub>O<sub>3</sub> catalyst developed by the Toyota company within a narrow temperature window of 300–400 °C.<sup>9–15</sup> 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<sub>2</sub>O<sub>3</sub> NSR catalyst significantly drops.<sup>16,17</sup> When the operating temperature exceeds 400 °C, the solid-phase reaction between BaO and Al<sub>2</sub>O<sub>3</sub> to form BaAl<sub>2</sub>O<sub>4</sub> will lower the surface area and reduce the NO<sub>x</sub> storage sites.<sup>18</sup> Pt sintering also hampers the reduction of NO<sub>x</sub> from cycle to cycle.<sup>19,20</sup> 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<sub>x</sub> storage capacity.<sup>18,21</sup> Thus, it is urgent to develop a NSR catalyst with good high-temperature performance.

<sup>a</sup>Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin Key Laboratory of Applied Catalysis Science and Engineering, School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, P. R. China. E-mail: xingang\_li@tju.edu.cn

<sup>b</sup>School of Chemistry and Chemical Engineering, Henan University of Technology, Zhengzhou 450001, P. R. China

<sup>c</sup>Shanghai Synchrotron Radiation Facility, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai, 201800, P. R. China

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It was reported that mixing an alkaline earth metal oxide with  $\text{Al}_2\text{O}_3$  could enhance the basicity of the support and also improve the thermal stability of the trapped nitrates.<sup>16</sup>  $\text{MgAl}_2\text{O}_4$ , as one of these mixed oxides, has been employed as support of high-temperature NSR catalysts. Through supported on  $\text{MgAl}_2\text{O}_4$ , the stability of nitrate species is strongly improved whether on potassium sites or barium sites,<sup>16,18</sup> and Pt sintering can also be effectively inhibited.<sup>17</sup> Additionally, the  $\text{MgAl}_2\text{O}_4$  support can provide extra storage sites for  $\text{NO}_x$ .<sup>22</sup> Hence, we chose  $\text{MgAl}_2\text{O}_4$  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  $\text{BaFeO}_{3-x}$ ,  $\text{LaCoO}_3$  and  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ .<sup>23–28</sup> The transition metal elements of manganese and copper were also studied as substitutes for platinum.<sup>29,30</sup> It was reported that  $\text{Cu/K}_2\text{Ti}_2\text{O}_5$  could be applied over a wide temperature range (200–600 °C) with the mutual transformation of different structures.<sup>31</sup>

As for the storage material, it is generally admitted that potassium-based catalysts have higher ability to storage  $\text{NO}_x$  at high temperatures (above 400 °C) than barium-based ones due to its stronger basicity and better mobility.<sup>32</sup> Potassium is more suitable as the storage element for the high-temperature NSR catalyst.<sup>17</sup>

Based on the above analysis, it is interesting to design a new NSR catalyst with CuO as the  $\text{NO}_x$  oxidation and reduction center, potassium as the  $\text{NO}_x$  storage element and  $\text{MgAl}_2\text{O}_4$  as the support material. To the best of our knowledge, the reasonably designed  $\text{CuO/K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  catalyst herein has not been reported before.

In this study, we prepared the  $\text{CuO/K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  catalyst by successive impregnation method. The  $\text{Al}_2\text{O}_3$ -supported catalyst with the same Cu and K loading was also prepared for comparison. The  $\text{NO}_x$  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),  $\text{H}_2$  temperature-programmed reduction ( $\text{H}_2$ -TPR), temperature-programmed desorption of  $\text{CO}_2$  ( $\text{CO}_2$ -TPD) and temperature-programmed desorption of  $\text{NO}_x$  ( $\text{NO}_x$ -TPD). Through the results of the above characterizations, we investigated the states of K- and Cu-species in  $\text{CuO/K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  and  $\text{CuO/K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalysts. We also discussed the thermal stability of nitrate on the catalysts and revealed how the  $\text{CuO/K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  catalyst improved the NSR performance at high temperatures.

## 2. Experimental section

### 2.1. Support and catalyst preparation

**2.1.1. Support preparation.** The  $\text{MgAl}_2\text{O}_4$  support was prepared by co-precipitation method. A certain amount of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved and mixed

with vigorous stirring. The pH value of the aqueous solution was adjusted to 9.5 by addition of  $\text{NH}_3 \cdot \text{H}_2\text{O}$ . The mixture was aged at 65 °C for 12 h and then filtrated. The obtained solid was dried at 120 °C for 12 h and then calcined at 800 °C for 5 h. The commercial  $\gamma\text{-Al}_2\text{O}_3$  support (Tianjin Chemical Research & Design Institute) was pre-treated at 600 °C before using.

**2.1.2. Catalyst preparation.** The  $\text{CuO/K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  catalyst was prepared by successive incipient wetness impregnation. The support was immersed into the solution of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ , dried at 120 °C and then calcined at 600 °C for 4 h. Subsequently,  $\text{K}_2\text{CO}_3$  was loaded on the above powder by incipient wetness impregnation. The final sample was obtained after calcination at 600 °C for 2 h. The weight loadings of Cu and K were both 10%.

For comparison, the  $\text{CuO/K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalyst was also prepared by incipient wetness impregnation with the same process. The weight loadings of Cu and K were both 10%. The  $\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$ ,  $\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ ,  $\text{CuO/MgAl}_2\text{O}_4$  and  $\text{CuO/Al}_2\text{O}_3$  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 ( $S_{\text{BET}}$ ) 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  $K\alpha$  radiation  $\lambda = 0.15418$  nm) operating at 40 mA and 40 kV. The diffraction data were collected in the 10 to 90° range at a step size of 0.02°. The crystallite sizes of CuO were calculated by using Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos \theta}$$

$D$  is the crystallite size.  $K$  is a constant.  $\lambda$  is the wavelength of the X-ray device.  $\beta$  is the full weight half maximum.  $\theta$  is the Bragg's angle.

XPS measurements were carried out by using a PHI-1600 ESCA spectrometer with Mg  $K\alpha$  (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.

$\text{H}_2$ -TPR experiments were carried out on the TP-5079 TPDRO apparatus (Xian quan). The reduction gas is 8 vol%  $\text{H}_2/\text{N}_2$  with a flow rate of 30 mL  $\text{min}^{-1}$ . 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  $\text{min}^{-1}$ .



CO<sub>2</sub>-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<sup>-1</sup>) from RT to 900 °C. The heating rate was 10 °C min<sup>-1</sup>.

NO<sub>x</sub>-TPD test was conducted in a quartz-tubular continuous flow reactor (i.d. = 4 mm). The samples were heated in pure N<sub>2</sub> (400 mL min<sup>-1</sup>) from 50 °C to 750 °C and the temperature ramp is 5 °C min<sup>-1</sup>. Before the measurements, the samples were saturated with NO<sub>x</sub> in the lean gas (400 ppm of NO, 5% O<sub>2</sub>, balanced by N<sub>2</sub>) 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<sup>-1</sup> with resolution of 4 cm<sup>-1</sup>. The spectra were recorded in air at RT.

### 2.3. Activity tests

The isothermal NO<sub>x</sub> 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% O<sub>2</sub>, balanced by N<sub>2</sub>; rich gas 1000 ppm C<sub>3</sub>H<sub>6</sub>, balanced by N<sub>2</sub>). The NO<sub>x</sub> concentrations were monitored online by a chemiluminescence NO–NO<sub>2</sub>–NO<sub>x</sub> analyzer (Model 42i-HL, Thermo Scientific). The total gas flow rate was 400 mL min<sup>-1</sup>, corresponding to a weight hourly space velocity of 100 000 mL g<sup>-1</sup> h<sup>-1</sup>. Meanwhile, the concentration of the byproduct N<sub>2</sub>O was monitored online by a N<sub>2</sub>O modular gas analyzer (S710, SICK MAIHAK).

The isothermal NO<sub>x</sub> storage experiments of the catalysts were carried out in the lean atmosphere (400 ppm of NO, 5% O<sub>2</sub>, balanced by N<sub>2</sub>) in the same reactor as above mentioned. The NO<sub>x</sub> concentrations were also monitored by the same analyzer. The total gas flow rate was 400 mL min<sup>-1</sup>, corresponding to a weight hourly space velocity of 100 000 mL g<sup>-1</sup> h<sup>-1</sup>.

The NO<sub>x</sub> reduction percentage (NRP) was calculated according to the steady lean/rich cycle as the following formula:

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

The NSC was taken after the NO<sub>x</sub> storage process prolonged 60 min and calculated as the following formula:

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

The storage ratio was calculated as the following formula:

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

[NO<sub>x</sub>] and [NO<sub>2</sub>] is the concentration of NO<sub>x</sub> and NO<sub>2</sub> 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*<sub>0</sub> is 22.4 L mol<sup>-1</sup>,

*m* is the weight of the sample, *t*<sub>1</sub> is the lean period in one L/R cycle, *t*<sub>2</sub> is 60 min, storage ratio is the percentage of the stored NO<sub>x</sub> to the introduced one.<sup>33</sup>

## 3. Results and discussion

### 3.1. NO<sub>x</sub> storage capacity measurement

NO<sub>x</sub> storage tests were carried out in the temperature range of 350–550 °C. The evolution of outlet NO<sub>x</sub> is depicted in Fig. 1. The NSC was calculated and summarized in Table 1. Fig. 1a shows the NSC profiles of the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst at the different temperatures. The NO<sub>x</sub> storage capacity of the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst varies with the increased reaction temperature. At 350 °C, the NO<sub>x</sub> trapping kinetics is too slow, inducing the low NSC. Fig. 1a shows that after introducing the feeding gas above 400 °C, a rapid NO<sub>x</sub> storage behavior occurs and the NO<sub>x</sub> signal diminishes sharply. Subsequently, the “lean trap” period is observed, namely the stage during which NO<sub>x</sub> is completely captured on the catalysts and no NO<sub>x</sub> is released. Then, the NO<sub>x</sub> concentration gradually recovers to the inlet level until saturation. Probably, CuO is activated above 400 °C for NO oxidation to generate NO<sub>2</sub>, which is beneficial to NO<sub>x</sub> storage under lean-burn conditions.<sup>34,35</sup> Meanwhile, the stored NO<sub>x</sub> gets thermally unstable. With the rising of the reaction temperature, the desorption rate of the released NO<sub>x</sub> from the catalysts is accelerated, as well as the equilibrium of the NO<sub>x</sub> storage process. The largest NSC uptake of the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst is obtained at 450 °C, which is the optimum

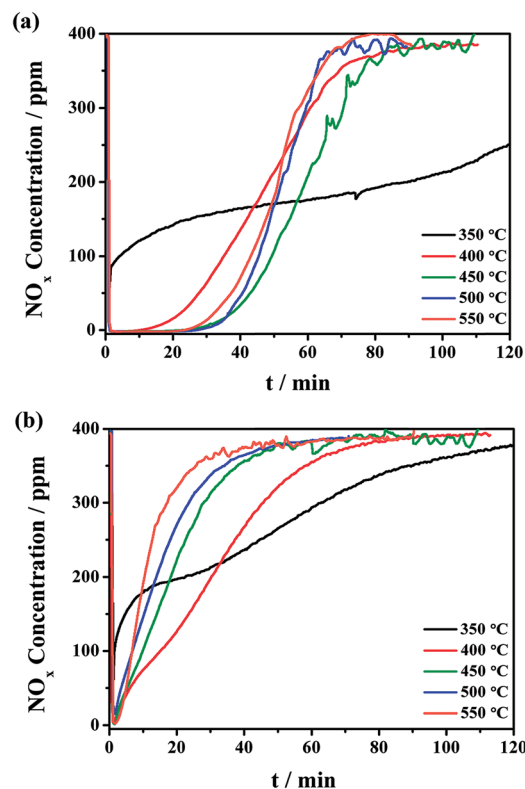


Fig. 1 Isothermal NO<sub>x</sub> storage curves of the (a) CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> and (b) CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts at the different temperatures.



Table 1 NRP, NSC and NO to NO<sub>2</sub> conversion of the catalysts

Catalysts	<i>T</i> (°C)	NRP (%)	NSC (mmol g <sup>-1</sup> )	NO to NO <sub>2</sub> conversion (%)
CuO/K <sub>2</sub> CO <sub>3</sub> /MgAl <sub>2</sub> O <sub>4</sub>	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/K <sub>2</sub> CO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	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<sub>x</sub> storage reaction. The “lean trap” period lasts for more than 20 min and the NSC value is 1.56 mmol g<sup>-1</sup> at 450 °C, which is comparable to or even better than the literature data.<sup>17,36</sup> When the reaction temperature continues to increase, the NSC of the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst decreases slightly because a small amount of the trapped NO<sub>x</sub> decomposes at high temperatures. Fig. 1b shows the NO<sub>x</sub> concentration profiles on the CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst at the different temperatures. Similarly, the CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> 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/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and the NSC value is 0.88 mmol g<sup>-1</sup>.

Differently from the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst, the CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst nearly presents no “lean trap” period in the NO<sub>x</sub> storage profiles. Additionally, the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst achieves maximum NSC value at 450 °C, which is 50 °C higher than that of the CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. With further increasing the reaction temperature above 400 °C, the NSC value of the CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst decreases seriously, whereas, the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst can maintain the large NSC values, making it suitable for the NSR reaction at high temperatures. The NO to NO<sub>2</sub> conversion of the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> and CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts was also measured, and the results were calculated and summarized in Table 1. The NO to NO<sub>2</sub> conversions of the two catalysts are very similar because the oxidation of NO to NO<sub>2</sub> is thermodynamically limited at high temperatures.<sup>5,37,38</sup>

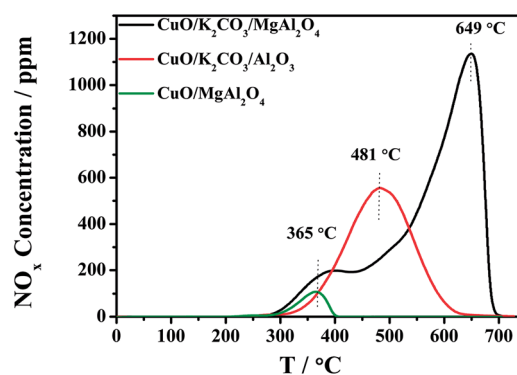
The distinct difference of the NO<sub>x</sub> storage behavior at high temperature between the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> and CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts probably results from the different thermal stability of the formed nitrate during the NO<sub>x</sub> storage reaction. To investigate the thermal stability of the trapped NO<sub>x</sub> on the catalysts, the NO<sub>x</sub>-TPD experiments were conducted after the saturated adsorption of NO<sub>x</sub> at 450 °C. Fig. 2 shows the NO<sub>x</sub>-TPD profiles of the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub>, CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and CuO/MgAl<sub>2</sub>O<sub>4</sub> catalysts. In the profile of the CuO/MgAl<sub>2</sub>O<sub>4</sub>, a single NO<sub>x</sub> desorption peak is observed at 365 °C, which is attributed to the decomposition of nitrates species formed on the MgAl<sub>2</sub>O<sub>4</sub> support, confirming that the support offers additional sites for NO<sub>x</sub> adsorption. It is likely caused by the strong

basicity of MgAl<sub>2</sub>O<sub>4</sub>. However, the MgAl<sub>2</sub>O<sub>4</sub> support is not the main NO<sub>x</sub> 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<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst can be ascribed to the decomposition of KNO<sub>3</sub> on it. Two desorption peaks are clearly observed in the profile of the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst. The first peak at 365 °C is assigned to the NO<sub>x</sub> desorption from the MgAl<sub>2</sub>O<sub>4</sub> support as mentioned above. The latter peak appearing at 649 °C can be attributed to the desorption of the stored NO<sub>x</sub> species on K<sub>2</sub>CO<sub>3</sub>. Thus, the K<sub>2</sub>CO<sub>3</sub> is identified as the main NO<sub>x</sub> storage sites according to the large desorption amount and high thermal stability. Meanwhile, a distinct difference in the decomposition temperatures of KNO<sub>3</sub> between the CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> (481 °C) and CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalysts (649 °C) is observed, suggesting the higher thermal stability of the nitrates on the K sites of the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst, which is the main reason of its higher NO<sub>x</sub> storage ability at high temperatures.

The components of CuO and K<sub>2</sub>CO<sub>3</sub> in the catalyst are designed to act as the NO<sub>x</sub> oxidation sites and storage sites, respectively. To clarify the roles of these two components, the stationary NO<sub>x</sub> storage tests were also performed over the K<sub>2</sub>CO<sub>3</sub>-free or CuO-free catalysts. In Fig. S1,† the K<sub>2</sub>CO<sub>3</sub>-free catalyst of CuO/MgAl<sub>2</sub>O<sub>4</sub> and CuO-free catalysts of K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> show the poor NO<sub>x</sub> adsorbability. The NSC of the CuO/MgAl<sub>2</sub>O<sub>4</sub> sample is only 0.11 mmol g<sup>-1</sup>, because of the absence of K<sub>2</sub>CO<sub>3</sub>, suggesting that K<sub>2</sub>CO<sub>3</sub> is the main NO<sub>x</sub> storage sites. The NSC values of the K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalysts are 0.43 mmol g<sup>-1</sup> and 0.60 mmol g<sup>-1</sup>, respectively. The decline in the NSC values suggests that the NO oxidation ability of CuO plays a significant role in the NO<sub>x</sub> storage process, because NO<sub>2</sub> oxidized from NO is considered to be more easily captured than NO over NSR catalysts.<sup>4,8,39</sup> The result above indicates that both the CuO and K<sub>2</sub>CO<sub>3</sub> play the important roles in the NO<sub>x</sub> storage process.

### 3.2. NO<sub>x</sub> storage/reduction in the lean-rich cycles

The NO<sub>x</sub> 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<sub>x</sub> is depicted

Fig. 2 NO<sub>x</sub>-TPD profiles of the catalysts.



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

Compared with the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalyst, the NSR performance of the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  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  $\text{NO}_x$  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  $\text{NO}_x$  storage at 450 °C. All of the diffraction peaks in Fig. 4a are well matched with spinel-type  $\text{MgAl}_2\text{O}_4$  phase (JCPDS 21-1152). It indicates that the  $\text{MgAl}_2\text{O}_4$  support is successfully synthesized after calcination at 800 °C with no other phase detected. Crystallized CuO phase (JCPDS 48-1548) with  $2\theta$  at 35.6°, 38.7° and 48.7° can be clearly identified on the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  and  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalysts. No characteristic peak of K-related species is detected on the pattern of the fresh  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  and  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalysts in Fig. 4b and c, suggesting that the K-related species may be highly dispersed or in amorphous state.<sup>40</sup> 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  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  and  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalysts is 24.4 and 22.4 nm, respectively.

The phase structure of the catalysts after  $\text{NO}_x$  storage was also characterized as shown in Fig. 4d and e. After the  $\text{NO}_x$  storage treatment at 450 °C, new diffraction peaks at 27.2°, 29.6° and 32.9° assigned to  $\text{KNO}_3$  phase (JCPDS 32-0824) emerge in the XRD patterns of the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  and  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalysts. The transformation of carbonates to nitrates is revealed on the K-related storage sites. Stronger peaks of  $\text{KNO}_3$

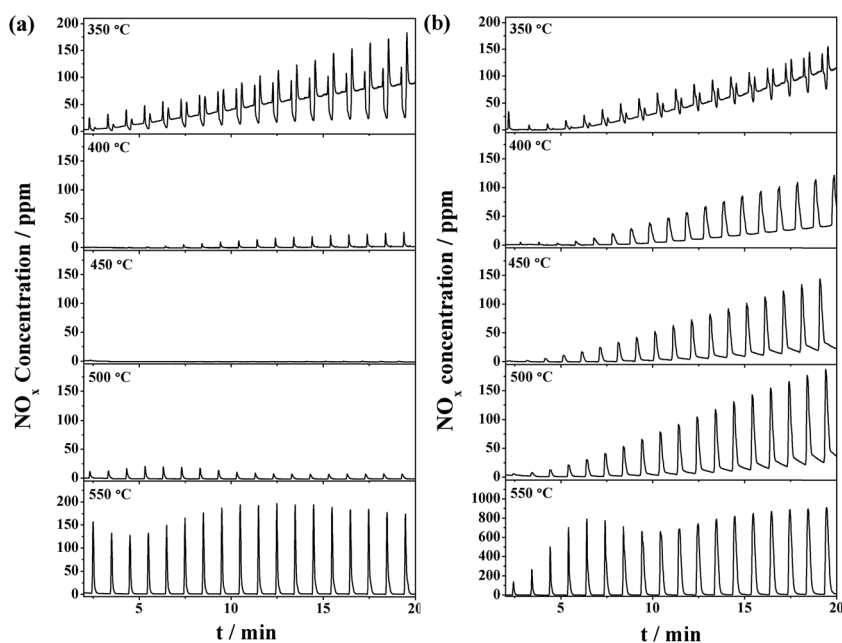


Fig. 3  $\text{NO}_x$  concentration curves during the lean/rich cycles over the (a)  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  and (b)  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalysts.



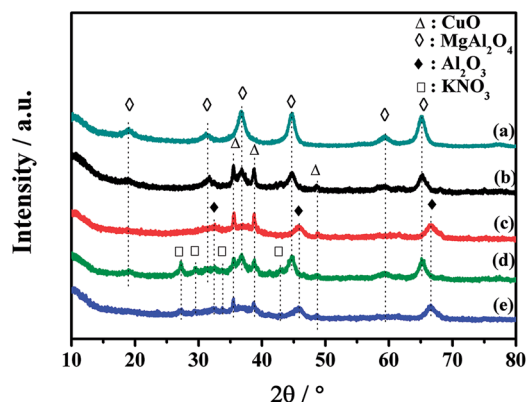


Fig. 4 XRD patterns of the catalysts: (a) fresh  $\text{MgAl}_2\text{O}_4$ , (b) fresh  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$ , (c) fresh  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ , (d)  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  after  $\text{NO}_x$  storage at  $450^\circ\text{C}$  and (e)  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  after  $\text{NO}_x$  storage at  $450^\circ\text{C}$ .

are observed in the XRD pattern of the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  catalyst than those of the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalyst, implying that more  $\text{NO}_x$  was trapped on the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  catalyst. It is in good agreement with the results of NSC. Additionally, after the  $\text{NO}_x$  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.<sup>29,41</sup>

We measured the specific surface areas of the catalysts by  $\text{N}_2$  physisorption. The  $\text{MgAl}_2\text{O}_4$  support has a specific surface area of  $100.2\text{ m}^2\text{ g}^{-1}$ , lower than the commercial- $\text{Al}_2\text{O}_3$  support ( $179.8\text{ m}^2\text{ g}^{-1}$ ). After loading the same amount of Cu and K, the surface areas of the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  and  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalysts drop to 60.5 and  $109.8\text{ m}^2\text{ g}^{-1}$ , respectively. Combined with the NRP and NSC results, the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  catalyst owns the higher NSR activity in spite of the smaller specific surface area compared with the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  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  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  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  $\text{MgAl}_2\text{O}_4$  and  $\text{K}_2\text{CO}_3$ .<sup>42</sup>

### 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  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  and  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  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  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  and  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalysts. For the two catalysts, the Cu 2p spectra are both composed of two typical peaks of  $\text{Cu}^{2+}$  at about 933.5 eV ( $\text{Cu } 2p_{3/2}$ ) and 952.9 eV ( $\text{Cu } 2p_{1/2}$ ) with a satellite shakeup at around 942.3 eV.<sup>43–46</sup> No Cu-related species other than CuO is observed, suggesting the  $\text{NO}_x$  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  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  and  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalysts. An apparent peak centering at about 296.1 eV ( $\text{K } 2p_{3/2}$ ) accompanied by a less intense peak at about 293.0 eV ( $\text{K } 2p_{1/2}$ ) can be assigned to  $\text{K}^+$ . 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.<sup>47</sup> The weak peak locating at 289.7 eV is related to surface carbonate species.<sup>48</sup> 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  $\text{K}_2\text{CO}_3$  were at 288.1 eV and 531.1 eV.<sup>47</sup> Therefore, the C 1s at 289.7 eV and O 1s at 531.1 eV may be assigned to  $\text{K}_2\text{CO}_3$  on the surface of the catalysts.<sup>49</sup> In the preparation process of the catalysts, a part of the  $\text{K}_2\text{CO}_3$

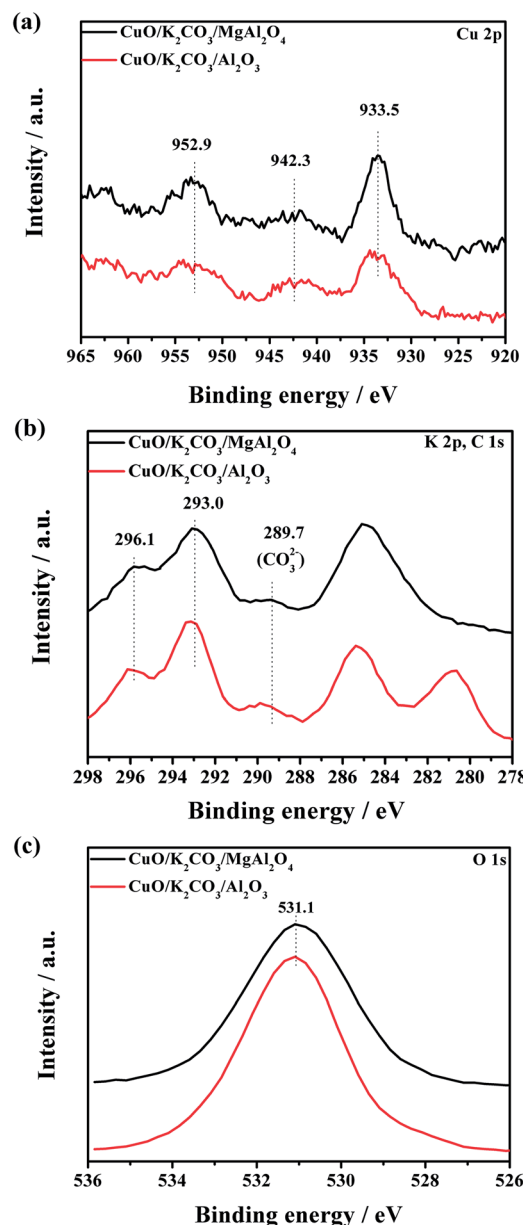


Fig. 5 XPS spectra of the fresh catalysts: (a) Cu 2p, (b) K 2p and C 1s and (c) O 1s.

precursor on the catalysts has decomposed into  $K_2O$  and  $CO_2$  during the calcination at  $600\text{ }^\circ\text{C}$ . 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.<sup>50</sup>

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  $CuO/K_2CO_3/MgAl_2O_4$  and  $CuO/K_2CO_3/Al_2O_3$  catalysts are much lower than their theoretical composition ( $Cu/K = 0.62$ ). It indicates that the  $K_2CO_3$  may partially cover the CuO phase on the surface of the catalysts. The surface Cu/K atomic ratio of the  $CuO/K_2CO_3/MgAl_2O_4$  catalyst is 0.29, larger than that of the  $CuO/K_2CO_3/Al_2O_3$  catalyst (0.24). As we discussed in Fig. S1,<sup>†</sup> the  $NO_x$  storage process will be substantially hindered without the aid of CuO. The higher surface Cu/K ratio of the  $MgAl_2O_4$ -supported catalyst reveals that there is more CuO existing and uncovered on the surface of  $CuO/K_2CO_3/MgAl_2O_4$  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  $CuO/K_2CO_3/MgAl_2O_4$  and  $CuO/K_2CO_3/Al_2O_3$  catalysts and the catalysts after  $NO_x$  storage at  $450\text{ }^\circ\text{C}$ . The reference samples are Cu,  $Cu_2O$  and CuO. Both of the two fresh catalysts show the similar shape and location of the adsorption edge to that of CuO.<sup>41</sup> There is no Cu and  $Cu_2O$  detected on the two catalysts. Therefore, the Cu species on the  $CuO/K_2CO_3/MgAl_2O_4$  and  $CuO/K_2CO_3/Al_2O_3$  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  $CuO/K_2CO_3/MgAl_2O_4$  and  $CuO/K_2CO_3/Al_2O_3$  catalysts.<sup>29,41,51</sup>

The  $H_2$ -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  $MgAl_2O_4$  support. For contrast, pure CuO shows a  $H_2$  consumption peak at  $350\text{ }^\circ\text{C}$ . CuO particles on the  $MgAl_2O_4$  support and  $Al_2O_3$  support can be reduced at much lower temperature of  $240\text{ }^\circ\text{C}$  and  $238\text{ }^\circ\text{C}$ , respectively. After 10% K loading on the  $CuO/MgAl_2O_4$  sample, the main reduction peak shifts to  $327\text{ }^\circ\text{C}$ , which is close to the unsupported-bulk CuO. Notably, a weak reduction peak at  $264\text{ }^\circ\text{C}$  is observed, which is assignable to the uncovered CuO on the  $CuO/K_2CO_3/MgAl_2O_4$  catalyst. While after 10% K loading on the  $CuO/Al_2O_3$  sample, the reduction of CuO occurs at above  $300\text{ }^\circ\text{C}$ . Herein, only the uncovered CuO on the  $CuO/K_2CO_3/MgAl_2O_4$  catalyst can be easy to contact to  $H_2$  and results in the similar reducibility of CuO as the CuO/

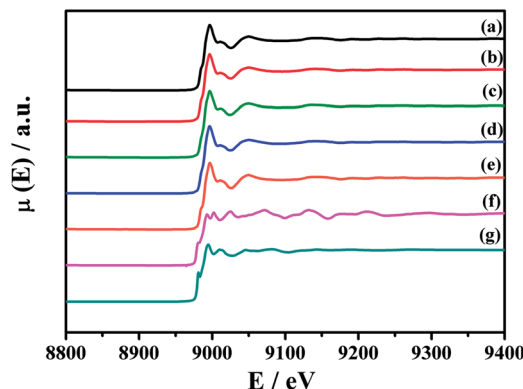


Fig. 6 XANES spectra of Cu K-edge of the samples: (a) fresh  $CuO/K_2CO_3/MgAl_2O_4$ , (b)  $CuO/K_2CO_3/MgAl_2O_4$  after  $NO_x$  storage at  $450\text{ }^\circ\text{C}$ , (c) fresh  $CuO/K_2CO_3/Al_2O_3$ , (d)  $CuO/K_2CO_3/Al_2O_3$  after  $NO_x$  storage at  $450\text{ }^\circ\text{C}$ , (e) CuO, (f) Cu and (g)  $Cu_2O$ .

$MgAl_2O_4$  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  $724\text{ }^\circ\text{C}$  and  $763\text{ }^\circ\text{C}$  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  $K_2CO_3$  species, the  $CO_2$ -TPD experiments of the fresh  $CuO/K_2CO_3/MgAl_2O_4$  and  $CuO/K_2CO_3/Al_2O_3$  catalysts were implemented, and the evolution profiles of  $CO_2$  are presented in Fig. 8. As reported in the literature, two kinds of  $K_2CO_3$  with different thermal stability can be distinguished as a function of decomposition temperature.<sup>41</sup> The reaction occurs as the following expression:  $K_2CO_3 \rightarrow K_2O + CO_2$ . For the  $CuO/K_2CO_3/MgAl_2O_4$  catalyst, the desorption of  $CO_2$  at  $304\text{--}640\text{ }^\circ\text{C}$  is regard to the decomposition of unstable surface  $K_2CO_3$  on the catalyst. The second desorption stage within  $640\text{--}840\text{ }^\circ\text{C}$  can be attributed to bulk/bulk-like  $K_2CO_3$  species with the high thermal stability. For the  $CuO/K_2CO_3/Al_2O_3$  catalyst, the desorption of  $CO_2$  initiates at  $245\text{ }^\circ\text{C}$ . The unstable surface  $K_2CO_3$  decomposes from  $245$  to  $763\text{ }^\circ\text{C}$ , and the bulk/bulk-like  $K_2CO_3$  decomposes from  $763$  to  $840\text{ }^\circ\text{C}$ . By the integration of the  $CO_2$ -TPD curves area, we find that the  $CuO/K_2CO_3/MgAl_2O_4$  and  $CuO/K_2CO_3/Al_2O_3$  catalysts have similar amount of  $CO_2$  desorption, suggesting that the amount of the desorbed  $K_2CO_3$  is similar on the two catalysts. However, the amount of bulk/bulk-like  $K_2CO_3$  on the  $CuO/K_2CO_3/MgAl_2O_4$  catalyst is much larger than that on the  $CuO/K_2CO_3/Al_2O_3$  catalyst, suggesting the higher thermal stability of the  $K_2CO_3$  on the  $CuO/K_2CO_3/MgAl_2O_4$  catalyst.

Table 2 Spectra parameters obtained by XPS of the fresh catalysts

Catalysts	Cu 2p <sub>3/2</sub> (eV)	K 2p <sub>3/2</sub> (eV)	O 1s (eV)	Cu/K (atomic%)
$CuO/K_2CO_3/MgAl_2O_4$	933.5	295.9	531.0	0.29
$CuO/K_2CO_3/Al_2O_3$	933.8	296.1	531.1	0.24



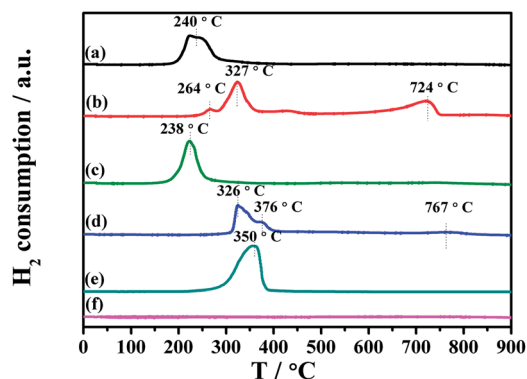


Fig. 7  $\text{H}_2$ -TPR profiles of the samples: (a)  $\text{CuO}/\text{MgAl}_2\text{O}_4$ , (b)  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$ , (c)  $\text{CuO}/\text{Al}_2\text{O}_3$ , (d)  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ , (e)  $\text{CuO}$  and (f)  $\text{MgAl}_2\text{O}_4$ .

In order to explicit the nature of  $\text{K}_2\text{CO}_3$  species, the FT-IR technique was carried out for the fresh  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  and  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalysts, as well as the references of the bulk  $\text{K}_2\text{CO}_3$  and  $\text{MgAl}_2\text{O}_4$ . Fig. 9 shows their FT-IR spectra. The characteristic peaks of the reference bulk  $\text{K}_2\text{CO}_3$  appear at  $1652\text{ cm}^{-1}$ ,  $1427\text{ cm}^{-1}$ ,  $1386\text{ cm}^{-1}$  and  $1110\text{ cm}^{-1}$ . The bands at  $695\text{ cm}^{-1}$  and  $518\text{ cm}^{-1}$  are assignable to typical  $\text{MgAl}_2\text{O}_4$  spinel structure. Compared with the bulk  $\text{K}_2\text{CO}_3$ , the FT-IR spectra of the loaded  $\text{K}_2\text{CO}_3$  on the fresh  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  and  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalysts shows an additional IR band at  $1530\text{ cm}^{-1}$ , belonging to chelating bidentate carbonates.<sup>52</sup> Thus, three kinds of  $\text{K}_2\text{CO}_3$  species, including bridging bidentate carbonates ( $1652\text{ cm}^{-1}$ ),<sup>53</sup> free ionic carbonate  $\text{CO}_3^{2-}$  ( $1410\text{ cm}^{-1}$  and  $1110\text{ cm}^{-1}$ )<sup>52</sup> and chelating bidentate carbonates ( $1530\text{ cm}^{-1}$ ), co-exist on the fresh catalysts.

The IR spectra of the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  and  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalysts after the  $\text{NO}_x$  storage reaction at different temperatures were also collected to investigate to the reactivity of the different types of  $\text{K}_2\text{CO}_3$ . Fig. 10a(2–6) shows the IR spectra of the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  catalyst after the  $\text{NO}_x$  storage reaction at different temperatures. As reported, both the ionic and bidentate nitrates presented on a series of  $\text{K}_2\text{O}/\text{Al}_2\text{O}_3$  catalysts after  $\text{NO}_2$  dosing.<sup>54</sup> The most intense peak at  $1380\text{ cm}^{-1}$  can be identified as ionic nitrates after the  $\text{NO}_x$  storage.<sup>52</sup>

The intensity of this peak varies with the reaction temperature of  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  catalyst, the tendency of which is consistent with the NSC order. The intensity of this peak becomes strongest when the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  catalyst reacts at  $450\text{ }^\circ\text{C}$ . Differently from the fresh  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  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  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  catalyst, suggesting most of carbonates on the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  catalyst participate in the  $\text{NO}_x$  storage. Fig. 10b(2–6) shows the IR spectra of the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalyst after the  $\text{NO}_x$  storage reaction at different temperatures. The peak at  $1380\text{ cm}^{-1}$  attributed to ionic nitrates can also be detected. However, the peaks at  $1652\text{ cm}^{-1}$  and  $1530\text{ cm}^{-1}$  do not completely disappear after the  $\text{NO}_x$  storage process, suggesting that a part of the bridging bidentate carbonate and chelating bidentate carbonate in the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalyst can not completely store  $\text{NO}_x$  at high temperatures. Comparing the IR spectra of the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  and  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalysts after the  $\text{NO}_x$  storage, there is more  $\text{K}_2\text{CO}_3$  on  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  transformed to nitrate. It suggests that the  $\text{MgAl}_2\text{O}_4$  can improve the  $\text{NO}_x$  storage efficiency of  $\text{K}_2\text{CO}_3$  at high operating temperatures. Additionally, after  $\text{NO}_x$  storage at  $450\text{ }^\circ\text{C}$ , the two catalysts were heated in the  $\text{N}_2$  flow at  $450\text{ }^\circ\text{C}$  for 10 min. The IR spectra of the two catalysts after  $\text{NO}_x$ -TPD are shown in Fig. 10a(7) and b(7). For the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  catalyst, the intensity of the peak at  $1380\text{ cm}^{-1}$  in Fig. 10a(7) has little change compared with Fig. 10a(4). For the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$  catalyst, a distinct decrease of peak at  $1380\text{ cm}^{-1}$  in Fig. 10b(7) is observed compared with Fig. 10b(4). The different behaviors at  $1380\text{ cm}^{-1}$  on the two catalysts reveal that the nitrates on the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  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  $\text{NO}_x$  storage reaction will limit their application at high operating temperatures.<sup>16</sup> In Fig. 2, the thermal stability of the nitrates on the K sites of the  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$  catalyst is

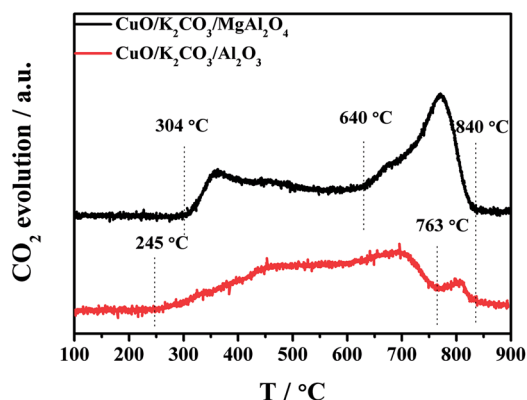


Fig. 8  $\text{CO}_2$ -TPD profiles of the fresh catalysts.

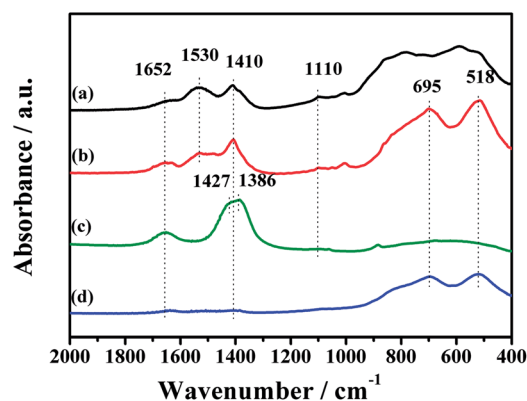


Fig. 9 FT-IR spectra of the samples: (a)  $\text{CuO}/\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3$ , (b)  $\text{CuO}/\text{K}_2\text{CO}_3/\text{MgAl}_2\text{O}_4$ , (c) pure  $\text{K}_2\text{CO}_3$  and (d)  $\text{MgAl}_2\text{O}_4$ .





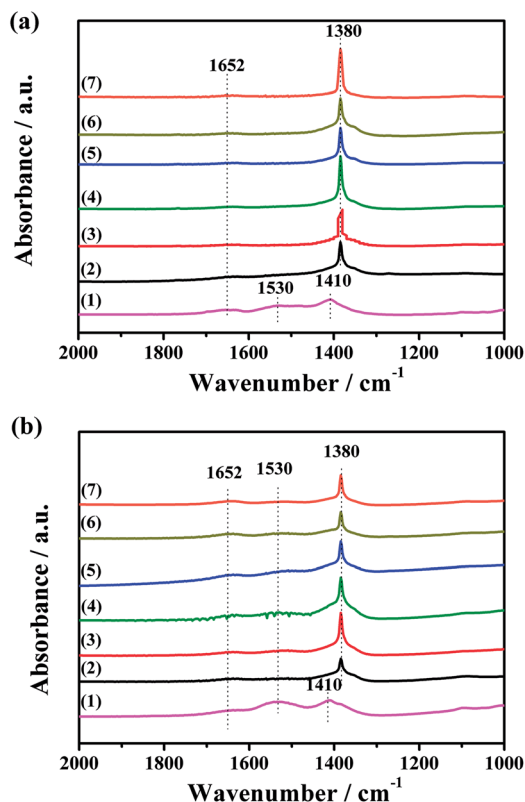


Fig. 10 FT-IR spectra of the (a) CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> and (b) CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts: (1) fresh catalyst, and the catalyst after NO<sub>x</sub> storage reaction at (2) 350 °C, (3) 400 °C, (4) 450 °C, (5) 500 °C and (6) 550 °C, and (7) the catalyst (4) heated at 450 °C in N<sub>2</sub> flow for 10 min.

higher compared with the CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> 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.<sup>17</sup> The charge density of Al<sup>3+</sup> and Mg<sup>2+</sup> is  $4.8 \times 10^{-3} \text{ e nm}^{-3}$  and  $7.5 \times 10^{-4} \text{ e nm}^{-3}$ . Lower extent of polarization of Mg<sup>2+</sup> makes N–O bond less prone to breakage, and thus the nitrates on the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> show the higher thermal stability.

Additionally, in our study, the temperatures of NO<sub>x</sub> desorption correlate to the temperatures of K<sub>2</sub>CO<sub>3</sub> decomposition as mentioned in Fig. 8. Thus, the thermal stability of nitrates is related to the thermal stability of K<sub>2</sub>CO<sub>3</sub>. In other word, the nitrates with high thermal stability may be transformed from the thermal stable K<sub>2</sub>CO<sub>3</sub>. As discussed in Fig. 10, there is more K<sub>2</sub>CO<sub>3</sub> with high thermal stability on the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst than that on the CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, and this part of K<sub>2</sub>CO<sub>3</sub> is the main storage sites in the high-temperature NSR reaction. Thus, the trapped nitrate on the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst shows the high thermal stability.

Through the above discussion, the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst can store much more NO<sub>x</sub> than CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> 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<sub>x</sub> storage capacity of the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> 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/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> 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<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst at high operating temperatures. As concerns of the NSR activity in successive 20 lean/rich cycles between 350–550 °C, the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst performs more effectively and steadily on De-NO<sub>x</sub> in alternative lean/rich atmospheres than the Al<sub>2</sub>O<sub>3</sub>-supported catalyst. Especially, the NO<sub>x</sub> reduction efficiency of the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst achieves a maximum value of 99.9% with a large NO<sub>x</sub> uptake of 1.56 mmol g<sup>-1</sup> at 450 °C. Meanwhile, a high N<sub>2</sub> selectivity of 99.7% was also obtained. The NRP of the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst maintains above 90% at 400–550 °C. While the NRP of the CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst decreases sharply with the increased reaction temperatures.

The states of CuO and K<sub>2</sub>CO<sub>3</sub> species have an apparent difference on the MgAl<sub>2</sub>O<sub>4</sub> and Al<sub>2</sub>O<sub>3</sub> supported catalysts. After K loading, CuO is probably covered by K<sub>2</sub>CO<sub>3</sub>. There is still a part of the uncovered CuO on the MgAl<sub>2</sub>O<sub>4</sub> supported catalyst, but none for the Al<sub>2</sub>O<sub>3</sub> supported catalyst. This part of CuO is beneficial for the oxidation and reduction of NO<sub>x</sub> 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 K<sub>2</sub>CO<sub>3</sub> on the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst can convert to nitrates, but only a part of them participates on the CuO/K<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. Moreover, our results show that the thermal stability of nitrate is consistent with the thermal stability of K<sub>2</sub>CO<sub>3</sub>. The formed nitrates during the lean operation on the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst have the high thermal stability, because of the high thermal stability of K<sub>2</sub>CO<sub>3</sub> supported on the catalyst. Accordingly, the CuO/K<sub>2</sub>CO<sub>3</sub>/MgAl<sub>2</sub>O<sub>4</sub> catalyst exhibits a high NSR activity at high operating temperatures and is a promising high-temperature NSR catalyst.

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