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The Catalytic Chemistry of Nitric Oxide

I. The Effect of Water on the Reduction of Nitric Oxide Over Supported Chromium and Iron Oxides

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The reduction of NO with CO over alumina supported iron oxide and chromium oxide is a relatively fast process. The reaction is strongly inhibited over both catalysts by small amounts (~0.7 mole %) of water. The reduction of NO by H_2 appears to be significantly slower than by CO, although this was shown to be due to inhibition by H_2O, which is a primary product of the NO–H_2 reaction. The product distribution from competitive experiments with mixtures of CO and H_2, shows that H_2 reacts preferentially to CO, over iron oxide.

The water-gas shift reaction occurs more readily over iron oxide than chromium oxide and the H_2 formed reduces NO to NH_3. The product distribution from the NO–H_2 reaction differs with the two catalysts. Over iron oxide the major product is NH_3, while with chromium oxide it is N_2. Since chromium oxide neither decomposes NH_3 nor promotes the NO–NH_3 reaction with any greater ease than Fe_2O_3, it is concluded that the reduction of NO with H_2 occurs by different mechanisms over the two catalysts.

INTRODUCTION

The presence of nitric oxide (NO) in automotive exhaust gases, and its role in the formation of photochemical smog, has stimulated much research into the catalytic reduction and decomposition of this compound. It has been shown (*1–3*) that although NO decomposition is a slow kinetically controlled process, its reduction with either carbon monoxide (CO) or hydrogen (H_2) is a very fast reaction (*4–7*). These latter reactions may be of considerable practical importance for the purification of auto exhaust gases; since CO is always present in varying concentrations and H_2 can be formed *in situ* by the water-gas shift reaction. The proposed mechanism for the reduction of NO with CO (*8*) is a typical redox process in which the catalyst surface is reduced by CO and then subsequently reoxidized by NO. The net reaction products are thus carbon dioxide (CO_2) and nitrogen (N_2), both of which can be safely released into the atmosphere. The reaction is strongly inhibited by oxygen (*8, 9*) due to competition between NO and O_2 for reoxidation of the reduced surface sites.

A catalytic activity sequence for the reduction of NO with CO over various supported metal oxides has been derived (*8*), and is in agreement with our results obtained in a dry reaction system:

$$Fe > Cu > Cr > Ni > Co > Mn > V.$$

There is, however, a lack of data comparing CO and H_2 as reducing agents, and on the effect of water vapor on catalytic activity. The latter is of special importance because of the presence of about 15 vol % water vapor in exhaust gases. Since high catalytic activity is of the utmost importance for any practical exhaust gas purification system, our studies were concentrated on Fe, Cu, and Cr oxides. The behavior of supported Cu oxide is quite distinct from the other two; therefore, these results will be reported separately. We wish now to report our results for the effect of water vapor on the catalytic reduction of NO by CO and H_2 over supported iron and chromium oxides.

Experimental Methods

Materials

All gases used in the experiments were used as supplied by Air Products & Chemicals, Inc. (Ar, 99.99%; H_2, 99.99%; No, 99.5%; CO, 99.6%).

Catalyst Preparation

γ-Alumina spheres (1/16 in. diam) supplied by Universal Oil Products Co. with a pore volume of 0.82 cc/g, average pore diameter of 85 Å, and 196 m^2/g surface area were used as the support. These were impregnated with aqueous solutions of chemically pure Fe or Cr nitrates and the concentration of the respective solutions was adjusted to give 10 wt % of metal on the finished catalyst. The impregnated spheres were dried at 120°C and calcined at 500°C in air. The total surface area of the finished catalysts was approximately 190 m^2/g.

Apparatus and Procedure

All activity data were obtained using a quartz flow reactor at atmospheric pressure. Five grams of catalyst (approx 10 cc) were placed between two quartz wool plugs at the bottom of a 500 mm long, 18 mm i.d. quartz reactor. The upper part of the reactor was packed with quartz chips and served as a preheater zone. The catalyst bed temperature was maintained constant with a maximum variation of ±1.5°C by an automatic temperature controller, and was constantly monitored by a multipoint recorder connected to an iron–constantan thermocouple positioned inside the reactor. The gaseous reactants were fed from individual cylinders through pressure regulators, Brooks rotometers and needle valves. Water was fed by a Harvard Apparatus Co. syringe pump through a quartz capillary immersed in the preheater zone. In a typical run a mixture containing 1.25 mole % NO, 2.50 mole % CO, 0.7 mole % H_2O, with the balance being Ar as carrier gas, was passed over the catalyst at a flow rate of 15,000 GHSV. The following standard procedure was used to start each run. After reaching equilibrium temperature in flowing Ar, CO or H_2 was admitted, then after successive 15-min intervals NO and H_2O were admitted. When shutting down the unit overnight, the reactants were turned off in the reverse sequence.

Analysis

The reactor effluent was continuously monitored for NO content with a Beckman 315A infrared analyzer having a total range between 0 and 2×10^4 ppm NO. In addition, the exit gases were continuously sampled by an A.E.I. MS-10 mass spectrometer having a rhenium filament, at a sampling pressure of 0.1 Torr, ionization voltage of 70 V and a trap current of 50 μA. The mass spectrometer was calibrated for the following pure gases: CO, CO_2, NO, N_2O, NH_3, N_2 and Ar. The fragmentation pattern of the instrument and the sensitivity coefficients for the pure gases are shown in Table 1. The quantitative analysis of all components was based on the nine following peaks: $m/e = 14, 16, 17, 18, 22, 28, 30, 40$, and 44. No corrections were made for ^{13}C, since estimates indicated that the results would not be significantly changed by such corrections. The peak at $m/e = 18$ was used to correct the peak at $m/e = 17$ (NH_3) for the presence of water in the system. It was not used to determine quantitatively the amount of water formed during the reaction. The peak at $m/e = 14$ was used to differentiate N_2 and CO. Mass spectral data have been calculated from a set of seven simultaneous equations which were readily solved by the use of a computer. Scanning of the mass spectrum was started only after a steady-state condition had been reached, the latter being indicated by a constant NO reading on the ir analyzer and a constant catalyst bed temperature. Ammonia formation in the reaction

TABLE 1
MS-10 MASS SPECTROMETER FRAGMENTATION PATTERN

No.	*m/e*	N_2	NH_3	H_2O	CO_2	N_2O	NO	CO	Ar
1	14	7.475	1.553			11.369	6.850	1.312	
2	16		81.210	1.305	8.133	4.557	0.816	2.124	
3	17		100	20.125					
4	18			100					
5	22				1.482				
6	28	100			8.044	11.021		100	
7	30					30.438	100		
8	40								100
9	44				100	100			
Relative sensitivity factor		1.000	1.380	1.415	1.221	1.256	0.838	1.103	0.699

was checked by chemical analysis. The reactor outlet gas was scrubbed with a saturated solution of boric acid and then titrated with 0.05 *N* hydrochloride acid.

RESULTS AND DISCUSSION

Reduction of NO with CO over Chromium and Iron Oxides

The relative activity of a catalyst for the reduction of NO with a given reagent can be conveniently expressed in terms of percentage of NO reaction versus catalyst bed temperature, at a fixed-flow rate. By arbitrarily choosing the temperature T_a, at which 90% NO reduction occurs as an activity indicator, any number of catalysts can be conveniently compared. Figure 1 shows the activity data obtained for the reduction of NO with CO over 10% chromium oxide on alumina; curve (a) represents the water-free system while points obtained in the presence of H_2O or H_2 are plotted on curve (b). Taking T_a as the activity indicator described above, it can be seen that the presence of 0.7 mole %

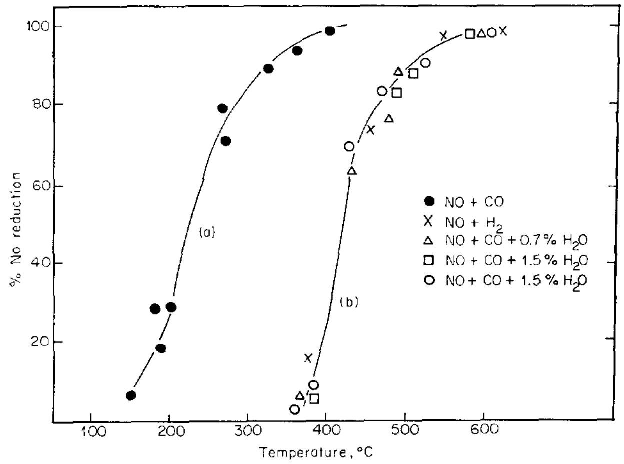

FIG. 1. Relative activity curves for NO reduction over 10% chromium oxide on Al_2O_3 with CO, H_2, and CO + H_2, in the presence and absence of H_2O. Reaction conditions: 1.25% NO, 2.5% CO, 3.2% H_2, in argon carrier at 15,000 GHSV. (a) for NO + CO system, (b) for NO + H_2, NO + CO + H_2, and NO + CO + H_2O systems.

H_2O increases T_a from 325 to 520°C. The addition of larger amounts of water had only a minor effect on T_a, e.g., increasing the H_2O level from 0.7 to 1.5 mole % had no effect; with 15 mole % of H_2O which is close to the practical case, T_a was 565°C.

Similar data are shown in Fig. 2 for iron oxide on alumina. The same overall pattern of activity was observed, but iron oxide was somewhat more active than chromium oxide both in the absence and presence of water. (For iron oxide, T_a was 280 and 485°C in the water-free and 0.7 mole % H_2O–CO systems, respectively.)

It is only when the product distributions for the various feeds are compared that some very distinct differences between chromium oxide and iron oxide become apparent. In the absence of water, the reaction may be represented simply by the equation $NO + CO \dashrightarrow CO_2 + 1/2\,N_2$. This was confirmed by mass spectral analysis of the reactor effluent, where all four compounds appeared in amounts which would be predicted by the above stoichiometry. A complete reactor effluent analysis as a function of temperature for the NO–CO–H_2O system is shown in Fig. 3 for chromium oxide and Fig. 4 for iron oxide. Over chromium oxide the concentrations of NO and CO decreased in the manner expected for a NO–CO reaction, although at NO conversions > 80%, trace amounts of NH_3 (0.02 mole %) were formed. The formation of NH_3 by reduction of NO with H_2

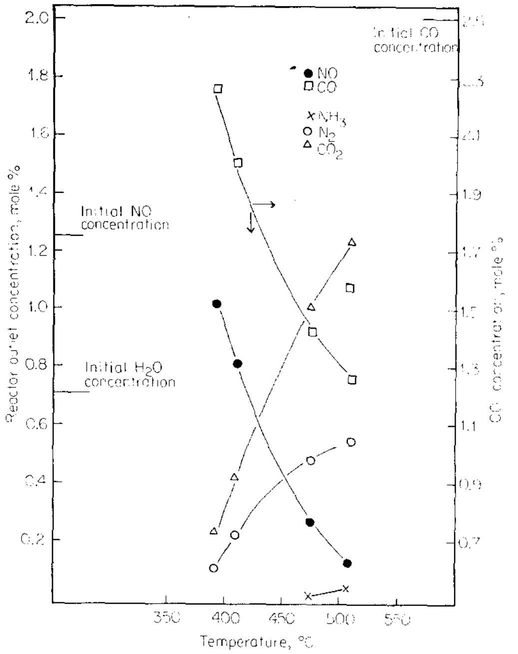

FIG. 3. Effect of temperature on the reactor outlet composition for the NO–CO reaction over 10% chromium oxide on Al_2O_3, in the presence of H_2O. GHSV = 15,000.

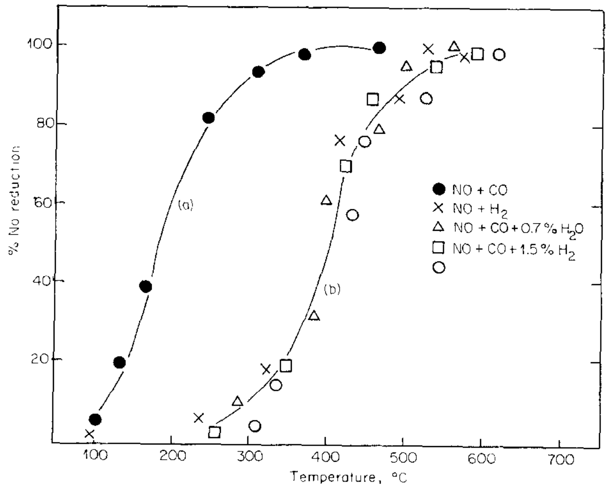

FIG. 2. Relative activity curves for NO reduction over 10% iron oxide on Al_2O_3 with CO, H_2, and CO + H_2, in the presence and absence of H_2O. Reaction conditions: 1.25% NO, 2.5% CO, 3.2% H_2, in argon carrier at 15,000 GHSV. (a) for NO + CO system, (b) for NO + H_2, NO + CO + H_2, and NO + CO + H_2O systems.

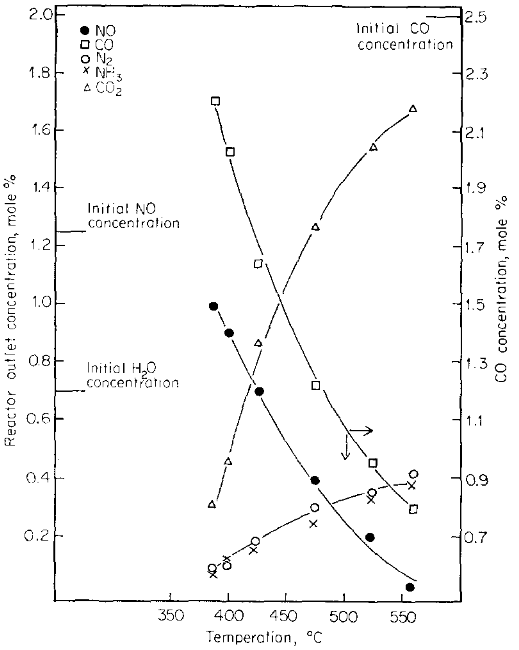

FIG. 4. Effect of temperature on the reactor outlet composition for the NO–CO reaction over 10% iron oxide on Al_2O_3, in the presence of H_2O. GHSV = 15,000.

can occur according to the equation $2NO + 5H_2 \dashrightarrow 2NH_3 + 2H_2O$. The H_2 necessary for this reduction could come from the water-gas shift reaction, $CO + H_2O \dashrightarrow CO_2 + H_2$.

In contrast with the above results, the product distribution from the iron oxide catalyst changed markedly when water was added to the feed. This is clearly depicted in Fig. 4. Over the whole temperature range studied, NH_3 appeared as a product in amounts comparable to N_2. In addition, a large excess of CO_2 (0.45 mole %) was formed above that expected from the stoichiometry of reduction of NO by CO. Together these facts demonstrate that the water-gas shift reactions occurs over iron oxide more rapidly than over chromium oxide, and that the H_2 produced is active for reduction of NO, at least in part, to NH_3. (When iron oxide and chromium oxide were compared in separate experiments for the reaction $CO + H_2O \dashrightarrow CO_2 + H_2$, approximately 50% CO was converted over iron oxide and less than 5% over chromium oxide.) Although the differing degrees to which the water-gas shift reaction occurs appear to rationalize the above results, data presented later will show that the system is more complex than indicated by this simple interpretation.

Reduction of NO with H_2 Over Chromium and Iron Oxides

In systems containing water, the possibility of H_2 formation exists; therefore, the activity of H_2 as a reducing agent for NO over iron oxide and chromium oxide must be considered. Such data are shown in Figs. 1 and 2 for the chromium oxide and iron oxide catalysts, respectively. The reaction of NO with H_2 was considerably slower than with CO, and over both catalysts the relative rates of the NO–H_2 reaction were about equal to those for the NO–CO–H_2O system. This was not surprising in the case of iron oxide, where the water-gas shift reaction occurred rather readily to produce H_2, but it was unexpected for chromium oxide where the shift reaction was much slower.

The product distributions for the two catalysts differed significantly as shown in Table 2. Over chromium oxide the nitrogen containing reaction products consisted of 97% N_2 and 3% NH_3 whereas for iron oxide 30% N_2 and 70% NH_3. Although similar differences were observed for NO–CO–H_2O systems, the occurrence of extensive water-gas shift reaction over iron oxide provided a reasonable explanation of these results. However, for the NO–H_2 reaction, the reactants are equivalent over

TABLE 2
DISTRIBUTION OF NITROGEN CONTAINING PRODUCTS FOR THE REDUCTION OF NO WITH H_2 OVER SUPPORTED Cr_2O_3 AND Fe_2O_3[a]

Catalyst	Outlet composition (mole %) NO	NH$_3$	N$_2$
Cr_2O_3	0.08	0.02	0.59
Fe_2O_3	0.08	0.61	0.26

[a] Inlet composition: 1.25% NO, 3% H_2 in Argon. Temp, 510°C, Press, 1 atm, 15,000 GHSV.

both catalysts. Hence, either a different mechanism is operating for the two catalysts or else any NH_3 formed over chromium oxide undergoes subsequent reactions in which it is destroyed. Two such possibilities for the latter are NH_3 decomposition into its elements, and the reaction of the NH_3 formed initially with unreacted NO according to the equation $6NO + 4NH_3 \dashrightarrow 5N_2 + 6H_2O$. Both of these reactions would give the experimentally observed products. The first hypothesis was tested by measuring the rate of NH_3 decomposition (1% NH_3 in Argon, 15,000 GHSV) over chromium oxide at temperatures up to 600°C. Since no decomposition was observed under any conditions, it is concluded that this reaction probably does not account for the absence of NH_3 in the products of NO reduction by H_2 over chromium oxide. The possibility of interaction between NH_3 and unreacted NO was checked by measuring the relative rates of this reaction over both iron oxide and chromium oxide. The results, shown in Fig. 5, clearly indicate that the reaction is faster over iron oxide than over chromium oxide. Since NH_3 was found in the products of reaction over iron oxide and not over chromium oxide, the subsequent reaction of NH_3 with unreacted NO does not explain our experimental results. We conclude that a fundamental difference in mechanism must exist, but the nature of this difference is not clear at this time.

TABLE 3

PRODUCT DISTRUBITION FOR THE REDUCTION OF NO WITH A CO/H_2 MIXTURE OVER SUPPORTED Cr_2O_3 AND Fe_2O_3[a]

Catalyst	NO	NH_3	N_2	CO_2	CO
Cr_2O_3	0.08	0.01	0.61	0.61	1.87
Fe_2O_3	0.07	0.60	0.28	0.02	2.47

[a] Inlet composition: 1.25% NO, 2.5% CO, 3.0% H_2 in Argon. Temp, 510°C, Press, 1 atm, 15,000 GHSV. H_2O and H_2 content was not measured.

Although our data indicate that the reduction of NO with CO is considerably faster than with H_2 over both catalysts, the reduction by a CO/H_2 mixture was investigated in order to obtain competitive rate data. The results plotted in Figs. 1 and 2 show that the reaction rate for the NO–CO–H_2 system was much slower than for NO–CO and was in fact about equal to that observed for the NO–H_2 and NO–CO–H_2 systems. (These results suggest that H_2 as well as H_2O has a strong inhibiting effect on the reduction of NO by CO.) However, product distribution data shown in Table 3 for the reduction of NO with a

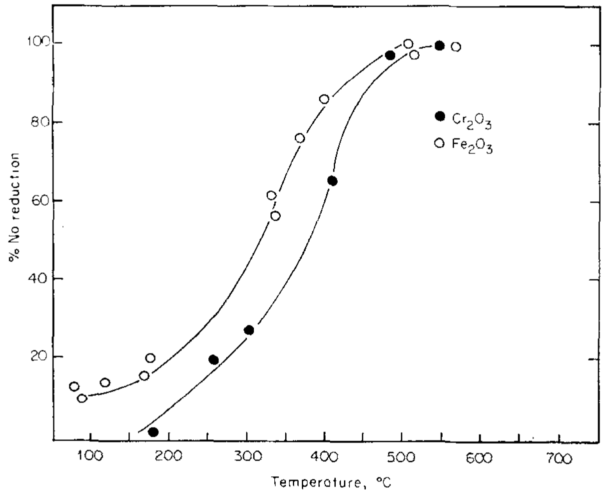

FIG. 5. Relative reactivity of supported chromium oxide and iron oxide for the reaction $6NO + 4NH_3 \dashrightarrow 5N_2 + 6H_2O$. Reaction conditions: 1.25% NO, 2.5% NH_3, in argon carrier at 15,000 GHSV.

mixture of 3.0 mole % H_2 and 2.5 mole % CO at 510°C, do not substantiate this idea. Over iron oxide the product distribution for the NO–CO–H_2 reaction is essentially identical with that observed for H_2 alone as the reducing agent, which indicates that in the NO–CO–H_2 mixture, CO does not take part in the reaction. This is further confirmed by the appearance of only 0.02 mole % CO_2 in the products.

While the results for the chromium oxide catalyst also indicate the equivalence of the NO–CO–H_2, NO–CO–H_2, and NO–H_2 in terms of activity, some differences in the product distribution do exist. For NO–CO–H_2 the formation of 0.61 mole % CO_2 shows that approximately half of the NO was reduced by CO and the remainder by H_2. From these competitive experiments, it must be concluded that over chromium oxide, the rates of reduction of NO by CO and H_2 were approximately equal, while over iron oxide the reduction with H_2 was considerably faster than with CO. This is, of course, contrary to the data obtained from the individual experiments with the NO–CO and NO–H_2 systems. However, the strong inhibiting effect of H_2O on the NO–CO reaction has been clearly demonstrated, and it must be noted that H_2O is a primary product of the NO–H_2 reaction. Thus, if initially NO was reduced rapidly by H_2 to form N_2 and H_2O, or even NH_3 and H_2O, it may be reasonable to expect that the H_2O produced would then have a strong inhibiting effect on further NO reduction.

The Mechanism of Inhibition by Water

Since water is always present in automobile exhaust gases, an understanding of the mechanism by which it inhibits the reduction of NO over chromium oxide and iron oxide may be of significant value in developing catalysts which are unaffected by water. Clearly the mechanism by which this inhibition operates must be associated with certain changes in the nature of the active catalyst sites. In order to develop a discussion of this problem, the nature of the active sites must be considered.

Burwell *et al.* (*10*) have proposed that the active sites on α-Cr_2O_3 comprise coordinatively unsaturated surface Cr^{3+} ions. These are formed as a result of condensation of surface hydroxyl groups to form water and coordinatively unsaturated Cr^{3+} and O^{2-} ions during heat treatment at 400°C. Chromia which has been treated in this way rapidly chemisorbs H_2, O_2 and CO at -78°C and is active for ethylene hydrogenation. On the other hand, chromia which has been heated only to 150°C, under which conditions surface hydroxylation does not occur, is not active for chemisorption of O_2 or CO, and will not hydrogenate ethylene.

In our studies, 10% chromium oxide supported on alumina was used as the catalyst rather than pure chromium oxide. At this level, however, it may be assumed that the supported chromia will be very similar to the pure material, and indeed our X-ray data for the catalysts show the presence of α-Cr_2O_3. Since these catalysts were activated by heating to 500°C, the formation of coordinatively unsaturated surface chromium ions, Cr^{3+} (cus), would be expected to occur according to the Burwell mechanism (*10*). It is these Cr^{3+} (cus) sites which we suppose are the active sites for NO adsorption and for subsequent reaction. In the presence of water vapor there will be competition between H_2O and NO for these active sites. Any effect of water on the rate of NO reduction will depend upon the relative strengths of the interaction of each specie with the Cr^{3+} (cus) ion.

The generation of a Cr^{3+} (cus) site is also accompanied by an O^{2-} (cus) neighboring site. This allows for the possibility of dissociative adsorption of water as H^+ OH^-, the proton being associated with the O^{2-} (cus) site and the hydroxyl with the Cr^{3+} (cus) site. (This is the reverse of the dehydroxylation reaction which initially generated the active sites, and will probably produce a surface layer of hydroxyl groups and so lead to an inactive catalyst.) Further, the interactions of H^+ with O^{2-} and OH^- with Cr^{3+} are all of the "hard acid–hard base" type (II) and are, therefore, predicted to be strong interactions. In these terms, the interaction of NO, a soft base, with the hard acid Cr^{3+} is not likely to be very strong. Thus, if the adsorption of water onto the active catalyst sites occurs by a dissociative mechanism, it is likely to be a very strong interaction, and would probably render the catalyst inactive for NO adsorption.

An attempt to gain some understanding of this adsorption and its role in inhibiting the reduction of NO was made through the series of experiments shown in Table 4. In Run No. 1 a reaction mixture of NO and CO was passed over the catalyst at 320°C, with almost complete conversion of NO being achieved. The introduction of an additional 1.5% H_2 (Run No. 2) caused the NO reduction to essentially cease. When the H_2 was turned off (Run No. 3) the catalyst activity did not return to its original level even though the reaction conditions were identical to those in Run No. 1. Finally, after the catalyst was heated to 500°C in flowing argon for 1 hr, a complete recovery of activity was achieved (Run No. 4).

As shown in Table 3, the product distribution indicates that the rate of NO reduction with CO and with H_2 were about equal over chromium oxide, so that in Run No. 2 of Table 4 water will be formed as a result of reaction of NO with H_2. This will then be adsorbed onto the active sites and inhibit any further reduction of the NO. If this adsorption is molecular rather than dissociative then one might expect that once the hydrogen was turned off (Run No. 3), the adsorbed water would be slowly desorbed and catalytic activity would return to its original level. The fact that this did not occur suggests a dissociative adsorption which will destroy the active sites by producing a completely hydroxylated surface. According to Burwell *et al.* (*10*), α-Cr_2O_3 with this type of surface would not be active for NO chemisorption and thus NO reduction could not occur. The surface can be dehydroxylated and new active sites generated by heating to at least 400°C. Thus in Run No. 4, catalytically active sites were regenerated and the reactivity for NO reduction with CO returned to its original level.

The above discussion has been essentially confined to the chromium oxide system, primarily because its surface chemistry and catalytic reactivity has been well studied by many workers (*10*). The similar behavior noted for chromium oxide and iron oxide suggest they may possess similar types of coordinatively unsaturated surface sites and that inhibition of NO reduction by water may be through analogous mechanisms. Discussion concerning the active sites has been confined to the nature of the site before the NO is actually adsorbed onto it. The possibility is recognized that oxidation state changes could occur at the Cr^{3+} (cus) sites following adsorption of the NO molecule. However, the present data provides no detailed information about the surface interactions, so that further speculation is unwarranted. Infrared, ESR and microbalance studies are now underway in an attempt to define the detailed

TABLE 4

THE EFFECT OF H_2 ON THE REDUCTION OF NO WITH CO OVER SUPPORTED Cr_2O_3 AND Fe_2O_3[a]

	Inlet composition (mole %)			Cr_2O_3	Fe_2O_3
Expt No.	NO	CO	H_2	% NO Conversion	% NO Conversion
1	1.25	2.5	—	100	100
2	1.25	2.5	1.5	2.7	8.3
3	1.25	2.5	—	2.8	7.1
4	1.25	2.5	—	100	100

[a] Reaction conditions: 320°C, press, 1 atm, 15,000 GHSV. Between runs Nos. 3 and 4, the catalyst was heated to 500°C in argon for 1 hr.

surface chemistry which occurs in the above systems.

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