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NOTES

Catalytic Properties of Oxygen Adsorbed on NiO–Sm_2O_3 Binary Oxides

Although the catalytic behavior of rare earth oxides has been investigated by many authors (*1–3*), that of the corresponding binary systems has received little attention. The rare earth oxides show catalytic activities for some catalytic oxidation reactions (*4–6*); they would, however, be more useful as promoters for oxidation catalysts. In the early stage of this study, catalytic activities of binary oxides of nickel and rare earth (La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Yb) for the oxidation of nitrogen oxide (NO) and TPD (temperature-programmed desorption) spectra of the adsorbed oxygen on these binary oxide systems were measured. On the basis of the preliminary experiments, NiO–Sm_2O_3 was chosen, because not only a promotion effect of samarium but also noticeable TPD spectra were found for the system. In this paper, catalytic activity of the NiO–Sm_2O_3 system for the oxidation of nitrogen oxide, TPD spectra of the adsorbed oxygen, and XPS (X-ray photoelectron spectroscopy) spectra of the binary oxide system are reported.

Nickel oxide (NiO), samarium oxide (Sm_2O_3), and six NiO–Sm_2O_3 binary oxides [1.25, 2.5, 3.75, 5, 10, and 20% (mol) Sm_2O_3], were used in this study. The binary oxides were prepared by calcination of oxalates coprecipitated from aqueous solutions of $Ni(NO_3)_2$ and $SmCl_3$ in a stream of oxygen at 800°C for 4 hr. The oxide powder was then formed into a pellet at a pressure of 100 $kg \cdot cm^{-2}$ and cut into cubes with dimensions 1–2 mm. The surface area measured by the BET method was as follows: NiO, 3.6 $m^2 \cdot g^{-1}$; 1.25% Sm, 4.9 $m^2 \cdot g^{-1}$; 2.5% Sm, 6.4 $m^2 \cdot g^{-1}$; 3.75% Sm, 8.9 $m^2 \cdot g^{-1}$; 5% Sm, 8.7 $m^2 \cdot g^{-1}$; 10% Sm, 14.9 $m^2 \cdot g^{-1}$; 20% Sm, 8.6 $m^2 \cdot g^{-1}$; and Sm_2O_3, 10.6 $m^2 \cdot g^{-1}$. For the measurement of catalytic activity, a reaction tube (10-mm ϕ) was set in a conventional flow system and a mixture (1 cm^3) of the catalyst (ca. 0.85 g) and SiC (9–20 mesh) was placed in the center. The catalyst bed was fixed with silica wool and its temperature was measured with an alumel-chromel thermocouple. The flow rate of the reactant gas (NO, 500 ppm; O_2, 5%; N_2, balance; total, 1 atm) was 1000 $cm^3 \cdot min^{-1}$. Quantitative analyses of NO and total NO_x were carried out with the "Saltzman method" and the "nitrate-selective electrode method," respectively. Before the measurement of catalytic activity, a gas mixture (O_2:N_2 = 1:4) was flowed through the catalyst bed at 450°C for 3 hr to clean the surface. During the NO oxidation reaction the catalyst temperature was kept at 320°C. The TPD apparatus could be evacuated to 10^{-5} Torr with a diffusion pump and TPD spectra were obtained by measuring the variation in pressure due to desorption of the gases from the samples with a highly sensitive pirani gauge (Dan Kagaku Model PS-12). Pretreatment of the sample (ca. 0.25 g) was carried out by repeated cycles of heating under 400 Torr of O_2 and evacuation at 700°C. XPS

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spectra were obtained by means of a Du Pont ESCA-650 spectrometer which was capable of heating the sample *in situ* up to 400°C. The specimens were kept in a vacuum capsule prior to mounting in the XPS spectrometer.

Catalytic activities of the NiO–Sm_2O_3 binary oxides in the oxidation of NO at 320°C are shown in Fig. 1. K_g is the rate of formation of NO_2 in units of μmol·(g of catalyst)$^{-1}$·min^{-1}, which was usually constant during the period of measurement ($\sim$1 hr), while K_s is the rate of formation of NO_2 in units of μmol·(m^2 of catalyst)$^{-1}$·min^{-1}. The catalytic activity K_g increased with increasing samarium content: The catalyst containing 3.75% Sm_2O_3 showed maximum activity and was 3.7 times as active as pure NiO. For catalysts with Sm_2O_3 contents higher than 3.75%, K_g decreased with increasing content. Pure Sm_2O_3 gave only very low activity. The catalytic activity K_s also showed a similar pattern, but the extent of the enhancement of activity by addition of samarium was lower than that for K_g. Therefore, some of the promotion effect by samarium could be caused by the increase in surface area by the addition of samarium. In this study, interest has subsequently focused on the adsorbed oxygen on the oxides.

Figure 2 shows the TPD spectra of the O_2–NiO–Sm_2O_3 system. The spectra (a)–(h) were obtained by the following operation: (1) heating the oxide sample *in vacuo* at 700°C for 1 hr in the cell, (2) introduction of 400 Torr of O_2 into the cell at 700°C, (3) gradual cooling to 20°C over a period of 2 hr, (4) evacuation of the gas for 30 min, and (5) linear increase in temperature (40°C·min^{-1}) during evacuation with the diffusion pump. The variation in pressure due to desorption of oxygen was followed on a recorder. Each spectrum (in group I, Fig. 2), except for pure Sm_2O_3, gave two desorption peaks: α (220–230°C) and β (370–380°C). The peak intensity was very weak on NiO but increased sharply with increasing samarium content. Above 3.75% Sm, however, it decreased with increasing samarium content. The TPD spectrum from Sm_2O_3 gave no clear peak in this experiment. It is noteworthy that the temperatures for both peaks (α and β) in these spectra (a)–(g) were almost the

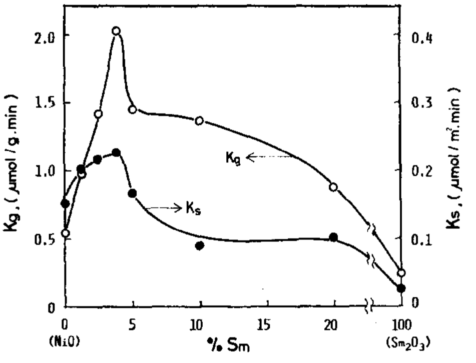

FIG. 1. Catalytic activities of NiO–Sm_2O_3 binary oxides in the oxidation of nitrogen oxide.

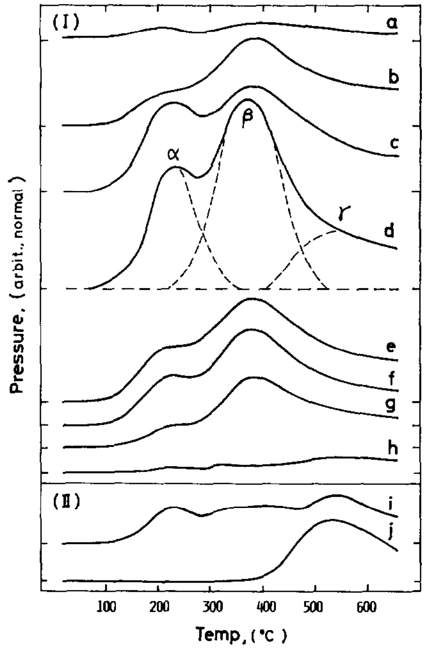

FIG. 2. TPD spectra of oxygen from NiO–Sm_2O_3 binary oxides. (I) (a) Pure NiO, (b) 1.25% Sm, (c) 2.5% Sm, (d) 3.75% Sm, (e) 5% Sm, (f) 10% Sm, (g) 20% Sm, (h) pure Sm_2O_3. Oxygen was adsorbed at 750°C and evacuated at 20°C. (II) 3.75% Sm. Oxygen was adsorbed and evacuated at 80°C (i) or 400°C (j).

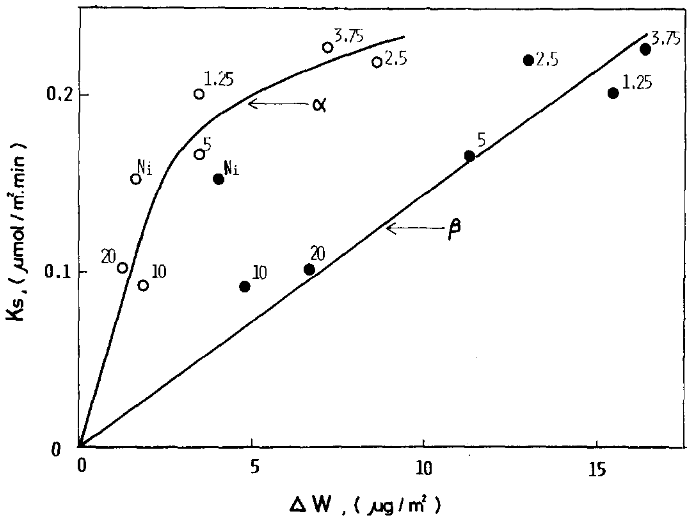

FIG. 3. Relation between the catalytic activity K_s and the amount of α or β peak oxygen. Numbers by each point give the samarium content. ΔW, amount of oxygen adsorbed.

same in spite of large differences in the amount of oxygen desorbed. This could suggest that the oxides, with the exception of pure Sm_2O_3, have active sites of the same type. Since all the β peaks have long tails to high temperature, certain experiments were performed using the 3.75% Sm_2O_3 catalyst. The procedure for the experiment was as follows: (1) heating the sample *in vacuo* at 700°C for 1 hr in the cell, (2) gradual cooling to 80°C [spectrum (i)] or 400°C [spectrum (j)], (3) introduction of 400 Torr of O_2 into the cell at each temperature for 30 min, (4) evacuation of the gas for 30 min at each temperature, (5) cooling to 20°C, and (6) linear increase in temperature ($40°C \cdot min^{-1}$) while evacuating with the diffusion pump. The spectra are shown in Fig. 2 (i) and (j) and clearly show the existence of a third peak γ (530–540°C). The β peak disappeared after an adsorption–evacuation procedure at 400°C [spectrum (j)], and the α peak disappeared after such a procedure at 220°C. No evidence for gas desorption was found in the TPD spectrum when no oxygen was introduced into the cell.

Concerning the temperatures for the peaks in the TPD spectrum of oxygen adsorbed on nickel oxide, Gay (*7*) has reported interesting results using NiO which was prepared by calcination of nickel nitrate at 850°C for 9 hr. He found two peaks for desorption of oxygen, at 320–360°C (strong) and at 650–700°C (medium), in the TPD spectrum when the oxide was exposed to oxygen at 200°C and evacuated. Moreover, he found three peaks, at about 200°C (strong), 500–530°C (weak), and about 730°C (medium), in the TPD spectrum of the oxide which was exposed to oxygen (200°C, at first) and N_2O (100°C, subsequently). The temperatures found in the present study almost correspond to his results. On the other hand, Iwamoto and co-workers (*8*) have also reported TPD spectra of the O_2–NiO system, and found four peaks at 30–40°C, 320–360°C, 420–450°C, and 520–550°C. Some of the temperatures for desorption of oxygen in their study agree with our results, but others do not. In particular he found no peak at ~220°C. This discrepancy could be caused by the difference in preparation temperature; they prepared their sample by decomposition of nickel carbonate *in vacuo* at 600°C for 17 hr.

To relate the catalytic activity to the chemisorbed oxygen species, the activity

K_s of each catalyst was plotted against the amount of oxygen desorbed from a unit surface area of each oxide. The result is shown in Fig. 3. It was then assumed that the distribution of the amount of oxygen in the peaks α and β was gaussian-like, as illustrated in Fig. 2(d). The weight of oxygen corresponding to the unit area of the TPD peak was evaluated by use of microgravimetry, i.e., the weight change caused by desorption of oxygen was followed with a microbalance. As shown in Fig. 3, the amount of adsorbed oxygen per unit area differred considerably from catalyst to catalyst. It is noteworthy that the catalytic activity increased, apart from a few exceptions, with increasing amounts of oxygen in each peak. However, the oxygen corresponding to the α peak should not play such an important role in the reaction, since the latter was carried out at 320°C. The linear relation between K_s and ΔW of the peak would suggest that the oxygen corresponding to the β peak is important for the oxidation of NO. This might be supported by the work of Gay, who reported the reaction of oxygen with N_2O at 320–360°C. The reason why only the pure NiO splits off from the straight line is still under consideration. The oxygen coverage corresponding to the β peak on the catalyst containing 3.75% Sm_2O_3 was 0.054, assuming that only (100) planes were present on the surface and that the oxygen species were atomic.

TABLE 1

XPS Binding Energies for the Nickel–Oxygen System[a]

	Binding energy (eV)	
	Ni $2p_{3/2}$	O1s
NiO	854.5 856.3 (MS)[b] 861.7 (ME)	529.9
Ni_2O_3	855.8 861.4 (ME)	531.7
$Ni(OH)_2$	856.6 862.4 (ME)	531.7
NiO_{ads}	~853.5	533.5

[a] After Kim and Winograd (9).

[b] MS, multiple splitting; ME, electron shake-up.

The XPS spectra of the catalyst containing 3.75% Sm_2O_3 heated *in vacuo* at

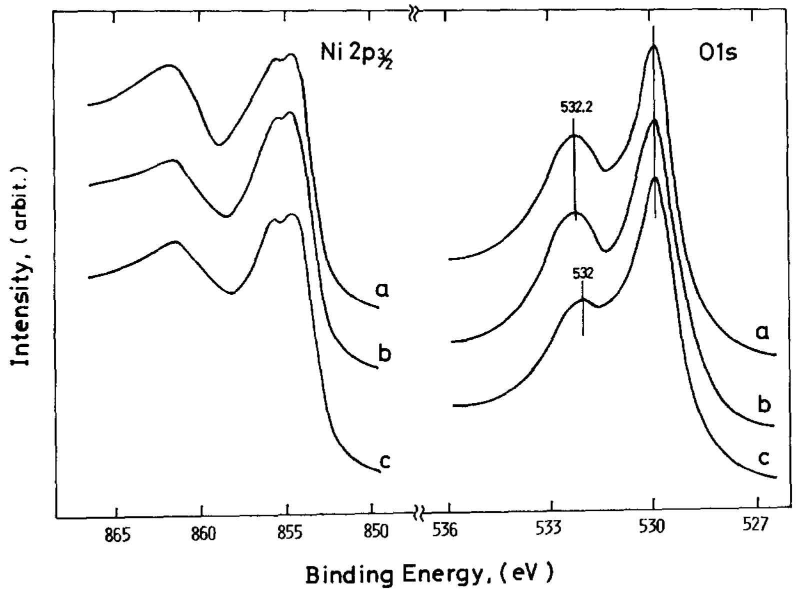

FIG. 4. XPS spectra of a NiO–Sm_2O_3 binary oxide [composition, NiO (3.75% Sm)]. Each spectrum shows the sample after heating in vacuum at (a) 100°C, (b) 230°C, and (c) 400°C.

various temperatures (100, 230, and 400°C) *in situ* are shown in Fig. 4. According to the assignments reported by Kim and Winograd (*9*) (Table 1), the surface layer with adsorbed oxygen corresponding to the α, β, and γ peaks [spectra (a)] showed a mixed spectrum of NiO- and Ni_2O_3-like oxide. Since the left O1s peak (532.2 eV) had 0.5 eV higher binding energy than that of their data (531.7 eV), the oxygen should not strictly be the lattice oxygen of Ni_2O_3. After heating *in vacuo* at 230°C, the oxide gave almost the same spectrum as that of (a), except for a decrease in the intensity of the satellite peak at 861.5 eV. A remarkable change in the spectrum occurred when the oxygen corresponding to the α and β peaks was removed from the oxide. Namely, the height of the left O1s peak was diminished and the binding energy was shifted to lower energy. The ratios of peak intensities at 529.9 to 532.2 eV [or 532.0 eV in the case of (c)] of (a), (b), and (c) were 0.58, 0.58, and 0.46, respectively. These suggest that the O1s peak at 532.2 eV is due to the oxygen corresponding to the β peak and that at 532.0 eV is due to the oxygen corresponding to γ and/or any other tightly adsorbed oxygen species on the oxide. Kim and Winograd have found only one peak at 529.9 eV in the spectrum of NiO which evacuated at 800°C. It is well-known that NiO, when subjected to evacuation at high temperatures, develops an inherent nonstoichiometry, due to a partial removal of lattice oxygens that generates both anion vacancies and a consequent transformation of certain Ni^{2+} ions to Ni^{3+} ions. The type-β peaks observed in the TPD experiments may partially reflect, for example, this loss of lattice O^{2-} ions, rather than a true "desorption" of adsorbed oxygen. Addition of low levels of Sm_2O_3, with its highly stable Sm^{3+} ions, may increase the stability or ease of formation of catalytically significant anion vacancies.

In conclusion, we can note that samarium behaves as a promoter in the NiO–Sm_2O_3 binary system, i.e., it causes not only an increase in surface area, but also an increase in oxygen adsorption sites per unit area. In the TPD spectra of the oxide system, three peaks [α(220–230°C), β (370–380°C), and γ (530–540°C)] were found between 20 and 660°C. The catalytic oxidation of NO on these binary oxides is considered to be closely related to the β peak oxygen.

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