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Reactivity and Microstructure of Rh and Rh–Ce in NO + CO[1]

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Changes in the activity and selectivity of Rh and Rh–Ce catalysts supported on Al_2O_3 and SiO_2 in the NO + CO reaction have been measured as a function of pretreatment. Rh–Ce/Al_2O_3 had very low activity following a pretreatment in H_2, which increased by a factor of ~10 after heating in NO, and increased further in CO and in NO + CO. Rh–Ce catalysts also had very low N_2 selectivity vs N_2O after treatments in H_2, CO, and NO + CO, but not after heating in air or NO, and had a lower activation energy for NO reduction than Rh catalysts. The activities of Rh/Al_2O_3 and Rh/SiO_2 catalysts correlate well with changes in microstructures. An increased dispersion produced an increased activity at low temperatures except for the air pretreatment which oxidized the Rh and produced the lowest activity. Selectivity to N_2 increased with increasing temperature below 300°C up to 100% for all pretreatments. All changes on alumina supported catalysts were reversible. The activity of Rh/SiO_2 decreased after heating in NO + CO because of volatilization of Rh. © 1994 Academic Press, Inc.

INTRODUCTION

The reaction between NO and CO is one of the most important reactions in the automotive catalytic converter because it eliminates two of the major pollutants. Rhodium is the metal primarily responsible for NO_x removal, and Ce is added to the catalytic converter as a promoter and stabilizer. The NO + CO reaction is a structure sensitive reaction on Rh (1), in that the rate is sensitive to the surface characteristics of the catalyst. Therefore, a change in microstructure would be expected to be accompanied by a change in rate. There are two possible reactions between NO and CO,

$$2\,NO + 2\,CO \rightarrow N_2 + 2\,CO_2,$$

which is desired, and

$$2\,NO + CO \rightarrow N_2O + CO_2,$$

which is not as desirable since N_2O is still a pollutant. However, this reaction might be an important intermediate step in the first reaction since N_2O can also react with CO (2),

$$N_2O + CO \rightarrow N_2 + CO_2,$$

a reaction which, unlike NO + CO, is not believed to be structure sensitive (3). Large amounts of Ce added to Rh have been shown to improve the selectivity and rate of NO + CO on alumina (4). Ce has also been shown to improve performance for CO hydrogenation on silica, but has little effect on ethane hydrogenolysis activity (5). Several mechanisms for Ce promotion have been proposed, including increasing the noble metal dispersion (6), providing oxygen storage by shifting between Ce_2O_3 under fuel-rich conditions and CeO_2 under fuel-lean conditions (7–9), promoting the water–gas shift reaction (10, 11), and stabilizing the alumina support (12). Ce has also been shown to hinder volatilization of Pt during high temperature oxidation (13) and loss of Rh in NO and CO at 300–400°C (14).

We have previously characterized the microstructures of Rh/Ce on SiO_2 and Al_2O_3 supports under reducing, oxidizing, and reaction conditions using transmission electron microscopy (TEM), high-resolution electron microscopy (HREM), electron energy loss spectroscopy (EELS), and X-ray photoelectron spectroscopy (XPS) (13–15). Substantial changes occur in the microstructures of Rh particles in NO and CO, including volatilization and dispersion of Rh particles. These changes are drastically different between alumina and silica supports. Previous studies had reported changes in the IR spectra of adsorbed CO on Rh (16), possibly due to the disruption of Rh particles in CO and acceleration of the disruption in NO + CO (17). This had been inferred from infrared spectroscopy (IR), XPS, and extended X-ray absorption fine structure (EXAFS), but had not been observed directly because of the very small size of the initial Rh particles. Cerium addition, which is examined in this paper, has been shown to retard the reductive agglomeration of Rh^1 to Rh_x, thus stabilizing disrupted Rh (18). Catalytic disruption has similarities to the transformations reported here, but several important differences exist. We report changes that occur at realistic reaction temperatures, 300

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to 400°C, and which would occur along with the reaction, while the other studies were conducted below 100°C with much smaller Rh particles.

Microstructures of Rh and Rh–Ce

Figure 1 shows a schematic diagram summarizing the microstructural evolution of Rh and Rh/Ce in H_2, air, NO, CO, and an NO + CO mixture as described from previous microstructure characterization by TEM, XPS, and EELS (5, 13, 14).

Without Ce, Rh forms metallic particles after heating in H_2 at 600°C on either support and this was the starting point for all TEM studies as indicated at the left in Fig. 1. Heating the sample in O_2 at 600°C oxidizes the Rh into Rh_2O_3 particles. In NO at only 300°C the Rh will disperse into small particles (on Al_2O_3) or form a thin film around the edges of the particles (on SiO_2). CO alone has very little noticeable effect on Rh particles but has a large effect after a treatment in NO. On Al_2O_3, CO causes the dispersed particles to sinter into the original particles leaving the microstructure very similar to before the treatments. However, on SiO_2, CO causes volatilization of the dispersed Rh at 300°C. Heat treatments in NO and CO mixtures have the combined effects of each species. The final effect is almost complete loss of Rh from SiO_2. This result was confirmed with EELS and EDS, which showed that no Rh remained on the TEM sample.

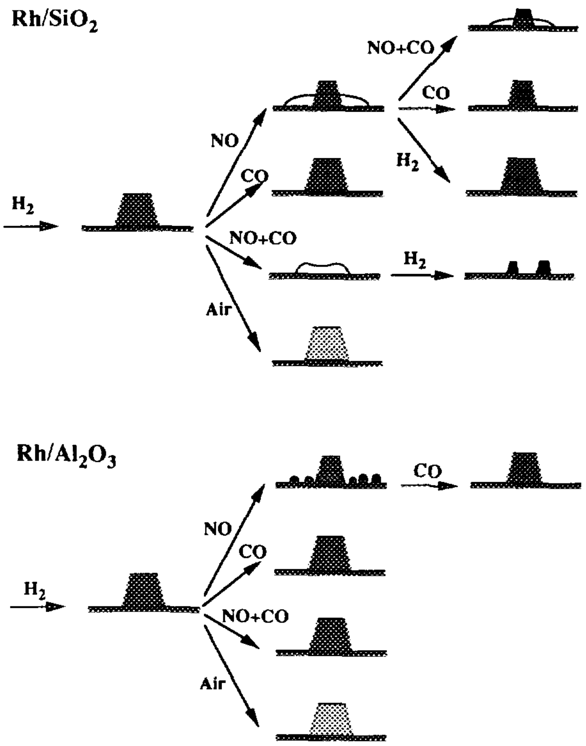

FIG. 1. Schematic of the microstructural changes of Rh particles after heating in NO, CO, NO + CO, and air.

Cerium has substantial effects on the Rh microstructure. Cerium lessens the effects of NO and CO treatments on either support. On Al_2O_3, Ce has little effect on the Rh microstructure during oxidation and reduction with H_2. However, Rh_2O_3 spreads into a thin layer on SiO_2 if Ce is present. Subsequent heating in H_2 causes Rh to sinter into particles larger than the initial Rh particles on SiO_2.

This paper examines the effects of these microstructural changes on catalytic activity. Many of the microstructural changes are reversible, so the reversibility of changes in reactivity is also important. Catalytic activity was measured after heating in different environments to determine the effect of catalyst pretreatment on reactivity and tested for reversibility.

EXPERIMENTAL

Catalytic activity was measured using powder catalysts prepared by standard aqueous impregnation techniques. $Rh(NO_3)_3 \cdot 2H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ were added to Aesar γ-Al_2O_3 (100 m^2/g) or Aerosil SiO_2 (200 m^2/g) and heated overnight in N_2 at 100°C before calcining at 400°C for 4 hr in O_2. About 150 mg of catalyst were placed in a Pyrex reactor and the activity was measured from 200–300°C.

Kinetic studies were done at atmospheric pressure with 5% NO, 5% CO, and 90% He at a flow rate of ~40 ml/min. Rate measurements were performed in 10° steps from 200–300°C, inclusive. Gas compositions were measured with a gas chromatograph. All data shown here were obtained on several samples with reproducible results.

TEM samples were prepared by depositing Pt or Rh and Ce on thin planar films of γ-Al_2O_3 or SiO_2 using techniques described previously (5). The metal and Ce could be deposited on halves of the grid by masking the other half of the grid during evaporation so it was possible to have different metal and Ce loadings on the same microscope grid, allowing for direct comparison of different compositions on the same sample. TEM samples were treated in the same reactor in which the kinetic experiments were done using the same gases.

Treatments

The emphasis of this paper is to determine the effects of various pretreatments on the low temperature activity of Rh catalysts and to relate these changes to the known, reversible changes in microstructure (Fig. 1). Catalyst pretreatments were done in the reactor in air, H_2, 5% NO, 5% CO, and a mixture of 5% NO and 5% CO with a diluent of ultrahigh purity He at 400°C for ~15 hr. CO was passed through a molecular sieve trap to remove carbonyls. An additional treatment in H_2 was used to test the reversibility of the cycle of treatments, that is, to differentiate microstructure changes (reversible) from sintering (irreversible). Treatments at 400°C were designed to alter the microstructures similar to what was observed with TEM.

Catalytic activity was measured by heating in 10°C steps to 300°C for ~1 hr each. The activity measurements were done at lower temperatures and shorter times than the treatments. Thus, reaction measurements did not change the microstructure of the catalyst significantly since the measured activity at a given temperature did not change at temperatures below 300°C.

RESULTS

Reactivity of Rh/Al_2O_3

Rh and Rh–Ce catalysts on Al_2O_3 were examined in more detail than on SiO_2 because of their importance, the many possible changes in microstructure, and the greatly reduced rate of metal loss compared to SiO_2 supports. A single sample of catalyst was treated sequentially in each gas and in H_2 again. Treatments were for ~15 hr in each gas at 400°C followed by reaction between 200 and 300°C. All rate measurements were done at steady state and repeated to eliminate the effects of transients.

The rate of CO conversion at 200°C after H_2, NO + CO, H_2, and NO + CO pretreatments is shown in Fig. 2. The activity is about 50% higher after the NO + CO pretreatment than after the H_2 pretreatment. This change is reversible in that the activity returns to its original levels for the second cycle. The difference between the two treatments is less for Rh/Al_2O_3 than for Rh–Ce catalysts. The sharp decline in the activity of the Rh/SiO_2 catalyst is due to metal loss.

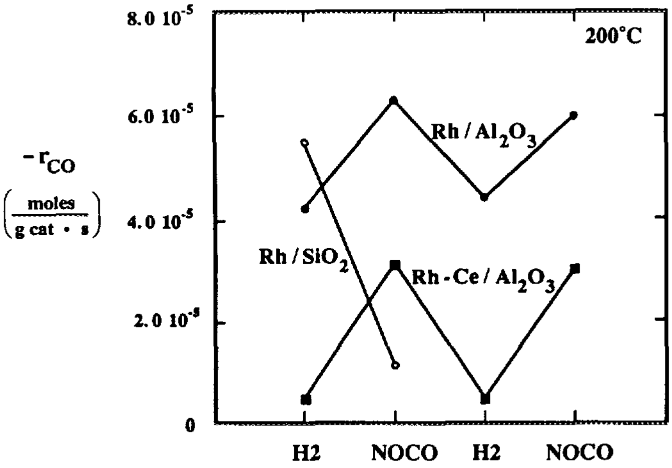

FIG. 2. Rates of CO conversion at 200°C after H_2 and NO + CO pretreatments at 400°C for each catalyst. The activity of the Rh/SiO_2 catalyst drops after the NO + CO pretreatment because Rh is lost from the catalyst. Both Rh and Rh–Ce on Al_2O_3 show reversible increases in activity after the NO + CO pretreatment. The decrease in activity of the Rh–Ce/Al_2O_3 catalyst is particularly large.

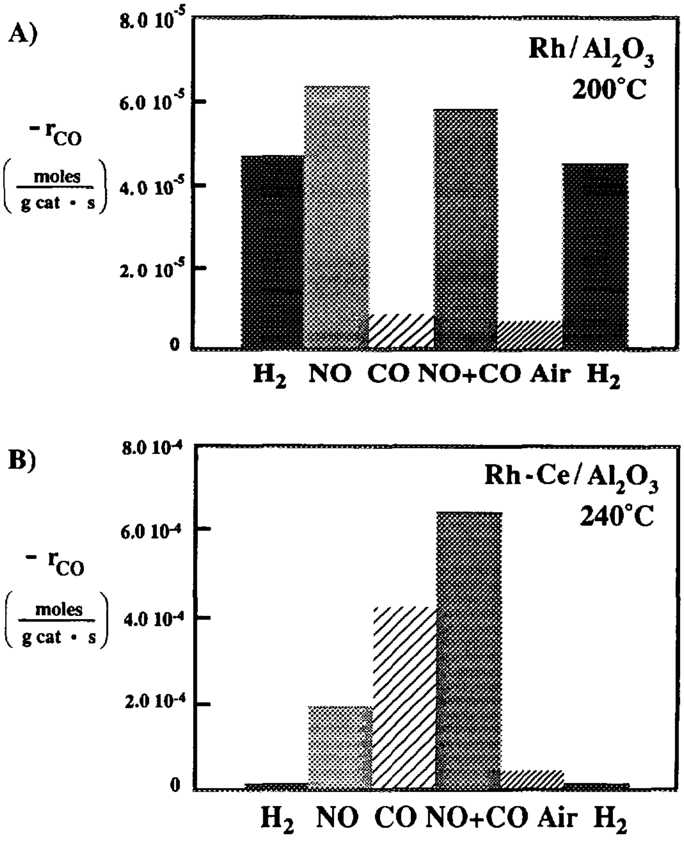

FIG. 3. Rates of CO conversion after pretreatments at 400°C in each environment for (A) the Rh/Al_2O_3 catalyst at 200°C, and (B) the Rh–Ce/Al_2O_3 catalyst at 240°C.

Figure 3A shows the catalytic activity of a Rh/Al_2O_3 catalyst at 200°C following heat treatments in each environment at 400°C. The activity changes for the Rh/Al_2O_3 catalyst at 200°C correlate well with the observed microstructural changes. The low temperature catalytic activity reached a maximum after heating in NO alone, which produced the smallest Rh particles and greatest dispersion. Heating the catalyst in CO alone caused the lowest activity for metallic Rh and the lowest dispersion in the TEM samples. The NO + CO treatment produced an intermediate activity indicating that the mixture has the combined effects of the individual components. Heating the catalyst in air oxidized the Rh and led to the lowest activity. The final H_2 treatment brought the activity back to its original level.

The NO conversion vs temperature for all pretreatments was also investigated for Rh/Al_2O_3 catalysts (Fig. 4A). As the temperature is raised above 200°C, the activity of the catalyst after heating in NO begins to lag the activity after treatments in H_2, CO, and NO + CO, but stays more active than after the air treatment, which is the

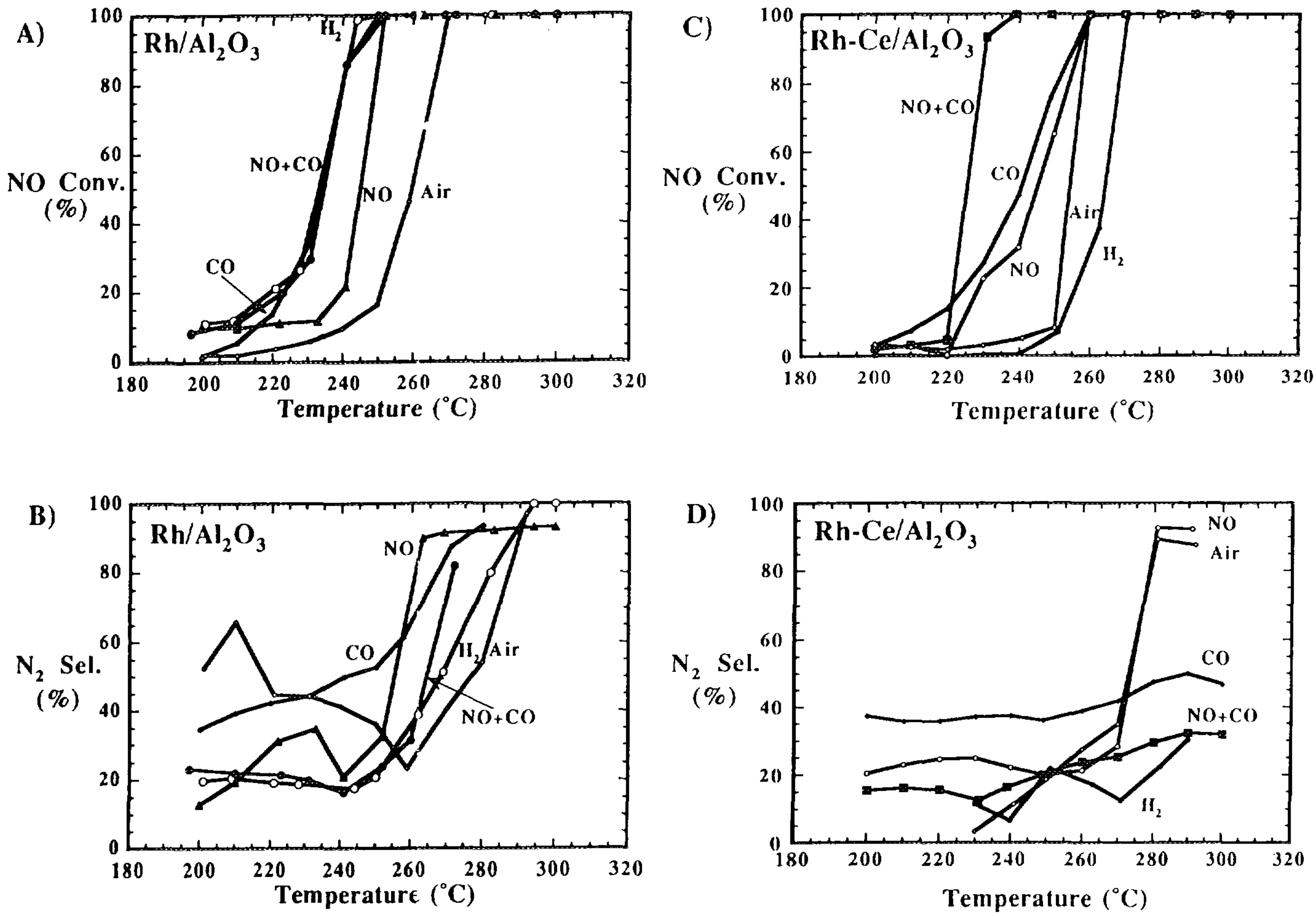

FIG. 4. NO conversions and N_2 selectivities following each pretreatment. The first graph, (A), shows the NO conversion vs temperature for the Rh/Al_2O_3 catalyst, while (B) shows the N_2 selectivity vs temperature for the same experiments. The upper right graph, (C), is the NO conversion vs temperature following each pretreatment for the $Rh–Ce/Al_2O_3$ catalyst, and (D) is the N_2 selectivity for the same experiments.

least active at all temperatures. The activity after the CO treatment is lower at 200°C than after the H_2 and NO + CO treatments, but all three treatments produce almost the same activity above 230°C.

Reactivity of $Rh–Ce/Al_2O_3$

When Ce is added to the Rh/Al_2O_3 catalyst, the activities no longer correlate simply to the dispersions. The rate of CO conversion at 200°C after H_2, NO + CO, H_2, and NO + CO pretreatments increases by more than an order of magnitude after the NO + CO pretreatment (Fig. 2). The change is reversible since a second H_2 pretreatment decreases the activity and an additional NO + CO treatment increases the activity again.

Figure 3B shows the catalytic activity of a $Rh–Ce/Al_2O_3$ catalyst at 240°C following heat treatments at 400°C overnight. The lowest activity occurred after reduction in H_2 even though the dispersion was not the lowest. The activity was so low after the H_2 pretreatment that it could not be reliably measured below 240°C. Heating the catalyst in NO alone increased the activity by a factor of ~10. Subsequent treatments in CO alone and in NO + CO increased the activity further. Heating the catalyst in air oxidized the catalyst and decreased the activity to a level slightly above the activity after reduction in H_2. Further treatment in H_2 returned the activity to its original low level.

The NO conversion vs temperature for all pretreatments for $Rh–Ce/Al_2O_3$ catalysts is shown in Figure 4C. The NO + CO pretreatment made the catalyst most active at most temperatures. The activity of the catalyst after the H_2 pretreatment was the lowest at all temperatures. The air treatment produced the second least active catalyst, while treatments in NO and CO alone produced very similar rates of NO conversion, but very different selectivities as discussed later.

Arrhenius plots for both catalysts after treatments in CO indicate a decrease in the activation energy with Ce addition (Fig. 5). At temperatures above ~250°C,

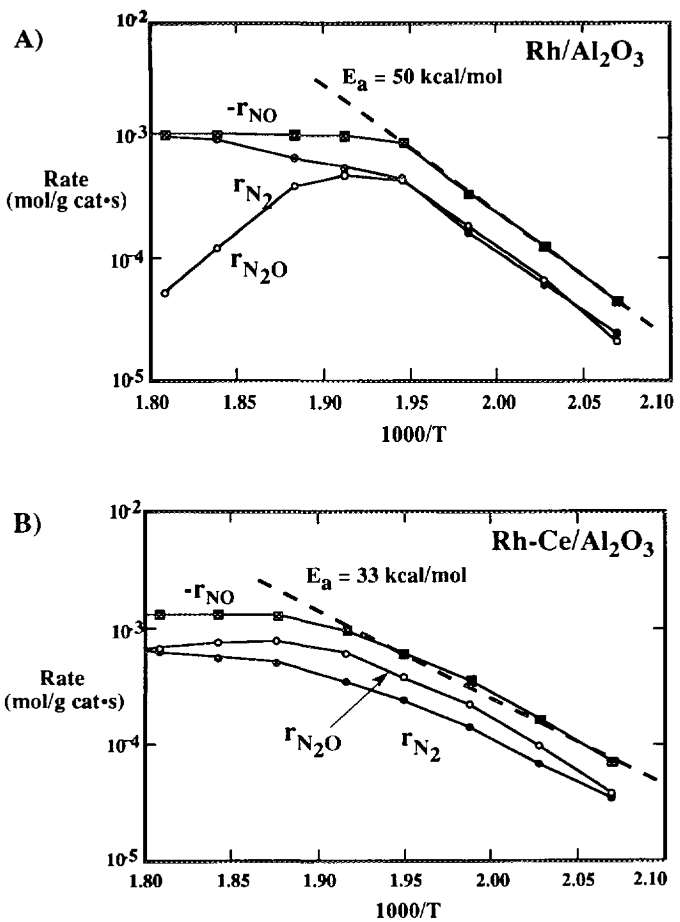

FIG. 5. Arrhenius plots for the (A) Rh/Al_2O_3 and (B) $Rh-Ce/Al_2O_3$ catalysts. The activation energy is decreased by the addition of Ce.

NO conversion was complete in both cases, although CO conversion was not. At lower temperatures, the activation energy is decreased by $\sim\frac{1}{3}$ by adding Ce to the catalyst.

Reactivity of Rh/SiO_2

The activity of Rh/SiO_2 catalysts at 200°C before and after heating in NO + CO at 300°C overnight decreased by a factor of 5 compared to the same catalyst following heating in H_2. This compares to Rh and $Rh-Ce/Al_2O_3$ catalysts which showed an increase in activity for the same treatment. Figure 2 compares the activities of the three catalysts before and after heating in NO + CO. The decrease in activity of the Rh/SiO_2 catalyst is due to loss of Rh from the catalyst through volatilization.

The Rh content of the powder catalyst was also measured by dissolving some Rh/SiO_2 catalyst and measuring the Rh content in a mass spectrometer to ensure that the Rh loss on the planar TEM sample would also occur on a powder catalyst, and was not just an effect of geometry. The unused catalyst had a Rh concentration of 4.62%, while other catalyst particles from the same batch that had been heated in NO + CO at 400°C for 40 hr had a Rh concentration of only 1.90%, which is less than half of the original Rh loading.

N_2 vs N_2O Selectivity

Figure 4B shows the N_2 selectivity vs temperature for the Rh/Al_2O_3 catalyst after each pretreatment. N_2 selectivity increased with temperature for all treatments. The N_2 selectivity reached its maximum after the NO pretreatment at 260°C, which was the lowest temperature for complete CO conversion. The N_2 selectivity following the air pretreatment was the lowest at higher temperatures. The high selectivity at low temperatures is probably not a reliable measurement because the conversion was so low, as discussed later. Complete conversion to N_2 was reached at or before 290°C for all pretreatments.

Figure 4D shows the N_2 selectivity vs temperature for the $Rh-Ce/Al_2O_3$ catalyst after each pretreatment. Ce decreased the selectivity to N_2 after most pretreatments. Only the treatments in NO and air produced complete conversion to N_2 at 300°C. For the other treatments, H_2,

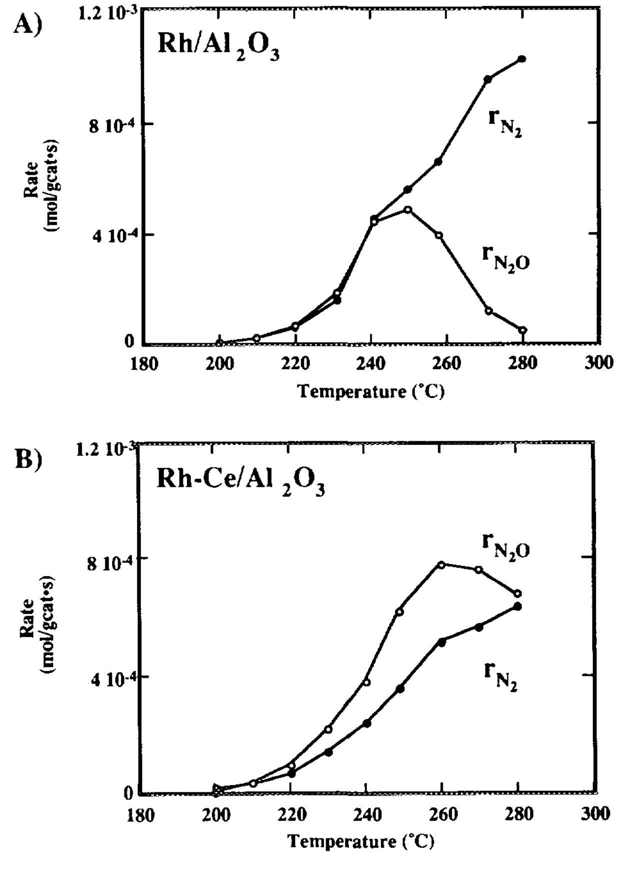

FIG. 6. Plots showing the relative rates of N_2 and N_2O production vs temperature for (a) the Rh/Al_2O_3 catalyst and (b) the $Rh-Ce/Al_2O_3$ catalyst. The N_2 selectivity is decreased by the addition of Ce.

CO, and NO + CO, the N_2 selectivity did not exceed 50%, even at 300°C, where there was complete conversion to N_2 without Ce. The selectivities following the H_2, CO, and NO + CO treatments show a slight increase with increasing temperature, but the increase is much less than the NO and air pretreatments or for the Rh/Al_2O_3 catalyst after any treatment.

The conversions to N_2 and N_2O on a linear scale after the CO pretreatments are shown in Fig. 6. The N_2 selectivity was much higher for the Rh only catalyst than the Rh–Ce catalyst. The N_2 and N_2O rates are almost the same for the Rh/Al_2O_3 catalyst below 240°C. At 250°C, the N_2 reaction becomes favored and its rate increases with increasing temperature, while the N_2O reaction rate decreases because the reactants are being consumed to make N_2. The N_2O reaction on the $Rh–Ce/Al_2O_3$ catalyst is always faster for the temperatures examined. Although the N_2 reaction might become the favored reaction at higher temperatures, above 280°C, this is 50° higher than the catalyst with no Ce.

DISCUSSION

Reactivity of Rh/Al_2O_3

All changes in microstructure and reactivity were reversible within experimental error under the different treatments for alumina-supported catalysts in that the microstructure and reactivity could be returned to what they were after any given treatment by pretreating the catalyst in the environment of interest. The catalytic activity and microstructure were not changed significantly by the activity measurements at temperatures used because the activity was the same before and after the measurements at a given temperature for a given treatment. The activity was measured at temperatures at or below 300°C, which is 100° lower than the pretreatments, and for ~1 hr at each temperature in 10° steps, which is shorter than the ~15 hr of treatment.

The results for the Rh/Al_2O_3 catalysts at 200°C match the higher dispersions seen in TEM with higher activities, with the exception of the treatment in air, which oxidized the Rh particles. Evidently, Rh_2O_3 is less active than Rh metal particles for the NO + CO reaction. It also appears that the dispersion is the controlling factor in the reactivity at low temperatures. As the temperature was increased from 200°C, the activity following the NO treatment, which had been the highest at 200°C, lagged behind the H_2, CO, and NO + CO treatments. This could be due to oxidation of some of the Rh particles during the NO treatment, which would cause the slight decrease in activity observed. A light oxidation of Rh/Al_2O_3 catalysts has been reported to trigger a transient in the activity for the water–gas shift reaction which temporarily increased the activity (19). These transients were on the order of a few seconds and since our results are at steady state after about an hour at each temperature, the increase in NO activity at low temperatures but not at higher temperatures is not due to the same effect. In separate experiments, we have used XPS to examine the effects of these treatments on the oxidation state of Rh. The oxidation state of Rh does not change in NO + CO in the temperature range we examined. Another possibility is that the treatment changes the microstructure on a level that is not noticeable with TEM. The activity following heating in air was much lower at higher temperatures than following any other environment. The temperature of 50% conversion is another measure of reactivity. The H_2, CO, and NO + CO treatments all produced a 50% conversion temperature of ~230°C, while the NO treatment was ~240°C, and the air treatment ~260°C.

A sudden increase in conversion, like what is seen here, is often an indication of hysteresis, or multiple steady states. As part of the experiment, the temperature was decreased in increments and the activity measured. The conversions and selectivities followed the same curve for decreasing temperature as they did for increasing temperature. If there is any hysteresis in this system, the hysteresis loop is too narrow for us to observe experimentally; we cannot see multiple steady states.

Reactivity of $Rh–Ce/Al_2O_3$

The most surprising aspect of the results on $Rh–Ce/Al_2O_3$ catalysts is the exceptionally low catalytic activity after heating in H_2. Others have seen that the addition of large amounts of Ce enhance the activity of Rh catalysts for this reaction (4) and that Rh/CeO_2 catalysts are more active than Rh/Al_2O_3 (9). In our experiments, the weight loadings of Rh and Ce were equal. This is not the case in a real catalytic converter or in the other experiments, which use a much lower Rh/Ce ratio. Hydrogen pretreatments have been shown to cause inhibitory strong metal support interactions (SMSI) for Rh/CeO_2 catalysts toward hydrogenation reactions (20) or to block the spillover process, leading to lower hydrogen chemisorption capacity (21). In our case, the Ce clearly has a detrimental effect on the Rh catalyst, possibly because of SMSI or decreasing the chemisorption ability of Rh toward NO, CO, or both. This exceptional deactivation only occurs after H_2, and produces the lowest activity of all pretreatments. Other environments restore catalytic activity. Further investigation is needed to determine the exact cause of this effect.

Treatments in NO, CO, and NO + CO did not cause the large microstructural changes in $Rh–Ce/Al_2O_3$ catalysts that were seen in Rh/Al_2O_3 catalysts. Unlike catalysts without Ce, a CO treatment produced a higher activity than NO and NO + CO produced the highest activity for all treatments. These treatments could be affecting the microstructure on a level that is too fine for direct observation in TEM, possibly changing the amount of exposed Rh, the exposed crystal planes, or the amount of stepped surfaces available for reaction. Heating the catalyst in air decreases the activity by an order of magnitude, similar to Rh only, which is once again most likely because of oxidation of the Rh particles. The NO + CO pretreatment also produced the lowest 50% conversion temperature, ~225°C. The temperatures for the individual NO and CO pretreatments were ~240°C, air was ~250°C, and H_2 was ~265°C, which is another indication of the surprisingly low activity following the H_2 treatment.

Most of the pretreatments caused the catalyst to light off and not give a uniform exponential increase in rate with temperature. When it was possible to measure an activation energy, after the CO pretreatment, the Rh/Ce catalyst had a lower activation energy than the Rh catalyst for the same pretreatment. The decrease in activation energy with Ce addition is in agreement with Oh (4), who reported a decrease in activation energy for CO_2 formation from 28 kcal/mol down to 18 kcal/mol by adding Ce to the catalyst. Our activation energies are higher (50 and 33 kcal/mol, respectively), but the trend is the same. Oh also reported an activation energy of 46 kcal/mol for NO + CO on Rh/Al_2O_3 (22), which is in better agreement with our measurement. We have also used much more Rh (5%) than he did (0.014%) and see greater activity at lower temperatures.

Reactivity of Rh/SiO_2

The loss of Rh from the Rh/SiO_2 catalyst due to heating in NO and CO at 400°C for only 40 hr is significant and agrees with our results on planar TEM samples. More than half of the Rh originally present in the catalyst is lost because of this relatively mild treatment. In our TEM experiments, almost all of the Rh on a planar sample was lost because of this treatment, so the geometry of a porous catalyst evidently prevents some Rh loss after volatilization, but not all. The decreased rate of Rh loss is most likely due to volatile Rh compounds being trapped in pores and condensing. The loss of Rh from the sample due to heating in CO is probably through the formation of volatile carbonyls which can only form from nitrosyl compounds, which are produced by heating in NO (14). Heating in both gases combines the effects of each. A similar experiment using an alumina supported Rh catalyst, on which volatilization is greatly reduced according to the TEM results, failed because the catalyst did not properly dissolve so the Rh content could not be measured in the mass spectrometer.

N_2 vs N_2O Selectivity

The increase in N_2 selectivity with increasing temperature for the Rh/Al_2O_3 catalyst is not surprising and has been reported before (4). All pretreatments gave complete conversion to N_2 before 300°C. The high selectivity at low temperatures after the air treatment might not be reliable because of the low activity. The N_2 entering the reactor as an impurity in the NO was assumed to be constant and subtracted from the measured N_2 in the product stream to determine the conversion. A small change in the flow rate of the NO would have a greater effect on the final selectivity measurement because of the low conversion.

Ce addition caused a significant decrease in N_2 selectivity after H_2, CO, and NO + CO treatments, although the rate of NO conversion was not affected as much. These treatments along with the Ce are altering the chemistry of the Rh catalyst as well as the microstructure since N_2O formation is greatly enhanced at the expense of N_2. The decrease in N_2 selectivity due to Ce addition does not occur following treatments in NO and air, which could produce CeO_2 (Ce^{+4}) instead of Ce_2O_3 (Ce^{+3}), which probably forms after the other treatments. If this is the case, Ce^{+3} promotes N_2O formation while Ce^{+4} does not have the same adverse effect on the N_2 selectivity.

SUMMARY

Different pretreatments have substantial effects on the catalytic activity of Rh and Rh–Ce for the NO + CO reaction. As we have shown previously, these treatments also affect the microstructures of the catalysts. In the case of Rh/Al_2O_3 and Rh/SiO_2 catalysts, the different microstructures and activities correlate very well with each other. In general, a decrease in dispersion or in metal loading caused a decrease in catalytic activity at low temperatures. Complete conversion to N_2 was obtained at 300°C for all pretreatments. All changes in microstructure and reactivity were reversible with the exception of Rh loss from the Rh/SiO_2 catalyst after heating in NO + CO.

When Ce was added to Rh/Al_2O_3 catalysts, the microstructures and activities did not correlate as simply. Treatment in H_2 caused an order of magnitude decrease in catalytic activity compared to NO, CO, and NO + CO, which could not be predicted based on the TEM results. Ce addition decreased the N_2 selectivity after H_2, CO, and NO + CO treatments to below 50%, even at 300°C, and with complete conversion of NO. $Rh–Ce/Al_2O_3$ catalysts also had a lower apparent activation energy of NO reduction.

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