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# The Decomposition of Nitrous Oxide on Chromia–Alumina Catalysts

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The successive slug, microcatalytic technique has been used to study the decomposition of $N_2O$ on chromia-alumina catalysts in the region 300° to 600°C. The results are interpreted to indicate that the reaction sites are oxygen anion vacancies in the chromia clusters on the catalyst surface.

## INTRODUCTION

The industrial importance of impregnation-type chromia-alumina catalysts has prompted a number of studies on the physical and chemical properties of the surfaces of these catalysts. Eischens and Selwood (*1*) used magnetic susceptibility measurements. Givaudon and co-workers (*2*) and Voltz and Weller (*3*) have employed analytical techniques combined with gas adsorption and electrical conductivity methods. The electron paramagnetic resonance technique has been applied by O'Reilly and MacIver (*4*) and an optical method by Pool and MacIver (*5*).

Information pertaining to the structure of a catalyst surface can also be obtained from a study of suitably chosen reactions. Nitrous oxide decomposition in conventional flow systems has been used to study the surfaces of many oxides, not, however, including chromia-alumina. The present work employs the successive slug technique and the microcatalytic gas chromatographic apparatus developed by Emmett and co-workers (*6–8*).

## EXPERIMENTAL

The apparatus consisted of a Perkin-Elmer Vapor Fractometer, Model 154-C, connected to a microreactor. The latter was made of Pyrex glass tubing 1 cm in internal diameter, 5 cm in length, and had 1-mm capillaries for connecting tubes. The catalyst, about 1.4 g, was held in the reactor between glass wool plugs. The reactor was mounted vertically to avoid channeling and was provided with manometers at the entrance and exit for measurement of the pressure gradient. A multiple coil furnace regulated with variable transformers and an Amplitrol controller (Barber-Coleman Instrument Co., Rockford, Illinois) provided a region of about 10-cm length in which the temperature was constant to $\pm 1$°C. A chromel-alumel thermocouple, calibrated against a standard Pt-Pt + 10% Rh thermocouple (Bureau of Standards, Washington) was used for temperature measurement.

For catalyst preparation, $Al(OH)_3$ was precipitated from $KAlO_2$ solution using $CO_2$, dried at 130°C, and calcined at 380°C to give gamma alumina. This was then impregnated with varying amounts of chromia following the method of Eischens and Selwood (*1*). All catalysts were initially reduced in $H_2$ for 16 hr at 500°C and then given various other pretreatments as described later. Surface area measurements by the BET method gave values between 50 and 58 $m^2/g$. The $N_2O$ employed was better than 99.5% pure as shown by gas chromatographic analysis.

In a typical run, 1-ml slugs of $N_2O$ were introduced into the carrier gas stream (helium, argon, or hydrogen flowing at 1 cc/sec) by means of the chromatograph gas valve. The reactor exit gases were analyzed gas chromatographically and the activity of the catalyst expressed as per cent $N_2O$ decomposed. No retention of $N_2$ on any of the catalysts was detected. The exit gas peaks were relatively sharp and narrow, indicating adequate equilibration in the reaction (*9*). The carrier gas flow rate at room temperature and pressure was kept constant in the activation energy series of runs.

## RESULTS

### *Reduced Catalysts*

In one series of experiments, a freshly reduced catalyst, containing 19.1% Cr and maintained at 590°C, was switched to helium flushing for about 10 min and then subjected to successive 1-ml slugs of $N_2O$ at 2-min intervals. Decomposition was 100% and no oxygen was present in the exit gas for the first three slugs. The per cent decomposition then began to decrease and the oxygen in the exit gases to increase until steady state values were reached. Thus the per cent decomposition finally remained constant at 38.4% and the amount of oxygen retained by the catalyst at about 90% of theoretical, from slug 14 to 19. It was then found that the catalyst could be regenerated to varying degrees by introducing periods of pure helium flushing longer than the 2 min occurring between slugs in the above sequence. After each such longer helium flushing, the 2-min sequence was run again until a steady state activity was reached. The per cent decomposition of the first slug in such a sequence on a catalyst regenerated by helium flushing was called the "initial activity." The data are given in Table 1 and plotted in Fig. 1.

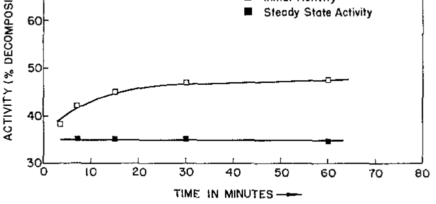

FIG. 1. Variation of activity of reduced catalyst with helium flushing time.

TABLE 1

ACTIVITY OF CHROMIA-ALUMINA CATALYST (19.1% CR) AS A FUNCTION OF DURATION OF HELIUM FLUSHING

| Helium flushing time (min) | Activity |  |
|---|---|---|
|  | Initial | Steady state (% decomposition) |
|  | *Reduced Catalyst* |  |
| 3.5 | 38.2 | — |
| 7 | 42.1 | 35.3 |
| 15 | 45.0 | 34.4 |
| 30 | 47.0 | 35.5 |
| 60 | 47.5 | 36.0 |
|  |  | Average 35.3 ± 0.4 |
|  | *Oxidized Catalyst* |  |
| 5 | 39.0 | 35.3 |
| 10 | 42.9 | 35.9 |
| 20 | 45.6 | 35.7 |
| 30 | 47.6 | 36.9 |
| 120 | 52.9 | 33.0 |
|  |  | Average 35.4 ± 0.9 |

Initial oxygen retention varied from 100% for 60-min helium flushing to about 91% for 3.5-min flushing. A similar behavior was obtained for a catalyst containing 3.8% Cr.

When hydrogen was used as a carrier gas with the 19.1% Cr catalyst, the activity remained constant at 100% decomposition for as many as 13 slugs at 590°C. At lower temperatures, for example at 405°C, considerable decrease of activity was recorded even in the first few slugs. In these runs, of course, no oxygen was detected in the exit gases. No attempt was made to determine water.

### *Oxidized Catalysts*

The standard reduced catalyst containing 19.1% Cr was exposed to an oxygen stream at 590°C for about 5 hr and then switched to the helium carrier gas. This catalyst was now found to behave in exactly the same manner toward decomposition of successive 1-ml slugs of $N_2O$ introduced at 2-min intervals, as the reduced catalyst which had been poisoned by the oxygen of decomposition. The data are also given in Table 1 and would give curves like those in Fig. 1. The average steady state activity of the oxidized catalyst was 35.4% ± 0.9%, in agreement with the value of 35.3% ± 0.4% obtained for the reduced catalyst. Oxygen retention data were also essentially the same as for the reduced catalyst. A few supplementary experiments also showed that when the time interval between successive 1-ml slugs was increased from 2 min to 5 min, the oxygen retention remained constant at 100% throughout the series, and there was no decrease in activity with successive slugs of a series.

The retention of oxygen by the catalyst at 590°C was proven directly by using successive 1-ml slugs introduced at 2-min intervals. As expected from the results reported thus far, it was found that the per cent of the initial slug retained increased with the duration of prior flushing with helium but that retention of subsequent members of a series converged to a common steady state value.

The gradual desorption of oxygen, into a helium atmosphere at 590°C, from a catalyst which had previously been treated with oxygen or over which a slug of $N_2O$ had been decomposed, was proven directly by isolating such a catalyst with stopcocks for say 10 min and then flushing the reactor contents into the chromatograph with the usual helium carrier gas stream. Definite peaks for oxygen were obtained. The amount of oxygen thus desorbed was found to decrease with increasing duration of prior flushing with helium.

Some of the $N_2O$ decomposition runs on an oxidized catalyst were repeated with argon instead of helium as the carrier gas. No difference in results was detected.

### *Pure Alumina*

Experiments similar to the above, performed on the pure alumina substrate, showed that the activity was much less, that there was no retention of oxygen from pure oxygen slugs nor progressive poisoning of the surface due to decomposition of successive $N_2O$ slugs, and that the catalytic activity was not altered by helium flushing.

### *Activation Energy*

Activation energies were determined on freshly reduced and oxidized catalysts, with chromium contents varying from 0% to 19.1%, by measuring the per cent decomposition of a 1-ml slug at various temperatures ranging between 300° and 600°C. A number of replicates were done for each set of conditions. Reproducibility was within 3%.

Since oxygen retention by the catalyst in the slug technique has been shown to be 100% for freshly reduced catalysts and 90% or more for oxidized catalysts (and only ½ mole of $O_2$ is produced per mole $N_2$), the rate equation for a first order reaction at constant volume in a conventional flow system may be used with sufficient accuracy in the present case (*9*). We may therefore write, including the Arrhenius equation,

$$k = 2.3(F/V)\log(N_0/N) = Ae^{-E/RT},$$

where $F$ is the flow rate corrected to the reactor temperature and average pressure, $V$ is the reactor free volume, and $N_0$ and $N$ are the moles of reactant entering and

TABLE 2

ACTIVATION ENERGY ON OXIDIZED AND REDUCED CATALYSTS

| Catalyst number | Chromium (wt %) | Activation energy (kcal/mole) |
|---|---|---|
| | *Reduced catalysts* | |
| — | 0.00 | 19.6 |
| 110 | 1.16 | 18.7 |
| 115 | 3.81 | 20.0 |
| 125 | 6.60 | 13.6 |
| 130 | 10.10 | 18.7 |
| 140 | 16.50 | 22.6 |
| 145 | 19.10 | 24.8 |
| | *Oxidized catalysts* | |
| — | 0.00 | 26.6 |
| 115 | 3.81 | 23.0 |
| 125 | 6.60 | 25.9 |
| 130 | 10.10 | 22.9 |
| 140 | 16.50 | 24.3 |
| 145 | 19.10 | 25.4 |

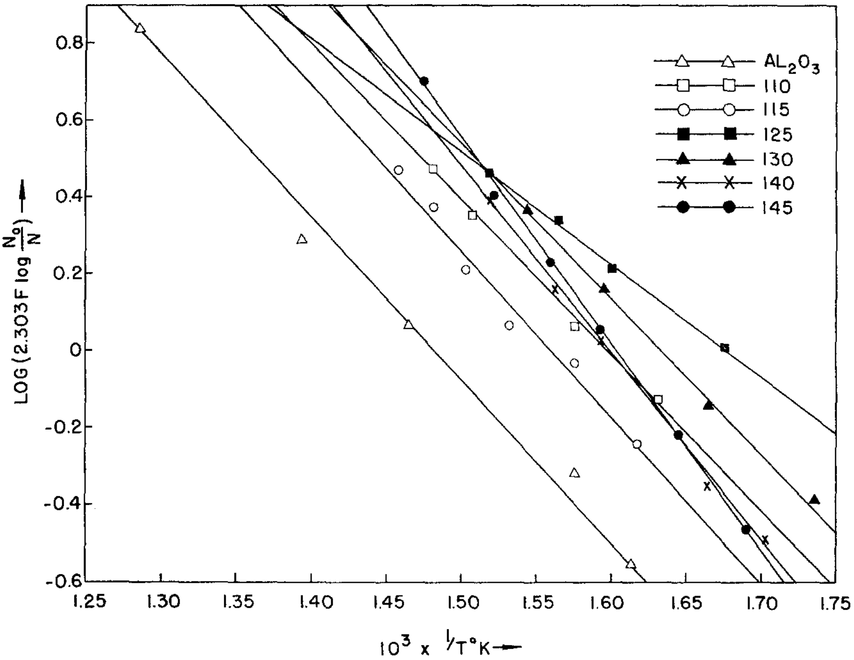

FIG. 2. Activation energy plot for reduced catalysts.

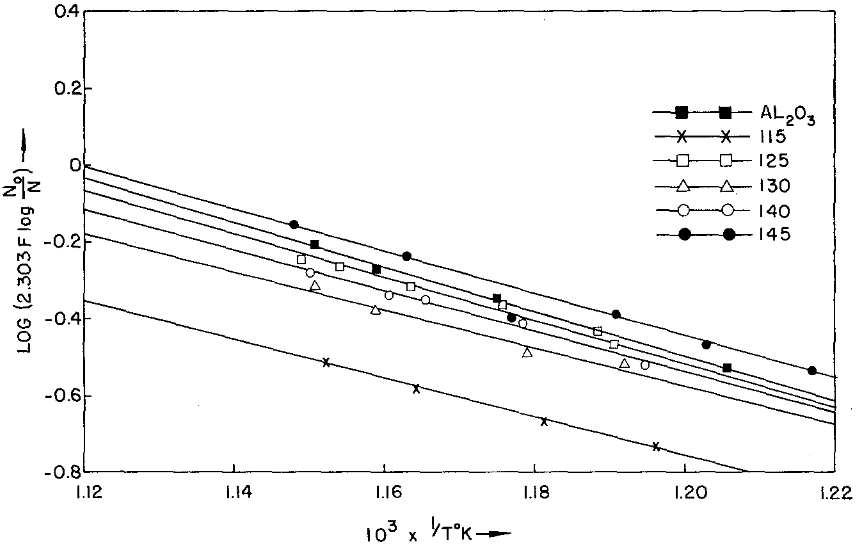

FIG. 3. Activation energy plot for oxidized catalysts.

leaving the reactor. The other symbols have their usual meaning. It therefore follows that a plot of log ($2.3F$ log $N_0/N$) against $1/T$ should be a straight line with negative slope $E/2.3R$. The excellent lines in Figs. 2 and 3 confirm the validity of the assumptions. Activation energies are given in Table 2.

## DISCUSSION

The mechanism of the $N_2O$ decomposition could, in general, be either reaction with hydrogen on the catalyst surface to give water and nitrogen, or donation of oxygen atoms from the $N_2O$ to anion vacancies in the surface with subsequent desorption of the oxygen as $O_2$ or $H_2O$. The results presented above show in a quite direct manner that the anion-vacancy mechanism is involved on both initially reduced and intially oxidized catalysts. Regeneration of catalytic activity by rare gas flushing can only be explained by creation of vacancies and this occurs for both types of catalysts. If chemisorbed hydrogen were significant in the mechanism, desorption of product water during helium flushing would decrease the activity.

The experimental observations are all concordant with the picture that the active sites on the chromia-alumina catalysts are oxygen anion vacancies created by hydrogen reduction or by slow desorption of oxygen at 590°C and are related to the chromia on the surface. When $N_2O$ slugs are decomposed on such a surface, the sites are poisoned by the oxygen which, however, slowly desorbs as helium flushing continues. Desorption of oxygen is a much slower process than decomposition of $N_2O$. The initial oxygen retention is partial or complete, depending on the activity of the surface. The oxygen from 100% decomposition of a 1-ml slug comprises only about 0.02 of the monolayer capacity of the catalyst. The vacancies can also adsorb atoms from molecular oxygen. No nitrogen is retained. When a consecutive series of slugs is passed over the catalyst, the activity decreases from its initial value and levels out at some steady state value which represents a balance between the degree of poisoning caused by the decomposition of one slug and the regeneration due to oxygen desorption during helium flushing between slugs. The final catalyst surface is the same whether the vacancies were initially created by reduction, or by desorption from an oxidized catalyst. The experiments with pure alumina show that the anion vacancies are related to the surface chromia and not to the alumina substrate. This will be developed further later. These conclusions agree in general with those drawn from results of entirely different types of experiments by prior workers, for example by Voltz and Weller (*3*).

Turning to the activation energy data in Table 2, it is seen that the values for the oxidized catalysts are independent of Cr content within experimental error. For reduced catalysts there is a systematic trend. As the Cr content increases the activation energy decreases to a minimum at about 6% Cr and then increases again, approaching the value for oxidized catalysts.

It has been shown by Selwood (*1*) that the $Cr_2O_3$ clusters present on $Al_2O_3$ are at least three atom layers thick. Assuming this to be the case on our catalysts, it can be calculated that a catalyst containing 6.6% Cr has 60% of its surface covered with the $Cr_2O_3$ clusters. It may be suggested that in this concentration range many of these clusters are sufficiently close together so that the gaps between them can be bridged by chemisorbed oxygen (from $N_2O$) and may in fact constitute the oxygen vacancies or sites for the reaction. The structure of these vacancies is such that they form energetically favorable sites, and hence the activation energy is low. At higher Cr concentrations on the surface, the clusters overlap more, gaps between clusters are minimized, and an increase in activation energy is observed. On the other hand, at lower Cr concentrations the clusters spread out and the gaps between clusters cannot be easily bridged. The more or less uniform value on all oxidized surfaces, on the basis of this model, is then due to the fact that such surfaces are saturated with oxygen which occupies most of the anionic vacancies. The activation energy is uniformly high and independent of Cr concentration.

Our model for the surface structure of chromia-alumina catalysts is supported by the EPR studies made recently by O'Reilly and MacIver (*4*) on similar catalysts. These studies indicated that as the total Cr content is gradually increased from 2% to 10%, the ratio of the Cr present in the delta phase ($Cr^{3+}$ isolated ions) to that in the beta phase (coupled $Cr^{3+}$ ions) shows a steep increase between 7% and 10%, indicating that more Cr is present as clusters than as isolated $Cr^{3+}$ ions. This is similar to our own results which indicate that in the region of 6% Cr most of the Cr is present as clusters close to each other. An exact agreement in the results is not expected because of differences in surface areas of the samples used. Further, O'Reilly and MacIver also observed that on oxidation of the catalyst a new gamma phase came into existence at the expense of the beta phase while the delta phase was unaffected. This fits in very well with our own model where it is envisaged that oxygen either from molecular oxygen or from $N_2O$ decomposition goes only into the vacancies in the clustered beta phase.

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