Structure-sensitive reaction over calcium oxide — decomposition of nitrous oxide

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Abstract

Decomposition of nitrous oxide (N_2O) was examined by using CaO catalysts having various surface areas, and structure sensitivity in the title reaction was discussed. The reaction rate of N_2O rapidly decreased with time-on-stream and then became almost constant. Temperature programmed desorption (TPD) after the reaction showed that produced oxygen is irreversibly adsorbed on CaO surface as a poisoning molecule. Photoluminescence spectra suggested that highly unsaturated sites were readily poisoned with adsorbed oxygen. The strong dependence of the initial activity and steady state activity on CaO surface area was observed, i.e., the reaction rate per surface area in the steady state increased linearly with the surface area, but that at the initial state depended more strongly on the surface area. Thus, it was found that N_2O decomposition over CaO is a structure-sensitive reaction demanding coordinately unsaturated sites. The highly unsaturated sites are extremely active for this reaction, but readily poisoned with oxygen. On the other hand, moderately and poorly unsaturated sites are responsible for the continuous catalytic activity of N_2O decomposition. The structure-sensitive dependence was rationalized by assuming the number of unsaturated sites having different coordination number, such as plane, edge, and corner sites, on geometric model of CaO crystallites. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Catalytic decomposition of nitrous oxide (N_2O) is an attractive subject from the environmental and scientific points of view. Since N_2O is thought to be responsible for the depletion of the ozone layer and for the global warming [1–3], it has been reported that various types of catalysts exhibit high activity for the decomposition of N_2O [4]. One of the most active catalyst is ion-exchanged zeolite, such as Co-, Cu-, Fe-, Rh-, and Ru-exchanged ZSM-5 [5–8]; however, the inhibition by oxygen is one of the problems. Previously, we have examined the catalytic conversion of N_2O over various metal oxide catalysts, and reported that CaO exhibits high activity for decomposition of N_2O without inhibitory effect of oxygen [9]. Although the detail was not clarified, it can be expected that

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the inhibitory effect of oxygen is strongly correlated to the adsorption of oxygen species over CaO surface.

The decomposition of N_2O can be described as an adsorption of N_2O on the active site, usually a coordinatively unsaturated surface site, followed by a decomposition giving formation of N_2 and a surface oxygen [4]. Accordingly, the N_2O decomposition has been applied extensively for characterization purpose, for example, the determination of the specific copper surface area over Cu/ZnO catalysts [10–13]. The molecular oxygen adsorption often causes the poisoning and inhibition to catalytic activity of N_2O decomposition. As for CaO catalysts, Nakamura et al. reported that adsorbed molecular oxygen species are appreciably produced through the decomposition of N_2O over CaO, and they indicated that the oxygen species are preferably held on surface sites with low coordination number [14,15].

From these reports, the adsorption of molecular oxygen and role of unsaturated sites are expected to be the key of the catalytic activity in N_2O decomposition. The activity in N_2O decomposition should be strongly affected by the surface structure of CaO. In this paper, the effect of surface area of CaO on N_2O decomposition was examined and the structure–activity relationship over CaO catalysts was discussed.

2. Experimental

Preparation of CaO, flow reaction of N_2O decomposition, temperature programmed desorption (TPD) of residual species, and BET surface area measurement were sequentially carried out in an in situ cell without exposure to external atmosphere. CaO catalysts were obtained from the calcination of $CaCO_3$ (Nakarai, GR grade) or $Ca(OH)_2$ (MERCK, GR grade). These powders were at first pressed, crushed and then sieved in the range of 28–48 mesh, and prescribed weights of the pellets were placed in a quartz tube. The pellets were heated above

1173 K in flowing He for 2 h. He was purified with molecular sieve 5A in cold trap at 77 K. Then, the decomposition of N_2O was performed in the same quartz tube at atmospheric pressure. In the catalytic runs, a mixture gas containing 1% N_2O diluted with He was fed to catalyst bed at a total flow rate of 100 cm^3 (STP) min^{-1}. N_2O was dehydrated with P_2O_5. Reaction products were analyzed by using a gas chromatograph equipped with columns of Porapak Q and Molecular Sieve 13X. After the reaction test, the catalyst was purged for 3 h in flowing He, and then TPD spectrum of residual species was measured in flowing He (30 cm^3 min^{-1}) with the heating rate of 7.5 K min^{-1}. The outlet gas was analyzed with TCD detector and mass spectrometer. Finally, BET surface area was measured in the same flow apparatus in a flow of 30% N_2/He mixture with N_2 as an adsorbate.

Photoluminescence spectra were recorded at 300 K with a Hitachi F-4500 photometer. Before recording spectra, the samples were heated with 13 Torr of O_2 at 773 K, followed by evacuation at 1173 K for 2 h, and then transferred in situ to the optical cell. Thermal gravimetry (TG) was performed with SEIKO TG-20 in flowing purified He. After the mount of 30 mg of sample and dehydration in flowing purified He at 303 K, the profile was measured from 303 K to 1273 K at the rate of 7.5 K min^{-1}. XRD patterns were recorded by a Rigaku RINT-1200 diffractometer with Cu $K\alpha$ radiation.

3. Results

3.1. Preparation of CaO from $CaCO_3$ and $Ca(OH)_2$

Table 1 shows the profiles of CaO catalysts. All the catalysts were calcined above 1173 K in flowing purified He for 2 h. It was confirmed by thermal gravimetry that $CaCO_3$ and $Ca(OH)_2$ completely decomposed to CaO above 1173 K. After the thermal decomposition above 1173 K,

Table 1
List of CaO catalysts used in this study

No.	Source material	Calcination temp./K	BET surface area/m^2 g^{-1}
1	CaCO$_3$	1373	32.2
2	CaCO$_3$	1173	32.7
3	CaCO$_3$	1173	28.1
4	Ca(OH)$_2$	1173	20.7
5	Ca(OH)$_2$	1273	6.1
6	Ca(OH)$_2$	1273	3.4
7	CaCO$_3$ → Ca(OH)$_2$[a]	1173	24.0

[a]CaCO$_3$ was calcined at 1273 K then hydrated in situ at 473 K.

only CaO phase was observed in XRD patterns. The difference in source materials and calcination temperatures resulted in the difference in BET surface area in the range of 3.4–32.7 m^2 g^{-1}. Surface areas of CaO from CaCO$_3$ were higher and less sensitive to calcination temperature than those of CaO from Ca(OH)$_2$. The catalyst No. 7 was prepared from calcination of CaCO$_3$ at 1273 K for 2 h, followed by hydration to Ca(OH)$_2$ in steam at 473 K overnight and calcination at 1173 K for 2 h. The surface area of this catalyst was in between those from CaCO$_3$ and Ca(OH)$_2$ sources.

3.2. Time-course of catalytic activity in N$_2$O decomposition

Fig. 1 shows the rate of N$_2$O decomposition per surface area and O/N$_2$ ratio with time-on-stream. In the case of the catalyst No. 1 having surface area of 32.2 m^2 g^{-1}, the initial reaction rate of N$_2$O was around 10 nmol m^{-2} s^{-1}. Then, the reaction rate steeply decreased within 100 min, and finally became 2.5 nmol m^{-2} s^{-1} with very slight decrease in the activity. The O/N$_2$ ratio was below unity at the initial stage of the reaction, and then increased and reached the stoichiometric ratio of the decomposition of N$_2$O.

$$N_2O \rightarrow N_2 + 1/2O_2$$
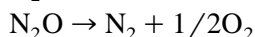
The deficiency of oxygen in the gas phase and the steep decrease in the activity at the initial stage suggest the adsorption of oxygen on CaO surface and poisoning of the reaction.
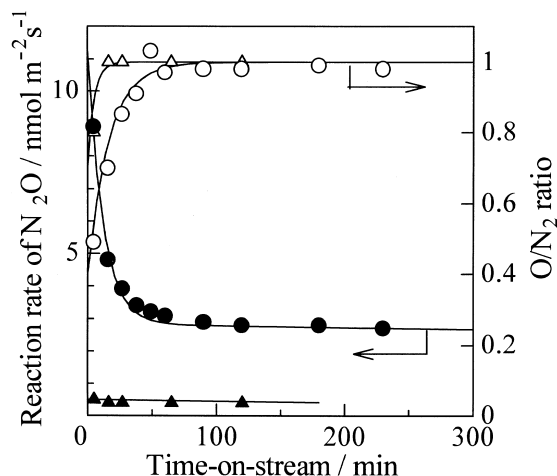

Fig. 1. Reaction rate per surface area (closed symbols) and O/N$_2$ ratio (open symbols) over CaO No. 1 (●○, 32.2 m^2 g^{-1}) and CaO No. 6 (▲ △, 3.4 m^2 g^{-1}) at 623 K.

On the other hand, in the case of the catalyst No. 6 having surface area of 3.4 m^2 g^{-1}, the activity per surface area was smaller than that over high surface area CaO. The accumulation of oxygen on the surface was very small, and the reaction rate of N$_2$O soon reached to a steady state. The trend in the transient state of reaction was strongly affected by the surface area of CaO.

3.3. TPD of residual species

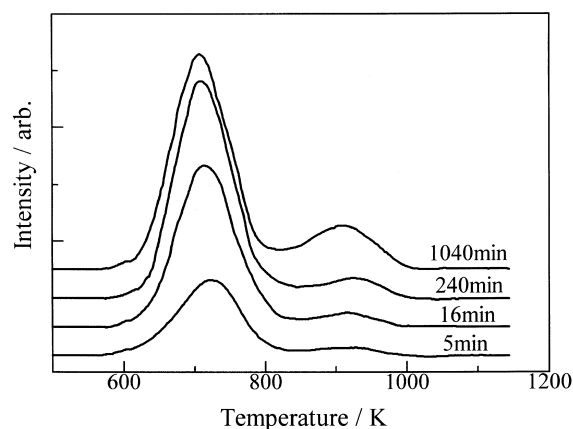Fig. 2 shows the TPD spectra of residual species after N$_2$O decomposition for various

Fig. 2. Effect of reaction time on TPD spectra of residual species from CaO catalyst after N$_2$O decomposition at 623 K. The catalyst was prepared by calcination of CaCO$_3$ at 1173 K.
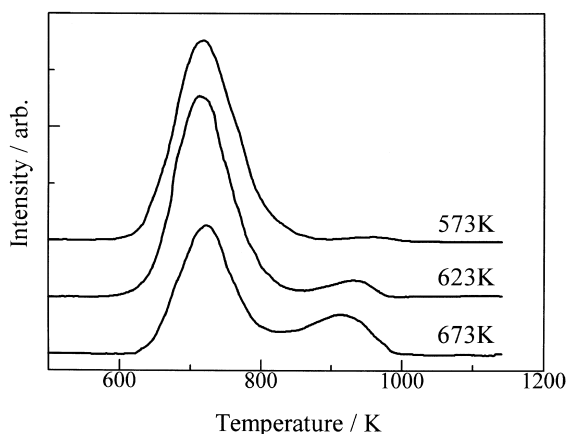
Fig. 3. Effect of reaction temperatures on TPD spectra of residual species from CaO after N_2O decomposition for 200 min. The catalyst was prepared by calcination of $CaCO_3$ at 1173 K.

times. Two desorption peaks were observed at ca. 700 K and above 850 K. From on-line mass spectroscopy and gas analysis with gas chromatography, the former peak is attributed to desorption of O_2 and the latter small peak is attributed to CO_2. The former O_2 peak increased with the reaction time, and the peak intensity was saturated after 240 min. The increase in the oxygen peak was in harmony with the low O/N_2 ratio at the initial stage of the reaction shown in Fig. 1. These spectra indicate that the produced oxygen is irreversibly adsorbed on CaO surface under the reaction condition. The desorption of CO_2 is due to small

amount of CO_2 impurity in feed gas. Since the intensity of CO_2 peak slightly increased with the time-on-stream, the slight decrease in the activity at the steady state should be due to the adsorption of CO_2 on CaO surface.

Fig. 3 shows the TPD spectra of residual species after N_2O decomposition at various temperatures. The intensity of the oxygen peak was the same at 623 and 523 K, but that was smaller at 673 K. In the case of former two spectra, the desorption peak started from ca. 623 K. The figure indicates that the irreversibly adsorbed oxygen can be removed above 623 K, i.e., the catalytic run below 623 K results in the maximum adsorption of oxygen species. The maximum number of adsorbed oxygen over CaO was 3.6 μmol m^{-2}. This value fairly agreed well with the deficient amount of oxygen in the gas phase during N_2O decomposition. The amount of adsorbed CO_2 after the reaction at 623 K for 200 min was 0.3 μmol m^{-2}, which was negligibly smaller than that of the adsorbed oxygen. Comparing with the crystallographic data, the coverage of oxygen was 25% of Ca^{2+} cation sites on (100) plane of CaO, which was in the same level as Nakamura et al. reported [14].

3.4. Photoluminescence spectra

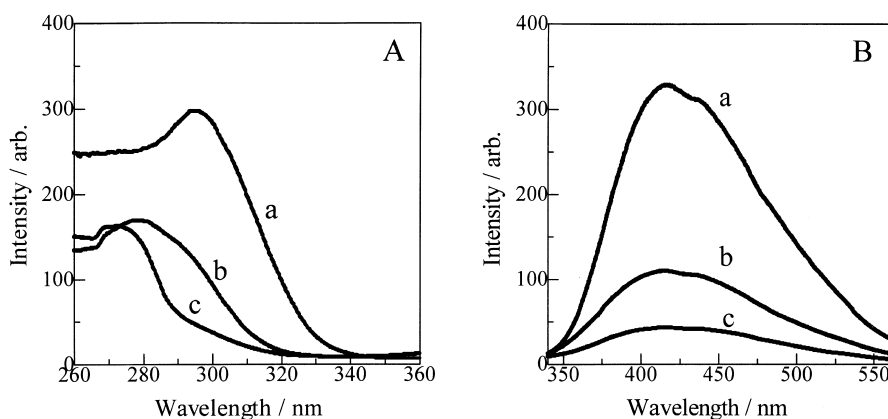Fig. 4 shows the photoluminescence spectra of CaO having various surface areas. In Fig. 4B,

Fig. 4. Photoluminescence excitation spectra of CaO catalysts of No. 1 (a, 33 m^2 g^{-1}), No.4 (b, 21 m^2 g^{-1}), and No.6 (c, 3 m^2 g^{-1}) at 300 K. (A, Left) Excitation spectra of 400 nm luminescence. (B, Right) Emission spectra excited at 298 nm.

the emission band centered at 410 nm was observed, and there was no difference in the position of emission band for all the CaO samples. On the contrary to this, the excitation spectra were affected by the surface area of CaO (Fig. 4A). The excitation maximum was observed at 295 nm for CaO having surface area of 33 m^2 g^{-1}, but at 270 nm for CaO having surface area of 3 m^2 g^{-1}. The higher surface area of CaO resulted in the lower excitation energy of photoluminescence. The similar photoluminescence spectra from CaO have been reported by Garrone et al. [16], Coluccia et al. [17], and Nakamura et al. [14]. According to their assignment, the photoluminescence spectra in Fig. 4 are identical with the surface absorption bands, and can be attributed to the surface unsaturated sites having coordination number of less than 5.

Fig. 5 shows the photoluminescence excitation spectra of CaO (33 m^2 g^{-1}) after the evacuation and introduction of N_2O. After introduction of 1.0 Torr N_2O, the photoluminescence excitation spectrum at around 300 nm was clearly reduced.
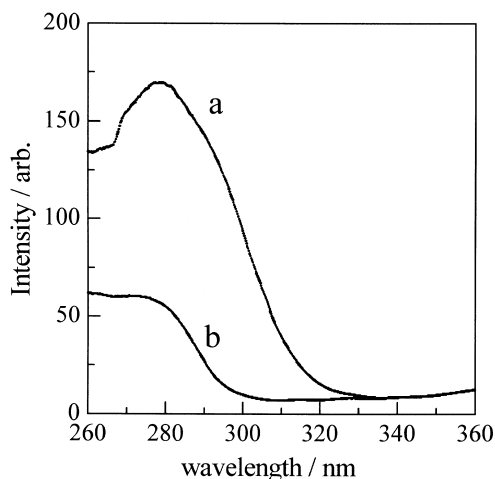

Fig. 5. Photoluminescence excitation spectra of CaO catalyst of No. 4 at 300 K (a) after evacuation at 1073 K and (b) after introduction of 1.0 Torr of N_2O at 623 K for 30 min. Spectra were recorded at 300 K by monitoring emission at 400 nm.

4. Discussion

4.1. Adsorption of oxygen and surface unsaturated sites

As shown in Fig. 1, the activity in N_2O decomposition steeply decreased with time-on-stream. From the low O/N_2 ratio at the initial stage of reaction and TPD of residual species, the decrease in the initial activity was clarified to be due to the adsorption of oxygen species on the CaO surface [14]. These results indicate that the high activity for N_2O decomposition in the initial stage is responsible for some surface sites that are readily poisoned by the surface oxygen produced during N_2O decomposition.

It is usually described that a coordinatively unsaturated surface site is the active center for the decomposition of N_2O, and the decomposition of N_2O results in O^- species on catalyst surface [4]. The existence of surface unsaturated sites over CaO was confirmed by photoluminescence spectra. In our results, CaO having higher surface area gave excitation spectra at longer wavelength, i.e., lower energy region. It is well known in other systems that the degree of surface unsaturated sites significantly affects the photoluminescence spectra [18,19]. Coluccia et al. investigated the relation between the surface morphology observed by electron micrograph and the photoluminescence spectra of MgO crystallites [20,21]. In their experiments, the exposure of cubic MgO crystallites to water vapor resulted in considerable increase in the surface unsaturated site which is involved in edge and corner and also in the significant enhancement in the photoluminescence emission excited at longer wavelength. Consequently, according to their reports, our luminescence spectra should represent the higher unsaturation of surface over CaO having high surface area.

As shown in Fig. 5, the exposure of CaO to N_2O led to the quenching of photoluminescence spectra. After the exposure to N_2O, the spec-

trum of high surface area CaO (Fig. 5b) became similar to that of low surface area CaO (Fig. 4Ac), of which the depletion of the catalytic activity was not significant. This suggests that the highly unsaturated surface sites are responsible for the initial depletion of the catalytic activity. Nakamura et al. [14] claimed that the adsorbed oxygen species were preferentially held on the highly unsaturated surface sites. These results suggest that the initial activity for N_2O decomposition is responsible for the surface highly unsaturated sites, and the moderate steady state activity is for the lower unsaturated sites. Previously, we reported the high durability of CaO catalyst against the inhibitory effect of oxygen in N_2O decomposition [9]. The above discussion suggests that the high durability of CaO catalyst should be due to the contribution of moderately or lower unsaturated surface sites.
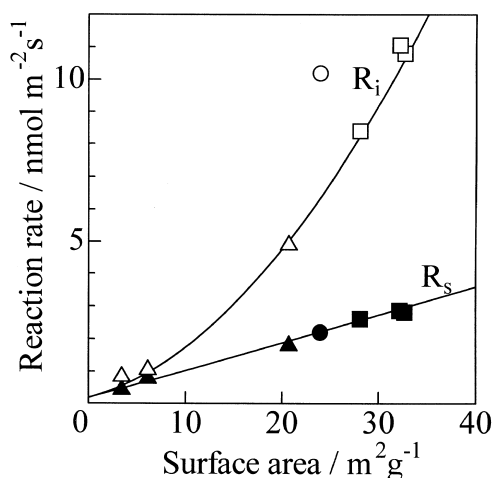

Fig. 6. Initial (open) and steady state (closed) reaction rates of N_2O decomposition at 623 K as a function of surface area of CaO prepared from $CaCO_3$ ($\square$ $\blacksquare$), $Ca(OH)_2$ ($\triangle$ $\blacktriangle$), and $CaCO_3$ followed by in situ hydration and thermal decomposition ($\bigcirc$ $\bullet$).

4.2. Structure sensitivity in decomposition of N_2O

As described above, the activity in N_2O decomposition can be divided into two features, the initial activity and the steady state activity. As shown in Fig. 1, the depletion curve exhibited two slopes, i.e., the fast depletion at the initial stage and the slow depletion after 100 min. These two types of the depletion curves were extrapolated to zero time, and defined as the initial state rate (R_i) and the steady state rate (R_s), respectively.

In Fig. 6, the reaction rates of N_2O per surface area in the initial state (R_i) and the steady state (R_s) were plotted as a function of the surface area of CaO. The steady state reaction rate, R_s, linearly increased with the surface area of CaO having a small intercept at zero surface area. On the other hand, the initial reaction rate, R_i, significantly increased with the surface area. It should be noted that this trend was independent of the source material of CaO. Thus, this strong dependence of the activity on the surface area of CaO is not due to the

chemical components, but to some structural difference in CaO crystallites. As discussed in Section 4.1, a significant difference in the degree of surface unsaturation was observed. The strong dependence of the activity on surface area should arise from the surface unsaturation, i.e., surface geometrical difference. Therefore, as an important conclusion, Fig. 6 clearly represents that the N_2O decomposition over CaO catalysts is the structure-sensitive reaction.

4.3. Activity pattern estimation

The structure sensitivity in N_2O decomposition over CaO should arise from the dependence of the number of unsaturated sites on catalyst surface. In general, there should be the three kinds of unsaturated sites on the surface of oxide crystallites, i.e., corner sites having coordination number of 3, edge sites having coordination number of 4, and plane sites having coordination number of 5 [20–22]. On the assumption that the morphology of CaO crystal is invariable with the crystal size, the number of plane (N_p), edge (N_e) and corner (N_c) sites per

surface area of a crystallite (S) should be described as:

$$N_p = \alpha a^2 / S \tag{1}$$

$$N_e = \beta a / S \tag{2}$$

$$N_c = \gamma / S \tag{3}$$

where a is an average side length of crystallites, and α, β, and γ are coefficients. The average side length of a, weight of CaO (w), and surface area of a crystallite (S) are correlated to BET surface area (S_{BET}) as follows:

$$a = \frac{\sigma}{S_{BET}} \tag{4}$$

$$w = \rho a^3 = \rho \left(\frac{\sigma}{S_{BET}} \right)^3 \tag{5}$$

$$S = S_{BET} w \tag{6}$$

where σ is a coefficient and ρ is the density of CaO crystal. From these equations, the surface concentration of plane, edge, and corner sites can be represented in the following equations.

$$N_p = \frac{\alpha}{\rho \sigma} \tag{7}$$

$$N_e = \frac{\beta}{\rho \sigma^2} S_{BET} \tag{8}$$

$$N_c = \frac{\gamma}{\rho \sigma^3} S_{BET}^2 \tag{9}$$

It should be noted that these equations, i.e., the correlation between the surface concentration of these sites and BET surface area, are available to CaO particle having any geometrical structure, such as cubic, rectangular, hexagonal and so on, as long as CaO particles have similarity in the geometry. As shown in Eqs. (7)–(9), the surface concentration of plane sites is independent of the surface area, while those on edge and corner sites are proportional to the surface area and square of it, respectively.

In Fig. 6, the plot of R_s was a straight line having an intercept, while the plot of R_i was a second-order curve, respectively. These relationships corresponded to the number of surface sites, i.e., R_i corresponded to linear combination of all sites, and R_s to the combination of plane and edge sites. One may suspect that the contribution of corner sites is too high when CaO is composed of ideal cubic crystallites. This may be due to extremely high activity of corner sites compared to other sites and due to complicated morphology of CaO crystallites. Although only the change in the number of sites was taken into consideration in above discussion, a good agreement with the experimental data was obtained as the first approximation.

5. Conclusion

From the examination of the dependence of the activity on the surface area of CaO, structure sensitivity in N_2O decomposition over CaO was demonstrated. The highly unsaturated sites are extremely active, but readily poisoned by oxygen, while the moderately and poorly unsaturated sites are responsible for the activity in the steady state. The structure-sensitive dependence was rationalized by using geometric model of CaO crystallites.

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