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Promotion by Co of a NiO-BaCO₃ catalyst for N₂O decomposition

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ABSTRACT

A series of $Co_xBa_{1.5}Ni_9$ catalysts prepared by a co-precipitation method were investigated for N_2O decomposition. Co improved the activity of NiO when $BaCO_3$ was present but had the opposite role when it was absent. This was because Co strengthened the Ni–O bond and decreased the surface area when added into pure NiO without $BaCO_3$, while in the presence of $BaCO_3$, it dramatically increased the surface area and amount of active sites of NiO.

1. Introduction

Nitrous oxide (N_2O) destroys the ozone in the stratosphere and it is a strong greenhouse gas [1,2]. The continuous increase of its concentration in the atmosphere is mainly from the tail gas of adipic acid and nitric acid plants [3]. This calls for the developing of efficient catalysts for its decomposition into N_2 and O_2.

In recent years, 3*d* transition metal oxides such as Co_3O_4 [4–12], NiO [13,14], Fe_3O_4 [15], and CuO [16] have been shown to exhibit high activity for N_2O decomposition. Fundamental and applied research has focused on these materials, in particular on Co_3O_4 based materials. Many additives have been studied to improve the catalytic activity of Co_3O_4. The alkali metals Na^+, K^+, Cs^+ [4,5,9–11] and alkaline earth metals Mg^{2+} [8], Ca^{2+}, Ba^{2+} [12] and some other transition metals like Ce [6], Ni, Zn [7,8] have been reported to be effective. On the other hand, although NiO has a comparable catalytic activity to Co_3O_4 [11], fewer additives for it have been investigated, apart form Cs [13] and Ce [14]. Concerning the mechanism of the additive promo-

tion of the NiO catalyst, it was reported that Cs [13] significantly facilitated the desorption of the oxygen produced from N_2O decomposition by weakening the Ni–O bond. In the case of Ce as additive, the promotional effect was attributed to a significant increase of the catalyst surface area since it did not much strengthen the Ni–O bond [14]. This influence of Ce on NiO was confirmed in our previous work [17], and on this basis, we suggested that $BaCO_3$ not only played the same role as Cs, but also increased the surface area of the catalyst.

In the present work, a Co-modified NiO-BaCO₃ catalyst was studied, and a significant promotional effect by Co on the activity of NiO in the presence of $BaCO_3$ was found.

2. Experimental

All catalysts were prepared by the co-precipitation method with the following procedure. A Na_2CO_3 aqueous solution (0.2 mol/L) was added dropwise to a mixed solution containing known amounts of $Ni(NO_3)_2·6H_2O$ and $Ba(NO_3)_2$ at 40 °C with strong stirring until the pH of the solution was 9.3. The slurry
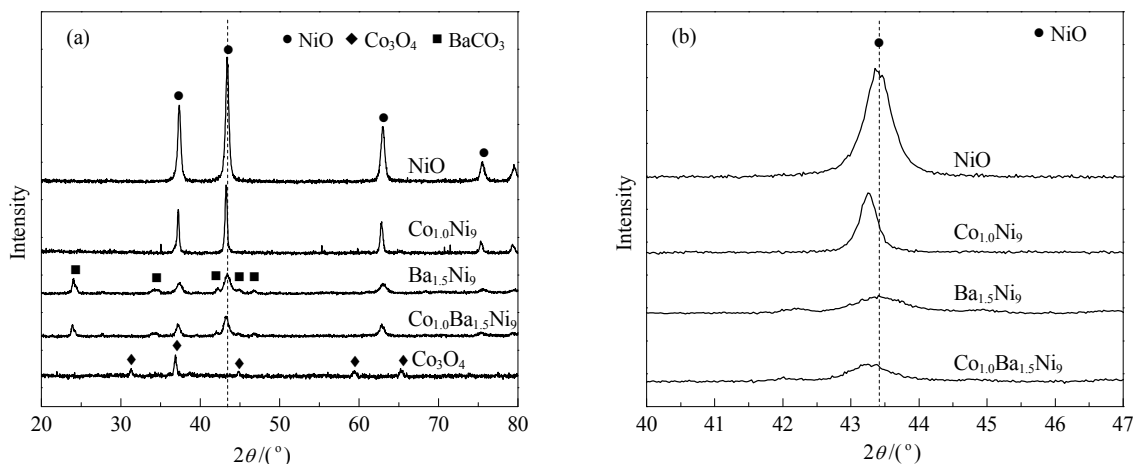
Fig. 1. (a) XRD patterns of the catalysts; (b) Amplification of the (200) (according to JCPDS 78-0643) reflection of NiO.

was stirred for an additional 2 h before it was filtered. Then the resultant precipitate was washed with distilled water until the pH of the filtrate reached 7. This sample was dried at 100 °C overnight, followed by calcination at 500 °C in air for 3 h. The catalysts were labeled as Co_xNi_9 or $Co_xBa_{1.5}Ni_9$ according to the mole ratios of $Co(NO_3)_2·6H_2O$ and $Ba(NO_3)_2$ to $Ni(NO_3)_2·6H_2O$ in the mixed solution used for the catalyst preparation.

The characterization of the catalysts with X-ray diffraction, H_2 temperature-programmed reduction, O_2 temperature-programmed desorption, N_2 adsorption-desorption for measuring the BET surface area, and the activity tests were the same as our previous work [17].

3. Results and discussion

3.1. Structural properties

Figure 1 presents the XRD patterns of the catalysts. No diffraction peak belonging to Co_3O_4 or other cobalt oxide was observed on the $Co_{1.0}Ni_9$ and $Co_{1.0}Ba_{1.5}Ni_9$ catalysts, indicating that the cobalt was well dispersed on them. Moreover, the diffraction peaks of NiO for the $Co_{1.0}Ni_9$ and $Co_xBa_{1.5}Ni_9$ catalysts were obviously shifted to lower angles as compared to pure NiO and $Ba_{1.5}Ni_9$, respectively. This resulted from the larger crystalline interplanar spacing of the (111), (200), (220), and (311) planes for $Co_{1.0}Ni_9$ and $Co_xBa_{1.5}Ni_9$ with respect to their counterparts (Table 1). This is consistent with the radius of Co^{2+} (72 pm) > Ni^{2+} (69 pm). The result indicated that Co^{2+} was incorporated into the NiO phase and partially replaced Ni^{2+} in the $Co_{1.0}Ni_9$ and $Co_{1.0}Ba_{1.5}Ni_9$ catalysts. Table 1 shows the BET surface areas

of the catalyst samples. The surface area drastically decreased due to the formation of a solid solution (Co dissolved into NiO) in $Co_{1.0}Ni_9$. Interestingly, when $BaCO_3$ was in the catalyst, the opposite occurred. For $Ba_{1.5}Ni_9$ and $Co_{1.0}Ba_{1.5}Ni_9$, the specific surface areas were 32 and 41 m^2/g, respectively, indicating that Co was effective for increasing the surface area of the $NiO-BaCO_3$ catalyst.

3.2. Chemical properties

Figure 2 exhibits the H_2-TPR profiles of the NiO, $Co_{1.0}Ni_9$, $Ba_{1.5}Ni_9$, and $Co_{1.0}Ba_{1.5}Ni_9$ catalysts. Three H_2 consumption peaks at 360, 408, and 435 °C appeared for pure NiO. The two peaks at the lower temperature were associated with the NiO reduction steps of $NiO→Ni^{\delta+}→Ni^{0.33}$ [14], while that at the higher temperature was due to the reduction of NiO and $Ni^{\delta+}$ inside larger NiO crystallines. Over $Ba_{1.5}Ni_9$, the last peak nearly did not appeared, which was associated with the small crystallite size of NiO in the sample (Table 1). Compared to the pure NiO, all of the H_2 consumption peaks of $Co_{1.0}Ni_9$ were shifted to higher temperature, which reflects that Co in the solid solution suppressed the reduction of NiO. Nevertheless, the shift of the reduction peaks on $Co_{1.0}Ba_{1.5}Ni_9$ with respect to $Ba_{1.5}Ni_9$ was less than that due to the presence of $BaCO_3$. This means that the

Table 1
Textural and crystal properties of the catalysts.

Catalyst	BET surface area (m^2/g)	Crystal size[a] (nm)	*d* values (nm)			
			(111)	(200)	(220)	(311)
NiO	29	18	0.2406	0.2083	0.1475	0.1258
$Co_{1.0}Ni_9$	9	21	0.2413	0.2090	0.1478	0.1260
$Ba_{1.5}Ni_9$	32	9	0.2406	0.2083	0.1475	0.1258
$Co_{1.0}Ba_{1.5}Ni_9$	41	13	0.2413	0.2090	0.1478	0.1260

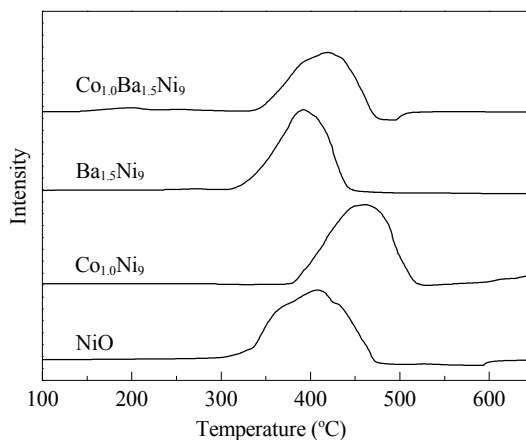[a] Calculated from XRD analysis according to Scherer's equation [18].

Fig. 2. H_2-TPR profiles of the catalysts.