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Direct decomposition of NO over BaO/Y_2O_3 catalyst

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NO direct decomposition on BaO/Y_2O_3 oxide catalyst was investigated and it was found that BaO supported on Y_2O_3 or Sc_2O_3 is highly active to NO decomposition into N_2. The highest N_2 yield of ca.90% at 1123 K was achieved at 5 mol% BaO supported on Y_2O_3. On this catalyst, NO conversion decreases with increasing oxygen partial pressure, P_{O_2}, however reasonably high N_2 yield (ca. 40%) was exhibited under co-feeding of 5% O_2 and P_{O_2} dependence is as small as −0.23. From NO-TPD results, large desorption peak of oxygen was observed around 773 K suggesting that weak adsorption strength of O_2 on BaO/Y_2O_3 catalyst. In case of NO, large NO desorption peak was also observed around 473 K and so NO adsorption was improved by loading BaO on Y_2O_3. In addition, part of NO desorbs as O_2 and NO, and small amount of N_2 desorbs at 773 K. This suggests that disproportional reaction of NO ($3NO = N_2 + NO_{3ad}$ or $NO = N_2O_{ad} + NO_{2ad}$) occurred and the surface of the catalyst was covered with nitrogen oxide species. In spite of small surface area of BaO/Y_2O_3 ($1.1\ m^2/g$), reasonably high N_2 yield (ca.30%) is shown at a high space velocity of $40{,}000\ h^{-1}$.

1. Introduction

Nitrogen oxides (NO_X), which are mainly formed by internal combustion engines such as diesel engine, are extremely toxic to a human body and also harmful to environment as a main source of both acid rain and photochemical smog. Recently, increase in NO emission in urban area becomes a significant environmental problem. Several methods have been practically used for NO_X removal such as 3-way catalyst [1] and selective catalytic reduction with NH_3 [2]. However, for diesel engines, applications of the conventional deNO_X process are difficult because of the high concentration of O_2 coexisted. Recently, selective reduction of NO_X with urea is partially applied for a practical exhaust gas treatment system for diesel engines [3]. However, urea is also harmful to environment and negative influence of leaked urea on environment is also anxious issues. On the other hand, direct decomposition of NO into N_2 and O_2 is the most ideal reaction for NO_X removal and several catalysts have been reported [4–11], however, activity of the proposed catalyst is still too low to use under a practical condition. In particular, NO decomposition activity under O_2 coexistence condition is still much lower than the demanded value. In the previous study, NO direct decomposition over perovskite and perovskite related catalyst has been investigated and it was found that $La_{0.7}Ba_{0.3}Mn_{0.8}In_{0.2}O_3$ [12] or $Ba_{0.8}La_{0.2}Mn_{0.8}Mg_{0.2}O_3$ [13] catalyst exhibits the high activity to NO direct decomposition. In addition, it was found that BaO supported on the oxide with perovskite related structure also shows the high activity to NO decomposition. On this catalyst, BaO/BaY_2O_3 which is obtained by decomposition of $Ba_3Y_4O_{9,}$ is highly active to NO decomposition [14]. Therefore, BaO in highly dispersed state seems to be active for NO direct decomposition into N_2 and O_2. In this study, NO decomposition activities of BaO/Y_2O_3 were studied as a simple model catalyst with highly dispersed state of BaO.

2. Experimental

BaO supported Y_2O_3 catalyst was prepared by a conventional impregnation method. Metal oxide support was prepared by the decomposition of a corresponding metal nitrate or acetate at 673 K for 2 h in air. Loading BaO is performed with conventional aqueous techniques, i.e., the obtained metal support oxide was suspended into Ba acetate aqueous solution followed by evaporation of water. The obtained powder was dried in oven at 333 K for 6 h and then calcined at 673 K for 2 h and 873 K for 6 h. The catalyst powder thus obtained was pressed into disks, crushed, and sieved into 16–32 meshes. XRD measurement suggests that $BaCO_3$ is formed after preparation and so the catalyst was calcined at 1123 K in He flow for ca. 6 h in reactor before reaction until no CO_2 formation was confirmed. Diffraction peaks from Y_2O_3 were only observed in XRD patterns of the catalyst and no $BaCO_3$ peak was observed

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Table 1
Direct NO decomposition on BaO loaded lanthanide oxide catalyst.

Catalyst	BaO loading (mol%)	S.A.* ($m^2\ g^{-1}$)	Conversion %	Yield/%			
			NO	N2	O2	N2O	NO2
BaO/Sc_2O_3	10	49.6	94.8	81.8	70.1	0.0	12.4
BaO/Y_2O_3	10	29.9	83.8	80.1	65.3	0.0	9.3
BaO/Sm_2O_3	10	15.8	93.8	75.9	61.1	0.0	16.4
BaO/Dy_2O_3	10	18.4	80.1	70.8	54.8	0.0	12.7
BaO/MgO	7	9.3	76.8	64.4	46.4	0.0	15.2
BaO/Nd_2O_3	10	13.4	73.3	57.1	39.2	0.0	17.1
BaO/Pr6O11	10	16.7	72.0	55.4	39.5	0.0	16.2
BaO/CeO_2	10	64.9	85.5	46.6	17.6	0.0	34.0
BaO/Gd_2O_3	10	1.7	61.0	42.8	24.9	0.0	18.1
BaO/Ho_2O_3	10	3.2	58.7	37.5	20.8	0.0	19.0
BaO/La_2O_3	10	15.5	71.7	30.7	0.0	0.0	36.6
BaO/SnO_2	10	3.7	11.7	6.3	1.9	0.0	4.9
Y_2O_3	0	41.8	54.4	36.6	20.2	0.0	17.1

Reaction temperature: 1223 K, NO: 1%, $W/F = 3.0\ g\ s\ cm^{-3}$.

* B.E.T. Surface area.

after He treatment. Therefore, state of Ba seems to be an oxide and highly dispersed state because of no XRD peaks from Ba compound observed in XRD patterns.

Direct decomposition of NO was performed with a conventional fixed-bed gas-flow reactor with a quartz glass tube. Gaseous mixture of 0.1–1.0% NO diluted with He was fed to a catalyst bed and the feed rate of the reactant was fixed at $W/F = 3.0\ g\ s\ cm^{-3}$ unless otherwise noted. NO was analyzed with online gas chromatography with a thermal conductivity detector (TCD). It is noted that NO_2 yield was estimated from the total nitrogen amount before and after reaction.

Temperature-programmed desorption of NO was performed after adsorption of NO at 775 K for 30 min. After evacuation of the catalyst at 773 K for 1 h, the catalyst was exposed to 10.1 k Pa NO for 30 min, and then cooled to room temperature. After evacuation at 323 K for 30 min, the catalyst was heating at 10 K/min and the desorbed gas was monitored by a quadrupole mass spectrometer (ANELVA, AQR-100R).

The adsorption state of NO on the catalyst was measured using an FT-IR spectrometer (JASCO type 610) with a diffusion reflectance measurement set-up by using an Hg–Cd–Te semiconductor (MCT) detector, which is a sensitive IR detector suitable for a diffuse reflectance system. About 100 mg of the catalyst powder was placed in an in situ measurement cell with KBr single crystal windows. Before the measurement, the catalyst was evacuated at 1123 K for more than 5 h and then cooled to room temperature. Background spectrum was measured at each measuring temperature before NO introduction. After 30 min of NO (ca. 10 kPa) was introduced at each temperature, IR measurement was performed under NO circulating condition.

3. Results and discussion

Table 1 shows the effects of support on the NO decomposition into N_2 and O_2. In general case of support, metal oxide with large surface area have been widely used, however, in this study, metal oxide with a basic property is requested and so, we mainly studied the effects of lanthanoid oxide as support oxide. As shown in Fig. 1, lanthanoid oxide support shows a large effect on NO decomposition activity of BaO catalyst. Obviously, there is no relationship between a surface area and NO decomposition activity. Therefore, dispersion of BaO is not an important factor for high NO decomposition activity, however chemical interaction seems to be more significant effects on NO decomposition. Among the examined oxides, it is evident that high NO decomposition activity is obtained on Y_2O_3, Sc_2O_3, and Sm_2O_3 oxide. From the view point of cost and activity, we mainly studied NO decomposition activity of BaO/Y_2O_3 catalyst. High activity of NO decomposition on BaO/Y_2O_3 is also reported by Tsuboi et al. [15]. Considering the high chemical stability of Y_2O_3 and BaO, high NO decomposition activity is highly interesting because redox property of the catalyst have been considered to be an important factor for NO decomposition catalyst in previous study [12,13].

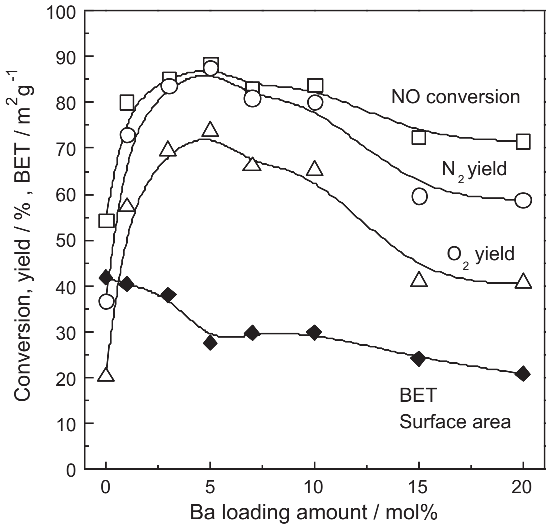

Fig. 1. NO decomposition activity on BaO/Y_2O_3 catalyst at 1123 K as a function of BaO amount loaded ($P_{NO} = 1.0\%$, $W/F = 3.0\ g\ s\ cm^{-3}$).

NO decomposition activity on BaO/Y_2O_3 catalyst at 1123K is shown in Fig. 1 as a function of BaO amount loaded. As shown in Fig. 1, NO decomposition reaction proceeds on Y_2O_3 suggesting that Y_2O_3 also works as the NO decomposition catalyst. However, NO conversion and N_2 yield increased drastically by loading BaO and the highest N_2 yield is achieved at 5 mol% BaO. At the amount of BaO higher than 5 mol%, N_2 yield slightly decreased with increasing BaO amount and this seems to be explained by the interface between BaO and Y_2O_3 is active site. This is because BaO shows no NO decomposition activity and works as just adsorption site for NO. In Fig. 1, BET surface area was also shown against BaO loading amount. In fact, BET surface area monotonously decreased with increasing amount of BaO and no relationship between surface area and the NO decomposition activity is observed. Therefore, as discussed above, surface area is not a important parameter for NO decomposition on this BaO/Y_2O_3 catalyst at a small SV value. Loading the excess amount of BaO just covers the surface of Y_2O_3 resulting in the decreased NO decomposition activity. In any way,

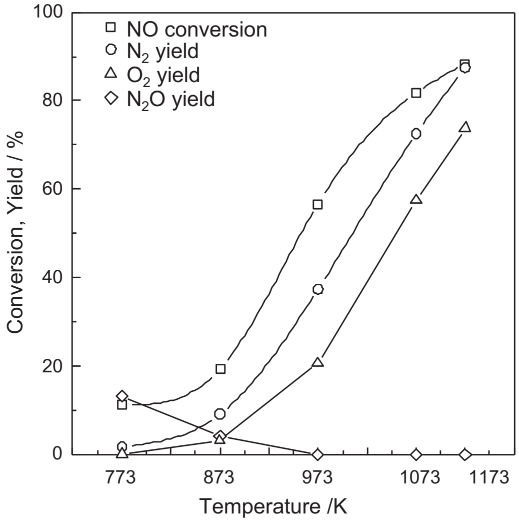

Fig. 2. Temperature dependence of NO decomposition on BaO/Y_2O_3 catalyst ($P_{NO} = 1.0\%$, $W/F = 3.0\ g\ s\ cm^{-3}$).

it is clear that the optimum amount of BaO is 5 mol% and the NO decomposition activity on this catalyst was studied in detail.

Fig. 2 shows the temperature dependence of NO decomposition activity of BaO/Y_2O_3 catalyst. NO conversion and N_2 formation is observed at temperature higher than 873 K and it monotonously increased with increasing reaction temperature. At temperature higher than 973 K, formation of O_2 is also observed and N_2 yield achieved a value of ca.90% at 1123K. Formation amount of O_2 is always smaller than that of N_2 and this could be explained by the formation of NO_2 in a cooling zone of reactor (from reaction temperature to room temperature). Formation of NO_2 is now planning to analyze with a chemiluminescence type NO_X analyzer and the results will be reported in future. On the other hand, at low temperature, N_2O formation is observed and it decreased with increasing temperature. As discussed later, N_2O formation may be related with the disproportionation of adsorbed NO ($3NO = N_2O + NO_2$). Therefore, it can be said that NO decomposition proceeds stoichiometrically to NO decomposition on this catalyst. Comparing with $Ba_{0.8}La_{0.2}Mn_{0.8}Mg_{0.2}O_3$, which is one of the most active catalyst reported, BaO/Y_2O_3 shows much higher N_2 and O_2 yield at 1123K [13]. Therefore, BaO/Y_2O_3 exhibits higher activity to NO decomposition reaction than that of $Ba_{0.8}La_{0.2}Mn_{0.8}Mg_{0.2}O_3$ and this catalyst is one of the most active catalysts reported.

Fig. 3 shows the N_2 yield at 1123 K as a function of the O_2 partial pressure (P_{O2}). In the conventional study, co-feeding of O_2 significantly lowered the catalyst activity to NO decomposition and there are limited number of the catalyst which exhibits the high NO conversion under coexistence of O_2. As shown in Fig. 3, negative effects of coexistence of O_2 are not large in case of BaO/Y_2O_3 and reasonably high N_2 yield is observed under O_2 coexistence condition. N_2 yield hardly decreased up to 1% O_2, however, it decreased to a value of 60% when 5% O_2 is co-fed. As a result, even under the oxygen partial pressure of 5%, it was found that N_2 yield of 60% was stably exhibited. Therefore, the negative effects of O_2 co-feeding are not serious and BaO/Y_2O_3 kept high activity in relatively high O_2 coexistence atmosphere. N_2 formation rate slightly decreased with increasing P_{O_2} and the P_{O_2} dependency is estimated to be −0.23, which is much smaller than that of the similar perovskite oxides reported. For example, it is reported that N_2 formation rate decreased with ${P_{O_2}}^{-0.81}$ for $La_{0.8}Sr_{0.2}CoO_3$ [9] and ${P_{O_2}}^{-0.53}$ for $La_{0.7}Ba_{0.3}Mn_{0.8}In_{0.2}O_3$ [12]. However, slightly larger comparing with that of $Ba_{0.8}La_{0.2}Mn_{0.8}Mg_{0.2}O_3$, i.e., ${P_{O_2}}^{-0.81}$ [13]. Therefore, the negative effect of coexisting O_2 on NO decomposition activity of this catalyst is much smaller than that of the conventional perovskite catalyst. Since co-feeding O_2 seems to accelerate the formation of NO_X surface species, which are strongly covered the active site for NO decomposition, small negative effects of O_2 on this catalyst can be explained by a weak adsorption state of NO_X surface species as discussed bellow.

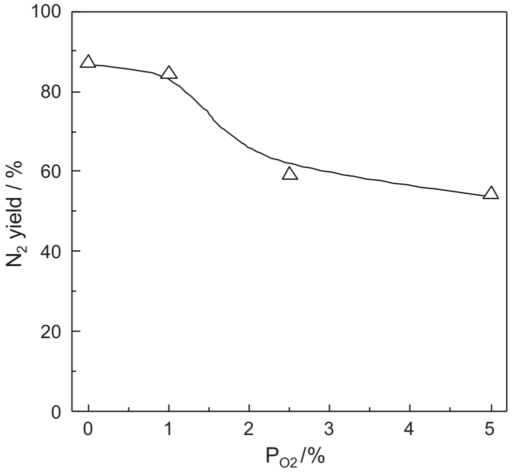

Fig. 3. N_2 yield at 1123 K as a function of the O_2 partial pressure ($P_{NO} = 0.5\%$, $W/F = 3.0\ g\ s\ cm^{-3}$).

Fig. 4 shows the N_2 yield at 1123 K as a function of NO partial pressure. In our previous study, it becomes clear that the N_2 formation rate increases with increasing NO partial pressure with ${P_{NO}}^{1.0}$ and so, the rate-determining step might be adsorption or activation of NO [9]. In the similar manner with that of doped perovskite, NO conversion slightly decreased with decreasing NO partial pressure. However, the formation rate of N_2 drastically decreased with decreasing P_{NO} less than 5000 ppm and at $P_{NO} = 1000$ ppm, N_2 yield is still reasonably a high value of ca. 40%. It is seen that the N_2 formation rate monotonously increased with increasing NO partial pressure and the dependence is ${P_{NO}}^{1.13}$, which is almost the same with that of $La_{0.7}Ba_{0.3}Mn_{0.8}In_{0.2}O_3$ [12] or $Ba_{0.8}La_{0.2}Mn_{0.8}Mg_{0.2}O_3$ [13] in our previous study. This suggests that the adsorption and/or the activation of NO are also the important step on BaO/Y_2O_3 catalyst.

For the application to the actual NO removal process from the automobile exhaust gas, the high NO removal rate should be exhib-

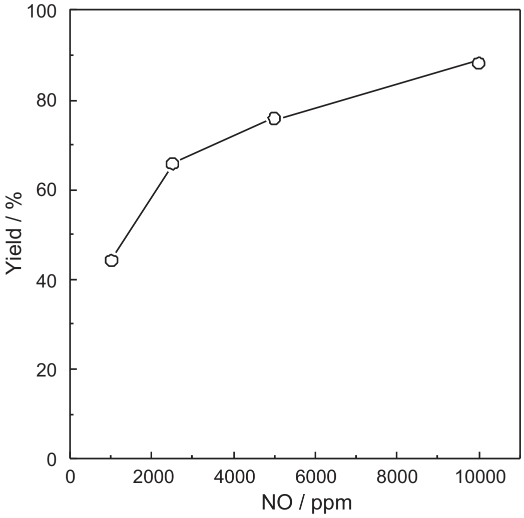

Fig. 4. N_2 yield at 1123 K as a function of NO partial pressure ($W/F = 3.0\ g\ s\ cm^{-3}$).

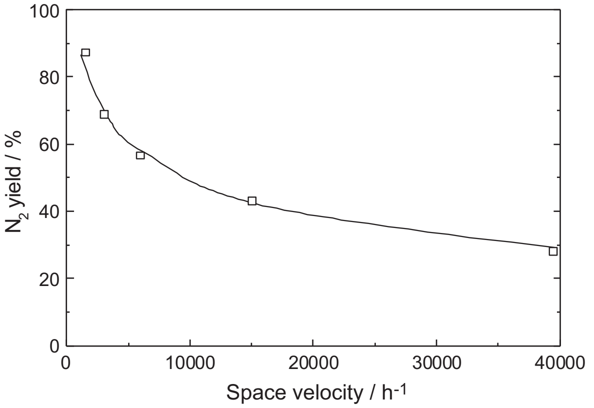

Fig. 5. N_2 yield at 1123 K as a function of the space velocity of NO (P_{NO} = 1.0%, W/F = 3.0 g s cm^{-3}).

ited at a high space velocity. Since NO decomposition reaction is considered a rather slow reaction comparing with the selective reduction reaction, the NO decomposition activity generally becomes lower with elevating the space velocity. Fig. 5 shows the N_2 yield as a function of the space velocity of NO. N_2 formation rate decreased with increasing space velocity, however, the reasonably high N_2 formation rate is still exhibited at a reasonably high space velocity of NO considering the small BET surface area of 1.1 m^2/g. The N_2 yield of 30% is still exhibited at SV = 40,000 h^{-1}. Although the high activity is requested even at few 100,000 h^{-1} for the commercial deNO$_X$ catalyst, the NO decomposition activity of BaO/Y_2O_3 catalyst is not high enough, however, reasonably high activity among the conventional NO decomposition catalyst. Considering the BET surface area of the present catalyst of 1.1 m^2/g, NO decomposition reaction under large space velocity might be diffusion limitation of reactant to active site and so, by enlarging the surface area, it is expected that the NO decomposition activity could be improved in a large space velocity value range.

Since adsorption and activation of NO seems to be the important step for NO decomposition on BaO/Y_2O_3, adsorption state of NO was studied with TPD in this study. Fig. 6 shows the NO desorption profiles from BaO/Y_2O_3. As shown in Fig. 6, NO desorption occurs mainly as NO, O_2, and N_2. It is also noted that N_2O desorption was not observed in this experiments. In the low temperature range, desorption of molecular NO is dominant. However, NO desorption cannot be observed at temperature higher than 873 K at which NO decomposition starts to proceed. In contrast, O_2 and N_2 desorption is mainly observed at 823 K. However, O_2 desorption is much larger than that of N_2. Therefore, some part of NO adsorption is dissociative ($3NO = N_2 + NO_{3ad}$ or $NO = N_2O_{ad} + NO_{2ad}$) and it is interesting that only small amount of N_2 desorbed over board temperature range. This suggests that large part of N remains on the catalyst as nitrogen oxide species like nitric, nitrate or nitrite one. On the other hand, the small amount of N_2 desorption is also observed around 623 K, at which temperature region, NO mainly desorbs. However, no desorption of oxygen was observed at this temperature. Therefore, it is considered that both molecular and dissociative NO adsorption occurred on this catalyst and molecularly adsorbed NO is weak and desorbed at relatively low temperature. However, some part of NO shows dissociative adsorption on the catalyst to form nitrogen oxide state (mainly nitrate species), which is strong adsorption species and covered the surface of BaO/Y_2O_3 catalyst. Formation of $NO_3{}^-$ species is also observed on $LaMnO_3$ [9] or $BaMnO_3$ oxide [13]. Since removing the surface nitrate requires rather high temperature, NO decomposition proceeds only at high temperature on this catalyst. Comparing with the catalysts studied in our previous work, desorption amount of O_2 is much larger and also desorption temperature is lower on BaO/Y_2O_3 catalyst. This may correspond to the small negative effects of O_2 coexistence on NO decomposition on this catalyst.

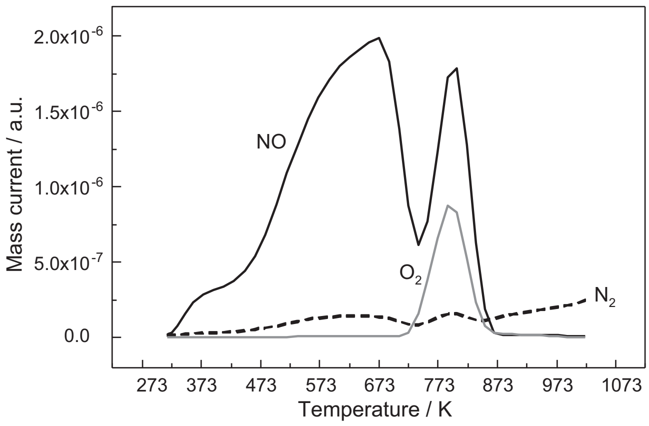

Fig. 6. Temperature programmed desorption of NO on BaO/Y_2O_3 catalyst. NO adsorption temperature: 773 K, Heating rate; 10 K/min.

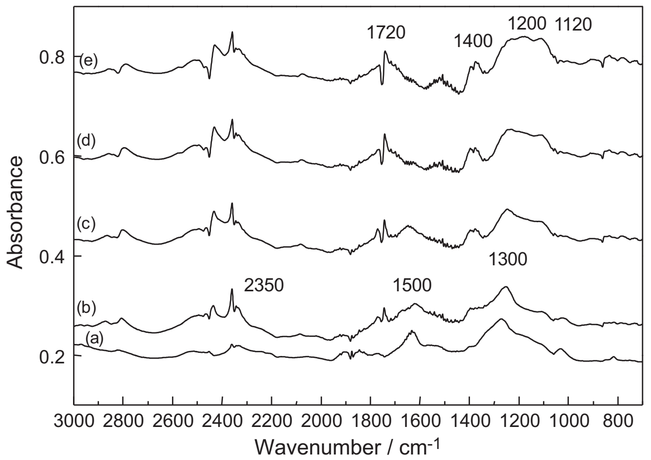

Fig. 7. FT-IR spectra of adsorbed NO on 5 wt% BaO/Y_2O_3 catalyst. Adsorption at (a) room temperature, (b) 473 K, (c) 573 K, (d) 673 K, (e) 773 K.

In order to further study the reactivity of adsorbed NO on BaO/Y_2O_3 catalyst, in situ FT-IR measurements were performed and Fig. 7 shows the IR spectra of NO at temperature from 298 to 773 K. Evidently, after exposed to NO at room temperature, the adsorption peaks around 1500 and 1300 cm^{-1} were appeared and these peaks were assigned to nitrate species (NO_2). Therefore, disproportionation reaction easily proceeds on this catalyst. On the other hand, with increasing adsorption temperature, absorption peaks around 2350, 1780, and 1200 cm^{-1} were newly appeared and that at 1500 cm^{-1} disappeared. The peaks around 2350 and 1780 cm^{-1} was assigned to N_2O and linear type NO (NO^-), respectively. As discussed above, N_2O seems to be the final intermediate species before formation of N_2. IR measurement also supports that N_2O is an intermediate species. On the other hand, the absorption bands around 1200 cm^{-1} can be assigned to those of NO_3, and these peaks became stronger with increasing temperature suggesting the strong adsorption of NO_3. Because the nitrate species strongly cover the active sites for NO decomposition, removal of the nitrate species from the surface was important to achieve high NO decomposition activities. Considering the low desorption temperature of NO_3 from BaO/Y_2O_3 catalyst comparing with that of conventional catalysts, high activity of NO decomposition on BaO/Y_2O_3 can be explained by removal of nitrate species at lower temperature. In any case, this study reveals that 5 mol% BaO/Y_2O_3 shows the high activity to NO decomposition and high NO decomposition activity is exhibited even under 5% O_2 coexistence condition.

4. Conclusion

NO decomposition activity of BaO supported on a lanthanide oxide was investigated and it was found that BaO/Sc_2O_3 or BaO/Y_2O_3 is highly active to NO decomposition. Although Y_2O_3 single oxide shows the NO decomposition activity, the activity is much improved by loading BaO and the highest N_2 yield was achieved when 5 mol% BaO was supported on Y_2O_3. On this catalyst, NO conversion increased with increasing reaction temperature, and NO conversion into N_2 and O_2 at 1123 K attained values of 88 and 74%, respectively. The NO decomposition rate increased with increasing NO partial pressure with $P_{NO}{}^{1.13}$. Therefore, the rate-determining step for NO decomposition on BaO/Y_2O_3 catalyst seems to be related with the adsorption or activation of NO. Co-feeding of oxygen decreased the N_2 yield with $P_{O_2}{}^{-0.23}$; however, N_2 yield of 55% could be exhibited even at 5% O_2 co-feeding at 1123 K. Therefore, negative effects of coexistence of oxygen are not serious on this catalyst. This could be related with a weak adsorption state of O_2 or NO_X, which is suggested by NO-TPD.

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