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The Dual State Behavior of Supported Noble Metal Catalysts

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In earlier NO reduction studies, difficulties in reproducing results with ruthenium catalysts were traced to some rather unusual pretreatment effects which were able to generate two states for ruthenium catalysts which differed in activity characteristics. This dual state behavior has subsequently been observed for other noble metal catalysts in a variety of reactions. The effect is most dramatic for the water–gas shift reaction, but was also observed for the CO–H_2 reaction, ammonia decomposition, and nitric oxide reduction. It was found that sulfur contamination eliminated the effect for ruthenium but not for platinum and palladium catalysts. Chemisorption measurements have shown that the effect is not a simple function of metal loading or dispersion. A mechanism involving surface reconstruction and/or metal–support interaction is proposed.

INTRODUCTION

Recent studies have shown that ruthenium catalysts promote the reduction of NO to N_2 with low NH_3 formation using feedstreams typical of auto exhaust (*1–4*). The complex nature of exhaust provides for several reactions to occur simultaneously and the relative concentrations of the reacting gases is a critical factor in determining the resultant product distributions (*3*). To further complicate the situation, the activity of the ruthenium catalysts in these reactions was dependent upon the catalyst pretreatment (*2*). Conversion of the catalyst between two activity states was reversible and accomplished by oxidizing or reducing the catalyst. Examination of the individual reactions which may be thought to occur in an exhaust converter revealed that catalyst reduction above 535°C leads to the exclusion of two of the reactions; namely, the water–gas shift reaction and ammonia decomposition (*3*).

This paper describes a series of experiments aimed at further characterizing this pretreatment dependent behavior of the ruthenium catalyst. Selectivity changes are compared for platinum, palladium, and ruthenium catalysts to see to what extent these properties are peculiar to ruthenium. Furthermore, several reactions are examined for which these catalysts exhibit the dual state activity. The dependence of catalytic activity on metal dispersion and metal loading on the alumina support was examined to determine to what extent the dual state behavior was dependent upon oxide formation, availability of metal sites, and metal–support interaction. The two states of the catalyst are referred to here by their method of preparation, oxidized or reduced, though it will be shown later that this terminology is not an accurate description of the dual states.

EXPERIMENTAL METHODS

The apparatus used to measure catalytic activity was described previously (*5*). Nondispersive ir (Beckman) provided continuous measurement of NO, CO, CO_2, and N_2O. A nondispersive uv instrument gave continuous analysis of NO_2. Oxygen was measured with a Beckman process oxygen monitor. The NH_3 was measured by the increases in the NO level following oxidation over a platinum catalyst (*5*). Hydrocarbon formation was monitored with a flame ionization detector. The gas hourly space velocity (GHSV) was generally 38,000 hr^{-1}. The feedstream referred to as the standard feedstream contained 0.1% NO, 1.0% CO, 0.3% H_2, 10% CO_2, and 10% H_2O in a N_2 atmosphere and simulates automotive exhaust gas. The catalysts were heated to 620°C and held for 30 min in the reactor in the standard feedstream prior to use. The temperature of the reactor was then lowered in steps and data points were taken for steady-state conversion at each temperature. Several points were checked in an increasing temperature sequence.

The apparatus used for the adsorption measurements was a conventional Pyrex vacuum system except for the dosing volume. The dosing volume of 15.59 cc consisted of the space between 3 Hoke bellows valves joining the vacuum line, gas inlet line, and sample cell with a connection to a MKS Baratron pressure gauge. The sample cell which was a Pyrex U-tube connected to the vacuum line via a Swagelok fitting had a needle valve on the other end to permit pretreatment of the catalyst under flowing hydrogen. The hydrogen was passed through a purifier (Bishop, Model A-1-DH) and Research Grade oxygen (Matheson) was used as received. Matheson UHP helium, which was used for the dead space measurements, was purified by passing it through a charcoal trap at −195°C. The weight of catalyst samples used in the adsorption experiments ranged from 1 to 5 g. The standard technique for pretreating the catalysts was reduction in hydrogen for 2 hr at 400°C followed by evacuation for 2 hr at the same temperature. Oxygen adsorption isotherms determined at room temperature and extrapolated to zero pressure were used as a measure of the ruthenium surface area (*6*). The stoichiometry of the oxygen chemisorption was found to be Ru:O by comparing the oxygen chemisorption result with the BET surface area for a sample of ruthenium powder and taking 9.03 $Å^2$ for the area occupied by a surface ruthenium atom (*7*). For ruthenium dispersions greater than 40%, that is greater than 40% of the metal atoms are surface atoms, surface areas were measured by hydrogen chemisorption at 100°C since oxygen uptake exceeded monolayer coverage for the smaller particles. We will report on the particle size dependence of the hydrogen/oxygen chemisorption ratio for supported ruthenium catalysts in a future publication (*8*). Crystallite sizes 1 were calculated from the surface areas from the relation $1 = 6/Sd$, where S is the surface area and d is the density of the metal.

The supported ruthenium catalysts used in this work were made up to contain 0.02 to 1.0% by weight of the metal. The catalysts were prepared by impregnating preformed alumina spheres (Kaiser KC/SAF, surface area = 260 m^2/g) with aqueous solutions of ruthenium chloride ($RuCl_3 \cdot 1\text{–}3\ H_2O$, Alfa Inorganics). The platinum and palladium catalysts were made by impregnating alumina spheres with aqueous solutions of chloroplatinic acid (10% solution $H_2PtCl_6 \cdot 6H_2O$, Matheson, Coleman, and Bell) and palladium chloride (5% solution $PdCl_2$, Matheson, Coleman, and Bell), respectively. After impregnation, the catalysts were all dried in air overnight. The dried catalysts were calcined in an air stream (GHSV = 500 hr^{-1}) for 4 hr at 500°C. Several ruthenium catalysts were calcined in 5% hydrogen in N_2 at 500°C instead. The metal loading was determined for each catalyst by X-ray fluorescence. The ruthenium sponge (Johnson Matthey Chemicals, Ltd., 99.99%) was used as received.

RESULTS AND DISCUSSION

In earlier work, it was found that the two forms of Ru/Al_2O_3 behaved differently in NO reduction (*2*). Thus, oxidized Ru/Al_2O_3 is more selective for N_2 formation and, in addition, is quite active in converting CO in the standard NO catalyst screening feedstream mentioned above. The two forms of the catalyst differ very little in their activity for NO removal.

In view of the complexity of the reactions that occur with this feedstream, the various reactions were examined separately.

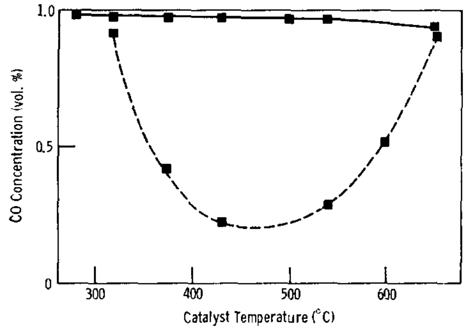

FIG. 1. The water-gas shift reaction over 0.081% Ru/Al_2O_3. Feedstream: 1.0% CO, 10% CO_2, and 10% H_2O in a N_2 atmosphere, GHSV = 38,000 (- - - -) oxidized catalyst; (———) reduced catalyst.

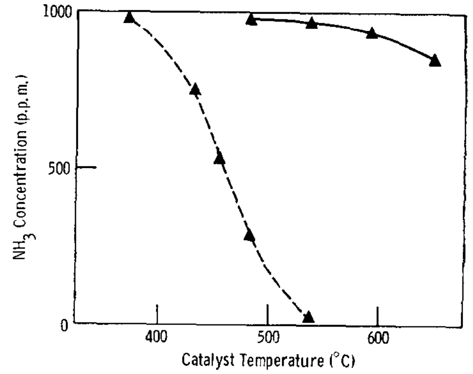

FIG. 2. Ammonia decomposition over 0.081% Ru/Al_2O_3. Feedstream: 1000 ppm NH_3 and 10% H_2O in a N_2 atmosphere, GHSV = 38,000 (- - - -) oxidized catalyst; (———) reduced catalyst.

The most striking difference between the two states of Ru/Al_2O_3 is shown in Fig. 1. Oxidized Ru/Al_2O_3 is active for the water-gas shift reaction, Eq. (1),

$$CO + H_2O = CO_2 + H_2, \qquad (1)$$

while the reduced form is essentially inactive for this reaction. This is not simply a space velocity effect since reduced Ru/Al_2O_3 was also inactive for this reaction at much lower space velocity, i.e., 9500 hr^{-1}.

To account for the difference in product distribution for NO reduction, the activities of these two catalysts were examined for ammonia decomposition (2) in the presence of water, Eq. (2),

$$2\ NH_3 \rightarrow N_2 + 3\ H_2. \qquad (2)$$

As in the previous reaction, oxidized Ru/Al_2O_3 is active for ammonia decomposition while reduced Ru/Al_2O_3 shows only the very low ammonia decomposition activity characteristic of the support alone (Fig. 2). It was shown recently that this reaction accounts very well for the selectivity difference for these catalysts in NO reduction (*9*).

A third reaction that showed the same phenomenon is the reaction of CO and H_2 to form hydrocarbon. Thus, oxidized Ru/Al_2O_3 forms hydrocarbon with considerable efficiency while hydrocarbon formation is nil over the corresponding reduced Ru/Al_2O_3 (Fig. 3). The addition of water to the feed stopped hydrocarbon formation over oxidized Ru/Al_2O_3 catalyst.

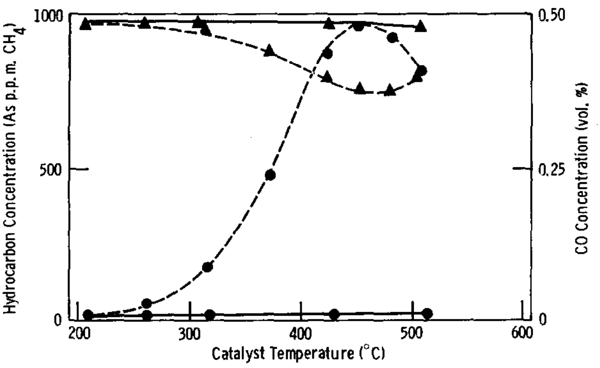

FIG. 3. Hydrocarbon formation over 0.081% Ru/Al_2O_3. Feedstream: 0.5% CO and 3.0% H_2 in a N_2 atmosphere, GHSV = 38,000 (- - - -) oxidized catalyst; (———) reduced catalyst; (○) hydrocarbon as CH_4, (△) CO.

The pretreatment conditions which resulted in the two activity states were examined in some detail. In the preparation of Ru/Al_2O_3, the more active or oxidized catalyst is formed because the calcination step is carried out in flowing air. Heating the catalyst in air at 500°C is then one way to form the oxidized Ru/Al_2O_3. The less active or reduced form of the catalyst is obtained by treating the catalyst with CO or H_2 at 650°C for 0.5 hr. The fact that both reducing agents produced the same effect argues against the possibility of deactivation due to metal poisoning by carbon. Heating the catalyst at 650°C in nitrogen did not give the reduced form of the catalyst which suggests the effect is not merely a thermal effect. The oxidized state can be regenerated quite easily by passing a feedstream containing a small excess of oxygen (e.g., 10% O_2) over the catalyst for 10 sec at temperatures of 200°C or above. Both NO and N_2O in the absence of excess reducing agent can be substituted for oxygen but require temperatures above 300°C. The reactions were studied directly on the oxides following the oxidation without a deliberate reduction step. The question pertaining to whether the catalyst remains oxidized in the presence of the reducing standard feedstream is dealt with below. If the catalyst is exposed to sulfur compounds (either SO_2 or H_2SO_4) the oxidized state of Ru/Al_2O_3 can no longer be generated.

In most cases, the conversion of the catalyst between the two states was reversible. The ease of conversion was examined with two reducing feedstreams. The instability of the oxidized state of the 0.086% Ru/Al_2O_3 catalyst was investigated by measuring the time required to convert the oxidized catalyst to the reduced form at 535 and 650°C. The time for the conversion using a CO(1.0%)-CO_2(10%)-H_2O(10%) in N_2 feedstream and monitoring the level of CO removal was 137 and 35 min at 535 and 650°C, respectively. Using a NO (0.1%)-H_2 (1.0%)-H_2O (10%) in N_2 feedstream and monitoring the level of NH_3 formation, the time for conversion to the reduced state was 120 and 80 min at 535 and 650°C, respectively. The results show that the oxidized catalyst is readily converted to the reduced catalyst at 650°C and moreover that at 535°C steady-state conversion is not achieved with the oxidized catalyst. The stability of the reduced state was not improved by reduction in H_2 for 18 hr at 730°C compared to 10 min at 650°C with H_2. Both catalysts responded similarly to oxygen treatment at 535°C.

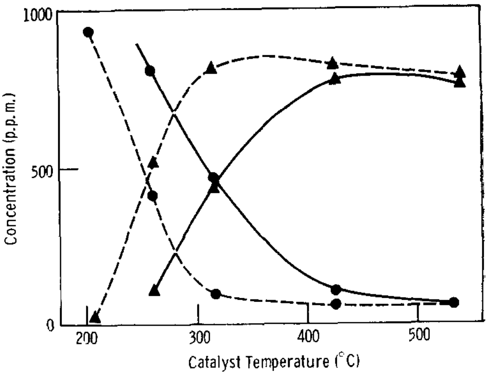

FIG. 4. The dual state behavior of 0.3% Pt/Al_2O_3 for nitric oxide reduction. Standard feedstream; GHSV = 38,000 (- - - -) oxidized catalyst; (———) reduced catalyst; (○) NO, (△) NH_3.

The dual state behavior for these reactions was not a property of the ruthenium catalyst alone. Supported platinum and palladium catalysts which were in the less active state following reduction in the standard feed stream at 650°C for 30 min were also changed to a more active form by treatment with an oxidizing atmosphere at 535°C (Figs. 4 and 5). In this case, how-

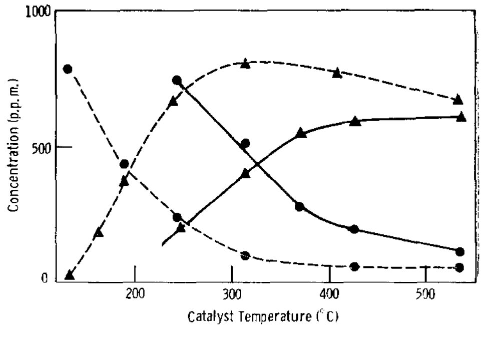

FIG. 5. The dual state behavior of 0.3% Pd/Al_2O_3 for nitric oxide reduction. Standard feedstream; GHSV = 38,000 (- - - -) oxidized catalyst; (———) reduced catalyst; (○) NO, (△) NH_3.

ever, the oxidized catalyst showed enhanced activity for nitric oxide removal. The temperature required for 50% NO removal was lower by 50 and 140°C for the platinum and palladium catalysts, respectively, after the oxygen treatment. These catalysts contained 0.3% of the precious metals. It should be noted that the 0.081% Ru/Al_2O_3 catalyst did not show enhanced activity for NO removal in the oxidized state. It is shown below, though, that the temperature for NO reduction is dependent on metal loading.

The water–gas shift reaction was examined over several platinum catalysts. A 0.1% Pt/Al_2O_3 catalyst showed a pronounced dual state behavior for CO removal (Table 1) whereas the 1.0% Pt/Al_2O_3 catalyst exhibited greater activity which did not appear to depend on pretreatment.

The oxidized forms of 0.1% Pt/Al_2O_3 and 0.1% Pd/Al_2O_3 promote the CO–H_2 reaction to form hydrocarbon (Table 2). As with ruthenium, the reduced form of these catalysts were devoid of activity for this reaction. The alumina support was inactive for this reaction also. Similar differences were found for ammonia decomposition over 0.1% Pt/Al_2O_3 (Fig. 6), but the reaction did not go well over either form of the catalyst.

TABLE 1
CARBON MONOXIDE REMOVAL

Catalyst	% CO removal[a] (425°C)	% CO removal[b] (425°C)
0.081% Ru/Al_2O_3		
Reduced	0.09	0.01
Oxidized	0.59	0.77
1.0% Pt/Al_2O_3		
Reduced	0.49	0.50
Oxidized	0.52	0.60
0.3% Pt/Al_2O_3		
Reduced	0.17	
Oxidized	0.31	
0.1% Pt/Al_2O_3		
Reduced		0.11
Oxidized		0.28
0.3% Pd/Al_2O_3		
Reduced	0.13	
Oxidized	0.21	

[a] Feedstream: 0.1% NO, 1.0% CO, 0.3% H_2, 10% CO_2 and 10% H_2O in a N_2 atmosphere; GHSV = 38,000.

[b] Feedstream: 1.0% CO, 10% CO_2, and 10% H_2O in a N_2 atmosphere; GHSV = 38,000.

TABLE 2
HYDROCARBON FORMATION OVER Ru, Pt, AND Pd CATALYSTS

Catalyst	Maximum hydrocarbon formation (ppm)[a] Oxidized	Reduced
0.081% Ru/Al_2O_3	970 (450°C)	0
0.1% Pt/Al_2O_3	180 (535°C)	8 (535°C)
0.1% Pd/Al_2O_3	330 (535°C)	0

[a] Feedstream: 0.5% CO, 3.0% H_2, and the balance N_2; GHSV = 38,000.

Treatment of the 0.3% Pt/Al_2O_3 catalyst with sulfuric acid initially eliminated activity for NO reduction with the standard feedstream; however, the activity was recovered following reduction at 650°C in the standard feedstream. Then unlike ruthenium the dual state behavior of the platinum catalyst can be recovered following the sulfur treatment.

The dual state behavior of the ruthenium, platinum, and palladium catalysts as de-

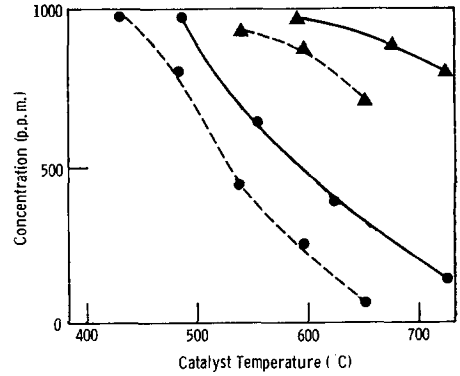

FIG. 6. Ammonia decomposition over 0.1% Pt/Al_2O_3. Feedstream: (○) 1000 ppm NH_3 in a N_2 atmosphere. (△) 1000 ppm NH_3 and 10% H_2O in a N_2 atmosphere, GHSV = 38,000 (- - - -) oxidized catalyst; (———) reduced catalyst.

scribed here was apparent from the difference in catalyst activity before and after high temperature reduction. It is, therefore, necessary to consider the possible effects of both the oxidation and the reduction in exploring this phenomenon. Experiments were carried out for the purpose of assessing the possible contribution of metal dispersion, oxide formation, and metal–support interactions to the dual state behavior of the catalysts.

To determine whether the dual state activity is dependent on the metal loading, several catalysts were made up with both higher and lower loadings of the precious metal. The metal content and metal surface areas for a series of ruthenium catalysts appear in Table 3. A decrease in dispersion, increase in particle size, and increase in ruthenium surface area accompanies the increase in ruthenium content of the Ru/Al_2O_3 catalysts which were all calcined in air at 500°C. No surface area is given for the 0.016% Ru/Al_2O_3 catalyst since the chemisorption technique does not measure this low level of ruthenium accurately. This catalyst showed two activity states for CO removal (Fig. 7) from the standard feedstream but did not start to remove NO until 290°C. The temperature dependent product distributions obtained for the standard feedstream with 0.37% and 0.82% Ru/Al_2O_3 are shown in Figs. 8 and 9, respectively. The 0.37% Ru/Al_2O_3 catalyst clearly showed two states, whereas reduced states were not obtained for the higher loaded ruthenium catalyst (0.82% Ru)

TABLE 3

RUTHENIUM CATALYSTS

Ru content (% by wt)	Dispersion	Specific surface area (m^2/g)	Crystallite size^b (Å)
0.016	—	—	—
0.081	0.12^a	0.05	73
0.37	0.091^a	0.18	102
0.82	0.063^a	0.28	142
0.40^c	0.40^e	0.87	23
0.086^c	0.55^e	0.26	16
0.086^{c,d}	0.33^a	0.15	28

[a] Determined by O_2 adsorption at room temperature.

[b] Assume $l = 6/Sd$.

[c] Ru Cl_3 decomposed in H_2.

[d] Surface area determined following oxidation and reduction at 400°C.

[e] Determined by H_2 adsorption at 100°C.

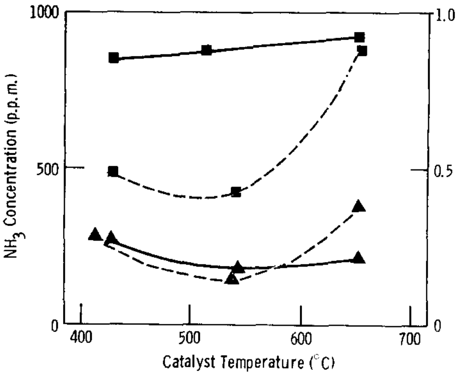

FIG. 7. The dual state behavior of 0.016% Ru/Al_2O_3 for nitric oxide reduction. Standard feedstream; GHSV = 38,000 (- - - -) oxidized catalyst; (———) reduced catalyst; (□) CO, (△) NH_3.

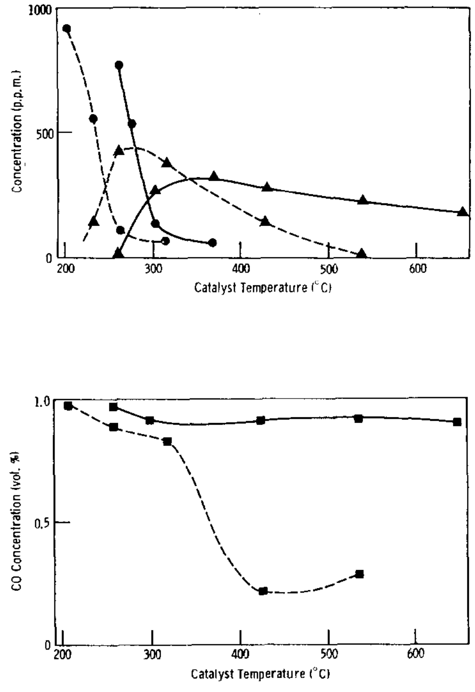

FIG. 8. The dual state behavior of 0.37% Ru/Al_2O_3 for nitric oxide reduction. Standard feedstream; GHSV = 38,000 (- - - -) oxidized catalyst; (———) reduced catalyst; (○) NO, (△) NH_3, (□) CO.

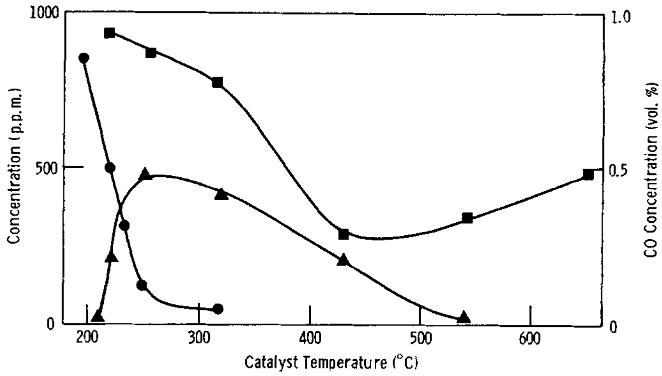

FIG. 9. Nitric oxide reduction over 0.82% Ru/Al_2O_3. Standard feedstream; GHSV = 38,000 (○) NO, (△) NH_3, (□) CO.

after 30 min at 650°C in a reducing atmosphere. It is possible that these conditions are not severe enough.

The specific activity of the oxidized catalysts for NO reduction at 232°C expressed as turnover numbers was determined by taking the ratio of the NO reacted per second to the number of metal sites calculated from the surface areas of the catalysts (Table 4). The lower temperature for NO reduction with increasing catalyst ruthenium content is shown to be due to the greater metal surface area with these catalysts since the specific activity expressed here as turnover numbers is essentially constant. The large magnitude of these turnover numbers is an indication of the high activity of the ruthenium for NO reduction.

TABLE 4
SPECIFIC ACTIVITY OF RUTHENIUM CATALYSTS AT 230°C

Catalyst	NO reacted[a] (ppm)	Metal area (m^2/g)	Turnover no. (sec^{-1})
0.081% Ru/Al_2O_3	100	0.054[b]	0.10
0.37% Ru/Al_2O_3	440	0.18[b]	0.13
0.82% Ru/Al_2O_3	690	0.28[b]	0.13
0.086% Ru/Al_2O_3	200	0.15[c]	0.07
0.40% Ru/Al_2O_3	860	0.87[b]	0.07

[a] Feedstream: 0.1% NO, 1.0% CO, 0.3% H_2, 10% CO_2, 10% H_2O, N_2 atmosphere; GHSV = 38,000.

[b] Surface area of fresh catalyst.

[c] Surface area following oxidation at 400°C then reduction in H_2 at 400°C.

The metal dispersion of the alumina supported ruthenium catalysts was greater by a factor of four if the decomposition of the ruthenium chloride following impregnation was carried out in H_2 rather than in air (Table 3). The catalysts prepared by this technique were also used to look for effects of metal dispersion on activity for NO reduction. The specific activity of these catalyst for NO reduction expressed as turnover numbers was the same as for catalyst with lower ruthenium dispersion (Table 4). This result shows that there are no crystallite size effects on the reduction. Though the measurements of the specific activity offer an explanation for the shift in the NO removal temperature with metal loading, they do not point to the difference between the oxidized and the reduced states of the catalyst.

To examine the possibility that these transformations involve a reversible change in dispersion, chemisorption experiments were carried out after a high temperature (600°C) hydrogen treatment of the 0.081% Ru/Al_2O_3 catalyst. The specific surface area of this catalyst was the same as for a 200°C pretreatment. Furthermore, the metal area of the catalyst samples which had been oxidized and reduced in the reactor were not significantly different following a pretreatment at 300°C *in vacuo* in the adsorption apparatus. We, therefore, have no evidence that the dual state of the catalysts represents a difference in metal area arising from a pretreatment dependent redispersion or sintering of the precious metals. It should be noted though that we have observed by X-ray line broadening a decrease in ruthenium particle size following reduction in CO of a 2% Ru/Al_2O_3 catalyst sintered in oxygen.

The fact that this phenomenon exists for the platinum and palladium catalysts also argues against dispersion effects. Recent work (*10*) has shown that Pt and Pd dispersions respond in a completely different manner to high temperature hydrogen and oxygen treatments. Palladium dispersions are extremely stable in oxygen but unstable in hydrogen. The reverse is true for platinum but the changes are less dramatic. The chemisorption results for 0.086% Ru/Al_2O_3 (Table 3) suggest that ruthenium behaves like platinum rather than palladium in spite of the easy formation of volatile ruthenium oxide (*11*).

To determine whether the oxidized state of the catalyst is in fact an oxide, chemisorption experiments were carried out to titrate the surface oxygen. Table 5 shows H_2 uptake for Ru/Al_2O_3 catalysts which had been given various pretreatments. The fresh catalyst after calcination at 500°C in air apparently contains some oxidized ruthenium. RuO_2 was not detectable in this catalyst, but could be found in heavier loaded ruthenium catalysts. The chemisorption results suggest the formation of about three layers of oxide for the fresh catalyst. On the other hand, the H_2 uptake for the so-called oxidized Ru/Al_2O_3 corresponds to only about three quarters of a monolayer. H_2 uptake for reduced Ru/Al_2O_3 was not very different and also corresponds to less than an oxygen monolayer. The oxidized and reduced Ru/Al_2O_3 catalysts were prepared in the reactor so that the state of the catalyst could be identified. It was shown that reduced Ru/Al_2O_3 catalyst was stable in air at room temperature and was not transformed to the other catalytic state in the transfer from the reactor to the chemisorption apparatus. These results indicate that ruthenium does not exist as the oxide in oxidized Ru/Al_2O_3. On the other hand, these results cannot rule out some residual oxygen on the surface since the titrations were carried out at 100°C, whereas 650°C was required for the transformation to the reduced state in the reactor.

TABLE 5

H_2 UPTAKE AT 100°C ON 0.086% Ru/Al_2O_3 (Air Calcined)

Catalyst	H_2 uptake (μmoles/g)	Oxygen monolayers as O/surface Ru
Reduced Ru/Al_2O_3[a]	0.7	0
Reduced Ru/Al_2O_3 with oxygen monolayer[b]	2.0	1
Fresh Ru/Al_2O_3[c]	9.2	6.5
Reduced Ru/Al_2O_3[d]	1.5	0.61
Oxidized Ru/Al_2O_3[e]	1.7	0.78

[a] Reduced at 400°C in H_2 and evacuated at 400°C.

[b] Oxygen chemisorbed at 25°C and not removed by evacuation at 25°C.

[c] Following calcination in air at 500°C.

[d] Reduced in the reactor at 650°C in the standard feedstream then cooled to 25°C in N_2.

[e] Oxidized in the reactor at 535°C by adding a dose of oxygen to the standard feedstream then cooled to 25°C in N_2.

One possible explanation for the dual state behavior would suggest that oxidation (followed by low temperature reduction) causes a surface reconstruction which may involve some buried oxygen. The more severe reduction step then would involve removal of the residual oxygen or annealing of the surface and the return to the less active surface structure. This kind of process is also possible on platinum and palladium catalysts. As a matter of fact, Ostermaier, Katzer and Manogue (*12*) have recently suggested a similar effect to explain their results on ammonia oxidation over platinum catalysts. Interestingly, the oxygen treatment deactivated the catalyst for ammonia oxidation. Infrared studies have detected that oxygen pretreatment enhances H_2 adsorption on platinum (*13*, *14*) and alters CO bonding over palladium (*15*). This change in CO adsorption would perhaps explain the reactivity effects associated with NO removal since CO inhibits NO reduction over Pt and Pd but not over ruthenium (*3*).

A possibility which we cannot rule out

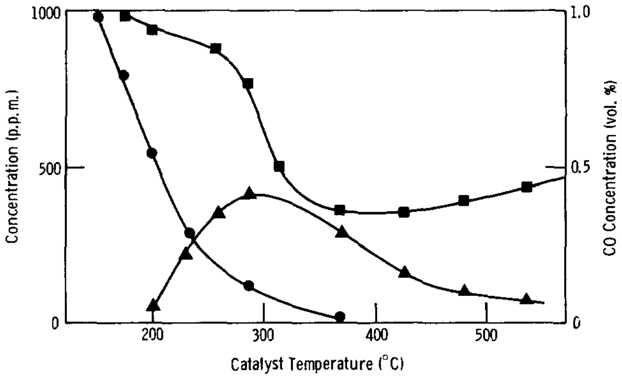

FIG. 10. Nitric oxide reduction over ruthenium sponge. Standard feedstream; GHSV = 272,000 (△) NH_3, (□) CO, (○) NO Sponge: 1.65 g, reduced.

is that the reduced catalyst is deactivated by interaction with the support and that the dual state activity arises from such an interaction. To look for this effect the catalytic activity of a sample of ruthenium sponge was examined for the reduction of NO in the standard feedstream. Figure 10 shows the product distribution obtained with the standard feedstream for 1.65 g of ruthenium which occupied 2.1 cc to give a GHSV of 272,000. The CO removal was not affected by a reducing pretreatment at 650°C in the standard feedstream or by oxidation at 535°C. The appearance of the oxidized state alone with the ruthenium sponge lends support to the hypothesis that the lower activity of the reduced state arises from interaction of the ruthenium with the support. However, it is not certain that more stringent conditions might be required for the reduction of bulk ruthenium. Deactivation by an impurity in the alumina support which can be removed by oxidation or reduction is unlikely since the state of a single catalyst sample was changed 10 times. Interestingly, the lower activity state is the only state observed with Ru/SiO_2. Amano and Taylor (*16*) have noted lower activity of Ru/SiO_2 catalysts vs Ru/Al_2O_3 for NH_3 decomposition.

CONCLUSIONS

The dual state phenomenon for alumina supported ruthenium catalysts has been extended to a number of new reactions. In addition, the phenomenon was shown to occur for platinum and palladium catalysts as well as ruthenium catalysts. Chemisorption studies indicate that the difference between the two states is not related to metal dispersion. Furthermore, the more active oxidized form of Ru/Al_2O_3 does not contain ruthenium oxide. It is suggested that the transformation to the more active oxidized catalyst state involves a reconstruction of the surface and/or destruction of inhibiting metal–support interactions.

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