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Direct decomposition of NO over alkaline earth metal oxide catalysts supported on cobalt oxide

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The direct decomposition of NO proceeds catalytically on alkaline earth metal oxides supported on Co_3O_4. Activity decreased in the order of $Ba/Co_3O_4 > Sr/Co_3O_4 > Ca/Co_3O_4 \gg Mg/Co_3O_4 \approx Co_3O_4$. The catalytic activity of supported alkaline earth metal oxides was found to be directly related to not only the number of surface basic sites, which corresponds to the surface density of alkaline earth elements, but also to the strength of basicity, suggesting that NO decomposition proceeds on alkaline earth metal oxides.

KEY WORDS: NO decomposition; alkaline earth metal oxides; Co_3O_4.

1. Introduction

Catalysis plays a very important role in solving air pollution problems caused by nitrogen oxides (NO_x). Among various catalytic methods for removing NO_x from exhaust gases, direct decomposition of NO ($2NO \rightarrow N_2 + O_2$) is the most ideal but also the most challenging NO_x abatement process. Until now, numerous studies have been made on this reaction, resulting in the discovery of a wide variety of catalysts, ranging from noble metals to ion-exchanged zeolites [1,2]. However, none has a level of activity that would enable practical application.

Numerous metal oxides have also been examined as candidates for NO decomposition catalysts [3]. Among them, cobalt oxide (Co_3O_4) was found to be one of the most active single metal oxides [4]. However, we have recently reported that NO decomposition takes place slowly, if at all, over Co_3O_4 [5]. The presence of small amounts of alkali metals has been revealed to be essential for the activity for NO decomposition. This interesting effect of alkali metals, particularly Na, was first reported by Kung and coworkers [6]. They proposed, based on their XRD results, that the presence of Na facilitates the formation of active Co^{2+} sites *via* the formation and decomposition of $NaNO_3$, suggesting the importance of a synergistic effect between alkali metals and Co_3O_4.

It has been reported that supported alkaline earth metal oxides such as Sr/La_2O_3 [7] and Ba/MgO [8,9] also show catalytic activity in the NO decomposition reaction. Although alkaline earth metal oxides appear to act as catalytically active components, no one has discussed the relationship between the properties of alkaline earth metal oxides and catalytic performance. This is probably because both the alkaline earth metal oxide and metal oxide support have similar catalytic properties, leading to difficulty in characterizing them independently.

In the present work, we studied the catalytic performance of Co_3O_4-supported alkaline earth metal oxides in NO decomposition. The use of Co_3O_4 makes it possible to characterize the properties, especially basicity, of supported alkaline earth metal oxides because of the quite low basicity of Co_3O_4. In this paper, we report on the relationship between catalytic performance and surface properties as revealed by catalyst characterization.

2. Experimental

2.1. Catalyst preparation

Cobalt oxide (Co_3O_4) was prepared by precipitation. To a solution of $Co(NO_3)_2 \cdot 6H_2O$ was added an aqueous solution of $(NH_4)_2CO_3$ as a precipitation agent at room temperature. The precipitate thus obtained was washed with distilled water, dried at 120 °C and then calcined at 400 °C for 4 h in flowing air. Addition of alkaline earth metal elements (Mg, Ca, Sr and Ba) on the Co_3O_4 support was performed by impregnation with an aqueous solution of alkaline earth metal nitrate, followed by drying at 110 °C. All the catalyst samples were finally calcined at 600 °C for 4 h in flowing air. The atomic ratio of alkaline earth metal to Co_3O_4 (M/Co) was varied from 0 to 0.2.

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2.2. Catalytic activity measurements

The direct decomposition of NO was carried out in a fixed-bed continuous flow reactor. The reaction gas composed of 1000 ppm NO with He as the balance gas was fed to a 0.5 g catalyst at a rate of 30 cm^3 min^{-1}. The effluent gas was analyzed by gas chromatography using a Molecular Sieve 5A column (for analysis of O_2 and N_2) and a Porapak Q column (for analysis of N_2O). Steady-state catalytic activity was measured at each temperature, with the reaction temperature raised from 500 to 750 °C in steps of 50 °C. In the present study, no formation of N_2O was observed.

2.3. Catalyst characterization

The BET surface area of the samples was determined using a conventional flow apparatus (Micromeritics Flowsorb II 2300) by nitrogen adsorption at liquid nitrogen temperature. The crystal structure of the samples was identified by XRD (Mac Science M18XHF^{22}) measurements using Cu Kα radiation at 40 kV and 150 mA.

Temperature-programmed desorption of CO_2 (CO_2-TPD) was performed using a TPD-1-AT-SP (Bell Japan Inc.) to determine the number of surface basic sites. Before each CO_2-TPD measurement, the sample was pretreated in a flow of He at 600 °C for 1 h and then cooled down to 50 °C. CO_2 adsorption was performed by passing a gas mixture of 0.5% CO_2/He through the sample bed at 50 °C for 1 h. After the adsorption gas was purged with He until no CO_2 was detected in the effluent, TPD measurement was carried out up to 600 °C at a heating rate of 10 °C min^{-1} in flowing He at a flow rate of 60 cm^3 min^{-1}. A quadrupole mass spectrometer was used to analyze the desorbed CO_2.

The diffuse reflectance FT-IR spectra were recorded using a Nicolet Nexus 670 FT-IR spectrometer, accumulating 64 scans at a resolution of 4 cm^{-1}. Prior to each experiment, 25 mg of a catalyst placed in a diffuse reflectance high temperature cell (Spectra Tech) fitted with CaF_2 windows was pretreated *in situ* by heating in flowing 10% O_2/He at 600 °C and then purged in He for 1 h, followed by changing to the desired temperature. The background spectrum of the clean surface was measured for spectra correction. The reaction gas containing 1000 ppm NO and He as the balance gas was fed to the catalyst at a flow rate of 30 cm^3 min^{-1}.

3. Results and discussion

3.1. NO decomposition over Sr/Co_3O_4 catalysts

Figure 1 shows the catalytic activity of Sr/Co_3O_4, calcined at 600 °C, with different Sr/Co atomic ratios for NO decomposition. As reported recently [5], Co_3O_4 showed little NO decomposition activity over the entire temperature range. Clearly, the addition of a small amount of Sr (Sr/Co = 0.01) drastically enhanced the activity of Co_3O_4 with respect to NO decomposition. The activity of Sr/Co_3O_4 increased with increasing Sr/Co atomic ratio, reaching a maximum at the Sr/Co atomic ratio of 0.1. Since O_2 was always detected, the direct decomposition of NO appears to proceed catalytically on Sr/Co_3O_4, although the O_2/N_2 ratio was less than unity due to the reaction of O_2 with NO to form NO_2 in the chromatography column. At higher temperatures, catalyst deactivation, probably due to the sintering of the catalysts, occurred.

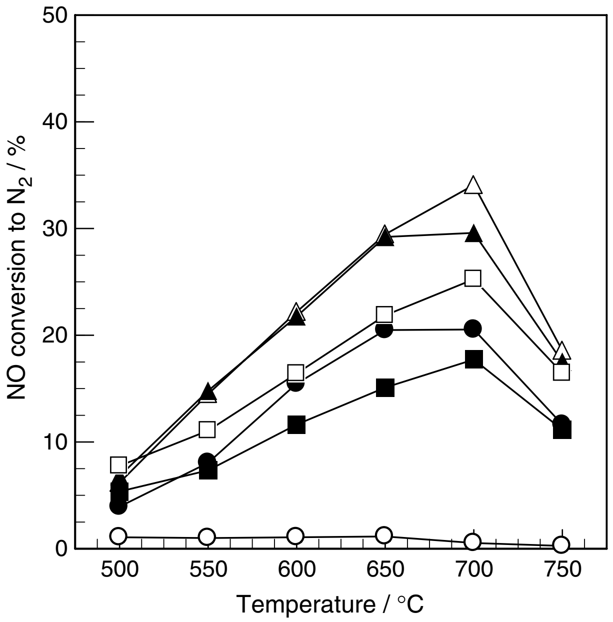

Figure 1. Catalytic activity of Sr/Co_3O_4 with different Sr/Co atomic ratios for NO decomposition. Conditions:NO = 1000 ppm, gas flow rate = 30 cm^3 min^{-1}, W/F = 1.0 gscm^{-3}. (□) Co_3O_4, (□) Sr/Co = 0.01, (≤) 0.017, (π) 0.05, (ρ) 0.1, (*fill*) 0.2.

Table 1 summarizes the BET surface area of fresh Sr/Co_3O_4 catalysts. Although the BET surface area of Co_3O_4 was significantly decreased from 48 to 9 m^2 g^{-1} after calcination at 600 °C, the Sr/Co_3O_4 catalysts still possessed a higher BET surface area. This suggests that the addition of Sr impeded the sintering of Co_3O_4. In table 1 are also given the specific activities, calculated by dividing the formation rate of N_2 in NO decomposition by BET surface area, of Sr/Co_3O_4 catalysts at 600 °C. The specific activity was significantly increased by addition of Sr, suggesting that added Sr increases not only the surface area but also the specific activity per unit surface area.

3.2. Physical properties of Sr/Co_3O_4 catalysts

XRD measurements were performed to identify the crystal structure of Sr/Co_3O_4 samples. The XRD patterns of Sr/Co_3O_4 with different Sr/Co ratios are shown in figure 2. XRD patterns of the samples with Sr/Co $\leq$0.017 showed only the peaks assignable to Co_3O_4 with a spinel

Table 1
BET surface area and NO decomposition activity of alkali earth metal oxide catalysts supported on Co_3O_4

Catalyst	M/Co atomic ratio	BET surface area (m^2 g^{-1})	Amount of CO_2 desorption[c] (mol-CO_2 g^{-1})	Activity at 600 °C	
				μmol-N_2 min^{-1} g^{-1}	nmol-N_2 min^{-1} m^{-2}
Co_3O_4[a]	–	48	–	–	–
Co_3O_4[b]	–	9.0	4.22×10^{-6}	0.14	15.0
Sr/Co_3O_4	0.010	26	4.08×10^{-5}	1.45	55.6
	0.017	30	5.58×10^{-5}	2.06	68.6
	0.050	21	7.41×10^{-5}	2.73	129.9
	0.100	34	7.04×10^{-5}	2.78	81.8
	0.200	23	3.48×10^{-5}	1.94	84.3
Mg/Co_3O_4	0.017	12	1.74×10^{-5}	0.10	8.7
Ca/Co_3O_4	0.017	21	5.43×10^{-5}	1.58	75.1
Ba/Co_3O_4	0.025	30	6.93×10^{-5}	2.89	96.4

[a] Co_3O_4 was calcined at 400 °C.
[b] Co_3O_4 was calcined at 600 °C.
[c] Amount of desorbed CO_2 was evaluated from the CO_2-TPD profiles given in figures 3 and 7.

structure. For the samples with $Sr/Co \geq 0.05$, additional peaks characteristic of $SrCoO_{2.5+\delta}$ [10] were also detected. The intensity of the $SrCoO_{2.5+\delta}$ peaks increased with increasing Sr content. In contrast to the formation of $SrCoO_{2.5+\delta}$, as can be seen in figure 1, the addition of too much Sr into Co_3O_4 ($Sr/Co \geq 0.2$) caused a decrease in activity. The formation of highly crystalline $SrCoO_{2.5+\delta}$ may reduce the surface density of Sr. This conclusion is supported by the results of the CO_2-TPD measurements described below. This is one reason for the presence of an optimal Sr/Co ratio for the NO decomposition reaction.

Since the surface density of Sr on the Co_3O_4 surface was suggested to be an important factor from the above XRD results, CO_2-TPD measurements were made to obtain information on Sr dispersion. Figure 3 shows the CO_2-TPD profiles of Sr/Co_3O_4 samples with different

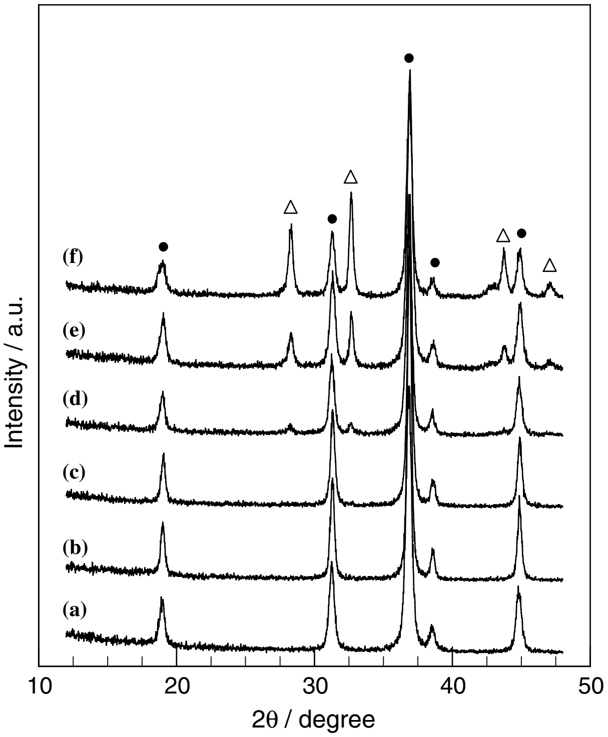

Figure 2. XRD patterns of (a) Co_3O_4 and Sr/Co_3O_4 with Sr/Co atomic ratio of (b) 0.01, (c) 0.017, (d) 0.05, (e) 0.1 and (f) 0.2. (●) Co_3O_4, (△) $SrCoO_{2.5+\delta}$.

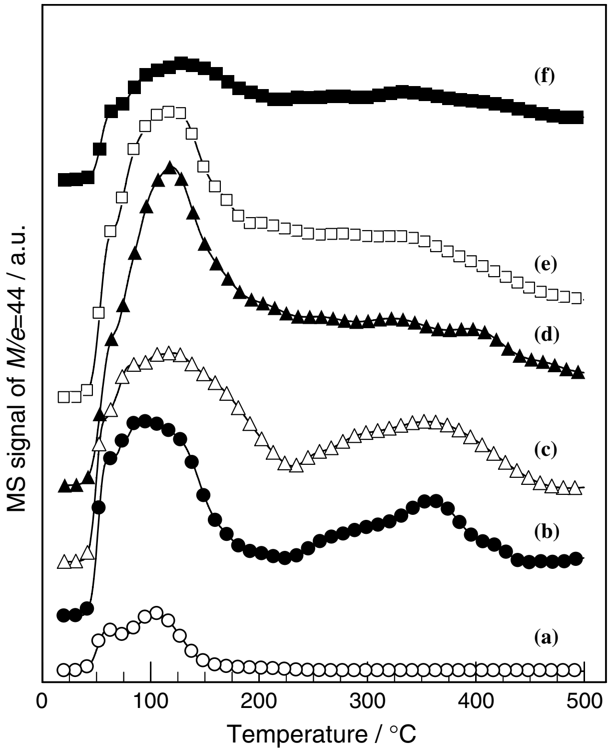

Figure 3. CO_2-TPD spectra for (a) Co_3O_4 and Sr/Co_3O_4 with Sr/Co atomic ratio of (b) 0.01, (c) 0.017, (d) 0.05, (e) 0.1 and (f) 0.2.

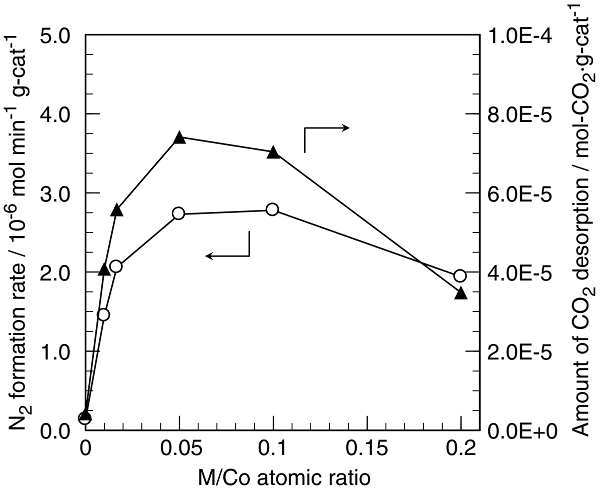

Figure 4. Effect of Sr/Co atomic ratio on NO decomposition activity at 600 °C (▲) and the amount of CO_2 desorption estimated from CO_2-TPD measurements (○) over Sr/Co_3O_4 catalysts.

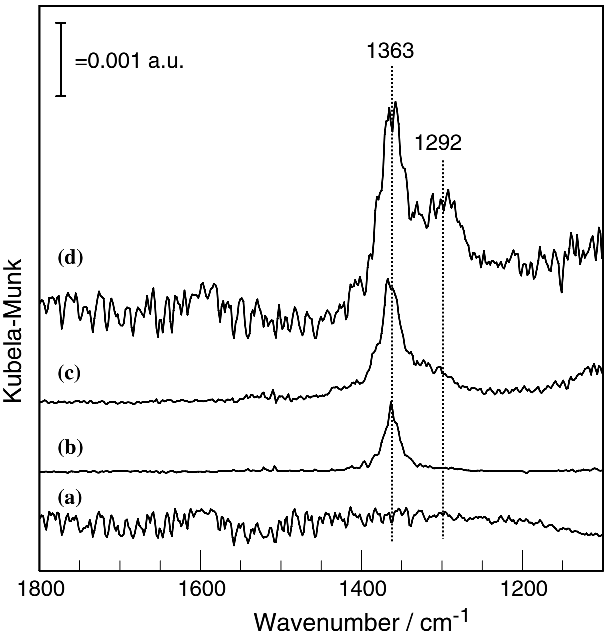

Figure 5. Diffuse reflectance FT-IR spectra recorded in flowing 1000 ppm NO/He over (a) Co_3O_4, (b) Sr/Co_3O_4 with Sr/Co atomic ratio of 0.01, (c) 0.017 and (d) 0.05 at 500 °C.

Sr/Co atomic ratios. Although desorption of CO_2 was observed for Co_3O_4, the intensity of desorption peaks was significantly increased by the presence of added Sr, strongly suggesting that CO_2 is preferentially adsorbed onto Sr sites because of its strong basic property. Figure 4 shows the change in the amount of desorbed CO_2, as well as the rate of N_2 formation at 600 °C, as a function of the Sr/Co atomic ratio. The amount of desorbed CO_2 increased with increased Sr/Co atomic ratio up to 0.05, and then decreased. Comparison with figure 2 indicates that the formation of highly crystalline $SrCoO_{2.5+\delta}$ causes a reduction of surface density of Sr. As can be seen in figure 4, a close correlation was observed between the amount of desorbed CO_2 and the NO decomposition activity, suggesting that the presence of highly dispersed Sr on the catalyst surface is essential for NO decomposition to proceed.

3.3. *Observation of surface species by FT-IR*

The surface species formed during NO decomposition over Sr/Co_3O_4 catalysts were measured using diffuse reflectance FT-IR spectroscopy. We recently reported that the exposure of NO to Co_3O_4 at room temperature gives rise to dinitrosyl and mononitrosyl species coordinated to Co^{2+} sites [11]. However, when 1000 ppm NO/He flowing gas was exposed to Co_3O_4 at 500 °C (figure 5(a)), no IR bands indicating adsorbed NO_x species were detected. This indicates that adsorbed NO_x species are not stable on the surface of Co_3O_4 at high temperatures. This is also supported by the fact that no desorption peak of NO was observed in the NO-TPD profile for Co_3O_4 at temperatures above 350 °C [5]. Taking into account the concept that catalytic reaction normally proceeds *via* the adsorption of reactant, the absence of adsorbed NO_x species at reaction temperatures is likely to be one of the reasons for the low catalytic activity of Co_3O_4 in the NO decomposition reaction.

On the other hand, a distinct IR band at 1363 cm^{-1} was observed for Sr/Co_3O_4 (Sr/Co = 0.01) figure 5(b)). This band can be assigned to polydentate nitrates (NO_3^-) coordinated with Sr^{2+} sites [12]. The band intensity increased with increased Sr/Co atomic ratio. Interestingly, a new IR absorption band at 1292 cm^{-1} appeared in addition to the 1363 cm^{-1} band as the Sr/Co atomic ratio increased up to 0.017 figures 5(c) and (d)). It is well known that the ν_3 split stretching vibration mode of monodentate and bidentate NO_3^- gives a pair of IR absorption bands at around 1550 and 1300 cm^{-1} [13]. Since no IR bands were detected at around 1550 cm^{-1} figure 5), the 1292 cm^{-1} band cannot be assigned to the NO_3^- -like species. This band is probably ascribable to a NO_2^- -like species [13]. It should be noted that the formation of NO_2^- species was observed on Sr/Co_3O_4, which possesses high catalytic activity for NO decomposition (figure 1).

Lunsford and coworkers [8, 9] reported that the NO_3^- species formed on Ba/MgO is a spectator species in NO decomposition reaction and poisons the reaction sites to which it is strongly adsorbed. They also proposed a reaction mechanism of NO decomposition over Ba/MgO, where the gas-phase NO reacts with a surface NO_x species such as NO_2^- on the barium surface. In the reaction over Sr/Co_3O_4, the same conclusion would be obtained from FT-IR results. Namely, the NO_2^- species formed on the Sr surface plays an important role in the process of NO decomposition, while the NO_3^- species does not participate in NO decomposition. A more detailed mechanistic study is now in progress.

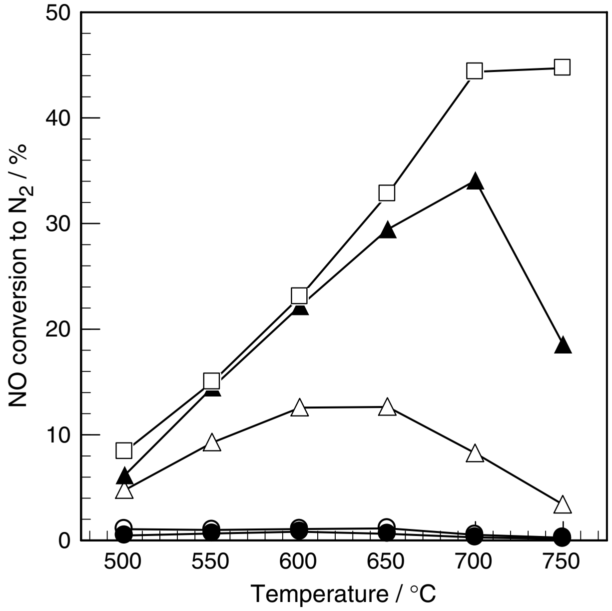

Figure 6. Catalytic activity of alkaline earth metal oxide supported on Co_3O_4 with an optimal M/Co atomic ratio for NO decomposition. Conditions: NO = 1000 ppm, gas flow rate = 30 cm^3 min^{-1}, W/F = 1.0 $gscm^{-3}$. (□) Co_3O_4, (▲) Mg/Co_3O_4 (Mg/Co = 0.017), (△) Ca/Co_3O_4 (Ca/Co = 0.017), (○) Sr/Co_3O_4 (Sr/Co = 0.1), (●) Ba/Co_3O_4 (Ba/Co = 0.025).

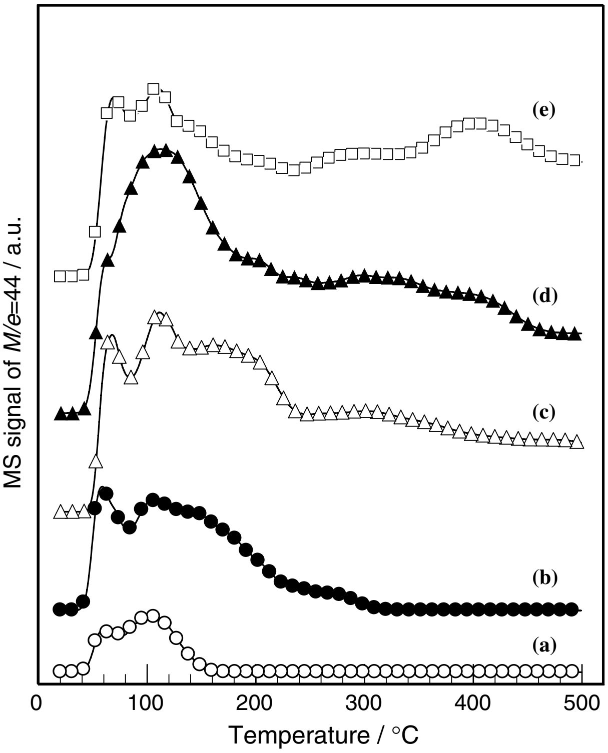

Figure 7. CO_2-TPD spectra for (a) Co_3O_4, (b) Mg/Co_3O_4 (Mg/Co = 0.017), (c) Ca/Co_3O_4 (Ca/Co = 0.017), (d) Sr/Co_3O_4 (Sr/Co = 0.1) and (e) Ba/Co_3O_4 (Ba/Co = 0.025).

3.4. *Activity of alkaline earth metal oxide catalysts supported on Co_3O_4*

The activity of other alkaline earth metal oxide catalysts supported on Co_3O_4 for NO decomposition was measured, where the M/Co atomic ratio was set at the optimal value (M/Co = 0.017 for Mg, 0.017 for Ca, 0.1 for Sr and 0.025 for Ba). The results are shown in figure 6. The NO decomposition reaction took place over Ca/Co_3O_4 and Ba/Co_3O_4, whereas Mg/Co_3O_4 showed little activity. As shown in table 1, since the specific activity of Ca/Co_3O_4 and Ba/Co_3O_4 was much higher than that of Co_3O_4, Ca and Ba appear to act as catalytically active sites for the NO decomposition reaction, as in the case of Sr/Co_3O_4.

It is apparent from figure 6 that the activity of supported alkaline earth metal oxide catalysts decreased in the order of Ba>Sr>Ca$\gg$ Mg. As described before, their catalytic activity is likely to be related to the surface density of alkaline earth elements. CO_2-TPD measurements were also made for all the catalysts. As shown in figure 7, Sr/Co_3O_4 and Ba/Co_3O_4, which showed high NO decomposition activity, gave large CO_2 desorption peaks, and the amount of desorbed CO_2 decreased in the order of Sr$\approx$ Ba>Ca>Mg (table 1). This order is in relatively good agreement with that of the NO decomposition activity. It is also noteworthy that Ba/Co_3O_4 gave a much stronger desorption peak at high temperatures above 300 °C compared with the other catalysts, indicating the presence of strongly basic sites. We can thus conclude that the activity of supported alkaline earth metal oxide catalysts for NO decomposition is related to not only the number of basic sites corresponding to the surface density of alkaline earth elements on the Co_3O_4 but also to the strength of basicity, irrespective of the type of alkaline earth elements.

4. Conclusions

(1) The addition of alkaline earth metal oxides to Co_3O_4 increases not only the surface area but also the specific activity per unit surface area. There is an optimal M/Co atomic ratio. Catalytic activity is related to not only the number of basic sites corresponding to the surface density of alkali elements on the Co_3O_4 but also to the strength of basicity, irrespective of the type of alkaline earth elements, suggesting that the presence of highly dispersed alkaline earth elements on the catalyst surface is essential for the NO decomposition to proceed.

(2) Nitrite and nitrate species are formed on the alkaline earth metal oxide surface, and the former species may serve as an intermediate, although the reaction mechanism remains unclear.

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