TITLE:

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CITATION:

Hong, Won-Jong ...[et al]. Direct Decomposition of NO on Ba Catalysts Supported on Ce-Fe Mixed Oxides. Catalysis Letters 2010, 135(3-4): 190-196

ISSUE DATE:

2010-04

URL:

<http://hdl.handle.net/2433/128948>

RIGHT:

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Direct decomposition of NO on Ba catalysts supported on Ce–Fe mixed oxides

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Abstract

Cerium-iron mixed oxides were prepared by a glycothermal method, and NO decomposition reactions over these oxides and barium catalysts supported on them were examined. Although Ce-Fe mixed oxides (Ce-Fe(x), $x = \text{Fe}/(\text{Ce}+\text{Fe})$ molar ratio) exhibited only low activities for the direct decomposition of NO into N₂ and O₂, Ba catalysts supported on these mixed oxides are active for this reaction. The highest NO conversion was achieved with 3 wt% BaO/Ce-Fe(0.02). The NO conversion on this catalyst increased with increasing reaction temperature, and NO conversion was 51 % at 800 °C. The high activity of this catalyst was maintained for more than 10 h and a relatively high NO conversion (23 %) was obtained even in the presence of 5 % oxygen. The XRD results indicated the formation of Ce-Fe(x) solid solutions with a cubic fluorite structure. The CO₂-TPD results indicated NO decomposition activities of the catalysts were correlated with their basicities.

1. Introduction

Exhaust gases from vehicle engines and industrial combustion facilities contain considerable amounts of nitrogen oxides (NO_x), which cause severe environmental problems. Practical NO_x emission control technologies such as three-way catalyst method for gasoline-fueled vehicles, NO_x storage-reduction (NSR) catalysts for lean-burn engine systems, and SCR processes for large-scale boilers have been developed; however, there is still a great research interest for the development of novel and more efficient de NO_x methods. Among various de NO_x strategies, direct decomposition of NO ($\text{NO} \rightarrow 1/2\text{O}_2 + 1/2\text{N}_2$) has been considered to be the most desirable method because this reaction is thermodynamically favorable at low temperatures and does not need any reductants such as NH_3 , H_2 , CO, or hydrocarbons. Hence, this reaction receives special interest of scientists, although no practical application has been reported until now.

A number of catalysts have been examined for this reaction, and several types of catalysts, such as precious metals [1,2], ion-exchanged zeolites [3,4], single-component metal oxides [5,6], and perovskites [7–10], were found to be active for this reaction. Recently, Imanaka et al. examined the direct NO decomposition on Gd–Y–Ba oxides [11] and Y–Zr oxides [12] with C-type cubic crystal structure and reported that these catalysts exhibited higher activities than the conventional perovskite-type catalysts. However, N_2 selectivity was quite low at temperatures below 600 °C. Accordingly, it is necessary to develop new active catalysts which can show both low-temperature activity and high thermal-stability.

We found that Ba–Ce–Co mixed oxides, composed of three phases, CeO_2 , Co_3O_4 , and $\text{BaCeO}_{3-\delta}$, showed high activities for NO decomposition reaction [13]. Then, to examine

the active sites of the catalysts, Ba catalysts supported on Co_3O_4 and CeO_2 were prepared, and it was found that the reaction rate was correlated to the number of basic sites of the catalysts [14].

Because of their unique oxygen-storage and redox properties, Ce-based mixed oxides have been widely used in many catalyses, such as catalytic conversion of light hydrocarbons [15], liquid phase oxidation reaction [16], and treatment of exhaust gases [17]. Therefore, the addition of the second component to CeO_2 was examined and it was found that Ba catalysts supported on Ce–Mn mixed oxides showed significantly improved activities for direct decomposition of NO [18]. In a previous paper [18], we also found that the addition of Fe to CeO_2 with Fe/Ce of 0.1 was also effective to improve the activity, although the promotion effect of Fe for CeO_2 was less significant as compared to that of Mn. However, iron is less expensive and environmentally harmless, which motivated us to explore the Ce–Fe system further. In this study, we prepared Ce–Fe mixed oxides with various Ce/Fe ratios, and the NO decomposition activities of Ce–Fe oxide catalysts and Ba catalysts supported on them were examined. The catalysts were characterized by several techniques and correlation between NO decomposition activities and physicochemical properties of the catalysts was investigated.

2. Experimental

2.1. Preparation of the catalysts

Ce–Fe oxide samples (designated as Ce–Fe(x), $x = \text{Fe}/(\text{Ce}+\text{Fe})$ molar ratio) were prepared by a glycothermal method. Appropriate amounts of $\text{Ce}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}(\text{CH}_3\text{COO})_2$ were added to 100 ml of 1,4-butanediol, and this mixture was set in a

300-ml autoclave. After the atmosphere inside the autoclave was completely replaced with nitrogen, the autoclave was heated to 300 °C at a rate of 2.3 °C min⁻¹ and kept at that temperature for 2 h. After cooling, the resultant powder product was collected by centrifugation, washed with acetone, air-dried, and calcined at 400 °C in air for 4 h.

Barium (up to 10 wt% as BaO) was loaded on Ce–Fe(*x*) by an impregnation method using an aqueous solution of barium nitrate, and the precursor was calcined at 800 °C for 1 h (designated as BaO/Ce–Fe(*x*)).

2.2. Direct NO decomposition reaction

The NO decomposition reaction was carried out in a fixed-bed flow reactor made of quartz glass tubing with an inner diameter of 10 mm. The catalysts were pressed into a pellet, pulverized into 10 to 22 mesh size, and charged to the reactor. After the catalyst bed was heated to 800 °C in a He flow, the reaction gas composed of 6000 ppm NO and 0–5% O₂ (He balance) was fed over 0.50–1.0 g of the catalysts at a rate of 20–300 ml min⁻¹ ($W/F = 0.2\text{--}3 \text{ g s ml}^{-1}$). The effluent gas was analyzed using a GL Science MicroGC 2002 gas chromatograph equipped with Molsieve 5A and Poraplot Q columns. The NO conversion was expressed on the basis of the formation of N₂:

$$\text{NO conversion} = \frac{2[\text{N}_2]_{\text{out}}}{[\text{NO}]_{\text{in}}},$$

where [NO]_{in} and [N₂]_{out} are concentrations of NO in the feed and of N₂ in the effluent, respectively.

Only a small amount of the by-product, N₂O, was formed for all the catalysts tested.

2.3. Characterization of the catalysts

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT 2500 X-ray diffractometer using CuK α radiation (scan rate, 0.02 ° 2 θ min⁻¹). Crystallite sizes of CeO₂ were calculated from the half-height width of the 111 diffraction peak (2 θ = 28.55 °) using the Scherrer equation. Specific surface areas were calculated by the BET single-point method on the basis of nitrogen uptakes measured at 77 K using a Micromeritics Flowsorb II 2300 sorptograph. The samples were evacuated at 300 °C for 30 min prior to the measurement.

Temperature-programmed desorption of CO₂ (CO₂-TPD) was carried out on a Bel Japan TPD-1-AT apparatus with a Q-MASS detector. Before performing CO₂-TPD experiment, the sample (50 mg) was treated in situ in a 50 ml min⁻¹ 20% O₂-He flow at 800 °C for 1 h, cooled to 50 °C in the same atmosphere, and purged with a 50 ml min⁻¹ He flow for 30 min. The sample was exposed to a 20 ml min⁻¹ flow of 19% CO₂ for 30 min, purged again with a 50 ml min⁻¹ He flow for 30 min, and then heated in the same flow from 50 °C to 800 °C at a rate of 10 °C min⁻¹ with monitoring the CO₂ desorption.

3. Results and Discussion

3.1. NO decomposition on Ba catalysts supported on Ce-Fe mixed oxides

Figure 1 shows the NO decomposition activities of Ce-Fe(x) and 7 wt% BaO/Ce-Fe(x) with various Fe contents. The Ce-Fe(x) mixed oxides showed quite low activities irrespective of the Fe contents. On the contrary, the Ba-loaded catalysts showed significant activities. As compared with the Ba catalysts supported on single-component carriers, CeO₂ ($x = 0$) and Fe₂O₃ ($x = 1$), which exhibited 18% and 5% of NO conversions, respectively, the Ba catalysts supported on Ce-Fe mixed oxides

showed enhanced activities. The highest activity was observed for 7 wt% BaO/Ce–Fe(0.02); 46% NO conversion to N₂ was attained at 800 °C.

Figure 2 shows the effect of the amount of BaO on the activity of the BaO/Ce–Fe(0.02) catalysts. Without the addition of BaO, the NO conversion was very low; however, the BaO loading significantly increased the activity, suggesting that Ba species is related to the active sites. The highest NO conversion was attained with 3 wt% BaO/Ce–Fe(0.02), and further increase in the BaO loading caused a gradual decrease in the activity. In the XRD pattern of the catalyst with 10 wt% BaO, small diffraction peaks due to BaCO₃ were detected, indicating low dispersion of the Ba species in this catalyst.

Figure 3 shows the stability of 3 wt% BaO/Ce–Fe(0.02) for the NO decomposition. At 550 °C, the conversion of NO to N₂ at the initial stage was 3% and it did not decrease after 10 h on stream, indicating that oxygen atoms formed by decomposition of NO were not accumulated on the catalyst. At 800 °C, a stable NO conversion, as high as 60%, was preserved over 10 h.

Figure 4 shows the effect of *W/F* on the NO decomposition on the 3 wt% BaO/Ce–Fe(0.02) catalyst measured by changing the flow rate. The NO conversion gradually increased with increasing the contact time. At 800 °C, quite a high NO conversion (75%) was attained at *W/F* = 3.0 g s ml⁻¹. On the other hand, even at a short contact time of *W/F* = 0.2 g s ml⁻¹, the catalyst exhibited 35% of NO conversion, indicating the high performance of this catalyst.

3.2. Characterization of the Ba catalysts supported on Ce–Fe mixed oxides

Figure 5 presents the XRD patterns of the 7 wt% BaO/Ce–Fe(x) catalysts. Diffraction peaks due to the CeO₂ phase with a cubic fluorite structure was recognized for all the catalysts except BaO/Ce–Fe(1). For $x \geq 0.5$, diffraction peaks due to Fe₂O₃ (JCPDS #39-1346) were observed in addition to the CeO₂ peaks. However, for $x \leq 0.17$, only diffraction peaks due to CeO₂ were observed, and no diffraction peaks due to Fe- and Ba-containing phases were recognized, indicating that Fe and Ba ions were highly dispersed in these catalysts.

Figure 6 shows the lattice parameters of the CeO₂ phase for Ce–Fe(x) calcined at 400 °C and for BaO/Ce–Fe(x) calcined at 800 °C. For the Ce–Fe(x) samples without BaO, the lattice parameter decreased remarkably with increasing Fe content, indicating the dissolution of Fe ions into the CeO₂ structure. However, the lattice parameter for $x = 0.5$ was almost same as that for $x = 0.17$, suggesting the existence of limitation of the Fe incorporation. This result is consistent with the report by Li et al. [19], who found that the Ce_{1- x} Fe _{x} O₂ solid solutions can be synthesized by a hydrothermal method until $x = 0.15$. For BaO/Ce–Fe(0), the lattice parameter was larger than that of CeO₂, indicating the incorporation of Ba ions into the fluorite structure. In the BaO–CeO₂ system, only one binary compound BaCeO₃ is found [20], and it is generally believed that Ba²⁺ ion does not dissolve in the CeO₂ matrix because ionic radius of Ba²⁺ is much larger than that of Ce⁴⁺ [21]. However, these statements do not rule out the possibility for the formation of the BaO–CeO₂ solid solution as a metastable phase. Actually, Ba-doped CeO₂ samples have been prepared and a large expansion of the lattice parameter of CeO₂ has been reported [22,23]. Pt–Ba–CeO₂ catalysts have been widely examined for the NO _{x} –storage–reduction strategy [24–30]. Although the phases developed by thermal treatment of these catalysts have been carefully examined, BaO–CeO₂ solid solutions

have never been detected in these works [24–26,31]. This is presumably because the catalysts were prepared by impregnation of CeO_2 with a barium acetate solution. Thermal decomposition of the acetate gives barium carbonate which is loaded on outer surface of ceria particles. Barium carbonate is fairly stable and the decomposition of this phase causes the formation of BaCeO_3 . In the present work, the CeO_2 sample prepared by the glycothermal method was impregnated with an aqueous solution of barium nitrate. Since the glycothermally prepared crystals have various types of defects [32,33], Ba^{2+} ions seems to be able to migrate into the CeO_2 matrix. For comparison, a 7wt% BaO/Ce-Fe(0.02) catalyst was prepared by impregnation of Ce-Fe(0.02) with an aqueous solution of barium acetate. As expected this catalyst showed a lower activity for direct decomposition of NO (data not shown) than the catalyst prepared from barium nitrate.

For the $\text{BaO/Ce-Fe}(x)$ samples, the lattice parameter increased with the increase in x up to 0.05, suggesting that a larger amount of Ba was soluble in the $\text{Ce}_{1-x}\text{Fe}_x\text{O}_2$ solid solution. However, further increase in x caused a gradual decrease in the lattice parameters of the CeO_2 phase.

In Table 1, physical properties of $\text{Ce-Fe}(x)$ and $\text{BaO/Ce-Fe}(x)$ are summarized. The addition of a small amount of Fe to CeO_2 increased the BET surface area of the product. However, the BET surface areas of $\text{Ce-Fe}(x)$ drastically decreased by calcination at 800 °C. For $\text{Ce-Fe}(x)$ with $x \geq 0.09$, the surface area gradually decreased with increasing the Fe content. This tendency was also observed for $\text{BaO/Ce-Fe}(x)$, and the crystallite size as well decreased with increasing the Fe content. When each primary particle is a single crystal, BET surface area should increase with the decrease in the crystallite size. Therefore, the primary particles of the present products are composed of

mosaic of crystallites. The correlation between the BET surface area and catalytic activities was not observed.

In order to estimate the basicity of the catalysts, CO₂-TPD experiments were carried out and the results are shown in Figure 7. The desorption profile for single-component CeO₂ showed a peak around 100 °C. On the contrary, the BaO-loaded CeO₂ samples showed a very broad peak at temperatures higher than 100 °C, indicating that they have considerably strong basic sites on the surface. Interestingly, the CO₂ uptake for BaO/Ce–Fe(0.02) was much larger than that of BaO/Ce–Fe(0), indicating an increase in the number of basic sites. In Figure 8, effect of x on the CO₂ uptake of the BaO/Ce–Fe(x) catalysts is shown. Although pure CeO₂ showed a significant CO₂ uptake, the BaO loading apparently increased the CO₂ uptake. Furthermore, the addition of Fe increased the CO₂ uptake markedly. This feature is probably due to the oxygen defects caused by the dissolution of Fe ions into the CeO₂ structure. The maximum CO₂ uptake was attained for the samples with $x = 0.02$, and further increase in the Fe content gradually decreased CO₂ uptake. This tendency is similar to the effect of Fe on the NO decomposition activity as shown in Figure 1, indicating that the NO decomposition activity of the catalyst is controlled by its basic property. As shown in Figure 6, a similar behavior was also observed in the change in the unit cell parameter of the CeO₂ phase, which suggests that the Ba species highly dispersed in the fluorite structure is the origin of the basic sites of the catalysts.

3.3. Influence of O₂ on the NO decomposition activity of BaO/Ce–Fe(0.02) catalyst.

The effect of the addition of oxygen to the reaction gas was investigated using 3 wt% BaO/Ce–Fe(0.02), since it is well known that oxygen suppresses the activities of NO

decomposition catalysts [8, 34]. Figure 9 shows NO conversion at 800 °C as a function of O₂ concentration. The NO conversion monotonically decreased with increasing the O₂ concentration. However, even in the presence of 5% O₂, the 3 wt% BaO/Ce–Fe(0.02) catalyst preserved a relatively high activity, 23%, at 800 °C. The reaction order with respect to the O₂ partial pressure became negatively large with decreasing the reaction temperature, indicating that retarding effect of oxygen become more significant at lower temperatures. However, the reaction order with respect to the O₂ partial pressure at 800 °C was -0.29 (Figure 10). The absolute value of this reaction order was relatively small, suggesting a potential of the present catalyst for practical deNO_x applications.

4. Conclusions

The direct decomposition of NO over Ba catalysts supported on Ce–Fe mixed oxides was examined, and it was found that Ba catalysts supported on Ce–Fe(0.02) mixed oxides exhibited quite high activities. The XRD analyses indicated that the Ce–Fe solid solutions with a cubic fluorite structure were formed. The CO₂-TPD results indicated the NO decomposition activities of the catalysts correlated with their basic properties. A high NO conversion, 60% at 800 °C in the absence of O₂ was attained over 3 wt% BaO/Ce–Fe(0.02), and even in the presence of 5% oxygen, this catalyst showed 23% NO conversion. The catalyst maintained the activity for over 10 h, suggesting a high potential of BaO/Ce–Fe mixed oxide catalysts for practical application in NO_x emission control.

Acknowledgments

This work was supported by a Grant-in-Aid from Ministry of Education, Culture, Sports, Science and Technology, Japan.

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Table 1. Physical properties of Ce–Fe(*x*) and 7 wt% BaO/Ce–Fe(*x*) catalysts.

<i>x</i>	BET surface area (m ² g ⁻¹)			Crystallite size ^{a)} (nm)		
	A	B	C	A	B	C
0	132	36	24	8	25	29
0.01	138	30	12	8	28	23
0.02	147	29	12	9	24	23
0.032	150	32	16	11	23	23
0.048	151	23	13	N.D.	N.D.	21
0.09	153	23	19	N.D.	N.D.	18
0.17	146	19	17	N.D.	N.D.	16
0.5	106	18	17	6	21	15
0.75	83	12	14	8	20	14
1	22	3	5	—	—	—

a) Calculated from the 111 diffraction peak of the fluorite phase.

A : Ce–Fe(*x*) calcined at 400 °C for 4 h.

B : Ce–Fe(*x*) calcined at 800 °C for 1 h.

C : 7wt% BaO/Ce–Fe(*x*) calcined at 800 °C for 1 h.

Figure captions

Figure 1. NO conversion to N_2 on Ce–Fe(x) and 7 wt% BaO/Ce–Fe(x) as a function of x , Fe/(Ce+Fe) ratio in Ce–Fe oxide. Catalyst, 0.50 g; reaction gas, 6000 ppm NO in He; flow rate, 30 ml min^{-1} ($W/F = 1.0 \text{ g s ml}^{-1}$); reaction temperature, 800°C .

Figure 2. Effect of Ba loading on the NO decomposition activities of BaO/Ce–Fe(0.02) catalyst. Catalyst, 0.50 g; reaction gas, 6000 ppm NO in He; flow rate, 30 ml min^{-1} ($W/F = 1.0 \text{ g s ml}^{-1}$).

Figure 3. Duration test of 3 wt% BaO/Ce–Fe(0.02) catalysts for direct decomposition of NO. Catalyst, 1.0 g; reaction gas, 6000 ppm NO in He; flow rate, 60 ml min^{-1} ($W/F = 1.0 \text{ g s ml}^{-1}$).

Figure 4. NO decomposition on 3 wt% BaO/Ce–Fe(0.02) catalyst as a function of W/F . Catalyst, 1.0 g; reaction gas, 6000 ppm NO in He; flow rate, $20\text{--}300 \text{ ml min}^{-1}$.

Figure 5. XRD patterns of 7 wt% BaO/Ce–Fe(x) calcined at 800°C .

Figure 6. Lattice parameters of CeO_2 for Ce–Fe(x) calcined at 400°C and 7 wt% BaO/Ce–Fe(x) catalysts.

Figure 7. CO₂-TPD profiles of CeO₂ and 7 wt% BaO/Ce–Fe(*x*) calcined at 800 °C. Prior to the measurement, the sample was treated again in situ in a 20% O₂–He flow at 800 for 1 h.

Figure 8. Amount of CO₂ desorbed from CeO₂ and 7 wt% BaO/Ce–Fe(*x*) calcined at 800 °C.

Figure 9. Effect of oxygen on the NO decomposition activity of 3 wt% BaO/Ce–Fe(0.02) catalyst. Catalyst, 1.0 g; reaction gas, 4000 ppm NO and 0–5% O₂ in He; flow rate, 60 ml min^{−1} ($W/F = 1.0 \text{ g s ml}^{-1}$).

Figure 10. N₂ formation rate on 3 wt% BaO/Ce–Fe(0.02) catalyst as a function of oxygen partial pressure.

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Figure 3. W.-J. Hong et al.

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Figure 10. W.-J. Hong et al.