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# Promotion Effects and Mechanism of Alkali Metals and Alkaline Earth Metals on Cobalt–Cerium Composite Oxide Catalysts for N<sub>2</sub>O Decomposition

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A series of alkali metal- and alkaline earth metal-doped cobalt–cerium composite oxide catalysts were prepared by the citrate method and tested for the decomposition of N<sub>2</sub>O. Strong promotion effects of alkali and alkaline earth metals on the activity of the catalyst were obtained in the order Li < Na < K < Rb < Cs and Mg < Ca < Sr, Ba. The promotion effects of alkaline earth metals were much weaker than the effects of alkali metals. To investigate the origin of the promotion effect, X-ray diffraction, Brunauer–Emmett–Teller surface area measurement, X-ray photoelectron spectroscopy, temperature-programmed desorption, and hydrogen temperature-programmed reduction methods were used to characterize the alkali metal-doped catalyst. The analytical results indicated that alkali metals improved the redox ability of active site Co<sup>2+</sup> by acting as electronic promoters. Catalytic decomposition of N<sub>2</sub>O proceeds through an oxidation–reduction mechanism with participation of electrons from Co<sup>2+</sup>, thus the increase in the redox ability of Co<sup>2+</sup> should lead to an increase in the activity of the catalyst.

## 1. Introduction

Catalytic decomposition of nitrous oxide (N<sub>2</sub>O) is an attractive proposition from an environmental point of view because N<sub>2</sub>O is considered to be responsible for the depletion of the ozone layer and for contributing to global warming (1–4). Although N<sub>2</sub>O is not the major contributor to global warming, it is much more potent than either of the other two most common anthropogenic greenhouse gases, CO<sub>2</sub> and CH<sub>4</sub>. It has 310 and 21 times the global warming potential (GWP) of CO<sub>2</sub> and CH<sub>4</sub>, respectively (3).

N<sub>2</sub>O is produced by both natural and anthropogenic sources. To control the emission of N<sub>2</sub>O from chemical processes, catalysts for N<sub>2</sub>O decomposition have been widely studied in the past decade; these catalysts include supported metals, transition metal ion exchanged zeolites, and pure and mixed oxides (1, 3, 5–14). Supported noble metal catalysts, such as Rh and Au catalysts (5–7), show high activities in N<sub>2</sub>O decomposition reactions at 200–300 °C. However, the high cost of the noble metal limits their application. Transition metal ion exchanged zeolite catalysts

such as Fe-ZSM-5 are more active in the selective catalytic reduction (SCR) of N<sub>2</sub>O by hydrocarbons than in the decomposition of N<sub>2</sub>O in a temperature range of 300–400 °C (3). In recent years, it has been found that various mixed oxide catalysts, such as calcined hydrotalcite and spinel oxide, showed relatively high activities.

One of the most active oxide catalysts is a mixed oxide containing cobalt spinel. Calcined hydrotalcites containing cobalt, such as Co–Al–HT (9–12) and Co–Rh–Al–HT (9, 11), have been reported to be very efficient for the decomposition of N<sub>2</sub>O. Yan et al. (13, 14) found that when the Co<sup>2+</sup> in Co<sub>3</sub>O<sub>4</sub> was partially replaced by Ni<sup>2+</sup>, Zn<sup>2+</sup>, or Mg<sup>2+</sup>, the catalytic activity of cobalt spinel could be greatly improved. In our previous work on the influence of preparation methods on the cobalt–cerium composite oxide catalyst, a remarkable promotion effect of residual K was observed (15). The greatly improved redox ability of active site Co<sup>2+</sup> induced by residual K was supposed to be the main reason for the high catalytic activity of the catalyst. The presence of ceria in this catalyst was very important, because it could also improve the cobalt catalyst's activity even in the presence of residual K (15, 16). However, the promotion effect of alkali metals was much greater than that of ceria. Therefore, a detailed study of effect of alkali and alkaline earth metals on cobalt–cerium composite catalysts is very necessary.

The promotion effects of alkali or alkaline earth metals on the catalytic decomposition of N<sub>2</sub>O have also been observed by other researchers. For instance, Farris et al. (17) found in a scale-up process that an appropriate amount of residual Na is very important for the catalytic activity of Co–Al hydrotalcite in N<sub>2</sub>O decomposition. Ohnishi et al. (18) reported that alkali and alkaline earth metals could promote the activity of a Co<sub>3</sub>O<sub>4</sub> catalyst for N<sub>2</sub>O decomposition. The alkaline earth metals showed much greater promotion effects than alkali metals in their study.

Alkali and alkaline earth metal compounds could serve as textural or electronic promoters for catalysts in various catalytic processes. Haber et al. (19) reported that doping with alkali metals could influence the dispersion of rhodium on Al<sub>2</sub>O<sub>3</sub>, and then influence its catalytic activity for the decomposition of N<sub>2</sub>O. Research by Konsolakis and Yentekakis on the SCR of NO by propene over Pt/Al<sub>2</sub>O<sub>3</sub> (20–22) showed that alkali and alkaline earth metals could promote the adsorption of NO (electron-acceptor) on the catalyst surface by acting as electronic promoters. The N–O bond was weakened at the same time, thus facilitating NO dissociation.

To clarify the role of alkali promoters in cobalt–cerium composite oxides (molar ratio of Ce/Co = 0.05) (15, 16), a series of alkali and alkaline earth metal-doped cobalt–cerium composite oxides were prepared and tested for the decomposition of N<sub>2</sub>O. A significant increase of catalytic activity was found when these promoters were present on the catalysts. Methods of X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area measurement, X-ray photoelectron spectroscopy (XPS), carbon dioxide temperature-programmed desorption (CO<sub>2</sub>-TPD), oxygen temperature-programmed desorption (O<sub>2</sub>-TPD), and hydrogen temperature-programmed reduction (H<sub>2</sub>-TPR) were used to characterize these catalysts in order to investigate the origin of this significant promotion effect.

## 2. Experimental Section

**2.1. Catalyst Preparation.** All catalysts were prepared by the citrate method. Nitrates of cobalt, cerium and alkali, or alkaline earth metals were used in appropriate quantities. The details of the method can be seen in the Supporting

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Information or in our previous paper (15). The catalyst is referred to as CC-M-*x* (M indicates the doping alkali or alkaline earth metal; *x* indicates the molar ratio of M/Co, so that *x* = 0 for the undoped catalyst).

**2.2. Catalytic Activity Measurement.** The catalytic reaction was carried out in a fixed-bed quartz flow reactor containing approximately 0.5 g of catalyst in all the experiments. The reactor was heated by a temperature-controlled furnace. A thermocouple was placed on the outside of the reactor tube. Prior to the reaction all samples were pretreated for 30 min with 20% O<sub>2</sub> in Ar at 400 °C to yield clean surfaces, followed by cooling to the reaction temperature in the same gas. A reaction mixture of N<sub>2</sub>O (1000 ppm) in Ar was then introduced into the reactor at a flow rate of 150 cm<sup>3</sup> min<sup>-1</sup>, yielding a space time (W/F) of 0.2 g s cm<sup>-3</sup>. Analysis of the reaction products was carried out using a gas chromatograph (Agilent 6890N equipped with Porapak Q for the analysis of N<sub>2</sub>O, CO<sub>2</sub>, and molecular sieve 5A columns for the analysis of N<sub>2</sub>, O<sub>2</sub> and NO). The reaction system was kept for 1 h at each reaction temperature to reach a steady state before analysis of the product was performed. In all tests, N<sub>2</sub> and O<sub>2</sub> were the only gaseous products that were observed.

**2.3. Catalyst Characterization.** The details for the catalyst characterization (X-rays diffraction (XRD), Brunauer–Emmett–Teller (BET), X-rays photoelectron spectroscopy (XPS)) can be seen in the Supporting Information.

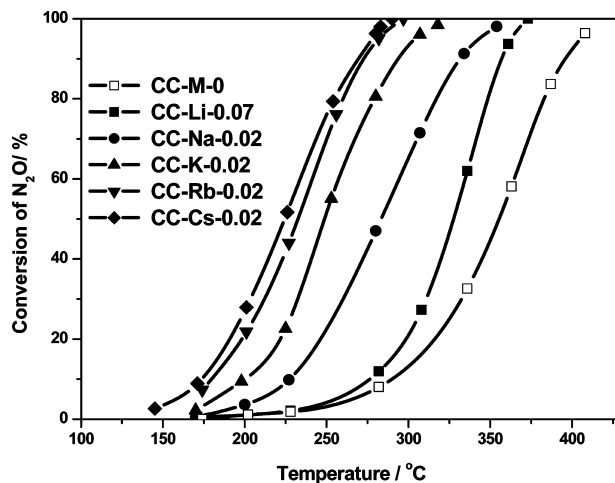
**2.4. O<sub>2</sub>-TPD, CO<sub>2</sub>-TPD and H<sub>2</sub>-TPR.** The O<sub>2</sub>-TPD experiments were performed in a flow of He (30 cm<sup>3</sup> min<sup>-1</sup>) over 200 mg of catalyst using a heating rate of 30 °C min<sup>-1</sup>. Prior to the TPD experiment, the catalysts were pretreated under a flow of 2% N<sub>2</sub>O/Ar (or 10% O<sub>2</sub>/He) at 400 °C for 1 h, followed by cooling to room temperature in the same flow. The decomposition of N<sub>2</sub>O over the catalyst would leave oxygen species adsorbed on the surface, which could be detected using a mass spectrometer (Hiden HPR20) in the TPD experiments. Similar devices were used in CO<sub>2</sub>-TPD and H<sub>2</sub>-TPR experiments and the detailed conditions can be seen in the Supporting Information.

### 3. Results and Discussion

**3.1. Catalytic Activity Measurements.** The amounts of alkali metals used for doping the cobalt–cerium composite oxide catalyst were *x* = 0.01–0.12. The *T*<sub>50</sub> and *T*<sub>90</sub> (the temperature needed to reach 50 or 90% N<sub>2</sub>O conversion) of alkali metal-doped cobalt–cerium composite oxide catalysts were used to optimize the molar ratio (*x*) of alkali metal to Co (Supporting Information Figure S1). The optimal doping amounts of alkali metals were *x* = 0.07 for Li and around *x* = 0.02 for Na-, K-, Rb-, or Cs-doped catalysts. For convenience of comparing the promotion effect of different alkali metals over a wide range of temperature, catalytic activities of catalysts doped with optimal amounts of alkali metals are shown in Figure 1. It can be seen that the alkali metals improve the activity of the cobalt–cerium composite oxide catalyst for N<sub>2</sub>O decomposition in the following order: Li < Na < K < Rb < Cs.

Doping amounts of alkaline earth metal to cobalt–cerium composite oxide catalyst were in the range *x* = 0.005–0.07. We also found that the optimal amount to be added was different for various alkaline earth metals. The catalytic activities of cobalt–cerium composite oxide catalysts doped with optimal amounts of alkaline earth metals are shown in Supporting Information Figure S2. From this result it can be seen that the alkaline earth metals improved the activity of the cobalt–cerium composite oxide catalyst in the order Mg < Ca < Sr, Ba. It should be noted that the promotion effects of alkaline earth metals were much weaker than the effects of alkali metals.

It is well-known that alkali and alkaline earth metals are poisons for the supported V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub> (MoO<sub>3</sub>)/TiO<sub>2</sub> catalysts



**FIGURE 1.** Catalytic activities of cobalt–cerium composite oxide catalysts doped with optimal amounts of alkali metals for N<sub>2</sub>O decomposition. Conditions: total flow, 150 cm<sup>3</sup> min<sup>-1</sup>; W/F = 0.2 g s cm<sup>-3</sup>; gas composition, 1000 ppm N<sub>2</sub>O/Ar.

used in the selective catalytic reduction (SCR) of NO<sub>x</sub> by NH<sub>3</sub> (23). The presence of the poisoning element could block both Brønsted acid and V<sup>5+</sup> = O sites of the catalysts, which play a crucial role in the SCR mechanism. The opposite effects of the same metals in the SCR reaction and the decomposition reaction are understandable because the two reactions use different catalyst and they have totally different catalytic mechanism.

Although Alkali metal oxides were reported to be good catalysts for the N<sub>2</sub>O-carbon reaction (24, 25), alkali and alkaline earth metal compounds are not active for N<sub>2</sub>O decomposition in comparison to oxides of transition metals (1, 26, 27). However, the activity test results suggest that trace amounts of alkali or alkaline earth metal could improve significantly the catalytic activity of cobalt–cerium composite oxides. Ohnishi et al. (18) have reported that alkali and alkaline earth metals could promote the activity of a Co<sub>3</sub>O<sub>4</sub> catalyst for N<sub>2</sub>O decomposition. However, they found that the promotion effect of alkali metals followed the order of Na < Li < Cs < K, and that the alkaline earth metals showed much greater promotion effects than the alkali metals did, which is quite different from the results of the current study. Such differences can be caused by the different doping amount of the promoters. In their study, the optimal doping amount of Na for Co<sub>3</sub>O<sub>4</sub> catalyst was around 1000 ppm (Na/Co = 0.0035), which was obtained by comparing the activities of catalysts prepared by different method. Therefore, the influence of preparation method on the catalyst's activity could not be excluded. Consequently, the order of promotion effect was quite different from each other. Actually, the optimal K/Co molar ratio was found to be 0.02 for Co<sub>3</sub>O<sub>4</sub> catalyst in their recent work (28), which was similar to our result.

In the present study, the promotion effect increases down the group, in both the alkali and the alkaline earth metals. This trend suggests that the promotion effect relates to the period of the element. According to the literature (1), catalytic decomposition of N<sub>2</sub>O proceeds by an oxidation–reduction mechanism with participation of electrons from active sites. In our previous work (15), we have found that traces of residual K in cobalt–cerium composite oxide catalysts improved catalytic activity by improving the redox ability of Co<sup>2+</sup>. Therefore, we deduce that the alkali and alkaline earth metals promote the activity of the catalyst by an electronic effect on Co<sup>2+</sup>. To obtain evidence to support this assumption, a series characterization was carried out on alkali-doped

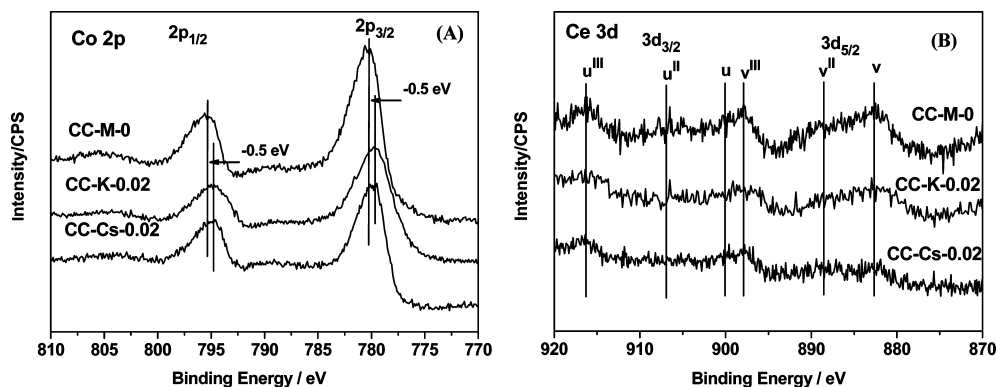


FIGURE 2. XPS spectra of Co 2p (A) and Ce 3d (B) for CC-M-0, CC-K-0.02, and CC-Cs-0.02 catalysts.

cobalt–cerium composite oxide catalysts, which showed the most significant promotion effects.

**3.2. XRD and BET Results.** The XRD patterns of the cobalt–cerium composite oxide catalysts doped with optimal amounts of various alkali metals are shown in Supporting Information Figure S3(A). Strong XRD reflections assignable to the cobalt spinel ( $\text{Co}_3\text{O}_4$ , JCPDS 80-1541) structure were detected for all the samples. Weak XRD peaks of  $\text{CeO}_2$  with a fluorite oxide-type structure (JCPDS 34-0394) were also present in the patterns of all the catalysts, especially for the CC-Li-0.07 catalyst. For the CC-Cs-0.02 catalyst, additional peaks characteristic of  $\text{CsNO}_3$  (JCPDS 81-1138) were observed, which indicates that the additive  $\text{CsNO}_3$  cannot decompose at the calcination temperature ( $400^\circ\text{C}$ ). Because of its small ionic size ( $r_{\text{Li}^+} = 0.068\text{ nm}$ ),  $\text{Li}^+$  may diffuse into the bulk of the  $\text{Co}_3\text{O}_4$  in the CC-Li-0.07 catalyst (29). Therefore, there are no other XRD peaks except those of  $\text{Co}_3\text{O}_4$  and  $\text{CeO}_2$ . In contrast, the ionic size of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ , or  $\text{Cs}^+$  is too large to allow diffusion into the bulk of the  $\text{Co}_3\text{O}_4$ . This may be an important reason for the optimal Li/Co molar ratio ( $x = 0.07$ ) being higher than the optimal molar ratios of the other alkali metals with Co ( $x = 0.02$ ). The absence of XRD reflections other than those of  $\text{Co}_3\text{O}_4$  and  $\text{CeO}_2$  on the CC-Na-0.02, CC-K-0.02 and CC-Rb-0.02 catalysts suggests that these three alkali metals might be highly dispersed or be amorphous on the surface of cobalt–cerium composite oxides. Although the existing state of alkali metals may be different in these CC-M- $x$  catalysts, and it may affect the promotion effect to some extent, however, it did not affect significantly the crystal phases of the catalyst. The alkaline earth nitrates, which are more easily crystallized, did not change the XRD pattern of the catalysts either, as can be seen in Supporting Information Figure S3(B).

The BET surface areas of CC-Li-0.07, CC-Na-0.02, CC-K-0.02, CC-Rb-0.02, and CC-Cs-0.02 are 80, 73, 78, 87, and  $82\text{ m}^2\text{ g}^{-1}$ , respectively. They were similar to the surface area of CC-M-0 ( $87\text{ m}^2\text{ g}^{-1}$ ). Therefore, it can be concluded that addition of various alkali metal promoters did not change the specific surface areas significantly.

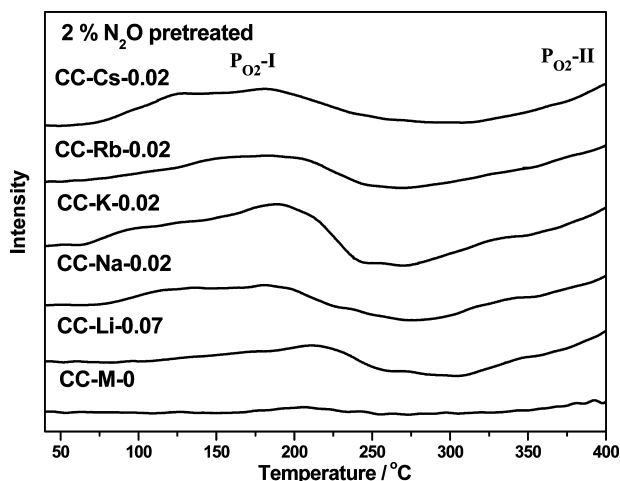
**3.3. XPS Results.** XPS measurements were performed to examine the influence of alkali metals on the valence states of Co and Ce. Figure 2(A) and (B) show the XPS spectra of Co 2p and Ce 3d of the CC-M-0, CC-K-0.02, and CC-Cs-0.02 catalysts, respectively. In Figure 2(A), for the CC-M-0 catalyst, the binding energy (BE) of the Co  $2p_{3/2}$  and Co  $2p_{1/2}$  was 780.2 and 795.3 eV, respectively. The  $2p_{3/2}$ – $2p_{1/2}$  spin orbit splitting ( $\Delta E$ ) was 15.1 eV, which is in good agreement with the reference data for  $\text{Co}_3\text{O}_4$  (30). As for CC-K-0.02 and CC-Cs-0.02 catalysts, BE of the Co  $2p_{3/2}$  and Co  $2p_{1/2}$  both shifted to a lower value compared with CC-M-0, whereas the  $\Delta E$  remained at 15.1 eV. According to literature, the BE of Co may be different in various chemical environments, whereas  $\Delta E$  is a very useful information for elucidating the oxidation state of the catalyst (30). Therefore, it is suggested that the

addition of alkali metals to the catalysts did not change the valance state of cobalt ( $\Delta E$  remained at 15.1 eV); however, the chemical environments of Co ions on the catalysts must be affected. The electronic effect of alkali metals was supposed to be an important reason for the change of the chemical environments of Co ions on CC-M- $x$  catalyst. A similar negative BE shift of Co  $2p_{3/2}$  in K-doped  $\text{Co}_3\text{O}_4$  was also reported by Haneda et al. (29). In that case, they concluded that addition of K was likely to lower the valence state of cobalt. As for  $\text{Co}_3\text{O}_4$ , however, both  $\text{Co}^{2+}$  and  $\text{Co}^{3+}$  exist and the BE of  $\text{Co}^{3+}$  is lower than that of  $\text{Co}^{2+}$ . Therefore, it is difficult to determine whether the valence state of cobalt can be lowered by the addition of K from the negative BE shift of Co  $2p_{3/2}$ . The BE of Co  $2p_{3/2}$ , Co $2p_{1/2}$ , and most importantly,  $\Delta E$  should be examined to verify their conclusion.

Figure 2 (B) shows the XPS spectra of Ce 3d. The three main  $3d_{5/2}$  features at 882.6, 888.5, and 897.9 eV correspond to the v,  $v^{\text{II}}$ ,  $v^{\text{III}}$  components, respectively. The  $3d_{3/2}$  features at 900.1, 906.9, and 916.3 eV correspond to the u,  $u^{\text{II}}$ , and  $u^{\text{III}}$  components, respectively. These three pairs of peaks arise from different Ce 4f electron configurations in the final states of the  $\text{Ce}^{4+}$  species (31, 32). There was no great difference in binding energy of Ce 3d between the doped and undoped cobalt–cerium composite oxide catalysts.

In our previous studies (16), we have found that the presence of ceria in the cobalt catalyst could improve its activity for  $\text{N}_2\text{O}$  decomposition by improving the surface area and redox ability of  $\text{Co}^{2+}/\text{Co}^{3+}$ . Subsequently, the promotion effect of K was found to be more significant than ceria (15, 16). Here, the influence of alkali metal additives on the chemistry environments of Co ions may be an important reason for their high activities.

**3.4.  $\text{CO}_2$ -TPD.** Addition of alkali metals to a catalyst may change the number of base sites on the catalyst. To clarify whether there is a relationship between the activity and the number of basic sites on the catalyst,  $\text{CO}_2$ -TPD experiments were performed over the catalysts doped with optimal amounts of various alkali metals, and the results are shown in Supporting Information Figure S4. The characteristic peaks of these profiles are assigned to their desorption temperatures, indicating the strength of surface basic sites. The  $\text{CO}_2$  desorption peaks located at ca. 50–160, 160–400, and 550–700  $^\circ\text{C}$  corresponded to weak, moderate and strong basic sites, respectively. The number of basic sites was characterized by the size of the corresponding peak. From Supporting Information Figure S4, it can be seen that the doping of alkali metals to the cobalt–cerium composite oxide increased the numbers of the weak and moderate base sites. This effect was strongest when the doping amount was high, as for the CC-Li-0.07 catalyst, or when a strong alkali metal such as Cs was added. However, on comparing the  $\text{CO}_2$ -TPD results and the catalytic activity measurement results, it can be seen that there is no clear relationship between the number of basic sites and the catalytic activities of these catalysts. Our



**FIGURE 3.** O<sub>2</sub>-TPD profiles of cobalt–cerium composite oxide catalysts doped with optimal amounts of alkali metals. Pretreatment condition: the catalysts were pretreated under a flow of 2% N<sub>2</sub>O/Ar at 400 °C for 1 h, followed by cooling down to room temperature in the same flow.

observation is similar to the findings of Obalová et al. (33, 34). Therefore, we conclude that the number of basic sites on the catalyst is not a key parameter in determining the catalytic decomposition of N<sub>2</sub>O.

**3.5. O<sub>2</sub>-TPD.** The decomposition of N<sub>2</sub>O is reported to proceed through an oxidation–reduction mechanism (1). Transition metal ions with more than one valence can act as the active site in this reaction. In the case of the cobalt–cerium composite oxide catalyst, Co<sup>2+</sup> in Co<sub>3</sub>O<sub>4</sub> serves as the active site. Therefore, the redox ability of Co<sup>2+</sup>/Co<sup>3+</sup> is very important for this decomposition reaction (eqs 1 and 2). To investigate the influence of alkali metals on the redox ability of Co<sup>2+</sup>/Co<sup>3+</sup>, O<sub>2</sub>-TPD experiments were carried out on undoped and alkali metal-doped cobalt–cerium composite oxide catalysts.

Prior to the TPD experiment, the catalysts were pretreated in a flow of 2% N<sub>2</sub>O/Ar at 400 °C for 1 h, followed by cooling to room temperature in the same flow. Adsorbed oxygen species derived from the decomposition of N<sub>2</sub>O would be left on the catalyst if the N<sub>2</sub>O decomposition step (eq 1) could proceed at temperatures lower than that required for the O<sub>2</sub> desorption step (eq 2).

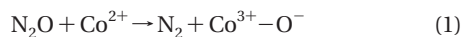


Figure 3 shows the O<sub>2</sub>-TPD profiles of all the catalysts pretreated with N<sub>2</sub>O. As there was no desorption peak of N<sub>2</sub> for all catalysts in the TPD experiments, the possibility of adsorbed N<sub>2</sub>O decomposes to form O<sub>2</sub> during heating process can be excluded. In Figure 3, the broad P<sub>O<sub>2</sub>-I</sub> obtained at 150–200 °C is ascribed to the desorption of surface oxygen species which are formed through the decomposition of N<sub>2</sub>O (eq 1), and the P<sub>O<sub>2</sub>-II</sub> above 350 °C for these catalysts belongs to the desorption of lattice oxygen in Co<sub>3</sub>O<sub>4</sub> (15). For better comparison, the amount of O<sub>2</sub> desorbed in P<sub>O<sub>2</sub>-I</sub> and that of Co<sup>2+</sup> calculated according to eq 2 are listed in Supporting Information Table S1.

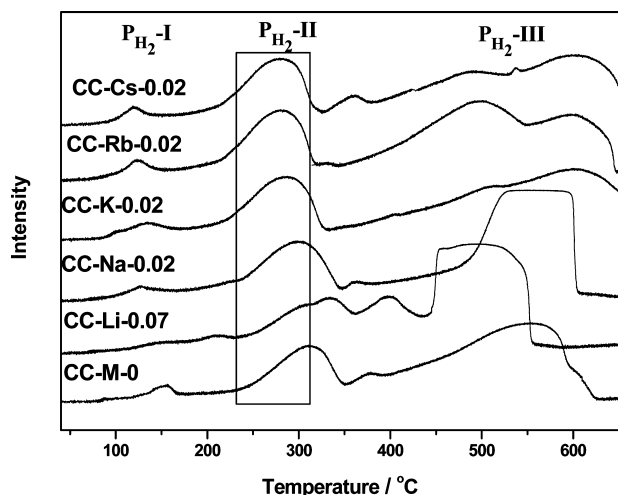
It can be seen from the TPD profiles in Figure 3 and Supporting Information Table S1 that P<sub>O<sub>2</sub>-I</sub> of the CC-M-0 catalyst was very weak, suggesting that Co<sup>2+</sup> in this catalyst should be inactive at low temperatures, thus few oxygen species could be formed on this catalyst after the N<sub>2</sub>O pretreatment. The N<sub>2</sub>O decomposition step (eq 1) is suggested to be the rate-determining step of the whole reaction at low temperatures in this case. When alkali metals were added,

however, P<sub>O<sub>2</sub>-I</sub> of CC-M-*x* became clearly strengthened compared with that of CC-M-0. The intensities of P<sub>O<sub>2</sub>-I</sub> were in the order of CC-Li-0.07 < CC-Na-0.02 < CC-K-0.02. This result suggests that the presence of alkali metals could facilitate the electron donation process of Co<sup>2+</sup> in the N<sub>2</sub>O decomposition step (eq 1), and thus more oxygen species were left on the catalyst after the N<sub>2</sub>O pretreatment at low temperatures (Supporting Information Table S1). The O<sub>2</sub> desorption step (eq 2) is suggested to be the rate-determining step at low temperatures over the alkali metal-doped catalysts. However, when Rb or Cs was added to the catalyst, the P<sub>O<sub>2</sub>-I</sub> became smaller than that of the K-doped catalyst. Considering that the Rb and Cs-doped cobalt–cerium catalysts showed higher measured activity than the K-doped catalyst, a possible reason for their small P<sub>O<sub>2</sub>-I</sub> might be that the desorption of surface oxygen species was easier on these two catalysts than on the K-doped catalyst. Therefore, few surface oxygen species were left on these catalysts after pretreatment.

To prove that the desorption of O<sub>2</sub> is easier on Rb and Cs-doped catalysts than on K-doped one, we also carried out a series of O<sub>2</sub>-TPD experiments over these three catalysts pretreated with O<sub>2</sub>. The O<sub>2</sub>-TPD profiles of these catalysts pretreated with O<sub>2</sub> are shown in Supporting Information Figure S5. Taking all the surface oxygen species into account, it is clear that the amount of oxygen species left on the surface of the CC-Cs-0.02 and CC-Rb-0.02 catalysts was much less than that on the surface of the CC-K-0.02 catalyst. This result suggests that the desorption of surface oxygen species on Cs and Rb-doped catalysts was much easier (or the ability of oxygen adsorption was lower) than on the K-doped catalyst, thus less oxygen was left after the pretreatment. Therefore, the rate-determining step was further accelerated over these two catalysts, and they showed much better activities than other catalysts.

All bonding orbitals in the N<sub>2</sub>O molecule are occupied. The principal catalytic action originates from charge donation into antibonding orbitals of N<sub>2</sub>O from the active site, weakening the N–O bond and lowering the activation energy and reaction temperature (1). Based on the results of the O<sub>2</sub>-TPD experiment, it is suggested that alkali metals present on the catalysts promote the electron donation property of the active site in the order Li < Na < K < Rb < Cs. In addition, doping with Rb or Cs could further facilitate the desorption of surface oxygen species produced from decomposition of N<sub>2</sub>O. Thus a significant promotion effect on catalytic activity could be obtained. This electronic promotion effect of alkali metals on cobalt–cerium for N<sub>2</sub>O decomposition is quite similar to that on the Ru/C catalyst for ammonia synthesis. Zeng et al. (35) have found that the presence of alkali or alkaline earth metals on the Ru/C catalyst could facilitate electron donation from active sites of Ru to the antibonding orbital of N<sub>2</sub>, which substantially weakens the NaN triple bond and facilitates the N<sub>2</sub>-dissociation reaction. In both cases the promotion effects of alkali metals were inversely proportional to the electronegativity of the promoters.

**3.6. H<sub>2</sub>-TPR.** According to the reaction mechanism (eqs 1 and 2), the reducibility of Co<sup>3+</sup> to Co<sup>2+</sup> is a very important property for the decomposition of N<sub>2</sub>O over cobalt containing catalysts, especially for the desorption of surface oxygen species derived from the decomposition of N<sub>2</sub>O. Therefore, H<sub>2</sub>-TPR experiments were carried out to examine the influence of the alkali metals on the reduction behavior of the cobalt–cerium composite oxide catalysts. The TPR profiles are shown in Figure 4. There were three reduction peaks in the profiles. The peak centered at ca. 120–150 °C (P<sub>H<sub>2</sub>-I</sub>) is attributed to the reduction of surface oxygen-containing species (36), P<sub>H<sub>2</sub>-II</sub> centered at 280–310 °C is due to the reduction of Co<sup>3+</sup> to Co<sup>2+</sup>, and P<sub>H<sub>2</sub>-III</sub> in the region of 350–650 °C is due to the reduction of Co<sup>2+</sup> to metallic cobalt Co<sup>0</sup> and partial reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup> (15, 37, 38).



**FIGURE 4.** H<sub>2</sub>-TPR profiles of cobalt–cerium composite oxide catalysts doped with optimal amounts of alkali metals. The rectangle represents the reduction region of Co<sup>3+</sup> to Co<sup>2+</sup> on the CC-M-0 catalyst.

From these profiles, it can be seen that the reduction behavior of the catalyst is greatly influenced by the addition of alkali metals. The reducibility of Co<sup>3+</sup> to Co<sup>2+</sup>, which could be represented by the temperature of P<sub>H<sub>2</sub></sub>-II, increases in the following order: Li < Na < K < Rb < Cs. This sequence is in the same order as that of the catalytic activity, suggesting that the increasing reducibility of Co<sup>3+</sup> to Co<sup>2+</sup> increases the catalytic activity of the cobalt–cerium composite oxide catalyst for the decomposition of N<sub>2</sub>O.

Based on the O<sub>2</sub>-TPD and H<sub>2</sub>-TPR results, it can be concluded that the addition of alkali metals to cobalt–cerium could improve the redox ability of active site Co<sup>2+</sup>. The promotion effect is closely related to the electron donation property of alkali metals. As a result, the reaction rates of eqs 1 and 2 were both increased on the alkali-doped catalysts. The alkaline earth promoters may have a similar effect on the active site. However they exhibited a weaker promotion effect than the alkali metals because of their higher electronegativity.

This study indicates that the addition of alkali or alkaline earth metals to a cobalt–cerium composite oxide catalyst caused a significant increase in catalytic activity for N<sub>2</sub>O decomposition. The promotion effect of these promoters followed the order Li < Na < K < Rb < Cs and Mg < Ca < Sr, Ba. According to the results of the characterization, the addition of the alkali metals did not have great influence on the crystal structure and specific surface area of the catalyst, and the number of basic site on the catalyst was not a key parameter in determining the catalytic decomposition of N<sub>2</sub>O. However, the chemical environments of Co ions appeared to be affected by doping with alkali metals. Based on the O<sub>2</sub>-TPD and H<sub>2</sub>-TPR results, the redox ability of active site Co<sup>2+</sup> was greatly improved by the alkali metals, which act as electronic promoters. The alkali promoters not only facilitate the electron donation process from Co<sup>2+</sup> to the antibonding orbital of N<sub>2</sub>O, but they also improve the reducibility of Co<sup>3+</sup> to Co<sup>2+</sup>, which is important for the desorption of adsorbed oxygen species derived from N<sub>2</sub>O decomposition, and thus the catalytic activity of cobalt–cerium composite oxide catalysts is improved. The alkaline earth promoters, which have higher electronegativity than alkali metals, exhibit a weaker promotion effect than the alkali metal promoters.

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### Supporting Information Available

Information about the details of catalyst preparation and characterization; additional figures and table. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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