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Alkali-doped Co_3O_4 catalysts for direct decomposition of N_2O in the presence of oxygen

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Abstract

Direct decomposition of nitrous oxide (N_2O) on various metal oxide catalysts was examined in the presence of oxygen. The NiO and Co_3O_4 catalysts showed high activities. Whereas the activity of the NiO catalyst was only slightly affected by the preparation conditions, the activity of the Co_3O_4 catalyst severely depended on the preparation conditions. It was found that the sodium content remaining in the precursor was the determining factor for the catalyst activity. Therefore, the effects of alkali doping on the performance of the Co_3O_4 catalysts were examined by using the catalysts prepared by impregnation of commercial $CoCO_3$ with alkali nitrates and subsequent calcination at 400 °C for 4 h. The alkali-doped Co_3O_4 catalysts showed higher activities than pure Co_3O_4. Strontium, calcium and barium ions had also favorable effects, but alkaline earth metals required higher concentration to exert the effects than that required by alkali metals.

Keywords: N_2O decomposition; Co_3O_4; Alkali modification

1. Introduction

Nitrous oxide (N_2O) has a high global warming potential, 310 times larger than that of CO_2 [1], and contributes to the destruction of the ozone layer in the stratosphere [2]. It is emitted from both natural and anthropogenic sources such as nitric acid and adipic acid plants and fluidized bed combustors for sewage-sludge or industrial wastes [3] besides the medical exhaust and biological and agricultural emissions. The concentration of nitrous oxide in the atmosphere continues to increase, and this increase appears to be caused mainly by human activities. With increasing concerns about protecting our environment, the catalytic removal of nitrous oxide from exhaust becomes very attractive. It was reported that nitrous oxide is easily decomposed to nitrogen and oxygen on various types of catalysts such as noble metals [2–5], metal oxides [6–10], and ion-exchanged zeolites [11–13]. However, few of them have been found to be active and stable enough for industrial applications, because their activities are severely inhibited by the presence of other gases such as O_2. Moreover, oxygen atoms formed by the decomposition of nitrous oxide are hardly desorbed from the catalyst surface and accumulated on the surface, finally causing catalyst deactivation [3,14]. Therefore, there is a need for further studies on the development of the catalysts from the following two points of view: (i) to find new active catalyst and (ii) to improve its activity and stability towards the inhibitory gases.

In this study, we have made a survey of various metal oxide catalysts for direct decomposition of nitrous oxide in the presence of oxygen and found that the Co_3O_4 catalyst prepared under specific conditions has a quite high activity. The effects of the modification of the Co_3O_4 catalyst with alkali and alkaline earth ions were examined in order to find the factors determining the catalytic activity.

2. Experimental

2.1. Materials

Commercial cobalt nitrate (Wako), nickel nitrate (Wako), copper nitrate (Nacalai), magnesium nitrate (Wako), sodium

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bicarbonate (Wako), sodium hydroxide (Nacalai), cobalt carbonate (Nacalai), and lithium (Nacalai), sodium (Wako), potassium (Wako), cesium (Wako), calcium (Wako), strontium (Wako), and barium (Wako) nitrates were used without further purification. Alkali content in the commercial cobalt carbonate sample was analyzed to be <50 ppm.

2.2. Preparation of various metal oxide catalysts

The precursors of the Co_3O_4 catalysts were prepared by the precipitation method. A cobalt nitrate solution held at a desired temperature was at once poured into a solution containing a large excess of sodium hydroxide or sodium bicarbonate kept at that temperature. The precipitate was aged, washed with water and dried at 80 °C. The Co_3O_4 catalysts were prepared by calcination of the precipitate at 400 °C for 4 h.

The sources of the other metal oxides used as catalysts are listed in Table 1, together with their BET surface areas. The MgO, NiO and CuO catalysts were prepared by precipitation method from the corresponding metal nitrate solutions with sodium hydroxide at 0 °C, followed by drying and calcination as described for the preparation of the Co_3O_4 catalysts.

Alkali-doped Co_3O_4 catalysts were prepared by impregnation of commercial $CoCO_3$ or Co_3O_4 (prepared by calcination of commercial $CoCO_3$ at 400 °C) with the aqueous solutions of alkali or alkaline earth metal nitrates. The dried catalysts were calcined in air at 400 °C for 4 h.

2.3. Catalyst test

Catalyst tests were carried out in a fixed-bed flow reactor. The catalyst was tabletted, pulverized into 10–22 mesh, and set in the reactor. The catalyst bed was heated to 500 °C in a helium gas flow and held at that temperature for 30 min. Then, the reaction gas composed of 5000 ppm N_2O, 2% O_2, and He balance was introduced to the catalyst bed at $W/F = 0.3$ g s ml^{-1}. The effluent gases from the reactor were analyzed every 5 min with an on-line micro-gas-chromatograph (CP 2002, Chrompack, Netherlands) (columns: 10 m molecular sieve 5A at 80 °C; 10 m Porapack Q at 40 °C). After the steady state was attained, reaction temperature was decreased from 500 °C to the temperature where the catalyst showed negligible N_2O conversion. N_2O was selectively decomposed to N_2 and no other nitrogen-containing products were detected by mass spectrometric analysis (Pfeiffer Vacuum Omnistar GSD 301). The catalyst activity is also expressed by the T_{50} value, which is defined as the temperature at which the catalyst exhibits 50% N_2O conversion under the above-mentioned conditions.

Table 1
Preparation conditions and BET surface area of the various metal oxide catalysts

Catalyst	Preparation conditions	BET surface area (m^2 g^{-1})	T_{50} (°C)
NiO	$Ni(NO_3)_2$ and NaOH at 0 °C	60	300
Co_3O_4	$Co(NO_3)_2$ and NaOH at 0 °C	26	382
CuO	$Cu(NO_3)_2$ and NaOH at 0 °C	11	365
MnO_2	Wako	49	~500
MgO	$Mg(NO_3)_2$ and NaOH at 0 °C	173	~500
Fe_3O_4	Nacalai	5.4	>500
CeO_2	Nacalai	1.3	>500
Al_2O_3	JRC-ALO-8[a]	173	>500
Cr_2O_3	Nacalai	3.5	>500

[a] Standard catalyst from Catalysis Society of Japan.

2.4. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XD-D1 diffractometer using Cu Kα radiation and a carbon monochromator. The specific surface area was calculated by BET single-point method on the basis of nitrogen uptake measured at 77 K. The Na/Co ratio in the cobalt precursor was determined by atomic absorption spectroscopy (Shimadzu, AA-6400F).

3. Results and discussion

3.1. N_2O decomposition over various metal oxide catalysts

The activities of various metal oxides for N_2O decomposition in the presence of 2% oxygen were examined (Table 1). The catalytic activity decreased according to the following order: $NiO > Co_3O_4 > CuO > MnO_2 \approx MgO > Fe_3O_4 > Al_2O_3 \approx CeO_2 \approx Cr_2O_3$. Although the activities of Ni- and Co-based catalysts were well documented [8–10,15–20], most of the works were devoted to the mixed oxide catalysts derived from

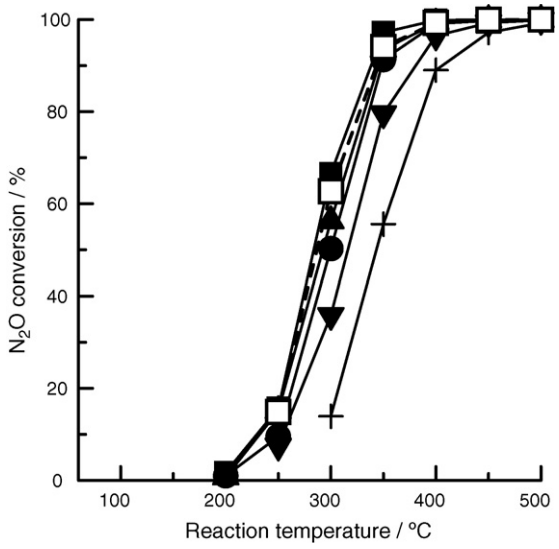

Fig. 1. N_2O decomposition activities of NiO catalysts prepared by calcination of the precursors formed from a $Ni(NO_3)_2$ solution at 0 °C with various precipitating agents: (●) NaOH; (■) $NaHCO_3$; (□) $NaHCO_3$ (prepared at 35 °C); (▲) Na_2CO_3; (▼) K_2CO_3; (+) $(NH_4)HCO_3$. Reaction conditions: N_2O, 5000 ppm; O_2, 2%; He balance; $W/F = 0.3$ g s ml^{-1}.

the hydrotalcite-like phases and therefore we tried to examined the activities of the NiO and Co_3O_4 catalysts.

3.2. The effect of the preparation conditions of the NiO and Co_3O_4 catalysts

The precursors of the NiO catalysts were prepared from nickel nitrate using various precipitating agents, and the activities of the NiO catalysts, obtained by calcination of the precursors at 400 °C, are shown in Fig. 1. The catalyst activity was only slightly affected by precipitation conditions.

On the contrary, the activities of the Co_3O_4 catalysts strongly depended on the preparation conditions, such as the kind of precipitating agents, mixing temperature and aging time (Fig. 2). We found that when cobalt carbonate was obtained as the precursor, the Co_3O_4 catalyst prepared by calcination thereof exhibited high activity. Detailed precipitation chemistry of the precursor of the Co_3O_4 catalysts will be discussed in a separate paper.

In order to find the factors determining the catalytic activity, the amount of sodium ions remaining in the precursors was determined by atomic absorption spectroscopy. Fig. 3 shows the T_{50} value of the catalyst plotted against the Na content remaining in the precursor as expressed by the Na/Co atomic ratio, which clearly indicates that the catalytic activity is closely connected with the Na^+ ion concentration. The optimal Na/Co molar ratio was 3.8×10^{-3}.

Interestingly, Haber et al. reported that doping the catalyst support with an adequate amount of alkali metals promoted the activity of a $Rh/\gamma\text{-}Al_2O_3$ catalyst [5]. However, they found that this promoting effect was brought about by an increase in dispersion of the Rh catalyst, and therefore this explanation cannot be applied for the present case since the surface areas (41–62 $m^2\ g^{-1}$) of the Co_3O_4 catalyst were essentially identical irrespective of the precipitating agent for the precursor.

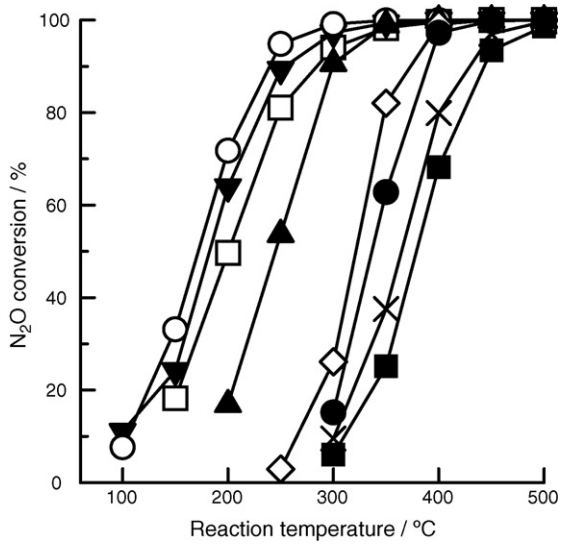

Fig. 2. N_2O decomposition activities of Co_3O_4 catalysts obtained by calcination of the precursors prepared with $NaHCO_3$ under various conditions (temperature, aging time, precursor phase, remarks if necessary): (○) 35 °C, 1 h, cobalt carbonate, synthesized in a large scale; (▼) 0 °C, 1 h at 0 °C and then for a week at room temperature, cobalt carbonate; (□) 35 °C, 1 h, cobalt carbonate; (▲) 35 °C, 1 h, cobalt carbonate, stirred during precipitation; (◇) 50 °C, 1 h, kambaldaite-like [21], $Co(NO_3)_2$ was added slowly with a micro tube pump; (●) 35 °C, 24 h, kambaldaite-like; (×) 35 °C, 1 h, hydrotalcite-like, stirred slowly; (■) 0 °C, 1 h, hydrotalcite-like. Reaction conditions: N_2O, 5000 ppm; O_2, 2%; He balance; $W/F = 0.3$ g s ml^{-1}.

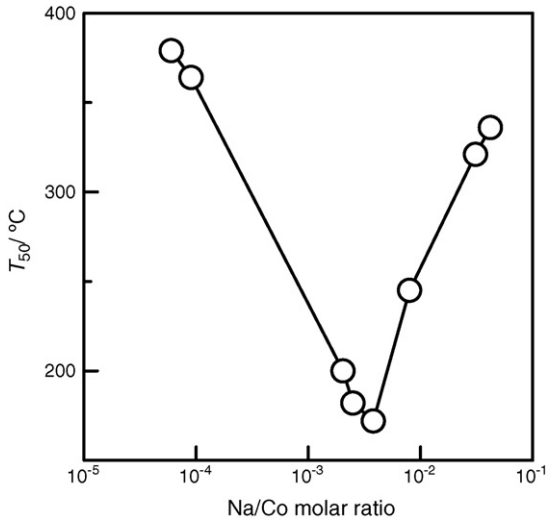

Fig. 3. Dependence of catalyst activity on the Na/Co ratio in the catalyst precursors which were prepared under various conditions described in the caption of Fig. 2. Reaction conditions: N_2O, 5000 ppm; O_2, 2%; He balance; $W/F = 0.3$ g s ml^{-1}.

3.3. Effects of the calcination temperature

The $CoCO_3$ precursor obtained by precipitation from $Co(NO_3)_2$ with $NaHCO_3$ was calcined at various temperatures and properties and activities of the thus-obtained catalysts are summarized in Table 2. Decomposition of the precursor took place below 300 °C, and all the catalysts showed the XRD peaks due to Co_3O_4. With the increase in the calcination temperature, BET surface area gradually decreased and the activity of these catalysts decreased as well. These results suggest that the catalyst activity depended on the surface area of the catalyst. Although the catalyst calcined at lower temperature showed higher activity, we adopted the calcination temperature of 400 °C, since the N_2O decomposition measurement started from 500 °C in this study. Note that the Co_3O_4

Table 2
Physical properties and activities of the catalysts obtained by calcination of the $CoCO_3$ precursor[a] at various temperatures

Calcination temperature (°C)	Phase detected by XRD	BET surface area ($m^2\ g^{-1}$)		Crystallite size (nm)	T_{50} (°C)
		Fresh	Used		
300	Co_3O_4	90	21	10	171
400	Co_3O_4	45	30	23	194
500	Co_3O_4	33	24	34	216
600	Co_3O_4	17	17	57	273

[a] The $CoCO_3$ precursor was obtained by precipitation from $Co(NO_3)_2$ solution with $NaHCO_3$ at 35 °C, followed by aging at the temperature for 24 h.

catalysts examined in this paper had high activities and essentially complete conversion of N_2O was attained at the temperature much lower than the calcination temperature.

3.4. Catalyst stability

Stability of the Co_3O_4 catalyst for N_2O decomposition was examined at 300 °C and the result is shown in Fig. 4. This catalyst maintained >90% N_2O conversion at least for 12 h. It is well known that noble metal catalysts have quite high activities for decomposition of N_2O, and a Rh catalyst was reported to catalyze the reaction even at room temperature [22]. However, oxygen atoms formed by the decomposition of N_2O were accumulated on the Rh surface, and, therefore, the activity of the catalyst decreased suddenly after keeping high N_2O conversion for a while. On the contrary, the present catalyst maintained high activity for more than 12 h, even in the presence of oxygen. This result suggests that oxygen formed by the decomposition of N_2O is easily desorbed from the surface of the present catalyst.

3.5. The effect of alkali modification

As mentioned above, the activities of the Co_3O_4 catalysts strongly depended on the amount of the sodium ions remaining in the catalysts. Therefore, effects of alkali modification of the Co_3O_4 catalyst on its activity were examined. The alkali components were impregnated on a commercial $CoCO_3$ sample having a low Na content (<50 ppm) and the loading of alkali metals was adjusted to 1000 ppm. For the Na-doped catalyst, this concentration corresponds to the Na/Co molar ratio of 3.5×10^{-3}. All the catalysts modified by alkali metals attained higher N_2O conversion (T_{50} values were 305, 311, 327, and 337 °C for the catalysts modified with Na, Li, Cs, and K, respectively) than the Co_3O_4 catalyst without modification (T_{50} = 354 °C); the catalysts modified by Li and Na showed high performance. The XRD patterns of the alkali-modified Co_3O_4 catalysts were identical with that of the Co_3O_4 catalyst without alkali modification (data not shown). Note that that alkali modification of the NiO catalyst exhibited a negative effect (T_{50} = 317 °C for Na-modified NiO catalyst; T_{50} = 310 °C for unmodified NiO catalyst), indicating that Na ions do not play as the active center but have a promoting effect on the Co_3O_4 catalyst.

The results of N_2O decomposition over the Co_3O_4 catalysts modified by various alkaline earth metals are shown in Fig. 5. The loading of alkaline earth metals was adjusted to 1 wt.%, because 1000 ppm Ba-doped catalyst showed almost the same activity as the Co_3O_4 catalyst (vide infra). As was the case for alkali modification, no difference in the XRD patterns of the Co_3O_4 catalysts was observed (data not shown). Although the activity of the Mg-modified catalyst was almost the same as that of the Co_3O_4 catalyst, modification by Ca, Sr and Ba improved the catalyst activity and the Ba/Co_3O_4 catalyst showed the highest activity. The T_{50} value of this catalyst was 209 °C, which is much lower than that of the unmodified Co_3O_4 catalyst (354 °C).

Fig. 6 shows the plot of the T_{50} value versus Ba content. The activities for N_2O decomposition depended on the amount of Ba loading. For the catalyst with Ba loading of 1000 ppm (Ba/Co molar ratio, 5.9×10^{-4}), the N_2O conversion of the Ba/Co_3O_4 catalyst was essentially identical with that of the Co_3O_4 catalyst. This result may be due to the presence of a small amount of Na (<50 ppm) in the precursor $CoCO_3$. When 5000 ppm Ba was doped to the Co_3O_4 catalyst, the activity for N_2O decomposition improved, and the T_{50} value of the catalyst

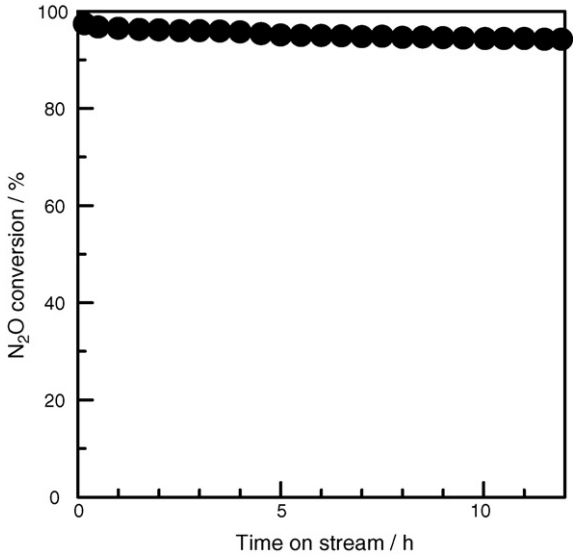

Fig. 4. Stability of the Co_3O_4 catalyst for the direct decomposition of N_2O at 300 °C. The catalyst was prepared by calcination of $CoCO_3$ formed by precipitation from a $Co(NO_3)_2$ solution with $NaHCO_3$ at 35 °C. Reaction condition: N_2O, 5000 ppm; O_2, 2%; He balance; W/F = 0.3 g s ml^{-1}.

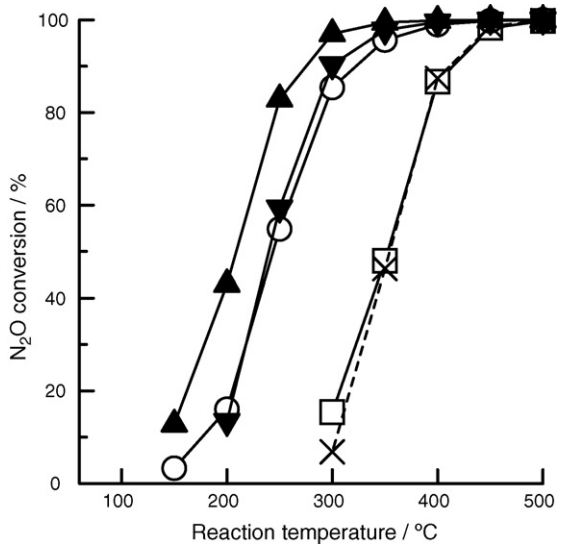

Fig. 5. N_2O decomposition activity of Co_3O_4 catalysts modified with: (□) Mg; (○) Ca; (▼) Sr; and (▲) Ba prepared by impregnation of a commercial $CoCO_3$ sample with the corresponding metal nitrate solution followed by calcination at 400 °C and (×) unmodified Co_3O_4 catalyst. The concentration of alkaline earth metals was 1 wt.%. Reaction conditions: N_2O, 5000 ppm; O_2, 2%; He balance; W/F = 0.3 g s ml^{-1}.

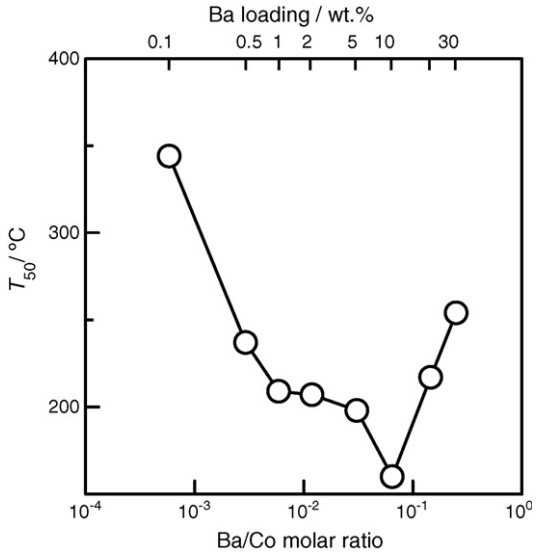

Fig. 6. Dependence of the catalyst activity on the Ba loading on the Co_3O_4 catalyst prepared by impregnation of $CoCO_3$ with $Ba(NO_3)_2$ and subsequent calcination at 400 °C. Reaction conditions: N_2O, 5000 ppm; O_2, 2%; He balance; $W/F = 0.3$ g s ml^{-1}.

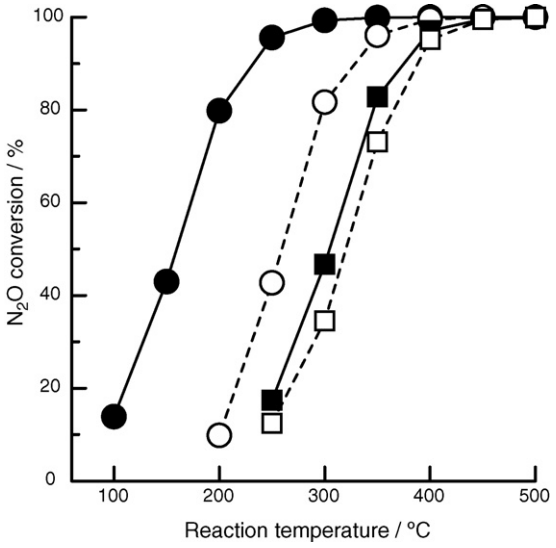

Fig. 8. N_2O decomposition activity of the Co_3O_4 catalysts doped with: (■, □) 1000 ppm Na; (●, ○) 10 wt.% Ba which were prepared by impregnation of: a commercial $CoCO_3$ sample (closed symbols) and the Co_3O_4 sample prepared by calcination of the $CoCO_3$ sample at 400 °C for 4 h (open symbols).

was 237 °C. Further increase in Ba loading gradually decreased the T_{50} values and the highest performance (T_{50} = 160 °C) was attained by Ba loading of 10 wt.% (Ba/Co molar ratio, 0.065). For the catalysts with higher Ba loadings (>10 wt.%), the XRD patterns (Fig. 7) showed the presence of the $Ba(NO_3)_2$ phase besides the peaks due to Co_3O_4, and therefore these catalysts exhibited low activities.

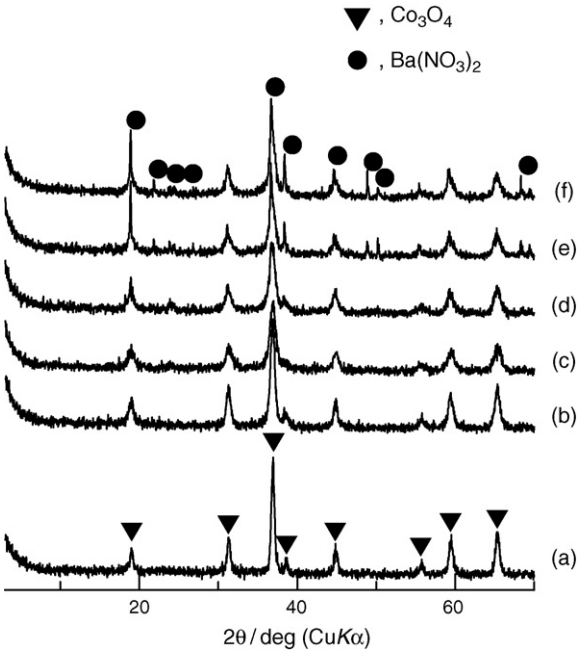

Fig. 7. XRD patterns of the Ba-doped Co_3O_4 catalysts prepared by impregnation of $CoCO_3$ with $Ba(NO_3)_2$ followed by calcination at 400 °C for 4 h. Ba loading: (a) 0 wt.%; (b) 1 wt.%; (c) 5 wt.%; (d) 10 wt.%; (e) 20 wt.%; (f) 30 wt.%.

3.6. The effect of the precursor for alkali-doped catalysts

In Fig. 8, the activities of the doped catalysts prepared by impregnation on $CoCO_3$ and Co_3O_4 are compared. For both the Na- and Ba-doped catalysts, those prepared by the impregnation of $CoCO_3$ with metal nitrate showed higher activities: for the Ba-modified catalysts, the T_{50} value of the catalyst prepared from $CoCO_3$ was 160 °C, while that of the catalyst prepared from Co_3O_4 was 260 °C. When $CoCO_3$ was used as the precursor, the decomposition of $CoCO_3$ itself occurred by calcination in addition to the decomposition of metal nitrate. Hedvall effect [23] during the decomposition of $CoCO_3$ possibly facilitates the migration of alkali into the Co_3O_4 lattice. After calcination, therefore, the alkaline ions are distributed not only on the surface but also in the bulk of the catalyst. Since excess alkali modification resulted in a decrease in the catalyst activity, the alkali component on the surface seems to be inactive. The alkali component migrated into the bulk seems to affect the electronic structure of Co_3O_4, thus promoting catalytic activity of Co_3O_4 for direct decomposition of N_2O. Further work is in progress to elucidate the role of alkali and alkaline earth components on the catalytic activities of the Co_3O_4 catalyst.

4. Conclusion

The Co_3O_4 catalysts showed high activities for the decomposition of N_2O in the presence of oxygen. However, the activity of the Co_3O_4 catalyst strongly depended on the preparation conditions, and the catalyst prepared by calcination of the $CoCO_3$ precursor, derived from $Co(NO_3)_2$ and $NaHCO_3$, showed the highest activity. The sodium content remaining in the precursors was the determining factor controlling the catalyst activity and the optimal the Na/Co molar ratio was

3.8×10^{-3}. Highly active catalysts were also prepared by impregnation of $CoCO_3$ with alkali nitrate solutions, while impregnation of Co_3O_4 with alkali nitrates resulted in relatively low activity. Doping with alkaline earth cations also had favorable effect and the barium-doped catalyst prepared by impregnation of $CoCO_3$ with barium nitrate and subsequent calcination exhibited the highest activity ($T_{50} = 160\ ^\circ C$) at Ba/Co molar ratio of 0.065 (about 10 wt.%). However, alkaline earth metals required higher M/Co molar ratios than those required by alkali metals.

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