

## Determination of the Number of Active Oxygen Species on the Surface of Cr<sub>2</sub>O<sub>3</sub> Catalysts

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The number of active oxygen species (O<sub>s</sub>) on the surface of Cr<sub>2</sub>O<sub>3</sub> catalysts was determined by using the rectangular pulse technique coupled with the reaction of NH<sub>3</sub> with a preoxidized catalyst, i.e.,  $2\text{NH}_3 + 3\text{O}_s \rightarrow \text{N}_2 + 3\text{H}_2\text{O}$  and  $2\text{NH}_3 + 4\text{O}_s \rightarrow \text{N}_2\text{O} + 3\text{H}_2\text{O}$ . The observed number of active oxygen species was found not to change with experimental variables such as temperature, carrier gas flow rate, weight of catalyst, and pulse width. The area occupied by a site, which is defined as the BET surface area divided by the number of active oxygen species, was almost constant for three kinds of Cr<sub>2</sub>O<sub>3</sub> catalysts prepared by different methods, and it was close to literature data.

### INTRODUCTION

Determination of the number of active sites on metal oxide catalysts has been one of the most important subjects of investigations in heterogeneous catalytic chemistry (1–13). In our previous studies (11–13), we have developed the rectangular pulse technique to determine the number of surface V=O species on vanadium oxide catalysts. In this study, we applied this technique to determining the number of active oxygen species on the surface of Cr<sub>2</sub>O<sub>3</sub> catalysts. Cr<sub>2</sub>O<sub>3</sub> catalysts are active for various reactions, such as oxidations of CO and hydrocarbons, dehydrogenations of butane, hydrogenation of ethylene, polymerization of ethylene and propylene, dehydrocyclization of paraffin to aromatics, synthesis of methanol, and reduction of NO with CO or NH<sub>3</sub> (14–29). Interesting methods have also been developed to determine the number of the surface oxygen species or of the coordinately unsaturated Cr ion, which include the hydrazine solution method, the KI method, the transient response method, and the chemisorption of NO, CO, or O<sub>2</sub> (1, 2, 16, 20, 30). We can therefore compare results obtained by using the rectangular

pulse technique with those obtained by these previous methods. It should be emphasized that, in addition to the number of the surface oxygen species, behaviors in the reoxidation of the surface by subsurface oxygen atoms can be investigated by using the rectangular pulse technique (11–13).

### EXPERIMENTAL

#### *Catalysts and Reagents*

Three kinds of Cr<sub>2</sub>O<sub>3</sub>, denoted by Cr<sub>2</sub>O<sub>3</sub>(A), Cr<sub>2</sub>O<sub>3</sub>(B), and Cr<sub>2</sub>O<sub>3</sub>(C), were used as catalysts. Cr<sub>2</sub>O<sub>3</sub>(A) was prepared by calcinating Cr<sub>2</sub>O<sub>3</sub> (Kishida Kagaku) in air at 723K for 3 h. Cr<sub>2</sub>O<sub>3</sub>(B) was prepared by thermal decomposition of ammonium chromate (Hayashi Junyaku) in a stream of O<sub>2</sub> at 773K for 3 h. Cr<sub>2</sub>O<sub>3</sub>(C) was prepared by the hydrolysis of chromium nitrate with an ammoniacal solution, followed by filtration and subsequent calcination in a stream of N<sub>2</sub> at 773K for 3 h. The catalyst was then pressed and sieved in the range 28–48 mesh.

A carrier gas (helium) was purified by the use of titanium metal sponge heated above 1073K, and a Molecular Sieve trap. Commercial NH<sub>3</sub>(99.9% purity), NO(99.5% pu-

urity), CO(99.9% purity), and O<sub>2</sub>(99.8% purity) were used without further purification.

#### Apparatus and Procedure

The rectangular pulse apparatus employed in this study was almost the same as that described previously (11–13, 31). When the selectivities to N<sub>2</sub> and N<sub>2</sub>O in the reaction of the rectangular pulse of NH<sub>3</sub> with the preoxidized catalyst were determined, a silica-gel column (50 cm in length) was used instead of the liquid nitrogen trap (13 in Fig. 1 of Ref. (11) or in Fig. 2 of Ref. (31) after the reactor to analyze N<sub>2</sub> and N<sub>2</sub>O chromatographically. Similarly, when the reaction of CO with the surface oxygen on the catalyst was examined, a Porapak Q column (2 m in length) was used instead of the liquid nitrogen trap. Unless otherwise specified, the rectangular pulse experiments were conducted under the following standard conditions: weight of catalyst, 0.01–0.2 g; flow rate of the carrier gas, 150 cm<sup>3</sup> min<sup>-1</sup>; pulse width, 60 s; reaction temperature, 525–643K. Initial concentrations of individual components in the rectangular pulse were as follows: C<sub>NH<sub>3</sub></sub><sup>o</sup> = 1.10 μmol cm<sup>-3</sup> for the rectangular pulse of NH<sub>3</sub>; C<sub>NO</sub><sup>o</sup> = 0.24 μmol cm<sup>-3</sup> and C<sub>NH<sub>3</sub></sub><sup>o</sup> = 0.96 μmol cm<sup>-3</sup> for the rectangular pulse of NO and NH<sub>3</sub> mixture; C<sub>CO</sub><sup>o</sup> = 1.10 μmol cm<sup>-3</sup> for the rectangular pulse of CO. Before every measurement, the catalyst was routinely preoxidized in a stream of O<sub>2</sub> (150 cm<sup>3</sup> min<sup>-1</sup>) for 20 min at 773K and cooled to a reaction temperature in the stream of O<sub>2</sub>. Then the O<sub>2</sub> supply was stopped and the carrier gas (helium) was introduced. The rectangular pulse of NH<sub>3</sub>, CO, or a mixture of NO and NH<sub>3</sub> was introduced at various times after introduction of the carrier gas.

An X-ray diffraction diagram of the catalyst was measured on a Rigaku GF-2035 X-ray diffractometer using a Cu target. An electron micrograph of the catalyst was obtained on a Hitachi H-700H electron microscope. The BET surface area of the catalyst was determined by using a conventional flow-type apparatus with N<sub>2</sub> as adsorbate.

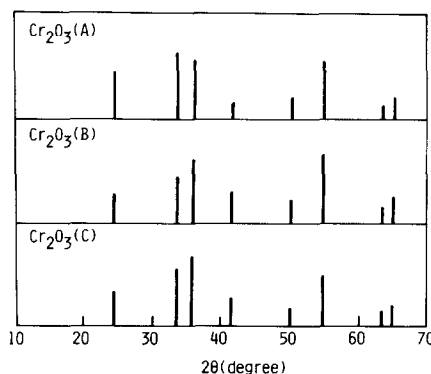


FIG. 1. X-Ray diffraction diagrams of Cr<sub>2</sub>O<sub>3</sub> catalysts.

## RESULTS

**X-Ray diffraction.** Figure 1 shows X-ray diffraction diagrams of Cr<sub>2</sub>O<sub>3</sub>(A), Cr<sub>2</sub>O<sub>3</sub>(B), and Cr<sub>2</sub>O<sub>3</sub>(C). All of the diffraction peaks were assigned to α-Cr<sub>2</sub>O<sub>3</sub>, while no peaks of other compounds such as CrO<sub>2</sub> and CrO<sub>3</sub> were observed in the diffraction diagrams. This indicates that the Cr<sub>2</sub>O<sub>3</sub>(A), Cr<sub>2</sub>O<sub>3</sub>(B), and Cr<sub>2</sub>O<sub>3</sub>(C) catalysts are mainly composed of α-Cr<sub>2</sub>O<sub>3</sub>.

**Concentration profiles of N<sub>2</sub> and the amount of the initial sharp N<sub>2</sub>.** The number of surface V=O species on vanadium oxide catalysts has been determined by the concentration profile of N<sub>2</sub> produced by the reaction of the NO and NH<sub>3</sub> mixture with the preoxidized V<sub>2</sub>O<sub>5</sub> catalyst (11–13). Preliminary experiments, however, indicated that this method cannot be applied to determining the number of active oxygen species on Cr<sub>2</sub>O<sub>3</sub>. This was because the reduced Cr<sub>3</sub>O<sub>3</sub> catalyst was also active for the reaction of NO with NH<sub>3</sub> and because the preoxidized Cr<sub>2</sub>O<sub>3</sub> oxidized NH<sub>3</sub> to form N<sub>2</sub> and N<sub>2</sub>O.

Figure 2 shows examples of the concentration profiles of N<sub>2</sub> produced by the reaction of the rectangular pulse of NH<sub>3</sub> with the Cr<sub>2</sub>O<sub>3</sub> catalyst. As shown, the concentration profile of N<sub>2</sub> consisted of two parts—initial sharp N<sub>2</sub> and tailing N<sub>2</sub>. Only the initial N<sub>2</sub> peak was observed at 536K. At higher temperatures such as 578 and

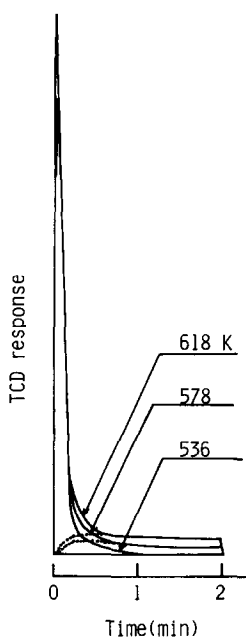


FIG. 2. Examples of concentration profiles of  $N_2$  produced by the reaction of the rectangular pulse of  $NH_3$  with the preoxidized  $Cr_2O_3(A)$  catalyst at various temperatures. Experiments were conducted under the standard conditions described under Experimental.

618K, the tailing of  $N_2$  appeared and the concentration of  $N_2$  at the tailing part became greater with increasing temperature. Similar profiles of  $N_2$  were observed for  $Cr_2O_3(B)$  and  $Cr_2O_3(C)$  catalysts also. Taking into account the results of simulation of the surface reaction and diffusion of oxygen in the metal oxide (11), the initial  $N_2$  peak was separated from the tailing part by the dotted line shown in Fig. 2. The amount of the initial  $N_2$  thus determined ( $A_{N_2}$ ) is shown in Fig. 3 as a function of temperature. As shown,  $A_{N_2}$  was almost constant at temperatures higher than 560K for all of the catalysts. It was also found that the constant value did not change with experimental variables such as the weight of catalyst, the carrier gas flow rate, or the time introducing the  $NH_3$  pulse after having changed the gas from  $O_2$  to He by turning the six-way valve.

**Selectivity to  $N_2$  and  $N_2O$ .** In addition to  $N_2$ ,  $N_2O$  was produced by the reaction of

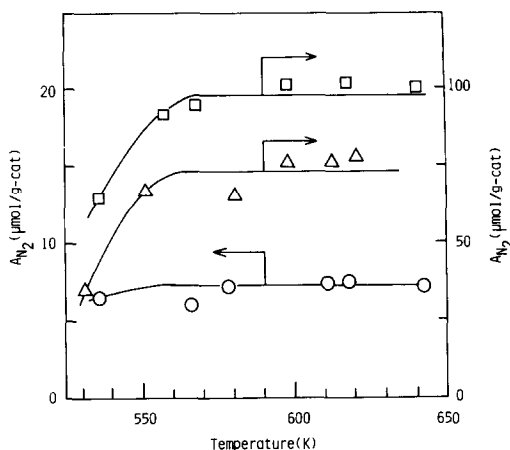


FIG. 3. The amount of the initial sharp  $N_2(A_{N_2})$  at various temperatures. Circles:  $Cr_2O_3(A)$ ; triangles:  $Cr_2O_3(B)$ ; squares:  $Cr_2O_3(C)$ . Experiments were conducted under the standard conditions.

the  $NH_3$  pulse with the preoxidized  $Cr_2O_3$  catalyst. Figure 4 shows the results of the selectivity to  $N_2O(S_{N_2O})$  at various temperatures.  $S_{N_2O}$  for the  $Cr_2O_3(A)$  was almost constant and independent of the reaction temperature.  $S_{N_2O}$  for the  $Cr_2O_3(B)$  and  $Cr_2O_3(C)$  slightly decreased with increasing reaction temperature.

**Amount of  $CO_2$  produced by the reaction of the  $CO$  pulse with the preoxidized  $Cr_2O_3$**

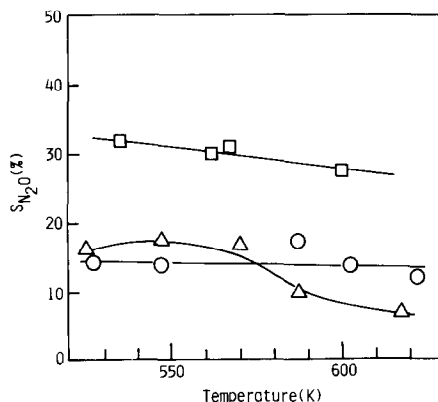


FIG. 4. Selectivity to  $N_2O(S_{N_2O})$  in the reaction of the rectangular pulse of  $NH_3$  with the preoxidized  $Cr_2O_3$  catalyst at various temperatures. Circles:  $Cr_2O_3(A)$ ; triangles:  $Cr_2O_3(B)$ ; squares:  $Cr_2O_3(C)$ . Experiments were conducted under the standard conditions using a silica-gel column instead of the liquid nitrogen trap.

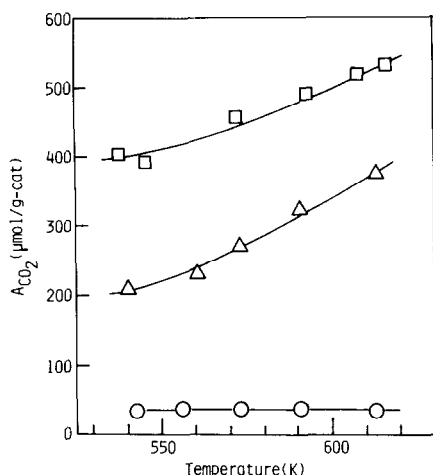


FIG. 5. Amount of CO<sub>2</sub> produced by the reaction of the rectangular pulse of CO with the preoxidized Cr<sub>2</sub>O<sub>3</sub> catalyst ( $A_{CO_2}$ ) at various temperatures. Circles: Cr<sub>2</sub>O<sub>3</sub>(A); triangles: Cr<sub>2</sub>O<sub>3</sub>(B); squares: Cr<sub>2</sub>O<sub>3</sub>(C). Experiments were conducted under the standard conditions using a Porapak Q column instead of the liquid nitrogen trap.

catalyst ( $A_{CO_2}$ ). Figure 5 shows results of  $A_{CO_2}$  at various temperatures.  $A_{CO_2}$  for the Cr<sub>2</sub>O<sub>3</sub>(A) was almost constant and independent of the reaction temperature, whereas  $A_{CO_2}$  for Cr<sub>2</sub>O<sub>3</sub>(B) and Cr<sub>2</sub>O<sub>3</sub>(C) increased monotonically with increasing temperature. Since the shape of the produced CO<sub>2</sub> was deformed considerably by the Porapak Q column, it was difficult to separate the produced CO<sub>2</sub> into the initial and tailing parts.  $A_{CO_2}$  was the total amount of CO<sub>2</sub> produced by the reaction of the CO pulse with the preoxidized Cr<sub>2</sub>O<sub>3</sub> catalyst.

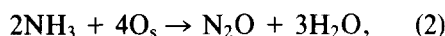
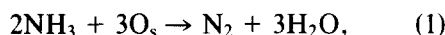
*Electron micrographs of catalyst.* Figure 6a shows an example of transmission electron micrographs of the Cr<sub>2</sub>O<sub>3</sub>(C) catalyst. From the micrographs, particle size distribution for the catalyst was determined as shown in Fig. 6b. The mean particle diameter and BET surface area of Cr<sub>2</sub>O<sub>3</sub>(C) were calculated from the distribution to be 14 nm and 83 m<sup>2</sup> g-cat<sup>-1</sup>, respectively. The calculated BET surface area does not differ significantly from the observed one (Table 1). This indicates that almost all of the catalyst particles were observed by the electron mi-

croscop. As can be seen from the electron diffraction pattern of the Cr<sub>2</sub>O<sub>3</sub>(C) catalyst in Fig. 6c, the catalyst exposed various crystal planes of α-Cr<sub>2</sub>O<sub>3</sub> to its surface.

## DISCUSSION

### *Number of Active Oxygen Species on the Surface*

According to the mechanism of the oxidation of NH<sub>3</sub> on metal oxide catalysts (32), N<sub>2</sub> and N<sub>2</sub>O are produced by the following equations:



where O<sub>s</sub> is an active oxygen species on the catalyst surface. These equations indicate that the number of active oxygen species responsible for the initial peak ( $A_0$ ) can be calculated from the amount of the initial sharp N<sub>2</sub> ( $A_{N_2}$ ) and selectivity to N<sub>2</sub>O ( $S_{N_2O}$ ) by

$$A_0 = A_{N_2} [3 + 4S_{N_2O} / (1 - S_{N_2O})]. \quad (3)$$

Figure 7 shows results of  $A_0$  at various temperatures which are calculated from the results of  $A_{N_2}$  and  $S_{N_2O}$  in Figs. 3 and 4. As shown in Fig. 7,  $A_0$  is almost constant at temperatures above 570K for all catalysts. Since the decrease of  $A_0$  at low temperatures is ascribable to unreacted O<sub>s</sub> species remaining on the catalyst because of the slower reaction rate at lower temperatures (11, 12), the value of  $A_0$  in the constant region indicates the number of active oxygen species on the catalyst surface. The aver-

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 ( $\sigma$ )

Catalyst	$S_{BET}$ (m <sup>2</sup> /g-cat)	$L$ (μmol/g-cat)	$L/S_{BET}$ (μmol/m <sup>2</sup> )	$\sigma$ (Å <sup>2</sup> )
Cr <sub>2</sub> O <sub>3</sub> (A)	3.5	26.3	7.5	22.1
Cr <sub>2</sub> O <sub>3</sub> (B)	23.4	255.0	10.9	15.2
Cr <sub>2</sub> O <sub>3</sub> (C)	64.7	463.4	7.2	23.2

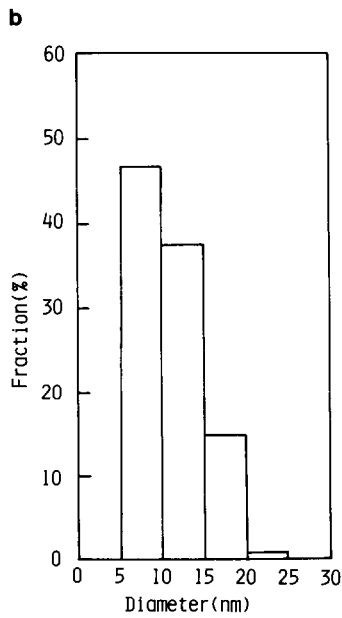


FIG. 6. (a) An example of transmission electron micrographs of the  $\text{Cr}_2\text{O}_3(\text{C})$  catalyst. (b) Particle size distribution determined by the electron micrographs of the  $\text{Cr}_2\text{O}_3(\text{C})$  catalyst. (c) Electron diffraction pattern of the  $\text{Cr}_2\text{O}_3(\text{C})$  catalyst.



FIG. 6—Continued.

age value of  $A_0$  in the constant region is defined as  $L$  and the result is shown in Table 1 for  $\text{Cr}_2\text{O}_3(\text{A})$ ,  $\text{Cr}_2\text{O}_3(\text{B})$ , and  $\text{Cr}_2\text{O}_3(\text{C})$ . This table also shows the area occupied by an active oxygen atom ( $\sigma$ ) which is defined as  $S_{\text{BET}}$  divided by  $L$  to-

gether with the concentration of the active oxygen species ( $L/S_{\text{BET}}$ ). As shown,  $\sigma$  does not differ significantly with the kind of catalysts, indicating the validity of the proposed method.

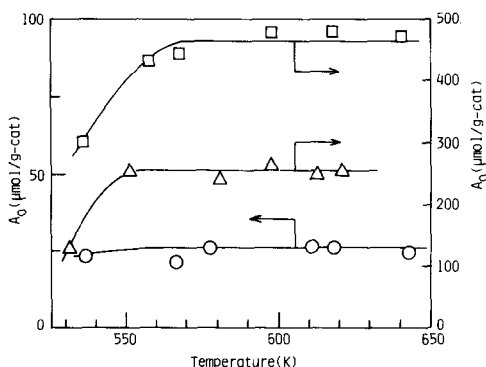


FIG. 7. The number of active oxygen species ( $A_0$ ) measured at various temperatures. Circles:  $\text{Cr}_2\text{O}_3(\text{A})$ ; triangles:  $\text{Cr}_2\text{O}_3(\text{B})$ ; squares:  $\text{Cr}_2\text{O}_3(\text{C})$ .  $A_0$  was calculated from the results of  $A_{\text{N}_2}$  (Fig. 3) and  $S_{\text{N}_2\text{O}}$  (Fig. 4) coupled with Eq. (3).

#### *Applicability of the Proposed Method to the Determination of the Number of Active Oxygen Species on $\text{Cr}_2\text{O}_3$ Catalysts*

Although almost constant value of  $\sigma$  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  $\text{N}_2$ .* As shown in Fig. 2, the concentration profile of  $\text{N}_2$  produced by the reaction of  $\text{NH}_3$  pulse with the catalyst shows the initial sharp  $\text{N}_2$  followed by the tailing part. The concentration at the tailing part increases with increasing temperature. According to the results of simulation of these processes (11), the ini-

tial sharp  $N_2$  is due to the reaction of  $NH_3$  with the surface oxygen species, while the tailing part is due to the reoxidation of the surface by subsurface oxygen species. 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 a behavior in the tailing part has been observed for the reaction of the NO and  $NH_3$  mixture with the  $V_2O_5$  catalyst (11, 12). An additive sometimes affects the diffusivity of oxygen atoms in metal oxide. The presence of the tailing part in the concentration profile of  $N_2$  shown in Fig. 2 indicates that this problem can be investigated by the rectangular pulse technique.

2. *Constancy of  $A_0$ .* Since the number of active oxygen species on  $Cr_2O_3$  is a quantity which depends only on the structure of the catalyst, it should not change with experimental variables such as the reaction temperature or the weight of the catalyst. The constancy of  $A_0$  above 570K (Fig. 7) satisfies the condition. As mentioned above,  $A_0$  did not vary with the carrier gas flow rate, the weight of the catalyst, or the pulse width. The desorption of the active oxygen species from the catalyst surface did not affect the measurements, provided that the catalyst was cooled to the reaction temperature in a stream of  $O_2$  after treatment with  $O_2$  at 773K.

3. *Stoichiometry of the reaction of the surface oxygen with  $NH_3$ .* According to Kobayashi and Kobayashi (20), the surface oxygen species ( $O_s$ ) on  $Cr_2O_3$  reacts with CO to form  $CO_2$ :



This means that the number of active oxygen species can alternately be determined by the reaction of CO with the preoxidized catalyst. The average value of the amount of the produced  $CO_2$  was determined from the results shown in Fig. 5 as follows: 34.6, 281.5, and 466.3  $\mu\text{mol g-cat}^{-1}$  for  $Cr_2O_3$ (A),

$Cr_2O_3$ (B), and  $Cr_2O_3$ (C), respectively. Taking into account the difference in the experimental conditions, these values are close to  $L$  determined by the reaction of the rectangular pulse of  $NH_3$  with the preoxidized catalyst coupled with the stoichiometries described by Eqs. (1) and (2). As shown in Fig. 5,  $A_{CO_2}$  increases with increasing temperature. Since the effect of the reoxidation of the surface by the subsurface oxygen is not separated from  $A_{CO_2}$ , this increase in  $A_{CO_2}$  is considered to be due to the reoxidation of the surface by the subsurface oxygen, which increases with increasing temperature. These data indicate the validity of the stoichiometries of Eqs. (1) and (2).

4. *Area occupied by a site ( $\sigma$ ).* As shown in Table 1,  $\sigma$  is almost constant for all of the catalysts. Strictly speaking, however,  $\sigma$  changes slightly with the catalyst. According to the results of electron microscopy, various crystal planes are exposed to the surface. Since the density of the active oxygen species may change with the crystal plane, the slight difference in  $\sigma$  may be ascribable to the difference in crystal planes exposed to the catalyst surface. The area occupied by a surface oxygen atom ( $\sigma$ ) for  $Cr_2O_3$  catalyst has been determined by Kobayashi and Kobayashi as follows: 13.4 and 11.6  $\text{\AA}^2$  by using the hydrazine solution method and the transient response method, respectively (20). According to Yao and Shelef (2), the area occupied by an adsorbed NO molecule is 15.4  $\text{\AA}^2$ . The results of oxygen chemisorption on unsupported  $Cr_2O_3$  obtained by Bridges *et al.* (16) and Gonzalez Tejuca and Pajares (30) lead to about 18–19 and 20  $\text{\AA}^2$ , respectively, as the value of  $\sigma$ . These values are close to the value of  $\sigma$  determined by using the rectangular pulse technique, indicating the validity of the proposed method.

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