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Article

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

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ABSTRACT

A series of Co_xBa_{1.5}Ni₉ catalysts prepared by a co-precipitation method were investigated for N₂O decomposition. Co improved the activity of NiO when BaCO₃ 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 BaCO₃, while in the presence of BaCO₃, it dramatically increased the surface area and amount of active sites of NiO.

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1. Introduction

Nitrous oxide (N₂O) 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 N₂ and O₂.

In recent years, 3d transition metal oxides such as Co₃O₄ [4–12], NiO [13,14], Fe₃O₄ [15], and CuO [16] have been shown to exhibit high activity for N₂O decomposition. Fundamental and applied research has focused on these materials, in particular on Co₃O₄ based materials. Many additives have been studied to improve the catalytic activity of Co₃O₄. The alkali metals Na⁺, K⁺, Cs⁺ [4,5,9–11] and alkaline earth metals Mg²⁺ [8], Ca²⁺, Ba²⁺ [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 Co₃O₄ [11], fewer additives for it have been investigated, apart from 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 N₂O 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 BaCO₃ 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 BaCO₃ was found.

2. Experimental

All catalysts were prepared by the co-precipitation method with the following procedure. A Na₂CO₃ aqueous solution (0.2 mol/L) was added dropwise to a mixed solution containing known amounts of Ni(NO₃)₂·6H₂O and Ba(NO₃)₂ at 40 °C with strong stirring until the pH of the solution was 9.3. The slurry

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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_xNi₉ or Co_xBa_{1.5}Ni₉ according to the mole ratios of Co(NO₃)₂·6H₂O and Ba(NO₃)₂ to Ni(NO₃)₂·6H₂O in the mixed solution used for the catalyst preparation.

The characterization of the catalysts with X-ray diffraction, H₂ temperature-programmed reduction, O₂ temperature-programmed desorption, N₂ 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 Co₃O₄ or other cobalt oxide was observed on the Co_{1.0}Ni₉ and Co_{1.0}Ba_{1.5}Ni₉ catalysts, indicating that the cobalt was well dispersed on them. Moreover, the diffraction peaks of NiO for the Co_{1.0}Ni₉ and Co_xBa_{1.5}Ni₉ catalysts were obviously shifted to lower angles as compared to pure NiO and Ba_{1.5}Ni₉, respectively. This resulted from the larger crystalline interplanar spacing of the (111), (200), (220), and (311) planes for Co_{1.0}Ni₉ and Co_xBa_{1.5}Ni₉ with respect to their counterparts (Table 1). This is consistent with the radius of Co²⁺ (72 pm) > Ni²⁺ (69 pm). The result indicated that Co²⁺ was incorporated into the NiO phase and partially replaced Ni²⁺ in the Co_{1.0}Ni₉ and Co_{1.0}Ba_{1.5}Ni₉ 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}Ni₉. Interestingly, when BaCO₃ was in the catalyst, the opposite occurred. For Ba_{1.5}Ni₉ and Co_{1.0}Ba_{1.5}Ni₉, the specific surface areas were 32 and 41 m²/g, respectively, indicating that Co was effective for increasing the surface area of the NiO-BaCO₃ catalyst.

3.2. Chemical properties

Figure 2 exhibits the H₂-TPR profiles of the NiO, Co_{1.0}Ni₉, Ba_{1.5}Ni₉, and Co_{1.0}Ba_{1.5}Ni₉ catalysts. Three H₂ 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^{δ+} → Ni^{0.33} [14], while that at the higher temperature was due to the reduction of NiO and Ni^{δ+} inside larger NiO crystallites. Over Ba_{1.5}Ni₉, the last peak nearly did not appear, which was associated with the small crystallite size of NiO in the sample (Table 1). Compared to the pure NiO, all of the H₂ consumption peaks of Co_{1.0}Ni₉ 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}Ni₉ with respect to Ba_{1.5}Ni₉ was less than that due to the presence of BaCO₃. This means that the

Table 1

Textural and crystal properties of the catalysts.

Catalyst	BET surface Area (m ² /g)	Crystal size ^a (nm)	<i>d</i> 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 Scherrer's equation [18].

Fig. 2. H₂-TPR profiles of the catalysts.

Fig. 3. O₂-TPD profiles of the catalysts.

Fig. 4. Schematic representation of the catalytic cycle of the active sites in N₂O decomposition.

Ni–O bond strengthening caused by Co was effectively reduced by BaCO₃ in the catalyst.

Figure 3 shows the O₂-TPD profiles of the catalysts. O₂ desorption started at 165 °C over pure NiO, while the starting temperature for O₂ desorption over Co_{1.0}Ni₉ was much increased to 217 °C. For the O₂-TPD profiles of Co_{1.0}Ba_{1.5}Ni₉ and Ba_{1.5}Ni₉ catalysts, their temperatures were quite close. Clearly, all the phenomena were consistent with the H₂-TPR results. Both indicated that the unfavorable effect of Co in suppressing O₂ desorption was greatly reduced when there was BaCO₃ in the catalyst. For N₂O decomposition, the catalytic cycle can be represented as shown in Fig. 4. The desorption of oxygen is widely accepted to be the rate determining step [19]. Thus the oxygen produced by N₂O decomposition on the active nickel sites (*) must be released at or below the reaction temperature, otherwise they would poison the active sites for the reaction. Hence, the active sites on each catalyst at 300 °C were calculated from the O₂ desorption area below 300 °C. As shown in Table 2, the active sites over NiO, Co_{1.0}Ni₉, Ba_{1.5}Ni₉, and Co_{1.0}Ba_{1.5}Ni₉ at the reaction temperature were 65.07, 52.17, 95.67, and 117.47 μmol/g, respectively, which was basically in

Table 2

Comparison of the catalysts and their active sites.

Catalyst	Amount at 300 °C (μmol/g)	Temperature of reduction peak in H ₂ -TPR (°C)	N ₂ O conversion for feed gas without O ₂ (%)
NiO	65.07	410	30
Co _{1.0} Ni ₉	52.17	465	4
Ba _{1.5} Ni ₉	95.67	390	90
Co _{1.0} Ba _{1.5} Ni ₉	117.47	415	100

Fig. 5. N₂O conversion over Co_xBa_{1.5}Ni₉ catalyst samples for feed gas 2000 ppm N₂O/Ar (a) and 2000 ppm N₂O/Ar+5% O₂/Ar (b).

proportion to the surface area of the catalysts (29, 9, 32, and 41 m²/g). This indicated again that Co gave the NiO based catalyst a special property, i.e. increasing its active sites, only when BaCO₃ also existed in the catalyst. As shown, the active sites decreased with the surface area due to the Co incorporation when BaCO₃ was absent from the NiO catalyst.

3.3. Catalytic performance

The conversion of N₂O at each reaction temperature over the Co_xBa_{1.5}Ni₉ ($x = 0, 0.5, 1.0, 1.5, 2.0$) catalysts are shown in Fig. 5. Interestingly, the Co_{1.0}Ba_{1.5}Ni₉ catalyst was much more active than Ba_{1.5}Ni₉ in the temperature range of 200–350 °C, regardless of whether the feed gas was with or without 5% O₂. Clearly, the superior catalytic activity of Co_{1.0}Ba_{1.5}Ni₉ can be attributed to the large increase of active sites caused by Co. On the other hand, comparing the conversion of N₂O over pure NiO and the Co_xNi₉ ($x = 1.0, 2.0, 3.0, 4.0$) catalysts at 350 °C (Fig. 6) showed that all the Co_xNi₉ catalysts displayed inferior activity

Fig. 6. N₂O conversion over the catalysts at 350 °C for a feed gas of 2000 ppm N₂O/Ar.

Graphical Abstract

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Cobalt as a co-additive with BaCO₃ in NiO significantly improved the activity of NiO for N₂O decomposition, although it played the opposite role when it was added to NiO alone without BaCO₃.

to pure NiO, and inferior BET surface area and active site amounts.

4. Conclusions

When an appropriate amount of cobalt as additive was incorporated into NiO-BaCO₃, a promotion of the catalytic activity for N₂O decomposition was observed. This was due to the increased surface area and active sites of the catalyst. However, introducing Co into pure NiO without BaCO₃ on the contrary decreased the surface area, amount of active sites, and activity of the catalyst. Hence, for the promotional effect of Co on the NiO-BaCO₃ catalyst to occur, BaCO₃ played a significant role.

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Co对NiO-BaCO₃催化剂催化N₂O分解的促进影响

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摘要: 采用共沉淀法制备了一系列Co_xBa_{1.5}Ni₉催化剂, 用于N₂O催化分解反应。研究发现, 尽管Co加入纯NiO对反应不利, 但在有BaCO₃存在的情况下, Co则能够显著提高NiO的活性。这是由于Co增强了Ni-O键而对反应不利, 但在BaCO₃存在下则大大增加了Ni基催化剂的比表面积及活性位数目。

关键词: 四氧化三钴; 氧化二氮分解; 碳酸钡; 氧化镍

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