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Catalytic disruption and volatilization of rhodium particles on silica in NO + CO *

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Initially reduced ≈ 100 Å diameter Rh metal particles on SiO_2 are found by TEM to be dispersed into an amorphous metal film by treatment in 5% NO + 5% CO in He at 260°C, leaving thin rings around the perimeter of the original particles. Electron diffraction shows that Rh is amorphous while XPS shows that the Rh is approximately zero valent in the dispersed state. Continued heating in this mixture resulted in irreversible volatilization of the Rh even at these low temperatures. Subsequent heating in H_2 at 650°C caused sintering and the reformation of crystalline Rh particles, but with a lower loading than observed initially. Treatment of Rh particles in 5% NO at 260°C causes Rh particles to shrink in diameter and to form thin shells around their perimeters. The only change observed after treatment in 5% CO alone at 260°C was slight sintering of adjacent Rh particles.

Keywords: Rhodium; silica; catalyst microstructure; disruption; carbon monoxide; nitric oxide; model catalysts

1. Introduction

Because Rh is primarily responsible for the removal of NO_x from automobile exhaust in the current automotive catalytic converter [1], the decomposition of NO and its reaction with CO on Rh have been studied for many years [2–5].

Adsorption of CO on Rh and its effect on Rh dispersion has also been examined extensively. Using infrared spectroscopy (IR), Yang and Garland first reported the formation of a gem-dicarbonyl, $Rh(CO)_2$ [6]. More recently, this has been studied in detail with IR by Solymosi et al. [7,8] and Yates et al. [9,10], with EXAFS by Prins et al. [11,12] on SiO_2, TiO_2, Al_2O_3, and MgO. Adsorption of CO was found to disrupt very small (≈ 20 atom) Rh clusters by the formation of the partially oxidized gem-dicarbonyl $Rh^1(CO)_2$. In all of these experiments,

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increasing the temperature of CO adsorption above 100°C was found to retard this effect due to the reducing nature of the CO. The addition of NO enhanced the CO-induced disruption of Rh [13] and the addition of Ce was found to inhibit the agglomeration of Rh as the temperature was increased [14]. Similar behavior has been seen for Ru [15–17]. IR studies of CO adsorption on supported Pd have been reported to cause only agglomeration of the Pd into larger particles [18]. To our knowledge, no attempts to directly observe this phenomenon with transmission electron microscopy (TEM) have been successful.

Over several years, we have developed techniques for observing microstructural changes in the same metal particles on planar supports after a series of treatments in various gases, and we have characterized the microstructure of Rh and Rb/Ce on SiO_2 [19,20] and on Al_2O_3 [21]. This method allows direct observation of catalytic disruption processes and further characterization of the conditions under which it occurs.

We report here observations of a related but different phenomenon than that produced in CO; this results in complete disruption of ≈ 100 Å Rh particles by low temperature treatment in NO + CO and a similar effect in NO alone.

2. Experimental

TEM sample preparation has been described in detail elsewhere [20]. An amorphous SiO_2 film (≈ 200 Å thick) was prepared on a gold TEM grid by vacuum depositing Si on formvar and heating to 800°C to decompose the formvar and convert the Si to amorphous SiO_2. A thin film (≈ 20 Å) of Rh was then vacuum deposited on top of the SiO_2, and the grid was heated in H_2 at 650°C for 10 h to disperse the Rh film into particles. TEM was performed on a Philips CM30 to obtain images and diffraction patterns.

Separate samples for X-ray photoelectron spectroscopy (XPS) were prepared by oxidizing the top ≈ 800 Å of a silicon wafer and then depositing Rh and heating as above. XPS was performed on a PHI 5400 spectrometer and the binding energy of adventitious carbon was referenced to 284.6 eV to compensate for charging. No evidence of differential charging was observed.

Treatments were in 5% NO, 5% CO, and 5% NO + 5% CO, all diluted in He, for times up to 40 h each in a furnace. The purity of the gases was $> 99\%$ and the CO was purified further by passing through molecular sieve.

3. Results

3.1. TREATMENT IN NO AND IN CO

Micrographs of two different Rh on SiO_2 samples after initial treatment in H_2 are shown in figs. 1A and 1C. The samples shown in figs. 1A and 1C were

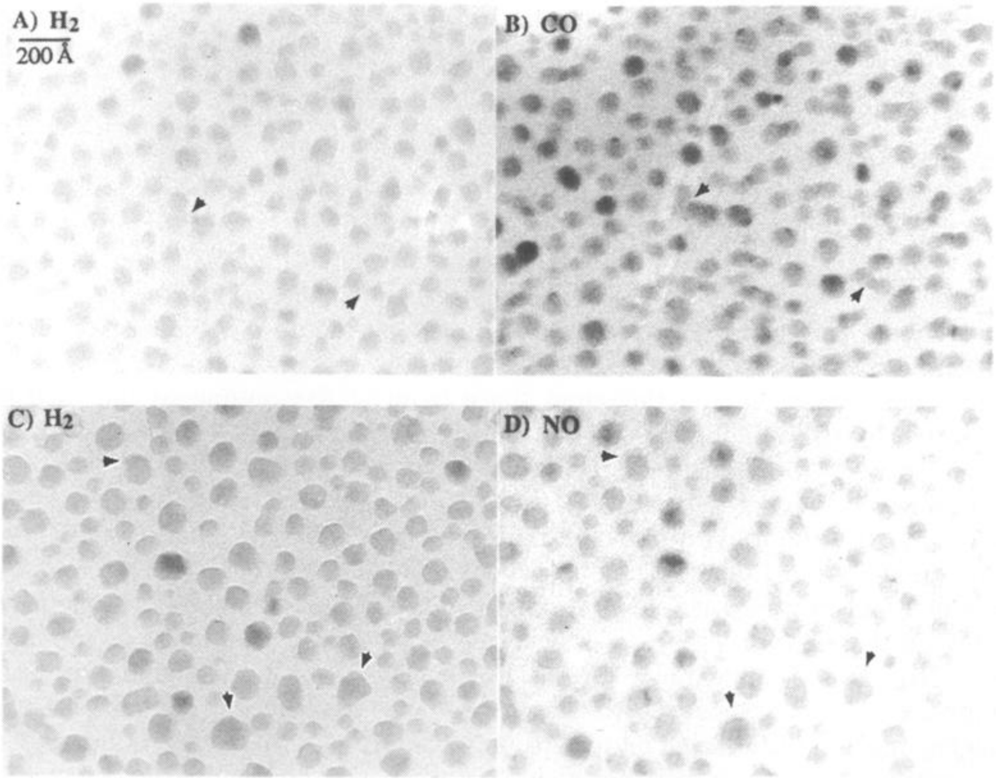

Fig. 1. Microstructure of Rh on SiO_2 after treatment in CO or NO alone. Micrographs (A) and (B) show the same particles (several indicated by arrows) after initial reduction and after treatment in 5% CO, respectively. No change in microstructure other than some sintering of adjacent Rh particles was observed after CO treatment. Micrographs (C) and (D) show the same particles (several indicated by arrows) on a different Rh/SiO_2 sample after initial reduction and after treatment in 5% NO at 260°C, respectively. After NO treatment, the smaller particles shrink and become thinner while a thin shell is formed at the perimeter of the larger particles.

then treated at room temperature in 5% CO and 5% NO, respectively, and no changes in the microstructure were observed. Further treatment of each sample at 260°C in the same environment for 40 h resulted in the microstructures shown in figs. 1B and 1D, where arrows identify the same particles before and after treatment. No changes in the microstructure other than some sintering of adjacent particles were observed in the sample treated in CO alone (fig. 1B).

After treatment in NO at 260°C, however, the smaller ($\leqslant$ 50 Å diameter) Rh particles were reduced in size. Also, the contrast of particles compared to the amorphous SiO_2 support was lower, indicating that particles were thinner than after the initial H_2 treatment. The larger particles also shrank in size, but a low contrast (thin) shell formed around the perimeter of each particle so that the diameter of shell plus particle after this treatment was the same as the particle diameter initially. Several examples are indicated by the arrows in fig. 1D. The changes in microstructure observed indicate that Rh particles are slowly disrupted by treatment in NO at 260°C.

3.2. TREATMENT IN NO AND CO

Rh is much more rapidly disrupted by treatment in NO + CO mixtures at 260°C. Figs. 2A–2C show the same area of a different Rh on SiO_2 sample after initial reduction, after NO + CO treatment at 260°C, and after reduction in H_2 at 650°C for 10 h, respectively. The low contrast region on the upper left edge is a hole in the SiO_2 support which was used to aid in location of the same area after each treatment and the same sharp bend in the outline of the hole is indicated by arrows in each micrograph. It is evident that all of the Rh particles disappeared to form a somewhat more granular film on the SiO_2.

Electron diffraction in the TEM and XPS of a planar bulk sample (lower right of fig. 2) after the initial reduction indicate that the Rh is present as metal. As after treatment in CO or NO alone, no changes were observed after treatments in NO + CO mixtures at temperatures up to 200°C (not shown). Treatment at 260°C in the mixture, however, caused nearly all the Rh particles to disappear (fig. 2B). The disappearance of the Rh particles was accompanied by the complete disappearance of Rh rings from the electron diffraction pattern, leaving only the diffuse ring pattern from the amorphous SiO_2. We estimate that any particles > 15 Å in diameter would be observable and should be detectable by electron diffraction.

XPS after this treatment shows no significant change in the valence state (Rh^0) of the Rh. Rh_2O_3 is easily produced by heating these samples in O_2 at ≈ 500°C for several hours; it exhibits a shift of the doublet in fig. 2 from 307.5 and 312.2 eV to 308.8 and 313.5 eV, a shift of 1.3 eV.

The same area after reduction in H_2 at 650°C for 10 h is shown in fig. 2C. Heating in H_2 caused the reformation of Rh metal particles, indicating that the Rh has not completely evaporated through formation of a volatile species. Many small ($\leqslant 50$ Å diameter) Rh particles have formed, and rings due to Rh metal are again observed by electron diffraction. As expected, XPS after H_2 treatment also indicates only Rh metal. The Rh particles continue to sinter with further treatment in H_2 but the final Rh loading appears lower that that present initially.

We have also observed the same disruption behavior on 5% Rh on SiO_2 catalyst prepared by aqueous impregnation of amorphous silica powder by $Rh(NO_3)_3$. Fig. 3 shows the same area of this catalyst (A) after reduction in H_2 and (B) after treatment in the same 5% NO + 5% CO in He mixture used for the planar samples at 300°C for 10 h. The images in fig. 3 are not as well defined as those in the previous figures mainly due to the three-dimensional nature of this sample. The arrows in fig. 3A indicate three ≈ 250 Å diameter Rh metal

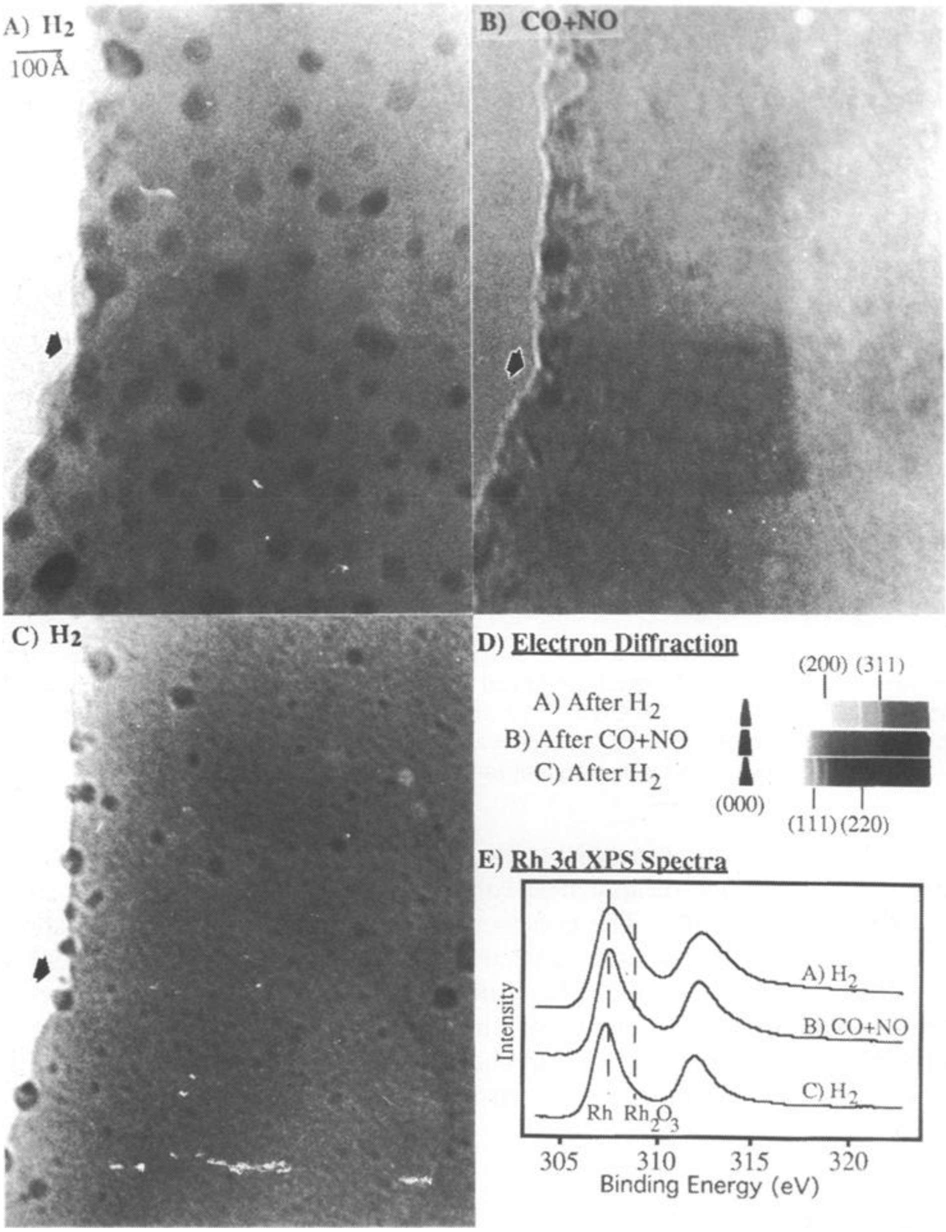

Fig. 2. Microstructure of Rh on SiO_2 after treatment in a 1:1 NO + CO mixture. Micrographs (A) and (B) show the same area after initial reduction and after treatment in 5% NO + 5% CO at 260°C, respectively. After treatment in NO + CO, nearly all Rh particles have disappeared, indicating their size is less than ≈ 15 Å diameter. Micrograph (C) shows the same area after heating in H_2 at 650°C. After treatment in H_2, the Rh has started to sinter and reform larger particles. Note the arrows in each micrograph indicate the same location in a hole in the SiO_2 film. Electron diffraction patterns in (D) show rings from fcc Rh metal after both treatments in H_2, but these rings disappear after treatment in NO + CO. Rh 3d XPS spectra in (E) show that the Rh peak area and valence state are unchanged by treatment in NO + CO.

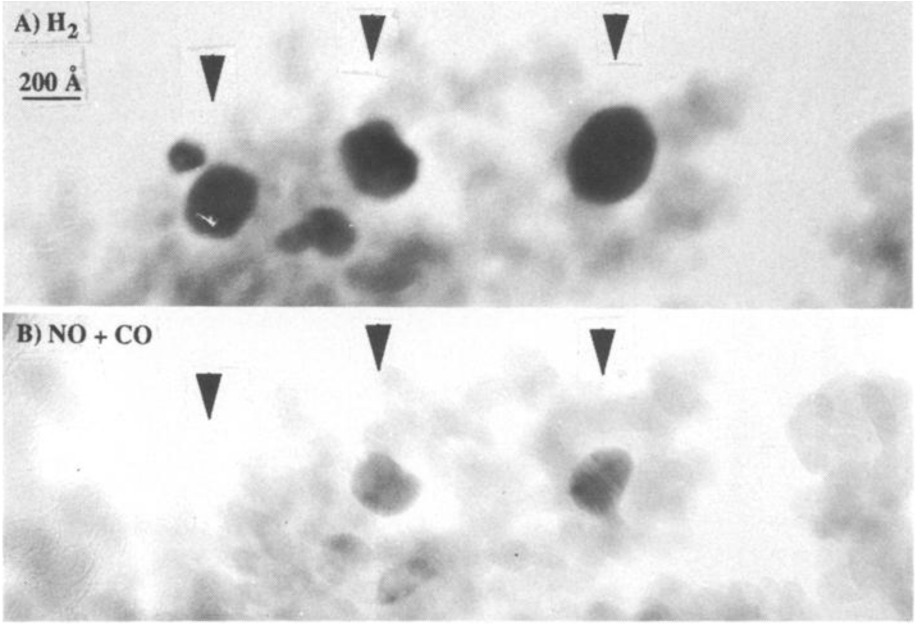

Fig. 3. Microstructure of typical area of 5% Rh on SiO_2 sample prepared by aqueous impregnation with Rh nitrate salt. Micrographs (A) and (B) show the same area after initial reduction and after treatment in 5% NO+5% CO at 300°C for 10 h, respectively. The arrows indicate the same Rh particles in both (A) and (B). The particle on the left has completely disappeared and the other two particles have significantly shrunk after treatment in NO+CO.

particles. After heating in NO + CO, the particle on the left, and the smaller nearby particle, have disappeared completely and the other two Rh particles have shrunk significantly. The presence and reduced size of the center and right Rh particles confirm that the left particle probably did not simply break away from the rest of the sample. The disruption of Rh is clearly seen to occur on both the planar and powder catalysts indicating that model catalysts can realistically represent the microstructural changes undergone by powder catalysts but allow a much more controlled system to study.

4. Discussion

We have directly observed the catalytic disruption of ≈ 100 Å diameter Rh particles on SiO_2 by treatment in NO + CO at 260°C and also its volatilization at this temperature. This microstructural behavior contrasts strongly with the reduction or oxidation of Rh caused by heating in pure H_2 or pure O_2, respectively, even at temperatures up to 650°C [19]. While this phenomenon is similar in effect to the disruption inferred with IR and EXAFS, its cause is clearly different. The particles in our experiments (1) are much larger, (2) require NO for disruption to occur, and (3) disrupt above ≈ 250°C while CO only causes disruption below ≈ 100°C.

Treatment in CO only at room temperature or at 260°C resulted in only a small amount of sintering of nearby particles even after 40 h, whereas treatment in NO only at 260°C caused more significant changes in the microstructure. The IR and EXAFS results infer that disruption occurs by room temperature exposure to CO only. Another important difference in the two phenomena is the effect of temperature. The rate of disappearance of Rh particles increases with increasing temperature in our experiments, but Rh particles reform above ≈ 100°C in the low temperature CO disruption because the partially oxidized $Rh^I(CO)_2$ is reduced by CO at higher temperatures.

The Rh appears amorphous by electron diffraction during the disruption, as evidenced by the disappearance of rings due to fcc metal, possibly by the formation of Rh^1 or formation of a Rh nitrile or carbonyl species. However, no significant change in the valence state of the Rh is detected by XPS after treatment in NO + CO at 260°C. This indicates that any oxide, nitrile, or carbonyl that is being formed must be very thin.

Many questions remain regarding the mechanism of catalytic disruption and the conditions that favor it. While conditions are far from equilibrium, there must be a thermodynamic driving force which alters the surface free energy of the Rh surface by producing a lower free energy of the film on the SiO_2 compared to isolated metal particles. This could be a high temperature nitrile or carbonyl or some partially or totally oxidized Rh species which has a low surface free energy and strong interactions with the SiO_2. This species must also have a very high surface mobility and appears to have significant volatility at the relatively low temperatures. We are unaware of any Rh compounds in the literature with significant volatility at these temperatures. Our observations of complete disruption of 100 Å particles in several hours requires a diffusion coefficient much larger than that expected for metals at these temperatures.

Disruption during exothermic catalytic reaction can also be assisted by local temperature increases. Even though treatment in NO only produced significant changes in the microstructure and disruption has also been observed with 1% NO + 1% CO, some heat effects cannot be ruled out.

We are currently studying the effects of temperature and gas composition and measuring reaction rates to better characterize this phenomenon. The possibility that other systems undergo catalytic disruption is also being investigated. In preliminary results, we find that the presence of Ce effects both the disruption of Rh in NO + CO and the return to particles in H_2 and that disruption of Rh supported on alumina occurs much slower.

5. Summary

We have shown that Rh is very mobile on SiO_2 when treated in NO + CO mixtures at temperatures as low as 260°C. The large change in Rh microstructure by treatment in a reactive environment at a relatively low temperature has important consequences on the understanding of noble metal catalysis. These results show that carefully prepared and characterized microstructures can be drastically altered under relatively modest reaction conditions, causing large changes in catalytic performance.

This dramatic change in the microstructure observed on both planar and powder catalysts by low temperature exposure to reactive environments clearly has impact on how metals can catalyze reactions. If catalysts can change rapidly and reversibly with their environment, then many characterization techniques which require different environments from reaction conditions are suspect.

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