



## Simultaneous soot combustion and nitrogen oxides storage on potassium-promoted hydrotalcite-based CoMgAlO catalysts

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### ABSTRACT

A series of potassium-promoted hydrotalcite-based CoMgAlO mixed oxide catalysts used for simultaneous soot combustion and nitrogen oxides storage were prepared by impregnation method. The techniques of TG/DTA, XRD, H<sub>2</sub>-TPR and *in situ* DRIFTS were employed for catalyst characterization. Over the catalyst containing 7.5% or 10% K, the soot ignition temperature ( $T_i = 260^\circ\text{C}$ ) and total removal temperature ( $T_f = 390^\circ\text{C}$ ) are decreased by  $180^\circ\text{C}$  and  $273^\circ\text{C}$ , respectively, as compared with the uncatalyzed reaction. The results of kinetic calculation show that the presence of K-promoted catalysts decreases the activation energy of soot combustion from 207 kJ/mol to about 160 kJ/mol. When 400 ppm NO is introduced, lower characteristic temperatures or higher reaction rate for soot oxidation is achieved. Simultaneously, relatively larger nitrogen oxides storage capacity is obtained. It is revealed by H<sub>2</sub>-TPR that the addition of K increases the amount of active Co sites and the mobility of bulk lattice oxygen due to the low melting point of K-containing compounds, the low valence of K<sup>+</sup> and the strong interaction between K and Mg(Al). For nitrogen oxides storage, different routes via chelating bidentate nitrates, monodentate nitrates and ionic nitrates are confirmed by *in situ* DRIFTS over the CoMgAlO catalysts with potassium loadings of 0, 1.5 and 7.5%, respectively.

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### 1. Introduction

Currently, diesel engines are widely used due to the high fuel efficiency, reliability and durability. Nitrogen oxides (NO<sub>x</sub>) and soot particulates are the main pollutants produced in the combustion of diesel fuels, which can cause serious environmental problems, such as photochemical smog, acid rain and some human diseases, like asthma [1]. As the legislation limitation is becoming more and more stringent, it is necessary to develop a practicable process to remove these harmful substances [2]. Within the last decade, the combination of NO<sub>x</sub> traps and soot oxidation catalysts has been found to be the most promising after-treatment technique [3].

Although numerous investigations on the soot combustion catalysts have been conducted and theoretical models for NO<sub>x</sub> storage have been developed [4–9], some problems still remain. Among them, the too high temperature of soot combustion and the relatively low NO<sub>x</sub> storage capacity (NSC) are the main aspects. How to simultaneously remove soot and NO<sub>x</sub> in the low and same temperature region, such as 200–400 °C, is still a challenging task. Thus,

exploring more active catalysts for simultaneous soot combustion and NO<sub>x</sub> storage is highly necessary.

Molten salt catalysts, especially the potassium salts due to their high mobility, possess promising activity for soot combustion under realistic conditions [10–13], by increasing their contacting efficiency with the soot. Up to now, extensive investigations on potassium-promoted catalysts for soot combustion [14–17], as well as NO<sub>x</sub> adsorbers [18], have been performed. Querini et al. reported that the Co, K/MgO catalysts are very active for soot combustion due to their improvement in surface mobility and/or volatility in the presence of potassium [19]. Moreover, Takahashi et al. found that the NO<sub>x</sub> storage ability of the potassium-based NO<sub>x</sub> storage material could be improved at high temperature by using the basic MgAl<sub>2</sub>O<sub>4</sub> spinel as support [20]. As a combination, potassium-loaded lanthana was designed and tested as a promising catalyst for the simultaneous soot combustion and NO<sub>x</sub> storage [3]. Recently, calcined hydrotalcite-like compounds (HTLcs) have attracted increasing attention, which are excellent catalysts or supports owing to their large surface areas, basic properties, high metal dispersions and high thermal stability [21,22]. Zhang et al. found that KNO<sub>3</sub> or K<sub>2</sub>CO<sub>3</sub>-supported Mg–Al hydrotalcite-based mixed oxide catalysts displayed high activity for catalytic combustion of diesel soot [23]. It is also reported that the hydrotalcite-based NO<sub>x</sub> storage–reduction (NSR) catalysts show higher activity than

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conventional Pt–Ba/Al<sub>2</sub>O<sub>3</sub> catalysts at the temperatures lower than 250 °C [24,25].

In this work, a series of potassium-promoted CoMgAl hydrotalcite-based mixed oxide catalysts were prepared and used for simultaneous soot combustion and NO<sub>x</sub> storage. It focuses on the promotional effects of potassium. Many techniques, such as TG/DTA, XRD, H<sub>2</sub>-TPR and *in situ* DRIFTS, are employed for catalyst characterization; the calculations of relevant kinetic parameters were also used to evaluate the performance of K-containing catalysts for soot combustion. Based on *in situ* DRIFTS results, different NO<sub>x</sub> adsorption and storage mechanisms were revealed and discussed.

## 2. Experimental

### 2.1. Catalyst preparation

The HTlc Co<sub>2.5</sub>Mg<sub>0.5</sub>/Al was prepared using constant-pH coprecipitation method by adding mixed salt solution and mixed basic solution dropwise into distilled water simultaneously under vigorous mechanical stirring. The mixed salt solution consists of metal nitrates of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O with the designed molar ratio. The mixed basic solution contains NaOH and Na<sub>2</sub>CO<sub>3</sub> with [OH<sup>-</sup>]=2.0 M and [OH<sup>-</sup>]/[CO<sub>3</sub><sup>2-</sup>]=16. Precipitates were kept in suspension at 60 °C under stirring for 4 h, then filtered and thoroughly washed with distilled water. After the cake was dried at 70 °C for 12 h and at 120 °C overnight, the precursor of HTlc was calcined at 600 °C for 4 h to get the desired catalyst (denoted as CMAO).

Catalysts promoted by potassium were prepared by impregnation method using KNO<sub>3</sub> as the precursor. Powder of CMAO was added into the solution of KNO<sub>3</sub> under stirring. Then, the slurry was dried at 120 °C and finally calcined at 600 °C for 2 h. The final catalyst was denoted as x% K/CMAO, where x represents the weight loading of potassium.

### 2.2. Catalyst characterization

The crystal structures of fresh samples were determined by X-ray diffraction measurement on an X'pert Pro rotatory diffractometer operating at 30 mA and 30 kV using Co K $\alpha$  as radiation source ( $\lambda = 0.1790$  nm). Data was recorded for  $2\theta$  values from 10° to 100° with a step size of 0.033°.

H<sub>2</sub>-TPR measurements were performed on a Thermo-Finnigan TPDRO 1100 instrument equipped with a thermal conductivity detector (TCD). The reducing gas was 5 vol.% H<sub>2</sub> balanced by pure N<sub>2</sub>, and a flow rate of 20 mL/min was used. The quartz tube reactor was loaded with 50 mg sample in powder form. The test was carried out from 100 °C to 800 °C at a heating rate of 10 °C/min.

A Perkin-Elmer Diamond TG/DTA instrument was used to obtain TG/DTA profiles. For clarity, the differential TG (DTG) curve was also presented. Each time, appropriate 10 mg of sample was heated at a heating rate of 10 °C/min.

*In situ* DRIFTS experiments were performed on a Nicolet Nexus spectrometer. The spectrometer was equipped with a MCT detector cooled by liquid nitrogen and a heating chamber allowing samples to be heated up to 600 °C. The DRIFTS spectra were recorded against a background spectrum of the sample purified just prior to introducing the adsorbates. In each run, about 15 mg of the sample in powder form was used. The NO<sub>x</sub> adsorption was carried out in order to reveal the NO<sub>x</sub> storage mechanism. The sample was pretreated under 5 vol.% O<sub>2</sub>/He with a flow of 20 mL/min at 350 °C for 30 min, and then exposed to a flow of 400 ppm NO. The spectra of

NO<sub>x</sub> adsorption at 350 °C were recorded at a spectral resolution of 4 cm<sup>-1</sup>.

### 2.3. Activity measurement

For soot combustion, the catalytic activity of the prepared samples was evaluated by TG/DTA technique using Printex-U purchased from Degussa as the model soot. The soot was mixed with the catalyst in a weight ratio of 1:20 in an agate mortar for 30 min to obtain a tight contact. The mixture was heated from room temperature to 800 °C at a heating rate of 5 °C/min in the flow of air. By comparing characteristic temperatures of TG/DTA profiles, catalytic activity of samples was evaluated. In this work, soot ignition temperature (denoted as  $T_i$ ), maximum conversion temperature of soot (denoted as  $T_m$ ) and complete conversion temperature of soot (denoted as  $T_f$ ) were used to evaluate the performance of catalysts. Besides, TG/DTA experiments in the flow of pure N<sub>2</sub>, as well as in NO<sub>x</sub> atmosphere were also carried out to study the reactivity of soot exposing to N<sub>2</sub>, air and NO<sub>x</sub>.

For NO<sub>x</sub> storage, experiments were carried out in a continuous fixed-bed quartz tubular reactor (i.d.=8 mm) mounted in a tube furnace at 350 °C under atmosphere pressure for 1 h, using 100 mg of catalysts with the gas mixture containing 400 ppm NO, 10 vol.% O<sub>2</sub> and N<sub>2</sub> for balance. TG/DTA experiments were performed to evaluate the NO<sub>x</sub> storage performance of the samples.

## 3. Results and discussion

### 3.1. Characterization of the precursor

The TGA profile of the sample during the preparation is shown in Fig. 1. Three stages corresponding to weight loss peaks are associated with the thermal decomposition of the hydrotalcite-like compound [26,27]. The first stage between 100 °C and 200 °C is attributed to the loss of inter-layer and adsorbed water molecules whereas the layered structure is still maintained. Removal of hydroxyl water and inter-layer nitrate anions is in progress around 250 °C. At this stage, part of the layered structure is collapsed. Upon heating to 600 °C, complete pyrolysis occurs and the layered structure is destroyed thoroughly.

Precursor of hydrotalcite-like phase can also be identified with the XRD pattern as shown in Fig. 2. The compound shows the typical diffraction peaks at  $2\theta = 13.4^\circ, 27.2^\circ, 40.1^\circ$  assigned to the (003), (006), (009) crystal planes in the layered structure with a rhombohedral symmetry (3R) [28,29].

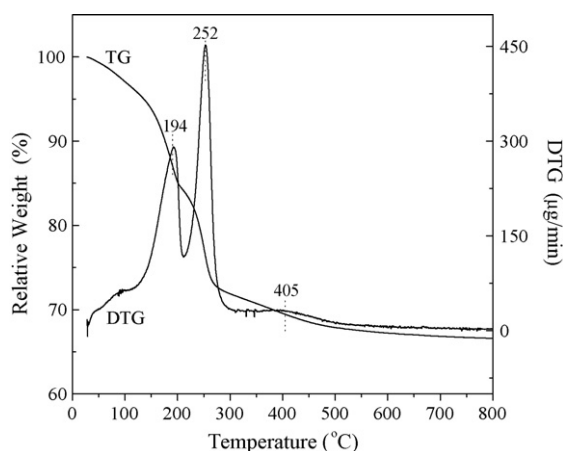


Fig. 1. The TGA profile for the precursor of CMAO catalyst.

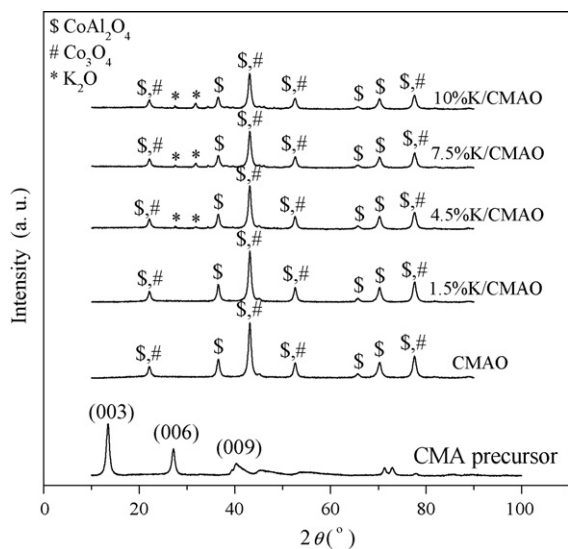


Fig. 2. The XRD patterns of the CMAO precursor and samples after calcination at 600 °C.

### 3.2. Characterization of K-promoted CMAO catalysts

Fig. 2 displays the XRD patterns of the hydrotalcite-based samples calcined at 600 °C. The  $Co_{2.5}Mg_{0.5}Al$ -HT (CMA-HT) is transformed into  $Co_{2.5}Mg_{0.5}Al$ -oxide (CMAO) that consists of a major Co-related phase ( $Co_3O_4$  and/or  $CoAl_2O_4$ ), which is characterized by diffraction peaks at  $\sim 22.1^\circ$ ,  $36.6^\circ$ ,  $43.1^\circ$ ,  $52.7^\circ$ ,  $65.7^\circ$ ,  $70.3^\circ$  and  $77.6^\circ$ . However, no crystalline of Mg oxide phase is detected because of its low content.

For potassium-promoted samples, a new phase of  $K_2O$  is segregated when greater amounts of metal alkali (4.5, 7.5 and 10 wt%) are added. The intensity of the diffraction peaks for Co-related phase decreases with the peak width at half height broadening to some extent after the addition of K ions, indicating the inhibition effects of potassium on the crystallization of  $Co_3O_4$  and/or  $CoAl_2O_4$  phases.

$H_2$ -TPR was employed to examine the redox properties of the catalysts. The results are given in Fig. 3. The profile of CMAO catalyst displays two reduction regions, one between 250 °C and 470 °C and the other above 500 °C. The former can be attributed to the reduction of  $Co^{3+}$  to  $Co^{2+}$  dispersed in the  $Co_3O_4$  phase [26], while the

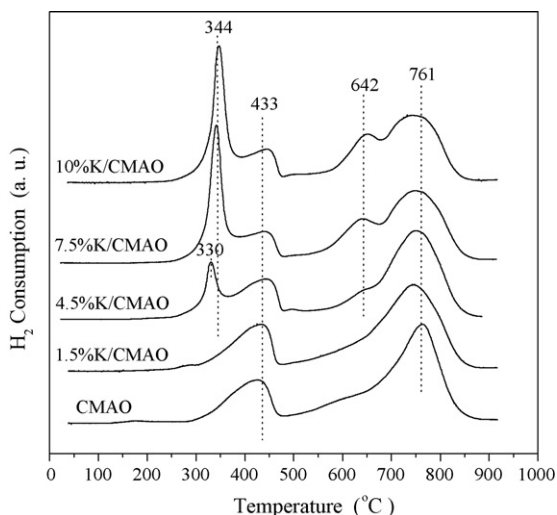


Fig. 3. The  $H_2$ -TPR profiles of the catalysts after calcination at 600 °C.

latter one extending from 500 °C to as high as 900 °C, should contain the reduction of both surface  $Co^{2+}$  ions and subsurface  $Co^{2+}$  ions in diluted  $Co^{2+}-Al^{3+}$  spinel or stoichiometric  $CoAl_2O_4$  [30]. These findings are in good agreement with the XRD results, suggesting the coexistence of  $Co_3O_4$  and  $CoAl_2O_4$  in view of the high Co content in the sample (molar ratio  $Co/Al > 2$ ). When a small amount of K (1.5 wt%) is introduced, no significant change is observed. But after more K is added, each reduction region becomes broader, splitting into two peaks and shifting toward lower temperatures to some extent with more  $H_2$  consumed. These results suggest that strong interactions between K and Mg(Al) species can weaken the bonds in  $CoAl_2O_4$  spinel and Mg(Al)-O. Similar conclusions were ever drawn by Zhang et al. on K/MgAlO catalysts [23]. Thus, active Co sites could be released, facilitating the mobility of bulk lattice oxygen species.

### 3.3. Catalytic soot combustion on K-promoted CMAO catalysts

Fig. 4 displays the TG–DTA curves for the soot combustion in air without catalysts. The results showed that the oxidation of soot started at  $\sim 440^\circ C$  and ended at  $\sim 663^\circ C$ . However, under the practical conditions, the temperature of diesel exhaust is in the range of 200–400 °C, so the activation energy of soot combustion reaction must be lowered.

Fig. 5(a) presents the DTG profiles of soot combustion in air over  $x\%$  K/CMAO catalysts ( $x=0, 1.5, 4.5, 7.5$  and 10). On the CMAO catalyst, the soot ignition and total removal temperatures are 345 °C and 508 °C, about 95 °C and 155 °C lower than those of the uncatalyzed reaction, respectively. With the addition of dopant potassium, the  $T_i$ ,  $T_m$  and  $T_f$  values decrease further. The lowest characteristic temperatures ( $T_i = 260^\circ C$  and  $T_f = 390^\circ C$ ) for soot combustion were observed on 7.5% K/CMAO and 10% K/CMAO catalysts, which are reduced by 180 °C and 273 °C, respectively, as compared with the uncatalyzed reaction under the same atmosphere.

The DTG curves of soot oxidation on K-promoted catalysts under  $NO_x$  atmosphere are illustrated in Fig. 5(b). When 400 ppm  $NO$  is introduced, lower characteristic temperatures are obtained on K-free and 1.5% K/CMAO catalysts. No obvious change is observed over 4.5% K/CMAO catalyst. When the amount of dopant K reaches 7.5%, higher oxidation rates are achieved, as indicated by the sharper peaks. Moreover,  $\Delta T(T_f - T_i)$  is lowered for all the catalysts except 1.5% K/CMAO, suggesting different kinetic mechanism from that under air, which is dependent on the amount of K. It is known that  $NO$  can be oxidized to  $NO_2$  over Co-containing catalysts, which can be stored as nitrates over the samples. So, it is inferred that  $NO_2$

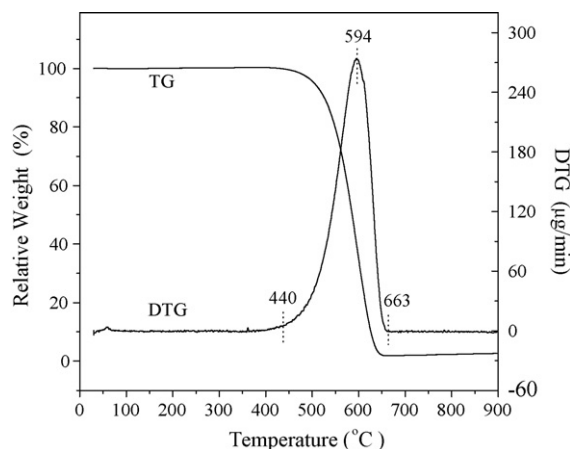


Fig. 4. The TGA curves for the uncatalyzed soot combustion in air.

**Table 1**  
Temperatures to the maximum combustion rate and the kinetic parameters for catalytic soot combustion in air over x% K/CMAO catalysts

Sample	$T_m$ (°C)	Activation energy (kJ/mol)	Frequency factor ( $\times 10^{10} \text{ s}^{-1}$ )	Temperature ranges (10–25% of soot combustion)
Uncatalyzed	594	207.3	0.9	526–557
CMAO	448	178.1	2.7	398–423
1.5% K/CMAO	393	160.5	1.2	353–374
4.5% K/CMAO	356	159.8	9.6	316–339
7.5% K/CMAO	348	156.1	4.4	308–330
10% K/CMAO	348	156.8	4.6	309–332

and/or nitrate species should play crucial role for soot combustion in NO<sub>x</sub> atmosphere.

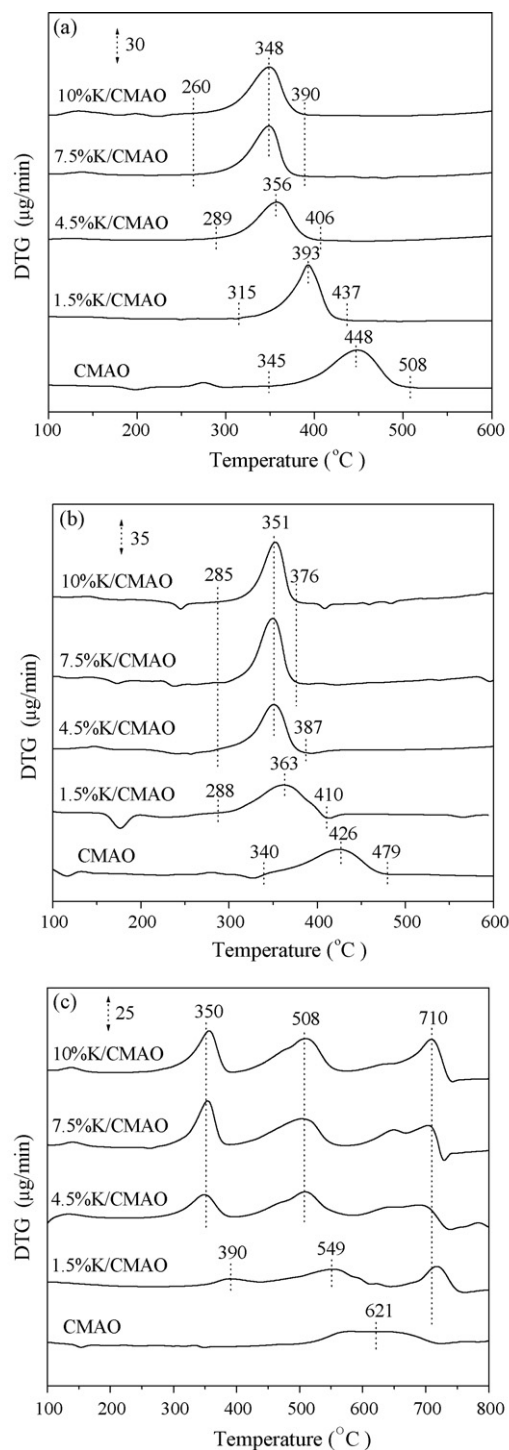
Based on these observations, it can be concluded that potassium plays an important role in enhancing the catalytic activity of CMAO for soot combustion under both air and NO<sub>x</sub> atmosphere. The effects can be attributed to the increase of released active Co sites, caused by strong interactions between K and Mg(Al) species. In addition, mobility of bulk lattice oxygen is also boosted in view of the weakening of the bonds in CoAl<sub>2</sub>O<sub>4</sub> spinel and Mg(Al)–O. This is in accordance with the TPR results as described in the former section. Moreover, in order to make a further confirmation, soot combustion with catalysts in inert gas (N<sub>2</sub>) was also studied as illustrated in Fig. 5(c). As K content was increased, the weight loss peaks appearing at lower temperatures become larger, indicating the easier mobility of bulk lattice oxygen, which is also in good agreement with the H<sub>2</sub>-TPR results. On the other hand, kinetic parameters were also acquired for soot combustion in air over x% K/CMAO catalysts, as shown in Table 1 [31]. It can be seen that the activation energy of reaction decreases from 207 kJ/mol to 178 kJ/mol when the catalysts are used. Subsequently, it is reduced to a lower value ( $\leq 160$  kJ/mol) once K is introduced. These data reveal that the reaction pathway of soot combustion is changed owing to the influence of potassium on the redox properties of the catalysts. The probable reason is that potassium improves the contacting efficiency between soot and the catalyst due to the low melting point of K-containing compounds. Besides, the low valence of K<sup>+</sup> leads to oxygen deficiency in lattice. Moreover, two new kinds of active Co sites are generated, released from Co<sub>3</sub>O<sub>4</sub> and CoAl<sub>2</sub>O<sub>4</sub> spinel, as described in TPR analysis. Thus, O<sub>2</sub> adsorbs on discrepant active sites compared to K-free catalysts, resulting in the difference in reaction pathways.

### 3.4. NO<sub>x</sub> storage behaviors

The NSCs of the catalysts are listed in Table 2, calculated by TG–DTA analysis from the weight loss of the samples after NO<sub>x</sub> storage. The storage experiments were carried out at 350 °C corresponding to the maximal conversion of soot under the same atmosphere. It can be seen that the K-promoted CMAO catalysts exhibit larger NO<sub>x</sub> storage capacities than those free of K. In addition, the NSC value is increased further as the potassium loading increases. However, when the weight loading of K reaches 4.5%, only very limited enhancement can be achieved even more potassium is added.

**Table 2**  
NO<sub>x</sub> storage capacities over CMAO and the K-promoted catalysts

Sample	NO <sub>x</sub> uptake (mg/g catalyst)
CMAO	24.10
1.5% K/CMAO	31.75
4.5% K/CMAO	51.88
7.5% K/CMAO	56.03
10% K/CMAO	61.24



**Fig. 5.** DTG profiles of soot combustion on x% K/CMAO catalysts ( $x=0, 1.5, 4.5, 7.5$  and  $10$ ) in different atmosphere: (a) air, (b) mixture of 400 ppm NO + 10% O<sub>2</sub> balanced by N<sub>2</sub> and (c) pure N<sub>2</sub>.

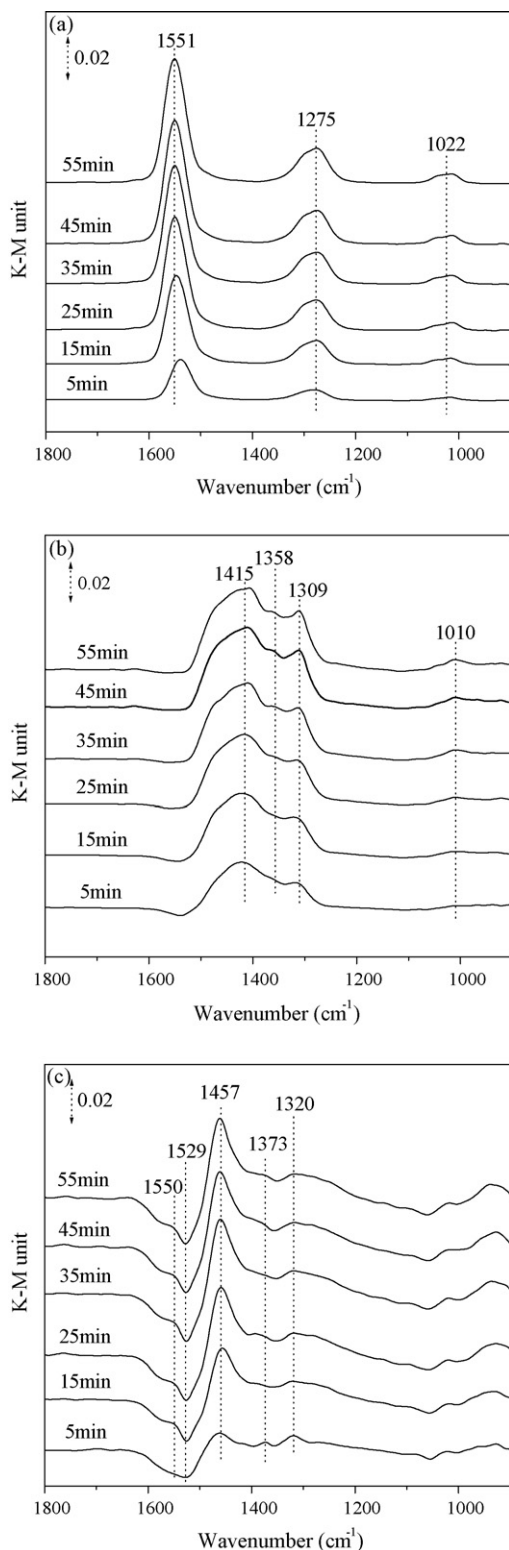


Fig. 6. The *in situ* DRIFTS spectra of NO<sub>x</sub> sorption on different samples: (a) CMAO, (b) 1.5% K/CMAO and (c) 7.5% K/CMAO.

In order to study the function of potassium, the *in situ* DRIFTS experiments were carried out to figure out the storage pathways. Thus, the storage mechanism of NO<sub>x</sub> can be revealed from the species formed during the adsorption process. Fig. 6 presents NO<sub>x</sub> storage results at 350 °C as the feed gas is switched to pass through the catalyst bed. It can be seen that on all catalysts, the adsorp-

tion process can reach a steady equilibrium in an hour. The relative amounts of NO<sub>x</sub> are dependent on the adsorption time and the catalyst composition.

On CMAO catalyst, the adsorption saturation was obtained after NO<sub>x</sub> passed through the sample for 25 min. Chelating bidentate nitrate (1551 cm<sup>-1</sup> and 1275 cm<sup>-1</sup>) is the major species, as presented in Fig. 6(a). For K-containing catalysts, illustrated as Fig. 6(b) and (c), the adsorption time seems to be shorter, testifying the enhancement of potassium on the storage rate. The appearance of negative bands at 1520–1530 cm<sup>-1</sup> in Fig. 6(c) is due to the decomposition of surface carbonates or their transformation to nitrates or nitrites during storage process. Peak at 1275 cm<sup>-1</sup> in Fig. 6(a) shifts to 1300–1550 cm<sup>-1</sup> in Fig. 6(b) and (c), attributed to monodentate nitrates (1358 cm<sup>-1</sup>, 1415 cm<sup>-1</sup> and 1309 cm<sup>-1</sup>) and ionic nitrates (1320 cm<sup>-1</sup>, 1373 cm<sup>-1</sup> and 1457 cm<sup>-1</sup>), respectively, with some other possible minor species such as bridging bidentate nitrate (1309 cm<sup>-1</sup>), chelating bidentate nitrate (1550 cm<sup>-1</sup>), N<sub>2</sub>O<sub>2</sub><sup>2-</sup> species (1415 cm<sup>-1</sup>), etc. [32–36]. It is worth noting that after further addition of K, the band at 1415 cm<sup>-1</sup> corresponding to monodentate nitrate in Fig. 6(b) becomes weaker, which is gradually replaced by another peak at 1457 cm<sup>-1</sup> in Fig. 6(c), arising from the formation of ionic nitrate.

The above results show that the introduction of K facilitates the formation of more kinds of stored N-containing species, corresponding to larger NO<sub>x</sub> trapping efficiency. The N-related species vary obviously as dopant K mounts up, shown in Fig. 7. Addition of K enhances the NSC to a great extent, probably due to the increase of active Co sites for NO oxidation, which is generally considered as the first and a crucial step for NO<sub>x</sub> storage [37]. The function of K in promoting the oxidation ability has been confirmed in TPR section. Several types of nitrates appeared on different samples, indicating different active sites were present as K was doped.

On K-free catalyst, NO<sub>x</sub> are stored in the form of chelating bidentate nitrates on Mg sites, as shown in Fig. 7(a). However, this is not the case for K-containing adsorbers. On 1.5% K/CMAO catalyst, monodentate nitrates are the major species as shown in Fig. 7(b), suggesting that the main storage sites are K-containing species instead of Mg species because of the stronger basicity of K species. When the loading of K is increased to a certain degree, monodentate nitrates transform into ionic nitrates as shown in Fig. 7(c). Toops et al. have also proposed the routes for the storage of NO<sub>x</sub> via ionic nitrates on Pt/K/Al<sub>2</sub>O<sub>3</sub> catalysts [38], where Pt is the active site for NO oxidation, and the highly dispersed K<sub>2</sub>O is thought to be the major potassium species, which is generated from the decomposition of K-containing precursor during the preparation process. In this work, over x% K/CMAO catalysts, similar lean NO<sub>x</sub> trap (LNT) mechanism is assumed, and the Co sites are believed to be responsible for the adsorption and activation of NO molecules. According to XRD (see Fig. 2) and TPR results (see Fig. 3), the addition of K has effectively inhibited the crystallization of Co phases, and enhanced the release of active Co phases, giving more interface area between K and active Co species. The strong electron-donating property of the basic component K may have increased the electronic density around Co sites, facilitating

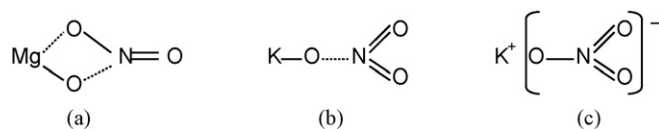
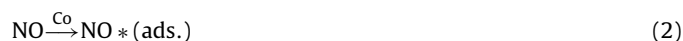
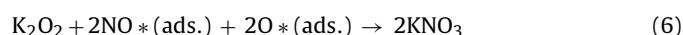


Fig. 7. The models of adsorbed NO<sub>x</sub> species over different samples: (a) chelating bidentate nitrate over CMAO, (b) monodentate nitrate over 1.5% K/CMAO and (c) ionic nitrate over 7.5% K/CMAO.

the adsorption and activation of the oxidative O<sub>2</sub> and NO molecules. The whole storage process can be described by the following reactions:



Some researchers have ever proposed the presence of other potassium oxides, such as K<sub>2</sub>O<sub>2</sub> [39,40], if it is so, the formation of ionic nitrates may be via the following reactions. However, in this work, no evidence is found to support the presence of K<sub>2</sub>O<sub>2</sub>.



#### 4. Conclusions

- (1) The hydrotalcite-based CoMgAlO catalysts promoted by potassium are active for both soot combustion and NO<sub>x</sub> storage in the same temperature range (200–400 °C). When the weight loading of K reaches 4.5%, the prominent enhancement effect is observed. For soot oxidation, the addition of K increases the amount of active Co sites as well as the mobility of bulk lattice oxygen species due to the low melting point of K-containing compounds, the low valence of K<sup>+</sup> and the strong interaction between K and Mg(Al). The presence of K-promoted catalysts decreases the activation energy of soot combustion reaction from 207 kJ/mol to about 160 kJ/mol, suggesting the change of reaction pathway.
- (2) With respect to NO<sub>x</sub> storage process, higher trapping efficiency was obtained over the K-promoted catalysts due to the formation of more kinds of stored N-containing species. The presence of electron-donating K species facilitates the adsorption and activation of gaseous oxygen and NO molecules on the active Co sites. As dopant K mounts up, N-related species vary from chelating bidentate nitrates to monodentate nitrates and ionic nitrates gradually. The main storage phase in K-containing samples is K<sub>2</sub>O.

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