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Reduction of Nitric Oxide with Carbon Monoxide and Hydrogen over Ruthenium Catalysts

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Ruthenium on alumina catalysts show five reproducible states with characteristic conversion patterns in the reduction of NO with a mixture of CO and H_2 in the presence of H_2O and CO_2. The Ru/Al_2O_3 catalysts are compared with bulk Ru. Two peaks in the NH_3 yield are distinguished; a CO-assisted NH_3 maximum at ~270°C and a H_2-assisted NH_3 maximum at ~350°C. The low-temperature NH_3 maximum increases with decreasing particle size of the Ru. The dual nature of Ru catalysts is proposed to be due to heavy coverage of the Ru surface with nitrogen in the reduced state and to partial coverage with oxygen in the oxidized state. NH_3 is not a gas-phase intermediate in the N_2 formation, but N_2O is. The watergas shift reaction has only a minimal effect on the selectivity, except at low temperature where the shift decreases the CO-assisted NH_3 yield. Oxidized Ru is active in the formation of CH_4 from CO and H_2.

INTRODUCTION

Metallic ruthenium is of considerable interest as catalyst for the conversion of the oxides of nitrogen present in automotive exhaust (*1,2*). It is favored because in comparison with other noble metal catalysts (*2*) or transition metal oxides (*1*), it is more selective towards the formation of N_2 rather than NH_3. Ruthenium is commonly used supported on alumina or silica–alumina (*1–3*). Ruthenium which is ionically bound in ruthenates (*4–6*) or in diluted form in perovskite-like manganites (*5*) is also an active and selective catalyst for NO reduction. Under reducing conditions of the tests, metallic ruthenium may precipitate on the surface of the ruthenates (*5,6*) and to a lesser extent, on the manganites (*5*). In our previous study of these catalysts, it was found that metallic ruthenium shows quite complex catalytic behavior. Earlier workers have noted the "dual state" behavior produced by alternatively oxidizing or reducing the catalyst (*1,3,7*). The reduced state of the dual nature Ru (RDN-Ru) is characterized by low activity in the watergas shift reaction and relatively high NH_3 yields (~20%) at $T \geqq 450°C$. The oxidized state of the dual nature Ru (ODN-Ru) shows high activity in the shift reaction and yields only minimal NH_3 at $T \geqq 450°C$.

The purpose of the present study is to find how the role of the Ru catalyst in the NO reduction is linked to its preparation and pretreatment. The reduction of NO in a mixture of NO, CO, H_2, H_2O and CO_2 in He is used to characterize Ru catalysts in their various reproducible states produced by different pretreatments. The products of the catalytic conversion are N_2, N_2O, NH_3, H_2, CO_2 and CH_4.

With little variation, the partial reactions which can explain the conversion process over oxidic ruthenium catalysts (*5*) can be invoked here too. NO, CO, and H_2 all adsorb strongly on ruthenium, in particular when its surface is reduced (*8–13*). NO and CO can be adsorbed in a molecular state, with the ir spectra indicating binding comparable to that in the nitrosyls and carbonyls (*9,11,13*).

$$NO + Ru \rightarrow Ru\text{-}NO, \quad (1)$$

$$CO + Ru \rightarrow Ru\text{-}CO. \quad (2)$$

The two molecules probably compete for the same sites (*2,14*). In addition, dissociative adsorption of NO is possible, as indicated by the adsorption and isotopic exchange of N_2 on Ru (*15,16*).

$$NO \rightarrow N_{ads} + O_{ads}. \quad (3)$$

Interaction of NO or N_{ads} with H_2 leads to N-containing fragments at the surface which are likely to be NH_2 or NH (*17*). Formation of N_2 and N_2O may then occur via:

$$2N_{ads} \rightarrow N_2, \quad (4)$$

$$NH_{2_{ads}} + NO_{ads} \rightarrow N_2 + H_2O, \quad (5)$$

$$N_{ads} + NO_{ads} \rightarrow N_2O. \quad (6)$$

The formation of NH_3 by hydrogenation of N_{ads} or $NH_{2_{ads}}$ appears to prevail at temperatures above 350°C, in accordance with the positive effect of the H_2 partial pressure on the rate of NH_3 formation (*3*).

$$2NH_{2_{ads}} + H_2 \rightarrow 2NH_3. \quad (7)$$

However, at low temperatures, the production of NH_3 is strongly enhanced by CO, in the presence of either H_2 (*3,14*) or particularly, H_2O (*14*). This has been explained by the presence of an isocyanate intermediate (*13*).

$$e + N_{ads} + CO_{ads} \rightarrow NCO^- \quad (8)$$

$$NCO^- + 2H_2O \rightarrow CO_2 + NH_3 + OH^- \quad (9)$$

This is also in accordance with the cocatalytic effect of NO on the watergas shift reaction (*3*):

$$CO + H_2O \rightarrow CO_2 + H_2. \quad (10)$$

However, adsorption of CO on NO-sites, thus reducing the surface concentration of N is also a possible explanation (*2*), as is the enhanced adsorption of H_2 in the presence of CO (*8,18*). It should be pointed out here, that the occurrence of the watergas shift reaction may either increase or decrease the NH_3 formation, since both CO and H_2 partial pressures have a positive effect on NH_3 formation.

In the NO reduction, H_2 and CO compete. The NO–CO reaction is faster at low temperature, the H_2–NO reaction is faster at higher temperature (*3*).

At high temperature, decomposition of NH_3 or $NH_{2_{ads}}$ is expected to become important in ensuring a selective conversion of NO to N_2 (*1,17*).

EXPERIMENTAL METHODS

The catalysts used were bulk ruthenium metal (Englehard Industries, Newark, NJ) with a BET surface area of 0.4 m^2/g and variously treated samples of Ru on alumina (Table 1). Fisher activated alumina pellets were impregnated with a solution of $RuCl_3$ (K & K Laboratories) slowly heated to 300°C in flowing H_2 and reduced at 300°C for 8 hr. The catalyst pellets were then crushed and the fraction of 37–250 μm (80–400 mesh) used. This stock was shown by chemical analysis and X-ray diffraction to consist of 0.8% Ru on γ-AlOOH, the surface area was 237 m^2/g. The Ru lines in X-ray diffraction were extremely broad and weak. The Ru/γ-Al_2O_3 catalysts used were obtained from this material by heating at 500–600°C for various lengths of time in H_2 or in a dilute H_2-NO-CO-H_2O-CO_2-He mixture (Table 1).

The catalytic properties of the catalysts were measured with a fixed-bed continuous flow reactor in which 0.3–1 cm^3 catalyst supported on a porous quartz disc was subjected to a downflow of a preheated mixture of 0.13% NO, 0.4% H_2, 1.3% CO, 3% H_2O and 3% CO_2 in He (mixture W) at GHSV 18,000 hr^{-1}. This composition was chosen to approximate the concentrations in automotive exhaust.

TABLE 1
PREPARATION AND PROPERTIES OF Ru CATALYSTS

No.	X-Ray diffraction and chemical analysis	Preparation	Surface area (m^2/g)
I	Ru bulk metal 1.00 g mixed with 0.50 quartz powder	Ru from Engelhard, as received	0.4[a]
IA	Same as I	I, 4 hr H_2 at 600°C, cooled in H_2	0.4
IB	Same as I	IA, 16 hr mixture W at 600°C, cooled in mixture W	0.4
IC	Same as I	IB, 17 hr H_2 at 625°C, cooled in H_2	0.4
II	0.8% Ru/γ-AlOOH $d_{Ru} < 100$ Å	Fisher activated alumina impregn. with $RuCl_3$; H_2 reduction at 300°C, 8 hr, cooled in H_2, exposed to air, pellets crushed to 37–250 μm	235
IIIA	0.8% Ru/γ-Al_2O_3 $d_{Ru} < 100$ Å	II heated in mix W, 1.5 hr at 520°C	
IIIB	Same as IIIA	IIIA heated in mix W, 11 hr at 627°C	145[b]
IV	0.8% Ru/γ-Al_2O_3 $d_{Ru} < 100$Å	II heated in H_2, 4 hr at 600°C, cooled in H_2, exposed to air	238
IVA	Same as IV $d_{Ru} < 100$ Å	IV heated in mix W, 15 hr at 620°C	157[b]
IVB	Same as IV d_{Ru} not measured	IV heated in mix W for several days, *in situ* reduced in H_2, 3 hr at 500°C, cooled in H_2	
IVC	Same as IV d_{Ru} not measured	IVB heated in mix W, 16 hr at 600°C	
IVD	Same as IV $d_{Ru} \gtrsim 500$ Å	IVC heated in mix W +1.7% O_2, 10 min at 540°C	138[b]

[a] Surface area of Ru powder only. Surface areas measured before use unless otherwise indicated.
[b] Measured after use.

The composition of the feed and of the effluent from the reactor were determined by analyzing dried samples by gas chromatography over Porapack Q and molecular sieve 13X columns used in series (*19*). The contents of H_2, N_2, NO, CO, N_2O and CH_4 were determined, and the NH_3 yield was calculated from the nitrogen balance. This analysis for NH_3 was confirmed by determination of the NH_3 content in the effluent by absorption and chemical analysis. An example of a gc analysis is given in Fig. 1. Occasionally, gas samples are analyzed by mass spectrometry to check the analysis procedure. The conversion of the inlet mixture was determined as a function of catalyst temperature at slowly ascending or descending temperature. The catalyst temperature was programmed (Bruce Controller and SRI programmer), up or down a terrace-pattern with a ramp of 2.5°C/min and a section of 5 min at constant temperature, at the end of which period the effluent sample was taken with an automatic sample valve.

RESULTS AND DISCUSSION

Bulk Ruthenium Metal

The conversion of NO, CO and H_2 as a function of temperature is given in Fig. 2. The top panel gives the yield of NO, N_2O and N_2 expressed as a percentage of the inlet NO, the middle panel does the same for NH_3, and the bottom panel gives the yield of H_2 and CO as a percentage of the inlet H_2 and inlet CO, respectively. The broken curves give the state of the as-received catalyst, and these surface characteristics are lost after the first heating to $T \geqslant 450$°C. In Fig. 3, the conversion of CO to CH_4 is expressed as ppm CH_4 in

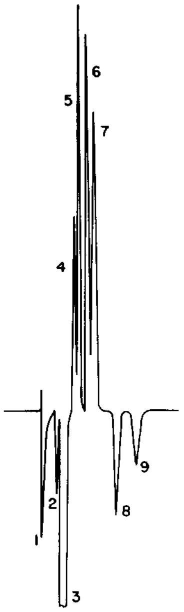

FIG. 1. Example of gc analysis. Peaks pointing down come from the Porapack Q column, peaks pointing up from the molecular sieve column. (1) Injection disturbance; (2) H_2; (3) combined CO, O_2, N_2, NO; (4) O_2; (5) N_2; (6) NO; (7) CO, × 1/20; (8) CO_2; (9) N_2O.

the effluent. The data for other catalysts are expressed similarly in the other figures.

The solid lines in Figs. 2 and 3 give the conversion over the catalyst at ascending temperature after pretreating the catalyst *in situ* in mixture W or in pure hydrogen for various lengths of time (Catalysts IA, IB and IC, Table 1). The results of the three pretreatments are virtually identical for the NO conversion (production of N_2, N_2O and NH_3; top two panels in Fig. 2) and for the watergas shift reaction (production of H_2 and concomitant conversion of CO, lower panel of Fig. 2). The CH_4 production however decreases continuously as the catalyst is subjected to the reducing pretreatments (Fig. 3). These results indicate that the RDN-Ru state cannot be reached here.

The striking feature in the product pattern is the presence of two peaks in the NH_3 yield, one spanning $T < 300°C$ and the other $300°C < T < 500°C$. It is likely that the low-temperature NH_3 peak is due primarily to a CO-assisted route to NH_3, perhaps the isocyanate route. This is in accordance with the strong promotion of NH_3 formation by CO in this temperature range found for Ru/Al_2O_3 (*3*) and for $Ru/SrRuO_3$ (*5*). It is also in accordance with the elimination of the NCO-ir band (*13*) and the selective elimination of the low temperature NH_3 formation (*20*) on $Ru/\gamma\text{-}Al_2O_3$ by treatment with SO_2. In the $NO\text{–}CO\text{–}H_2O$ system, a peak in NH_3 production at 200–300°C and rapid decline thereafter has also been observed (*14*). The second, high temperature NH_3 peak may be assumed to be due primarily to a H_2-assisted mechanism in which CO is not involved. This is in accordance with the positive effect of H_2 on the NH_3 formation on Ru/Al_2O_3 above 350°C (*3*) and with the absence of an effect of the CO concentration on NH_3 formation over $Ru/SrRuO_3$ above 350°C (*5*).

Up to 270°C, the selectivity of the NO conversion $S = (2N_2 + 2N_2O)/(2N_2 + 2N_2O + NH_3)$ is nearly constant, possibly as a result of a competition between N_2 formation through Eq. (6) followed by N_2O decomposition, and NH_3 formation through Eqs. (8) and (9). This would be reasonable in view of the similar molecular adsorption of CO and NO on Ru and of the limited role of H_2 in the reduction process up to that temperature (Fig. 2). The precipitous decrease of the NH_3 yield at 270°C cannot be due to changes in the NO or CO adsorption but may be the result of the start of the reaction of Eq. (5) of $NH_{2_{ads}}$ with NO (*17*) or of the surface diffusion of N_{ads} leading to Eq. (4).

The present reduced bulk Ru catalyst is active in the watergas shift reaction (see lower panel of Fig. 2), and does not produce NH_3 beyond 500°C. Both facts are in contrast with the behavior of the RDN states of $Ru/SiO_2\text{–}Al_2O_3$ (*3*) and $Ru/\gamma\text{-}Al_2O_3$ (see below). The occurrence of the

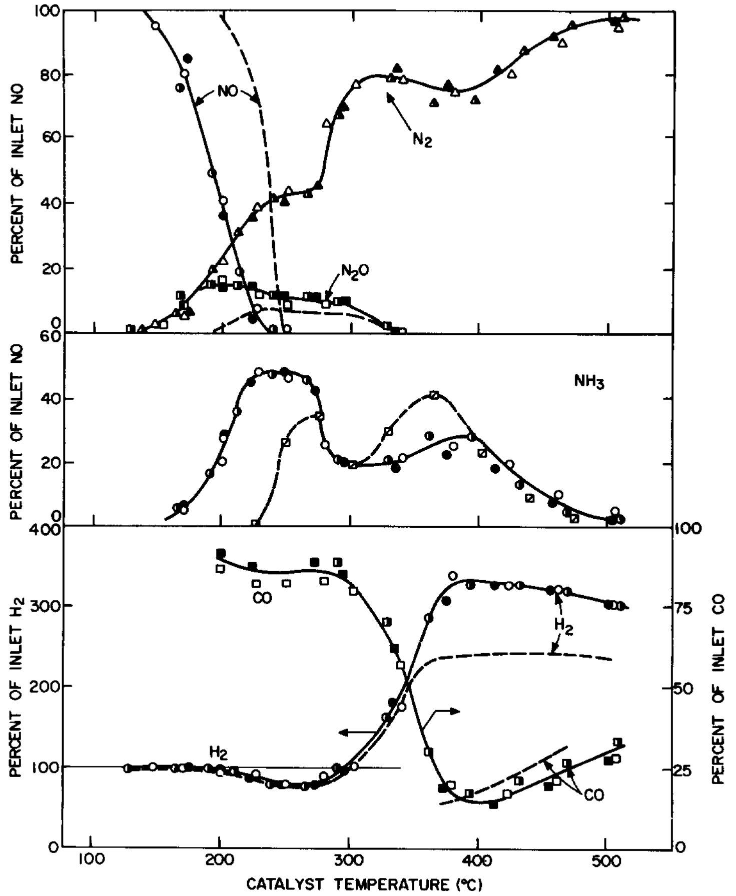

FIG. 2. Conversion of NO-CO-H_2-H_2O-CO_2-He (mixture W) over bulk ruthenium. (--) Received catalyst (CAT I); (—) CAT IA (◑), CAT IB (○) and CAT IC (●). GHSV 33,000 hr^{-1}.

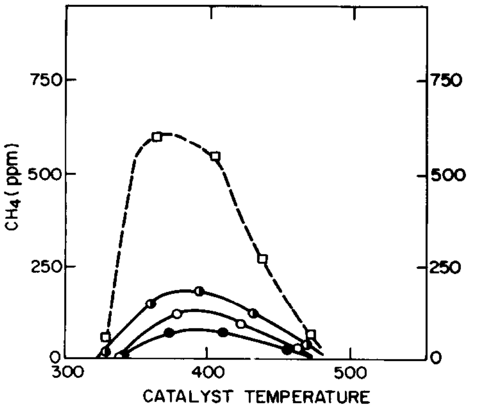

FIG. 3. Conversion of mixture W over bulk ruthenium. CH_4 production. See caption Fig. 2 for symbols. GHSV 33,000 hr^{-1}.

shift has only a negligible effect on the NH_3 formation.

The as-received bulk Ru, with a presumably oxidized surface, shows less activity for NO conversion (broken curves in Fig. 2). This is especially true at the lower temperatures, where CO is the main reducing agent. The CO-assisted NH_3 formation is diminished. These two effects are explained by the lower adsorption strength of CO and NO on oxidized Ru. The H_2 production is lower for the as-received Ru beyond 350°C, and H_2 might be consumed in the reduction of the surface oxide. The CH_4 formation on the oxidized surface is five fold higher than on the reduced surface (Fig. 3).

Ruthenium on γ-Al_2O_3, d > 500 Å

In a series of experiments on finely dispersed Ru/γ-Al_2O_3, we were initially unable to reproduce the "dual state" behavior of Ru reported by the G.M. workers (*1,3,7*). However, after many repeated oxidation and reduction treatments including use of the catalyst in mixture W at 600°C for many hours, the dual state behavior started to develop. The eventually resulting catalyst, which in X-ray showed a very well developed Ru diffraction pattern characteristic of particles larger than 500 Å (*21*) has catalytic properties as given in Fig. 4 (CAT IVC). The full lines give the reduced state (RDN-Ru), reached by treating in mixture W at 600°C for more than 16 hr after *in situ* reduction in H_2 for 3 hr at 500°C. In accordance with the earlier reports, the reduced catalyst is producing appreciable amounts of NH_3 at 500 and 530°C; and is fairly inactive in the H_2 formation. The reduced state does not promote the hydrogenation of CO to CH_4.

Following treatment of the RDN-Ru catalyst at 540°C for 10 min with an excess of O_2 (1.7%) added to mixture W, the catalyst (CAT IVD) was in a state similar to the oxidized state (ODN-Ru) reported before (*1*). The conversion of mixture W was measured at descending catalyst tem-

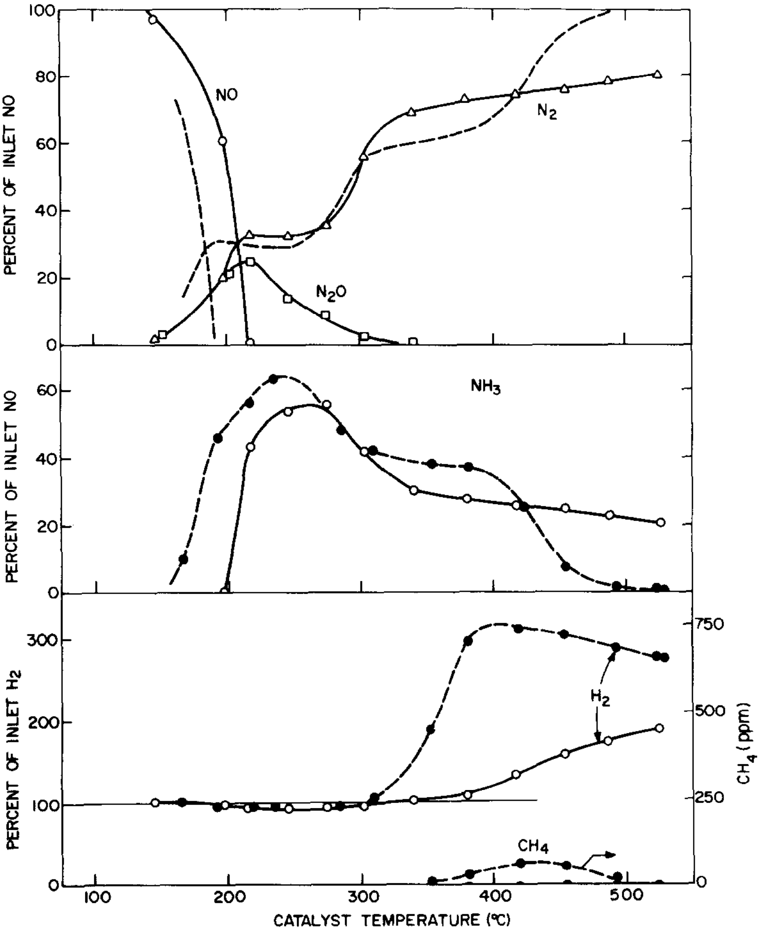

FIG. 4. Dual nature behavior of Ru/γ-Al_2O_3. (—) Reduced state (CAT IVC), (--) oxidized state (CAT IVD). GHSV 18,000 hr^{-1}.

perature (broken lines in Fig. 4). The watergas shift activity has increased very substantially and the NH_3 production is nil at 500°C and above.

Ruthenium on γ-Al_2O_3, $d < 100$ Å

Ru/γ-AlOOH (Cat II) and Ru/γ-Al_2O_3 (Cat IV), which were preheated in H_2 for 8 hr at 300°C and for an additional 4 hr at 600°C, respectively, were exposed to air in the course of transfer and storage. The catalytic profile of CAT II in the first run at ascending temperature is given in Fig. 5 (broken lines). The profile for CAT IV (not shown) is closely similar in all respects, notwithstanding the differences in support structure. Comparison with the as-received bulk Ru catalyst (broken lines in Fig. 2) shows that all these catalysts which have been exposed to air have very similar characteristics, witness the total NO conversion, the NH_3 formation and the watergas shift reaction. In comparison with the bulk Ru, the present supported catalysts differ only in the absence of the NH_3 minimum at 300°C and the initially much lower CH_4 formation.

A short period (< 90 min) of heating these catalysts in the flowing mixture W at 18,000 hr^{-1} space velocity and 520°C produces a reproducible state characterized by the solid curves in Fig. 5. Two different runs are shown, measured on catalysts IIIA and IIIB at descending temperatures. In between, the sample was heated in mixture W at 627°C for 11 hr. Another sample, pretreated *in situ* in mixture W at 620°C for 15 hr (CAT IVA) showed a virtually identical profile (not given). The N_2O yields are very similar to that shown in Fig. 4. Compared to similarly treated bulk Ru, the present catalysts differ mainly by the substantially higher low-temperature peak in the NH_3 yield. This is the peak which was ascribed to CO-assisted NH_3 formation. It may be significant in this respect that highly dispersed Ru catalysts chemisorb up to two or three CO molecules per surface Ru atom, whereas bulk Ru adsorbs only one CO (*9,12*).

On these finely dispersed Ru catalysts,

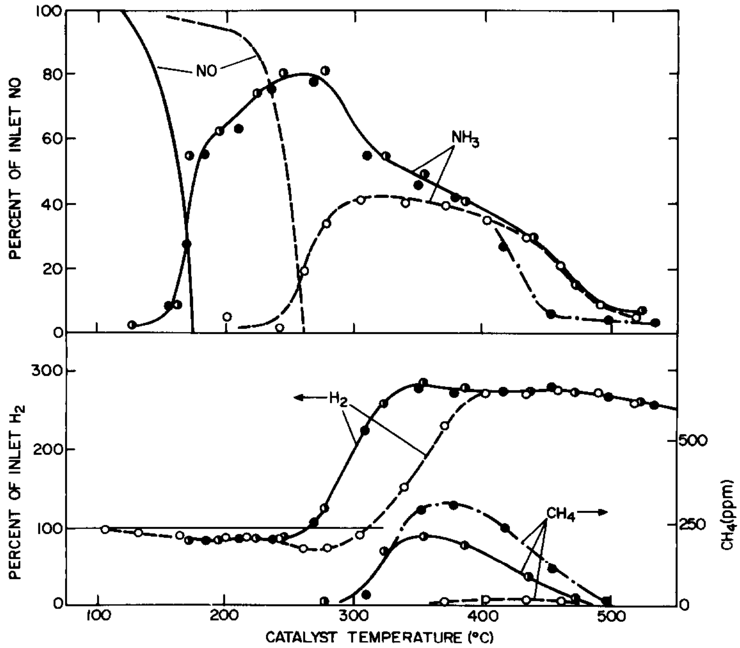

FIG. 5. Conversion of mixture W, over Ru/alumina. (--) Ru/γ-AlOOH, Cat II (○); (—) Ru/γ-Al_2O_3, CAT IIIA (●) and CAT IIIB (◐). GHSV 18,000 hr^{-1}.

the watergas shift reaction starts at 250°C. Its start correlates with a drop in the NH_3 yield. This substantiates earlier observations (*5,14*) that in the temperature range where NH_3 formation is assisted by CO, conversion of CO by the shift reaction decreases the NH_3 yield.

Treatments of the catalyst for periods of up to several days in mixture W at temperatures up to 630°C are expected to yield the RDN-Ru (*3*), in particular in view of the fact that the same catalyst after repeated oxidation and reduction under similar conditions eventually does show the dual state behavior. However, the present reduced state shows little NH_3 formation at 500°C and active H_2 formation from the shift reaction at $T \geqq 250°C$, unlike the RDN-Ru (Fig. 4 and Refs. (*1,3*).

An effort was made to contribute to the knowledge of the mechanism of the conversion of NO on this reduced state by studying the yields of the conversion products as a function of space velocity. A fresh sample of $Ru/\gamma\text{-}Al_2O_3$ (CAT IV) was treated with mixture W at 620°C for 15 hr (CAT IVA). It then showed a catalytic profile (yields of NH_3 and H_2) which was virtually identical to that shown by the solid curves in Fig. 5. The CH_4 yield corresponded to that of the higher CH_4 curve in Fig. 5. The N_2 and N_2O yields were similar to those in Fig. 4 and have been reported earlier [Ref. (*5*), Fig. 1]. The space velocity effects in Fig. 6 are for 212°C (solid curves) and 401°C (broken curves). These temperatures correspond approximately with the maxima of the first NH_3 peak and the N_2O peak for 212°C and of the second NH_3 peak and the CH_4 peak for 401°C.

At 212°C the N_2O/N_2 ratio is markedly dependent on the space velocity, increasing by a factor 2.5 for an increase of GHSV from 4000 to 38,000 hr^{-1}. This is in line with the proposed intermediacy of N_2O in part of the N_2 formation. At the same time, the NH_3 yield drops from 80 to 60%, which might indicate that reaction of N_{ads} with NO_{ads} is somewhat faster than

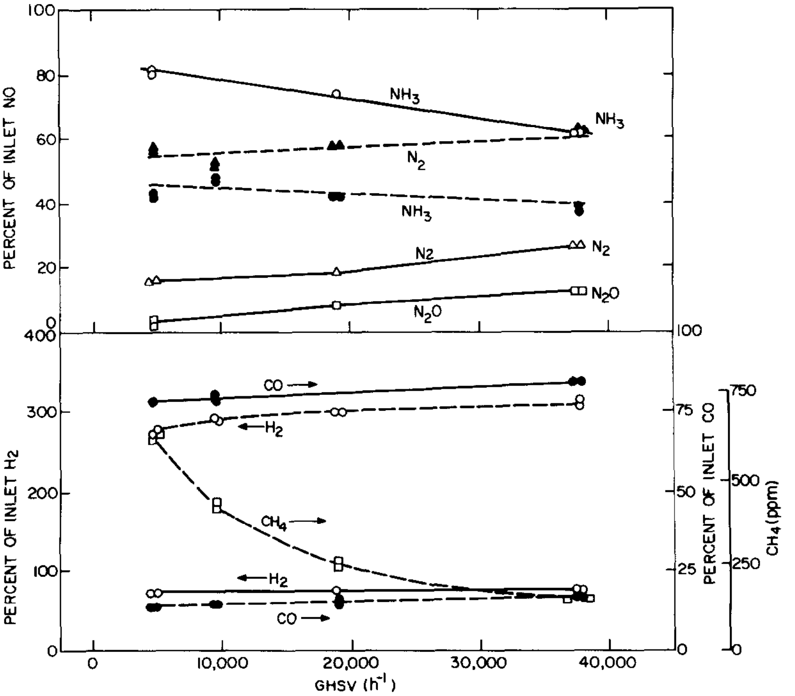

FIG. 6. Effect of space velocity on the conversion of mixture W over $Ru/\gamma\text{-}Al_2O_3$ (CAT IVA). (—) 212°C, (--) 401°C.

the reaction of N_{ads} with CO_{ads} and hydrolysis to NH_3. At any rate, a gas-phase NH_3 intermediate is unlikely. The last conclusion holds also for 401°C, where the variations of the NH_3 and N_2 yields are insignificant. A similar conclusion was reached for the RDN-Ru/SiO_2–Al_2O_3 (*3*). The CH_4 content strongly decreases with increasing space velocity at 401°C. However, the CH_4 yield (mole/hr) calculated from the product of the space velocity and the CH_4 content of the effluent actually increases by a factor 2 between GHSV 4000 and 38,000 hr^{-1}. Since the partial pressures of H_2 and CO are not changing sufficiently to account for this even if, for the sake of argument, the rate is supposed to vary with $p_{CO} \times p_{H_2}{}^3$, it must be assumed that another constituent, perhaps NO, plays a role in the CH_4 formation.

Development of the Dual State Nature of Ru/γ-Al_2O_3

Fresh Ru/γ-Al_2O_3 catalysts after air exposure are easily reduced to a reduced state which is active in the watergas shift reaction and which does not promote NH_3 formation at 500°C and above. The reduced state of the fresh catalyst is thus very different from the more extensively used RDN-Ru catalysts and in fact resembles more closely the reduced state of bulk Ru. It is therefore of interest to report in some detail the development of the dual nature behavior. The relevant series of experiments is shown in Fig. 7. A fresh sample of CAT IV, which had been prereduced in H_2 at 600°C, exposed to air and reduced in mixture W at ascending temperature up to 530°C showed behavior closely similar to the fresh reduced state in Fig. 5, as shown in Fig. 7 (Run No. 2, broken curves). After a few days' use in mixture W at varying space velocities at temperatures up to 540°C, the NH_3 yield had changed somewhat (Fig. 7, Run No. 5) but the NH_3 yield at 500°C was still very low and the activity in the watergas shift reaction (H_2 formation) has not changed. Subsequent oxidation at 540°C for 10 min in pure O_2 at 50 cm^3/min and flushing with pure He for 30 min at 540°C yielded the activity profile of Run No. 6, measured at descending temperature. Subsequently, the oxidation treatment was repeated in mixture W to which 1.7% O_2 was added (10 min at 540°C) and the activity was measured at descending temperatures (Run No. 7). It is quite clear that oxygen treatment has not affected the NH_3 yield at all, while the watergas shift activity is somewhat decreased and the CH_4 formation is almost eliminated.

At this point, when efforts to produce the dual state behavior by oxidation or reduction consistently led to behavior associated with the ODN-Ru catalysts described earlier (*1*), the catalyst was reduced in a flow of 100 cm^3/min of pure dry H_2 at 500°C for 3 hr, cooled in H_2 and kept in the H_2 flow at 25°C for 48 hr (CAT IVB). Subsequently, Run Nos. 8 and 9 (Fig. 7) were measured at ascending temperatures. The watergas shift activity had decreased significantly, as expected on the basis of the earlier reports, but the NH_3 formation has diminished instead of increased, with NH_3 yield at 500°C practically nil, again behavior which is associated with the ODN-Ru catalysts described earlier. The profile in Fig. 7 is stable at the temperatures (<520°C) reached in Run Nos. 8 and 9. It is only after heating for 16 hr at 600°C in mixture W (CAT IVC) that the NH_3 yield finally increased, especially in the range of 400–550°C. There was no increase in the overall NO conversion activity. In this way, the pattern of the RDN-Ru catalyst developed as shown in Fig. 4 (solid curves). This was easily converted into the ODN-Ru catalyst by treatment for 10 min at 540°C with mixture W to which 1.7% O_2 had been added (CAT IVD, Fig. 4, broken curves).

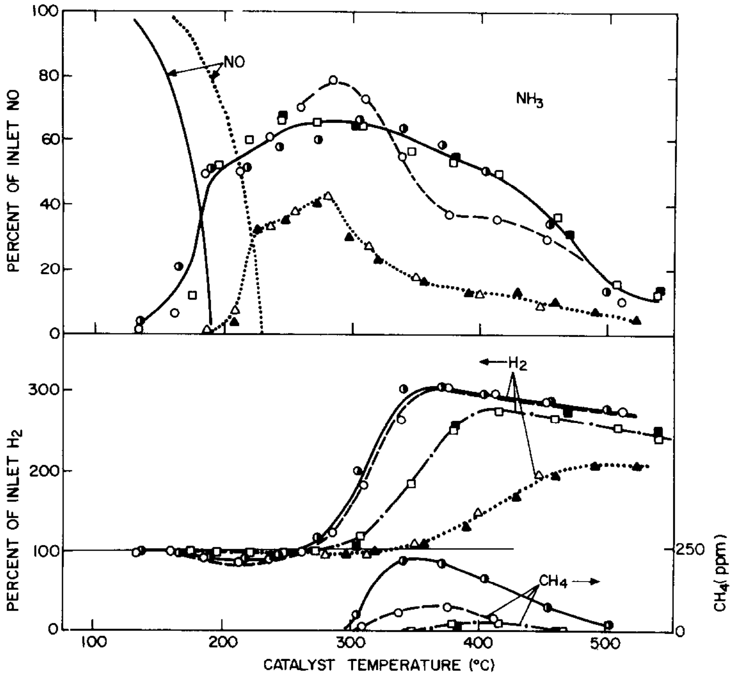

FIG. 7. Development of the dual nature of Ru/γ-Al_2O_3. Conversion of mixture W. GHSV 18,000 hr^{-1}. (○) CAT IV, run No. 2; (◑) CAT IV, run No. 5; (□) CAT IV, run No. 6; (■) CAT IV, run No. 7; (△) CAT IVB, run No. 8; (▲) CAT IVB, run No. 9; see text.

Proposed Explanation of the Dual Nature Effect

The explanation of the dual nature effect has been sought in redispersion effects brought about by the oxygen treatment (*7*). Some redispersion is indeed indicated by the increase in overall NO activity resulting from the oxygen treatment (Fig. 4). However, there is no correlation between the particle size of the Ru and the observation of the ODN-Ru behavior. The latter is exhibited by bulk Ru (Fig. 1), and by Ru/γAl_2O_3 with particles of at least 500 Å as in Fig. 4 (this size determination was done for the oxygen treated catalyst), but is also shown by Ru/γ-Al_2O_3 with particles of 100–500 Å (Fig. 7) or with particles of < 100 Å (Fig. 5).

On the other hand, the RDN-Ru behavior cannot be reached even by *in situ* reduction of bulk Ru in pure H_2 followed by treatment in mixture W for 17 hr at 620°C, and is only reached with difficulty on a Ru/γ-Al_2O_3 catalyst by H_2-reduction *in situ* at 500°C if followed by protracted use in mixture W above 520°C.

It is proposed that the deciding feature of the RDN-Ru catalysts is surface contamination by a nitrogen-containing layer, possibly a Ru-nitride layer (*22*). It must be assumed that formation of this layer is inhibited when the surface contains oxygen and only forms relatively slowly in mixture W at high temperatures where the surface is depleted of oxygen and NH_3 is not sufficiently stable to carry the N off the surface at the low H_2 partial pressure used. The stability of bulk Ru against the formation of the RDN (i.e., nitrogenated) state may be due to diffusion of oxygen from the bulk to the surface or to the difficulty for N atoms to penetrate the surface (*23*). The deciding disadvantage of the reduced state, its promotion of NH_3 formation at 500°C and higher, would be readily understood from the low activity of metal nitrides for NH_3 decomposition (*24*). Oxygen treatment is assumed to remove the nitrogen from the surface as NO or NO_2. The oxidation of Ru nitride should occur readily at 500°C. The greater difficulty experienced by us in obtaining the RDN-Ru state as compared with earlier workers (*1,3*) may be due to the fact that we used a He diluent rather than N_2. N_2 is adsorbed on finely dispersed Ru after reducing pretreatments (*22,25,26*) and could possibly serve as an additional source of N atoms for nitriding the surface. It is significant that N_2 is a stable ligand on Ru complexes (*27*).

If the explanation of the RDN behavior as being due to nitrogen covering the surface is correct, it may be expected that incorporation of K or K_2O impurities in the catalyst plays a role, since promotion of Ru catalysts with alkali leads to enhanced establishment of equilibrium of the N_2-H_2-NH_3 system (*16,28*) and enhances the adsorption of nitrogen on Ru (*29*). In bulk Ru, these impurities are not present, but they may be derived from the Al_2O_3 in the supported samples.

The reduced state produced by treatment of Ru catalysts with SO_2 (*3,20*) is similarly promoting NH_3 formation in mixture W at $T \geqq 500$°C. However, this sulfided reduced state is different from the nitrided reduced state in that the former eliminates the CO-assisted NH_3 formation as well as the NCO^- ir band, whereas the nitrided state still shows high activity for NH_3 formation at low temperature.

Effect of Ru Particle Size on NH_3 Yield

It may be noted that the low-temperature NH_3 maximum for all these catalysts showing the oxidized state is correlated with the particle size, increasing from 50% (bulk Ru) to 65% (≧500 Å), to 79% (100–500 Å), to 82% (< 100 Å). This is as expected for the CO-assisted NH_3 formation since the number of CO molecules adsorbed per Ru surface atom increases with decreasing particle size (*9,12*).

CONCLUSIONS

The formation of NH_3 in the conversion of NO-CO-H_2-H_2O-CO_2-He over Ruthenium catalysts proceeds mainly through a CO-assisted mechanism at low temperature ($T < 300$°C), and mainly through a H_2-assisted mechanism not involving CO

TABLE 2

Characteristic States of Ruthenium/Alumina Catalysts

Name	Surface[a]	50% NO converted[b] at T (°C)	NH_3 yield[b] (% of NO inlet) 175–275°C	275–450°C	>450°C	Shift reaction 200% H_2 at T (°C)	Stable[b] in mix W, up to T (°C)
α	Reduced, H_2 at 600°C	215	30–40	~20	<10	460	≧500
β	Oxidized, exposed to air	245	≲30	~40	<10	350	<400
γ	Some oxygen coverage[c]	175	60–80	~40	<10	300–350	>630
δ	Nitrogen covered[c]	200	~50	~30	~25	>530	>530
ε	SO_2 treated[cd]	260	≲30	~40	~30	>530	—

[a] See text.

[b] Under test conditions: mixture W, GHSV 18,000 hr^{-1}.

[c] RDN-Ru is in the δ or ε states, ODN-Ru is in the γ-state.

[d] Ref. (*20*).

at high temperature (300–500°C). The CO-assisted mechanism becomes increasingly important as the Ru particles become smaller.

The dual nature of ruthenium catalysts develops through the interaction of small, well-reduced ruthenium particles ($d \leqq 500$ Å) with the $NO-CO-H_2-H_2O-CO_2-He$ mixture. It is suggested that nitrogen incorporated in the ruthenium surface is responsible for the high NH_3 production and low NH_3 decomposition activity at $T \geqq 500°C$ associated with the "reduced state" of dual nature catalysts. The presence of oxygen in the surface passivates it for nitrogen incorporation and under oxidizing conditions the surface nitrogen is removed, restoring the "oxygen treated" state of the catalyst. Catalysts which are thoroughly reduced *in situ* in hydrogen show very low NH_3 formation, but this condition is not stable. An overview of the properties of the various "states" of Ru is given in Table 2.

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