

A Measure of the Number of Active Oxygen Atoms on the Surface of Co_3O_4 Catalysts

We have previously developed the rectangular pulse technique to determine the number of active oxygen atoms on the surface of V_2O_5 and Cr_2O_3 catalysts (1-3). This paper demonstrates that the number of active oxygen atoms (O_s) on Co_3O_4 catalysts can also be determined by using the rectangular pulse technique coupled with the reaction of NH_3 with the preoxidized catalyst, i.e.,



Adsorptions of NO and CO on Co_3O_4 catalysts have been well investigated (4-6). It is then interesting to determine the number of active oxygen atoms on the catalyst and discuss the site of the active oxygen atom since the catalyst is active for the oxidation of various reactants, such as CO, NH_3 , and hydrocarbons (e.g. (7-17)).

Two kinds of Co_3O_4 , denoted by $\text{Co}_3\text{O}_4(\text{A})$ and $\text{Co}_3\text{O}_4(\text{B})$, were used as catalysts. $\text{Co}_3\text{O}_4(\text{A})$ was prepared by thermal decomposition of cobalt(II) carbonate in a stream of O_2 at 773 K for 3 h. $\text{Co}_3\text{O}_4(\text{B})$ was prepared by hydrolysis of cobalt(II) nitrate with sodium hydroxide solution, followed by filtration and subsequent calcination in a stream of O_2 at 773 K for 3 h. The catalyst was then pressed and sieved in the range 28-48 mesh. Diffraction peaks in the X-ray diffraction diagrams of the catalysts were all assigned to the Co_3O_4 phase. Apparatus and procedure of the rectangular pulse technique were almost the same as those described previously (1, 2, 18). This technique is based on Reactions 1 and 2 together with the introduction of NH_3 in a

rectangular pulse shape onto the preoxidized catalyst and the detection of the concentration profile of N_2 produced by Reaction 1. Unless otherwise stated, experiments were conducted under the following standard conditions: Weight of catalyst = 0.1-0.2 g. Flow rate of carrier gas(He) = $150 \text{ cm}^3 \text{ min}^{-1}$. Pulse width = 2 min. Initial concentration of NH_3 in the rectangular pulse = $1.10 \mu\text{mol cm}^{-3}$. Before every measurement, the catalyst was routinely preoxidized in a stream of O_2 ($150 \text{ cm}^3 \text{ min}^{-1}$) for 20 min at 773 K and cooled to the reaction temperature in a stream of O_2 . The selectivities to N_2 and N_2O in the reaction of the rectangular pulse of NH_3 with the preoxidized catalyst were determined by using a silica-gel column (50 cm in length) instead of the liquid-nitrogen trap [13 in Fig. 1 of Ref. (2) or Fig. 2 of Ref. (18)].

Figure 1 shows examples of the concentration profiles of N_2 produced by the reaction of the rectangular pulse of NH_3 with the preoxidized Co_3O_4 catalyst. As shown, the concentration profile of N_2 consisted of two parts—initial sharp N_2 and tailing N_2 . The concentration of N_2 at the tailing part became greater with increasing temperature. The initial sharp N_2 is due to the reaction of NH_3 with the surface oxygen atoms, while the tailing N_2 is due to the reoxidation of the surface by subsurface oxygen atoms (1). Taking into account the results of simulation done on surface reaction and diffusion of oxygen in the metal oxide (2, 3), the initial N_2 peak was separated from the tailing part by the dotted line shown in Fig. 1. The amount of the initial N_2 thus determined [$A(\text{N}_2)$] is shown in Fig. 2 as a function of temperature. In addition to N_2 , N_2O

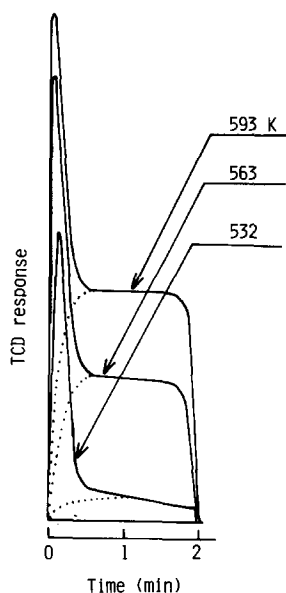


FIG. 1. Examples of concentration profiles of N_2 produced by the reaction of the rectangular pulse of NH_3 with the preoxidized $Co_3O_4(A)$ catalyst at various temperatures. Experiments were conducted under the standard condition. Weight of catalyst = 0.145 g. All curves in this figure were obtained on a single sample.

was produced by the reaction of the NH_3 pulse with the preoxidized Co_3O_4 catalyst. Figure 3 shows results of the selectivity to $N_2O[S(N_2O)]$ at various temperatures.

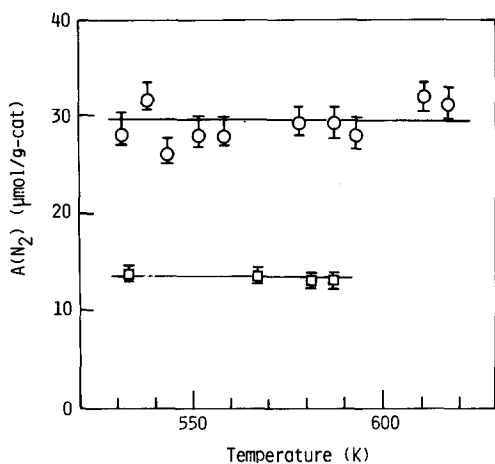


FIG. 2. The amount of the initial sharp N_2 [$A(N_2)$] produced by the reaction of the rectangular pulse of NH_3 with the preoxidized Co_3O_4 catalyst at various temperatures. Circles: $Co_3O_4(A)$. Squares: $Co_3O_4(B)$. Error bar resulted from the uncertainty of the dotted line to separate the initial N_2 from the tailing N_2 .

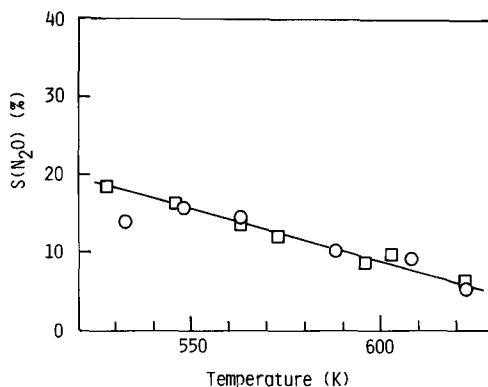


FIG. 3. Selectivity to N_2O [$S(N_2O)$] in the reaction of the rectangular pulse of NH_3 with the preoxidized Co_3O_4 catalyst at various temperatures. Circles: $Co_3O_4(A)$. Squares: $Co_3O_4(B)$.

According to the mechanism of the oxidation of NH_3 on metal oxide catalysts (9), N_2 and N_2O are produced by Eqs. (1) and (2). These equations indicate that the number of active oxygen atoms responsible for the initial peak (A_0) can be calculated by

$$A_0 = A(N_2)\{3 + 4S(N_2O)/[1 - S(N_2O)]\} \quad (3)$$

Figure 4 shows results of A_0 at various temperatures which are calculated from the results of $A(N_2)$ and $S(N_2O)$ in Figs. 2 and 3. As shown, A_0 is almost constant at any of the temperatures examined. The average value of A_0 is defined by L and the result is shown in Table 1. This table also shows the

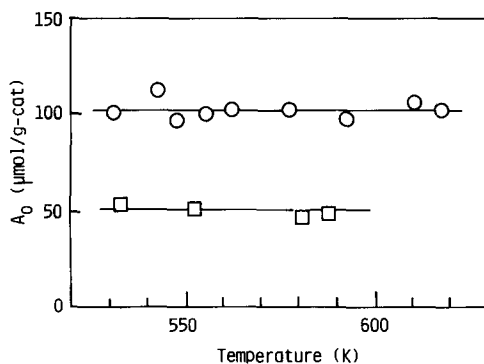


FIG. 4. The number of active oxygen atoms (A_0) measured at various temperatures. Circles: $Co_3O_4(A)$. Squares: $Co_3O_4(B)$.

TABLE I

The BET Surface Area (S_{BET}), Number of Active Oxygen Atoms (L), Concentration of Active Oxygen Atoms (L/S_{BET}), and Area Occupied by an Active Oxygen Atom (σ)

Catalyst	S_{BET} ($\text{m}^2/\text{g-cat}$)	L ($\mu\text{mol}/\text{g-cat}$)	L/S_{BET} ($\mu\text{mol}/\text{m}^2$)	σ (\AA^2)
$\text{Co}_3\text{O}_4(\text{A})$	31.3	102.0	3.3	51
$\text{Co}_3\text{O}_4(\text{B})$	18.6	51.0	2.7	61

BET surface area (S_{BET}), concentration of the active oxygen atoms (L/S_{BET}), and area occupied by an active oxygen atom (σ) which is defined as S_{BET} divided by L . As shown, σ does not change significantly with the catalyst. According to the electron diffraction patterns of the catalysts, the slight difference in σ may be ascribable to the difference in crystal planes exposed to the catalyst surface. It should also be noted that the value of σ is close to that determined by the temperature-programmed desorption method (56 \AA^2) (19).

Although almost constant value of σ indicates the availability of the proposed method, the following points should be discussed as further evidence for the validity of the method.

1. *Concentration profile of N_2 .* As shown in Fig. 1, the concentration profile of N_2 produced by the reaction of NH_3 pulse with the catalyst shows the initial sharp N_2 followed by the tailing part. The concentration at the tailing part increases with increasing temperature. According to simulation results of these processes (2, 3), the tailing part is due to the reoxidation of the surface by subsurface oxygen atoms. The increase in the concentration at the tailing part with increasing temperature means that the reoxidation of the surface takes place more readily at higher temperature. Such behavior in the tailing part has also been observed in the V_2O_5 and Cr_2O_3 catalysts.

2. *Constancy of A_0 .* Since the number of active oxygen atoms on Co_3O_4 is a quantity which depends only on the structure of the catalyst, it should not change with experi-

mental variables such as reaction temperature or catalyst weight. The constancy of A_0 satisfies the condition. Furthermore, A_0 did not vary with the carrier gas flow rate, the catalyst weight, or the pulse width. As indicated by error bars in Fig. 2, the way the initial and tailing parts were separated (dotted line in Fig. 1) did not affect the measurement significantly (on the average $\pm 6\%$).

According to the results of adsorptions of NO and CO on Co_3O_4 catalysts, one surface Co ion can adsorb approximately one NO or CO molecule. The area occupied by one adsorbed NO or CO molecule is $12.8\text{--}23.3 \text{ \AA}^2$ (2, 3) which is considerably smaller than that for the active oxygen atom ($51\text{--}61 \text{ \AA}^2$). This indicates that, on the average, 3–4 surface Co ions can provide a site for an active oxygen atom.

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REFERENCES

- Miyamoto, A., Ui, T., and Murakami, Y., *J. Catal.* **80**, 106 (1983).
- Miyamoto, A., Yamazaki, Y., Inomata, M., and Murakami, Y., *J. Phys. Chem.* **85**, 2366 (1981).
- Inomata, M., Miyamoto, A., and Murakami, Y., *J. Phys. Chem.* **85**, 2372 (1981).
- Farrauto, R. J., *AIChE Symp. Ser.* **70**, 9 (1974); and references therein.
- Yao, H. C., and Shelef, M., in "The Catalytic Chemistry of Nitrogen Oxides" (R. L. Klimisch and J. G. Larson, Eds.), p. 45. Plenum, New York, 1975; and references therein.
- Pope, D., Walker, D. S., Whalley, L., and Moss, R. L., *J. Catal.* **31**, 335 (1973).
- Goodsel, A. J., *J. Catal.* **30**, 175 (1973).
- Hertl, W., *J. Catal.* **31**, 231 (1973).
- Il'chenko, N. I., and Golodets, G. I., *J. Catal.* **39**, 57, 73 (1975).
- Yao, H. C., and Bettman, M., *J. Catal.* **41**, 349 (1976).
- Maliński, R., Akimoto, M., and Echigoya, E., *J. Catal.* **44**, 101 (1976).
- Pope, D., Walker, D. S., and Moss, R. L., *J. Catal.* **47**, 33 (1977).
- Moyes, R. B., and Roberts, M. W., *J. Catal.* **49**, 216 (1977).
- Ai, M., *J. Catal.* **54**, 223 (1978).

15. Mehandjiev, D., and Nikolova-Zhecheva, E., *J. Catal.* **65**, 475 (1980).
16. Murakami, Y., Kosaki, Y., Motokawa, M., Ooyabu, Y., and Miyamoto, A., *Nippon Kagaku Kaishi* 612 (1977).
17. Kosaki, Y., Miyamoto, A., and Murakami, Y., *Bull. Chem. Soc. Jpn.* **52**, 617 (1979).
18. Miyamoto, A., Yamazaki, Y., Hattori, T., Inomata, M., and Murakami, Y., *J. Catal.* **74**, 144 (1982).
19. Iwamoto, M., Yoda, Y., Yamazoe, N., and Seiyama, T., *J. Phys. Chem.* **82**, 2564 (1978).

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