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The Mechanism of the Reaction of Nitrogen Oxide with Ammonia over Cr_2O_3–Al_2O_3 and Cr_2O_3 Catalysts

I. Characterization of the Catalysts

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Catalytic activities of various Cr_2O_3–Al_2O_3 catalysts for the reaction of nitrogen oxide (NO) with ammonia (NH_3) were determined. The activity, when plotted against Cr contents, showed two maxima, at 9.3% Cr and 100% Cr, respectively. X-Ray examination showed that γ-phase and α-phase solid solution occurred at low and high Cr contents, respectively. The BET area, reducibility and the amount of irreversibly adsorbed NO also showed their maxima at 9.3% Cr. Such properties explain, at least partially, the activity pattern in the low Cr-content region.

INTRODUCTION

In a preceding paper (*1*), the mechanism of the reaction of NO + NH_3 over Fe_2O_3–Al_2O_3 catalyst was studied by means of the isotope-labeling technique. Information concerning the nature of the active sites for the reaction was, however, not available. One purpose of the present two articles is to confirm the validity of the proposed mechanism over Cr_2O_3–Al_2O_3 as catalyst. Fe_2O_3–Al_2O_3 and Cr_2O_3–Al_2O_3 show similar catalytic behavior in several reactions. For example, the two catalysts show similar catalytic activity (NO conversion) and selectivity (N_2/N_2O ratio) in the NO + H_2 reaction (*2*). Another objective is to clarify the nature of the active sites, since this was not discussed in the preceding paper.

Various chromium atoms having different valency as well as excess oxygen are known to be present on the surface of Cr_2O_3–Al_2O_3 and Cr_2O_3 catalyst, and these are responsible for the catalytic action in many reactions (*3*, *4*). In view of the many studies devoted to the surface chemistry of Cr_2O_3–Al_2O_3 and Cr_2O_3, such catalysts may be regarded as suitable systems for elucidating the nature of the active sites for the NO + NH_3 reaction. The effects of pretreatments on the activity and selectivity for the reaction were especially studied, because the active sites on the catalyst are extremely sensitive to the pretreatments (*3*, *4*).

The present paper (Part I) describes the characterization of the catalyst employed in this study. The reaction mechanisms as well as the roles of the active sites are discussed in the succeeding paper [Part II (*10*)].

EXPERIMENTAL METHODS

Catalysts

Chromia–alumina catalysts having different compositions were prepared by a coprecipitation method. An aqueous mixture of chromium nitrate and aluminum nitrate was poured into an excess amount of aque-

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ous ammonia under mild stirring. The precipitate was washed several times using a decantation method and dried at 100°C for 24 hr. It was then calcined at 600°C for 3 hr under a continuous air flow. Upon heating to 600°C, the catalysts of high Cr content underwent a glow phenomenon at about 300°C, as demonstrated by a sudden temperature rise in the catalyst bed. The atomic fractions of Cr, $[Cr/(Cr + Al)] \times 100$, were 2, 7.5, 9.3, 15, 25, 50, 80, and 95%. Al_2O_3 (0% Cr) and Cr_2O_3 (100% Cr) were also prepared by the same method. The reagents, $Cr(NO_3)_3 \cdot 9\ H_2O$ and $Al(NO_3)_3 \cdot 9\ H_2O$, were of reagent grade.

Reaction

The reaction was carried out in a conventional gas circulation system, the total volume of which was 274 cm^3. A weighed amount of catalyst (1.0 g) was placed in the reactor and was subjected to the following pretreatments: pumping at 200°C for 1 hr, prereduction with 300 Torr of H_2 at 300°C for 1 hr, and pumping at 200°C for 1 hr under 10^{-4} Torr. The reactants, NO and NH_3, were independently introduced from a gas holder into the gas circulation system, but bypassing the reactor. They were mixed by a circulation pump until a homogeneous gas composition was established throughout the system. The changes in total pressure, gaseous composition and isotope composition were followed by a manometer, by gas chromatography and by a mass spectrometer, respectively. Water produced during the reaction was trapped by KOH-packed columns located before and after the reactor. Reaction runs were repeated several times with no intervening treatment other than evacuation to 10^{-4} Torr at reaction temperature for 1 hr.

Gases

NO gas (supplied from Matheson Chem. Co.) was treated with KOH particles in order to eliminate potential impurities (NO_2, CO_2, etc.). It was further purified by vacuum distillation. NH_3 gas (supplied from Takachiho Chem. Co.) was purified by the same method. No impurities other than a trace of N_2 was found in the gas chromatographic analysis after such treatments. Correction was made for the presence of N_2, but it was within the experimental error.

NO Adsorption

The amount of NO adsorbed at 0°C was measured by the following procedure. One gram of catalyst placed in a U-tube, was heated at 500°C for 30 min under a continuous He flow. NO was passed through the catalyst bed at 0°C for 30 min. Weakly held and gaseous NO was washed out of the catalyst bed with the He flow. Then the reactor was heated to 500°C. Desorbed products, N_2, N_2O, and NO, were analyzed by gas chromatography, from which the amount of NO originally adsorbed on the catalyst at 0°C was calculated.

RESULTS

Preliminary Studies

The catalytic activity for the NO + NH_3 reaction was found to be very sensitive to the pretreatments. Either prereduction or preoxidation brought marked improvements in the catalytic activity. A typical example for Cr_2O_3 catalyst is shown in Fig. 1. The other catalysts showed a more or less similar behavior. Prereduction had a more marked effect on the catalysts of lower Cr contents. Both N_2 and N_2O formation increased after such treatments. The improvements were significant in the very initial stage; however, the activities of either (prereduced or preoxidized) catalyst settled to its unique stationary value after 5 min in the case of the preoxidized catalysts or after two to four runs in the case of the

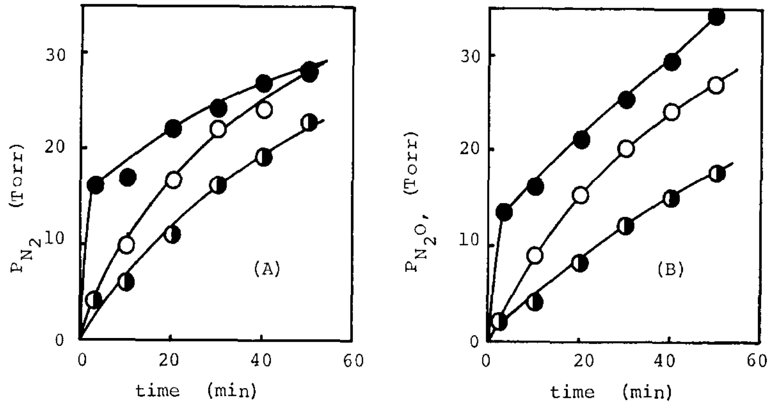

FIG. 1. The formation of N_2 (A) and N_2O (B) with time over oxidized (●), reduced (○) or stationary catalyst (◑). (●) Oxidized catalyst: treated with 300 Torr of O_2 at 300°C for 1 hr; (○) reduced catalyst: treated with 300 Torr of H_2 at 300°C for 1 hr; (◑) stationary catalyst: after several runs for the reaction; reaction temperature, 200°C; initial pressures: $P_{NO} = P_{NH_3} = 150$ Torr; catalyst: Cr_2O_3, 1.0 g.

prereduced catalysts. N_2 and N_2O were the only products under any reaction conditions.

When NO alone contacted the reduced catalyst, N_2 and N_2O were produced, while the reaction took place to a far lesser extent over a stationary catalyst. When NH_3 alone was contacted, little reaction took place either on prereduced or stationary catalysts. In this first paper, our primary concern is limited to the stationary activity. The effects of pretreatment gave information about the nature of active sites and are discussed in Part II (*10*).

Correlations of Catalytic Activity with Cr Content

The catalytic activity of a stationary surface was tested at 300°C for a series of catalysts having various Cr contents. Figure 2 illustrates the activity versus Cr content. Two maxima appeared at 9.3 and 100%. Quite interestingly, similar plots made for the NO + CO reaction over the same series of catalysts showed the same pattern (*5*) as that given in Fig. 2. This indicates that some similarities exist in the mechanisms of both reactions. The NO + NH_3 reaction was carried out at 300°C in this series of experiments in order to show the relative magnitude of activity for all the catalysts under the same conditions. At 200°C, which was the standard experimental condition in the subsequent paper, the rate of reaction over the less active catalysts was too low to measure. It should be noted that the rate of mass

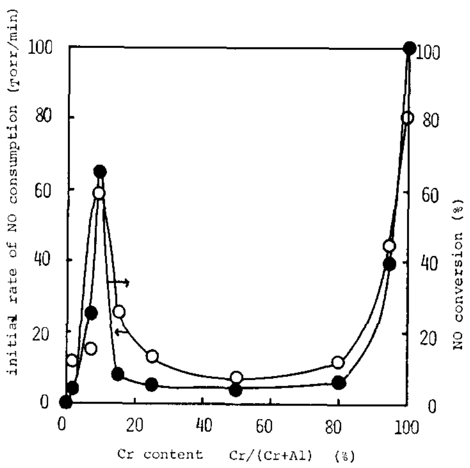

FIG. 2. Catalytic activity vs Cr content for NO + NH_3 and NO + CO (*5*) reaction. (○) NO + NH_3 reaction (this work): weight of the catalyst, 1.0 g; reaction temperature, 200°C; initial pressure of NO and NH_3, 150 Torr; (●) NO + CO reaction [Ebitani *et al.* (*5*)]: weight of the catalyst, 0.05 g; reaction temperature, 400°C; feed gas: 100 cm³/min (NO, 5%; CO, 10%; He balance).

transfer from the bulk gas stream to the surface of the catalyst affected the global rate at 300°C over highly active catalysts. Accordingly, the absolute values for 9.3 and 100% catalyst may be higher than the ones given in Fig. 2. This, however, does not influence the qualitative discussion given here.

Correlations of Physicochemical Properties with Cr Contents

Several physicochemical properties were measured as a function of Cr content in order to explain the interesting activity pattern given in Fig. 2.

Figure 3 illustrates the hydrogen consumption per gram of catalyst or per Cr atom versus Cr content. Such consumption occurred during pretreatments with 300 Torr of H_2 (1 Torr = 133 N m^{-2}) at 300°C for 1 hr. A maximum in the H_2 consumption per gram of catalyst vs Cr content appeared between 7.5 and 15%, which nearly corresponds to the first maximum in the activity vs Cr content plots.

Since one hydrogen atom reduces the valency of Cr by one unit, three hydrogen atoms are necessary to reduce Cr^{3+} to Cr^0. The value of the ratio, H atoms consumed/Cr atoms, was close to a 3 for low Cr contents, which indicated that chromium ions were almost fully reduced. It should be noted, however, that not only Cr^{3+} but also higher valency Cr ions might be present initially in the catalyst, such that the initial average valency is higher than 3. As a matter of fact, the presence of Cr^{5+} was confirmed by esr measurements for low Cr content catalysts (*5*).

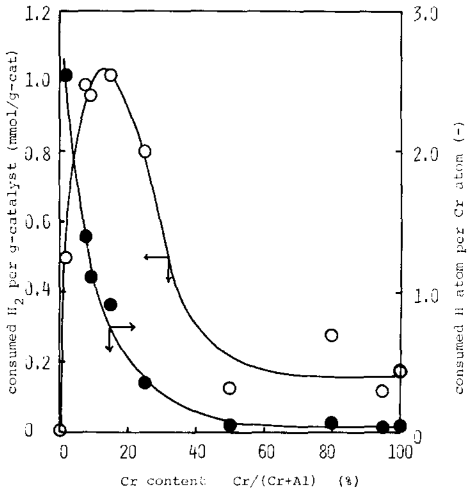

FIG. 3. Hydrogen consumption per g-catalyst or per Cr atom vs Cr content. (○) consumed H_2 per g-catalyst; (●) consumed H atom per Cr atom; reduction temperature, 300°C; time of reduction, 1 hr; initial H_2 pressure, 300 Torr.

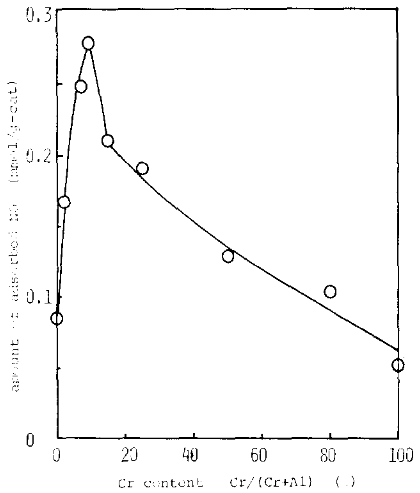

FIG. 4. The amount of irreversibly adsorbed NO at 0°C vs Cr content. Pretreatment of the catalyst: 500°C, 30 min with He flow.

Figure 4 shows the plots of the amount of NO irreversibly adsorbed on the catalysts against their Cr contents. Again, the maximum appeared at 9.3% Cr content.

Figure 5 shows the plot of BET area against Cr contents. A maximum appeared at 7.5–9.3% Cr content, which nearly corresponded to the first maximum in the activity vs Cr content plots. Poole and McIver (*3*) stated the surface area of Cr_2O_3–Al_2O_3 catalyst prepared with a similar method to ours, and our data showed rather surprisingly good agreement with theirs. They also made low temperature adsorption measurements of oxygen, from which the area of chromia exposed on the Al_2O_3 support was calculated. Good pro-

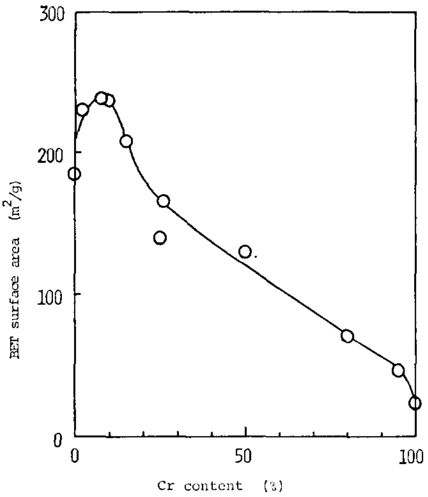

FIG. 5. BET surface area as a function of Cr content.

portionality between BET area and Cr_2O_3 area was observed. Such proportionality may also be expected in our case.

X-Ray diffraction patterns for the series of catalysts are given in Fig. 6. Drastic changes were observed between the regions of low and high Cr content. In the low Cr content region (0–15%), very similar patterns to that of γ-Al_2O_3 were found; however, some shift in peak positions indicating lattice expansion due to the formation of Cr_2O_3–Al_2O_3 solid solution was observed. On the other hand, only the α-phase (probably α-Cr_2O_3–Al_2O_3 solid solution) was found in the high Cr-content region (above 50%). In the intermediate region, both phases were observed.

Electron spin resonance studies were presented elsewhere (*5*); however, it is useful to state the general features. The γ-signal which was attributed to Cr^{+5} (*3*) was predominant in the low Cr-content region: the intensity of the signal was highest for 2% Cr catalyst and decreased with increase of Cr content. No such signal was observed after the catalyst was reduced with hydrogen. The β_N and β_W signals attributed to clustered Cr^{3+} were not separated from each other. They were observed for Cr_2O_3–Al_2O_3 catalyst of higher Cr contents than 7.5%. The δ signal, which was attributed to isolated Cr^{3+}, was found for 2 and 7.5% Cr catalyst.

DISCUSSION

Eischens and Selwood (*6*) suggested that two-dimensional dispersion of Cr_2O_3 was established over an impregnated catalyst, while three-dimensional dispersion (formation of solid solution) occurred in a coprecipitated catalyst. Rubinshtein and Slinkin (*3*, *7*) measured the magnetic susceptibility for a series of Cr_2O_3–Al_2O_3 catalysts having different compositions. They found drastic changes in the Weiss constant at 14, 33, and 60 wt% of Cr_2O_3. In the lowest Cr_2O_3 region, all the chromium ions are dispersed in a matrix of Al_2O_3 lattice. In the intermediate region, there is a mixture of chromia–alumina solution phases, some rich and some poor in chromia. In the highest region, free chromia appears. Such changes may be responsible for the changes

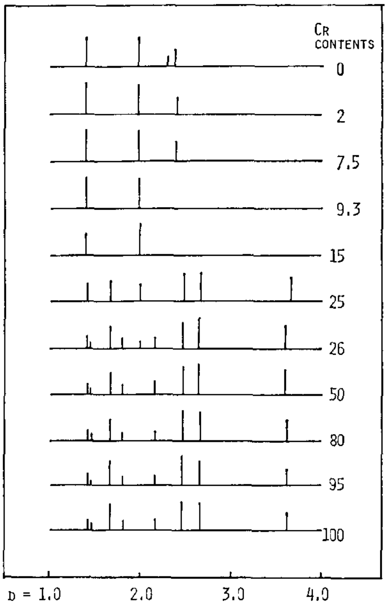

FIG. 6. X-Ray diffraction patterns for a series of Cr_2O_3–Al_2O_3 catalysts. The peak heights are relative to that of maximum strength for each catalyst.

in catalytic activity, redox properties and/or adsorption capacity. Egerton *et al.* (*8*) also classified α-Cr_2O_3–Al_2O_3 catalyst into three groups depending upon Cr contents. Their results on the activity for the decomposition of N_2O vs Cr content also showed two maxima in catalytic activity, at 5 and 100% Cr. Marcilly and Delmon (*9*) reported that γ-phase oxide was still observed after the calcination of low Cr-content catalysts at 900°C, while only α-phase was observed for high Cr-content catalyst. They also showed that, for the dehydrogenation of paraffin, the γ-phase solid solution was more active than the α-solid solution in the low Cr-content region.

In view of these results in the literature and also of our X-ray results given in Fig. 6, it is beneficial for the discussion to classify the catalysts according to their Cr contents, viz., the low Cr-content region (2–25%) and the high Cr-content region (50–100%).

Low Cr-Content Region

Catalysts consist of γ-phase crystallites of small size. An approximate evaluation of crystallite size from X-ray line broadening gave 40 Å which was almost independent of Cr content from 0 to 15%. After the calcination in air, they are in a highly oxidized state (esr results). However, they are readily reduced to a lower oxidation state (probably lower than Cr^{3+}) when treated with H_2 at 300°C.

Reducibility per unit weight of catalyst, surface area and the amount of irreversibly adsorbed NO all showed similar patterns when plotted against Cr content. Such patterns are not so sharp as that of catalytic activity vs Cr content, although the maximum of the former pattern occurred at the same Cr content as that of the latter. This indicates that not only the number of active sites but also the activity per unit number of active sites is largest for 9.3% Cr catalyst. As described in Part II (*10*), surface oxygen is considered as the active sites for the reaction. Since the γ-phase is a metastable phase, the bond strength, Cr–O, of γ-phase oxide is smaller than that of α-phase oxide: oxygen is activated on the surface of the former oxide. In other aspects, the BET area is an index of crystallite size; the larger the area, the smaller the crystallite size and thus the larger the surface energy. Such views qualitatively explain the activity pattern in terms of the reducibility and BET area.

High Cr-Content Region

Only the α-phase, probably α-Cr_2O_3–Al_2O_3 solid solution, was found. The size of the crystallites evaluated from X-ray line broadening was larger (300 Å for 50 and 85% Cr catalyst and 250 Å for Cr_2O_3 catalyst). They are difficult to reduce. No simple explanation for the activity pattern given in Fig. 2 can be offered at the present time: BET area, reducibility or NO adsorption data which, at least partially, interpret the activity pattern for the low Cr-content region were not helpful. Nevertheless, one speculative interpretation might be worth presenting. Auger spectroscopy suggests that there is a great difference between the bulk and surface concentrations. Since α-Cr_2O_3 is more readily formed than α-Al_2O_3, the former is first formed upon calcination of the catalyst, and the latter is deposited on it. This means that the surface concentration of Cr_2O_3 is very much lower than that expected from the bulk concentration.

The key feature of the present results for our subsequent work has been to give a criterion for the choice of catalyst for the studies on reaction mechanism. In the following paper, we try to clarify the reaction mechanism over two typical catalysts, namely, 9.3% Cr_2O_3–Al_2O_3 and Cr_2O_3.

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