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The Redispersion of Sintered Pt, Rh, and Pt/Rh Catalysts

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Sintered Pt/alumina catalysts can be readily redispersed by treatment with chlorine, chlorine/air mixtures, or bromine at temperatures above 400°C. The redispersion of Pt has been verified by hydrogen chemisorption, high resolution transmission electron microscopy, and catalytic activity measurements. Sintered Rh/alumina catalysts can be redispersed by a chlorine treatment at 500°C, but only when this treatment is preceded by a hydrogen treatment at or above 700°C. Sintered bimetallic Pt–Rh/alumina catalysts can be partially redispersed by direct treatment with chlorine at 500°C and more completely redispersed if the chlorine treatment is preceded by a hydrogen treatment at 700°C. However, unlike Pt/alumina, improvements in the catalytic activity of Rh/alumina or Pt–Rh/alumina do not necessarily accompany improvements in dispersion. For these catalysts, activity appears to be dominated by the recent oxidation or reduction history of the catalyst. © 1988 Academic Press, Inc.

INTRODUCTION

There are two primary processes which result in the deactivation of alumina-supported Pt, Rh, or Pt/Rh automotive catalysts. Chemical deactivation, or poisoning, occurs when contaminating materials such as phosphorus, lead, sulfur deposit on the catalyst, reducing its activity by either physical (pore blockage) or chemical (by direct interaction with a catalytically active site) mechanisms (*1–4*). Thermal deactivation, or sintering, occurs when a catalyst is exposed to high temperatures. This exposure results in the loss of catalytically active metal surface area through the growth of active metal particles (*5, 16–23*). The reversal of chemical deactivation in pelleted automotive catalysts has been addressed in a recent patent (*6*); this report will focus on the reversal of thermal deactivation.

Thermal deactivation is often a problem in processes which utilize supported metal catalysts. Alumina-supported reforming catalysts containing Pt alone or in combination with another metal such as Sn, Re, or Ir are the most commonly studied catalysts in terms of their thermal aging characteristics. Also, because of their cost and widespread use, the redispersion of the metal on this type of catalyst is commonly practiced and is the subject of many studies (*7–11*) and patents (*12–14*). The general process used for redispersion involves treating a thermally deactivated catalyst with a strong gaseous oxidant such as chlorine or phosgene at elevated temperature. Both reagents readily attack bulk noble metals to form chlorides or volatile carbonyl chlorides. Redispersion results from the movement of these oxidation products over the support, either by gas phase transport or by surface migration. Subsequent decomposition of the dispersed oxidation product at a relatively low temperature (e.g., H_2 at 400°C) leads to metal in a more dispersed state.

The purpose of this work was to investigate the redispersion of thermally aged automotive catalysts containing Pt, Rh, or bimetallic Pt/Rh using high temperature chlorine treatments. A redispersion treatment, coupled with poison removal (*6*), could be developed into a catalyst rejuvenation process with several possible applications. From a fundamental point of view, such a process would be helpful in estimating the

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relative contribution of thermal and chemical deactivation processes on a given catalyst's performance. From an applied point of view, such a process could be used as an alternative to catalyst replacement to help meet automotive high mileage requirements (e.g., light duty trucks), or to provide a less costly source of catalyst for the automotive catalytic converter after market.

EXPERIMENTAL

I. Catalysts

The support used for all catalysts in this study was W. R. Grace LBD alumina spheres, 3.2 mm (nominal) in diameter, consisting primarily of θ-alumina with a BET surface area of 110 m^2/g, a bulk density of 0.48 g/ml, and a total pore volume of 1.1 ml/g. This material was dried before use in flowing lab air (1 scfh) for 2 h at 300°C.

A 0.1% Pt/alumina catalyst was prepared by an acetone-based impregnation technique reported earlier (*15*). A 1000-g portion of dried support was divided into eight 125.0-g samples and each sample placed in a 1-liter round-bottomed flask. Each sample was prewetted with 300 ml of reagent grade acetone, the excess being decanted after 15 min. Each sample was then treated with a solution prepared from a 25.00-ml aliquot of a stock H_2PtCl_6/acetone solution (3.35 g $H_2PtCl_6 \cdot 6H_2O$ in 250 ml of acetone, 5.08 mg of Pt/ml by AA analysis) diluted with 200 ml of acetone. The samples were mixed gently at frequent intervals for 1 h, after which the acetone was decanted and the catalyst spread out to air dry in a hood overnight. Analysis of the spent impregnation solvents indicated 99.4% of the Pt had been adsorbed. After air drying, the catalyst was calcined in flowing lab air (1 scfh) for 2 h at 500°C. This calcination produces a catalyst which displays stable CO and hydrocarbon oxidation activity in the reactor evaluation described below. In the area of automotive emission control, such a catalyst is considered to be in a fresh state even though the Pt dispersion is somewhat low (39% by hydrogen chemisorption).

A 0.079% Rh/alumina catalyst was prepared by the standard incipient wetness procedure. A 500-g portion of dried support was treated with a solution of 0.965 g $RhCl_3 \cdot 3H_2O$ (40.8% Rh lot analysis) in 500 ml of water, this volume being completely adsorbed by the support. The impregnated support was air-dried in a hood overnight and then calcined in flowing (1 scfh) lab air for 2 h at 500°C.

A co-impregnated 0.15% Pt/0.075% Rh/alumina catalyst was prepared by the standard incipient wetness procedure. A 500-g sample of dried support was treated with a solution of 1.875 g $H_2PtCl_6 \cdot 6H_2O$ (40.0% Pt lot analysis) and 0.882 g $RhCl_3 \cdot 3H_2O$ (42.5% Rh lot analysis) in 500 ml of water. The impregnated support was air-dried in a hood overnight and then calcined in flowing (1 scfh) lab air for 2 h at 500°C. A sequentially impregnated 0.15% Pt/0.075% Rh/alumina catalyst was prepared similarly except that the Rh was deposited first, followed by a drying/calcination step. The Pt was then deposited in a second step, followed by drying/calcination.

Thermally aged samples of each catalyst were prepared by calcining in flowing laboratory air (1 scfh) for 4 h at 800°C.

II. Chlorination Experiments

All experiments involving chlorine were conducted in a well-ventilated hood. Catalyst samples, typically 8–10 g, were treated in a one inch tube furnace in a quartz tube. Water-saturated chlorine was used for all experiments and was produced by passing 99.5% chlorine from a cylinder through a glass gas washing bottle partially filled with water. The water in the washing bottle was saturated with chlorine before the final flow rate was set via the monel cylinder needle valve. All interconnections between cylinder needle valve, gas washing bottle, and tube furnace were made with glass or Teflon tubing. Chlorine was scrubbed from the tube furnace exit gas with a concentrated (>1 *M*) aqueous solution of potassium hydroxide, which was replaced frequently. Wet gases were used at all times to maintain constant and reproducible states of support surface hydration, a factor which may influence the migration of species over the support surface.

The general experimental procedure followed throughout the study involved first pretreating the catalyst (in either dry flowing air or dry 5% H_2/N_2) and then maintaining the pretreatment gas flow while adjusting the sample temperature to that required for the chlorination step. Once the desired chlorination temperature, T_C, was reached, a water-saturated chlorine flow of 60 ml/min was established and maintained for 30 min. After this time, the system was either (1) purged with wet air to remove the chlorine in the tube if $T_C \leq 500°C$, the temperature raised to 500°C, and held for 1 h in a wet air flow of 125 ml/min, or (2) cooled to 500°C in the wet chlorine flow if $T_C > 500°C$, the chlorine purged from the tube with wet air, and a wet air flow of 125 ml/min maintained for 1 h. In either case, the furnace was cooled after 1 h to 400°C in flowing wet air and the gas flow switched to wet 5% H_2/N_2, 125 ml/min, which was maintained for 1 h. After this time, the sample was cooled to room temperature in the wet 5% H_2/N_2 flow and removed from the tube. The postchlorination treatment was held constant for all samples, while the pretreatment and chlorination conditions were varied. These conditions are abbreviated in the following text as pretreatment gas, pretreatment temperature/Cl_2, chlorination temperature. For example, an experiment involving a pretreatment in 5% H_2/N_2 at 700°C followed by chlorination at 500°C is denoted H_2, 700°/Cl_2, 500°C.

Experiments involving bromine were conducted as for chlorine, above, except the wet bromine gas source was a gas washing bottle containing equal volumes of water and bromine. Air passed through this bubbler provided the wet, gaseous bromine source (partial pressure 200–300 Torr) used in the experiments.

III. Catalyst Characterization

Dispersion measurements were made using a Micromeritics ChemiSorb 2800 automated, five station static chemisorption instrument. A sample size of ~2 g was used with the following pretreatment procedure: (1) heat sample to 450°C (10°C/min) in flowing 5% O_2/N_2 (40 ml/min) and hold for 1 h, (2) evacuate at 450°C to $<1.5 \times 10^{-2}$ Torr, (3) treat at 450°C in flowing 5% H_2/N_2 (40 ml/min) for 1 h, (4) evacuate for 2 h at 450°C after reaching 1×10^{-3} Torr, and (5) cool to 35°C (10°C/min) while evacuating and continue evacuation for 2 h after reaching 1×10^{-4} Torr. The H_2 (99.9999%) adsorption isotherm was then determined at 35°C over the 20–200 Torr equilibrium pressure range at 20 Torr increments. The adsorption isotherm was redetermined after evacuation below 5×10^{-5} Torr at 35°C. The zero pressure intercept for each isotherm was determined by a least squares fit of the 80, 120, 160, and 200 Torr points to a straight line. The difference between the least squares intercepts of the two isotherms was taken as the amount of irreversibly adsorbed H_2 and the dispersion calculated assuming $H/M = 1.0$.

Catalyst samples were tested in a laboratory reactor consisting of a quartz tube (2.5 cm i.d.). The front 30 cm of this tube was filled with cylindrical quartz beads (2 × 2 mm) and surrounded by a tube furnace which served as a preheater upstream from the catalyst. The catalyst bed, which contained 5 g of catalyst, followed the quartz beads and started at the end of the tube furnace. The section of tube containing the catalyst was wrapped with 2 cm of Fiberfrax insulation. Temperature measurements were made at the inlet to the catalyst bed. The net oxidizing feed composition used contained 1.0 vol% O_2, 0.77 vol% CO, 0.2 vol% H_2, 500 ppm NO, 300 ppm HC (as C_3H_6), 10 vol% CO_2, 10 vol% H_2O, 20 ppm SO_2, and the balance N_2. The light-off test used to characterize catalyst samples was conducted by measuring the HC and CO conversions as the catalyst was heated from 200 to 500°C at 5°C/min in the oxidizing feedstream. At least three light-off tests were performed on each catalyst. Between tests the catalyst was cooled in flowing 0.25% H_2/N_2. Data were taken when two consecutive run-ups agreed to within ±5°C at the 50% conversion point.

Scanning electron microprobe (SEM) and transmission electron microscopy (TEM) characterizations were conducted by the Analytical Chemistry Department, General Motors Research Laboratories, Warren, Michigan. Samples for SEM were half-beads mounted in resin. TEM samples were 100- to 150-nm thick slices of a catalyst bead prepared using standard techniques on a DuPont Sorvall MT6000 ultramicrotome.

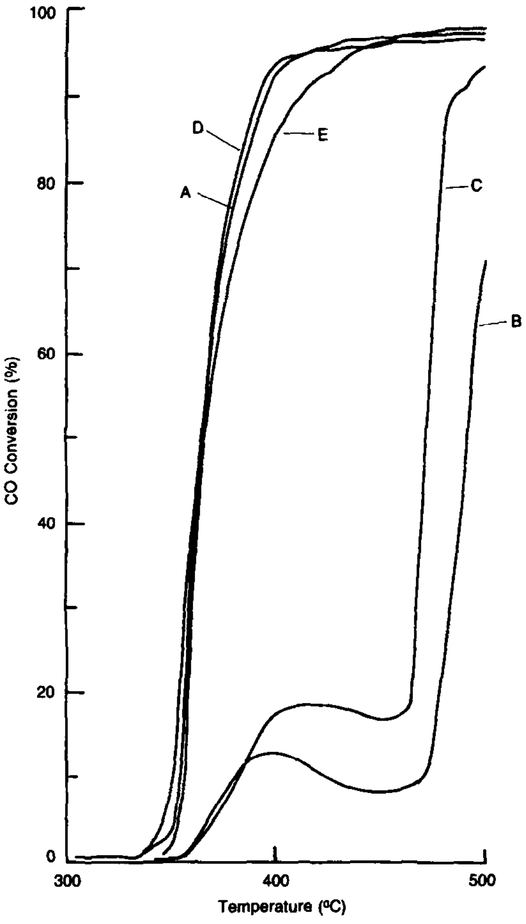

FIG. 1. Carbon monoxide light-off test results for 0.1% Pt/alumina. (A) Fresh; (B) aged, 800°C/4 h/air; (C) aged, after Cl_2, 350°C; (D) aged, after Cl_2, 400°C; (E) aged, after Cl_2, 450°C.

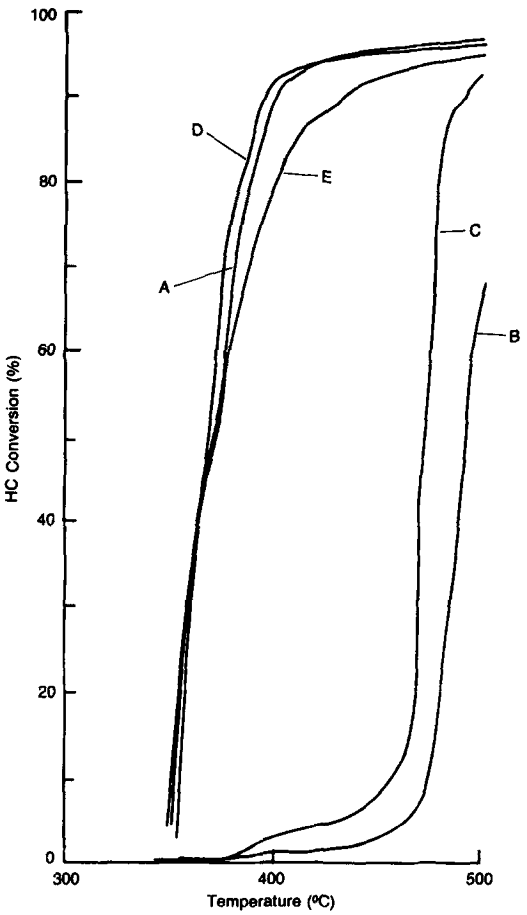

FIG. 2. Hydrocarbon light-off test results for 0.1% Pt/alumina. (A) Fresh; (B) aged, 800°C/4 h/air; (C) aged, after Cl_2, 350°C; (D) aged, after Cl_2, 400°C; (E) aged, after Cl_2, 450°C.

RESULTS AND DISCUSSION

I. Pt/Alumina

The consequence of thermal treatments on the properties of Pt/alumina have been examined in some detail (*16–23*). Generally, increases in supported metal particle size and declining catalytic activity are observed. For example, the performance of fresh 0.1% Pt/alumina in the CO and HC light-off tests is shown in Figs. 1 and 2, curve A. Thermal aging of this catalyst at 800°C for 4 h in air results in the poorer performance illustrated in Figs. 1 and 2, curve B. The 50% conversion temperatures (a convenient reference point for this type of activity curve) for CO and HC increased by 124 and 119°C, respectively, while the catalyst dispersion dropped from 39 to 2%. These changes represent a significant deterioration in catalyst performance. Attempts to recover the activity of this catalyst by treatment in air/$CHCl_3$, air/HCl, or 5% H_2/N_2 at temperatures in the 400–600°C range were unsuccessful. However, treatments with chlorine over the 250–500°C range revealed significant improvement in the activity of the catalyst when the temperature of the treatment was above 350°C. The CO and HC oxidation light-off tests for the aged 0.1% Pt/alumina catalyst after Cl_2, 350°C; Cl_2, 400°C; and Cl_2, 450°C treatments are shown in Fig. 1C–1E and Fig. 2C–2E, respectively. The performance of the catalyst treated at 400°C is virtually identical with the performance of the fresh catalyst.

Another way of looking at the effect of the chlorine treatment temperature is shown in Fig. 3 as a plot of the 50% CO conversion temperature vs the chlorine treatment temperature. The fresh and aged catalyst performances are marked on the left axis line for comparison. Treatment temperatures below 350°C provide little improvement in activity while those above 350°C yield performance equivalent with the fresh catalyst. The corresponding dispersions observed after the chlorination treatment are also plotted in Fig. 3, with fresh and aged catalyst dispersions marked on the right axis line. The changes in dispersion with the chlorine treatment temperature parallel the improvements observed in catalyst performance in the expected manner: as the dispersion increases, the 50% CO conversion temperature decreases. Similar trends are also ob-

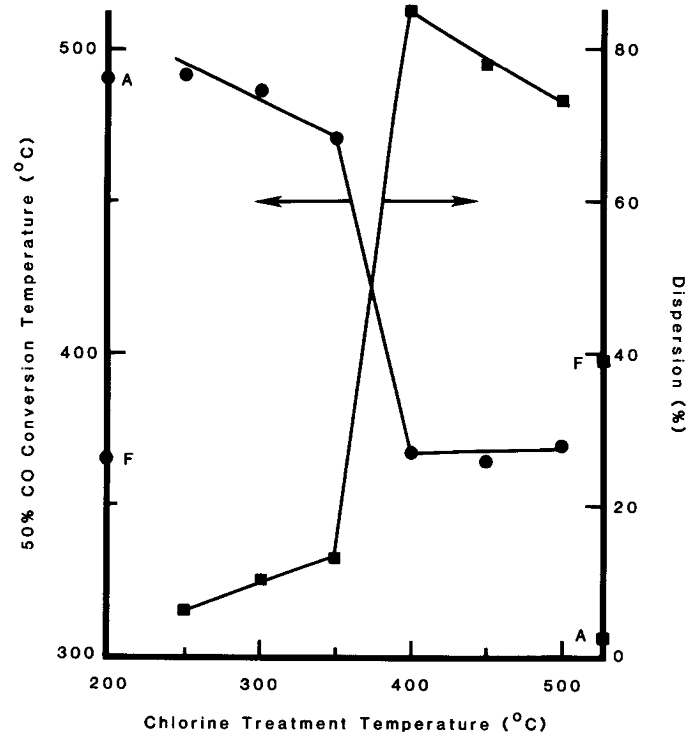

FIG. 3. The effect of chlorination temperature on the 50% CO conversion temperature and dispersion of aged 0.1% Pt/alumina. Fresh (F) and aged (A) reference points are marked on each vertical axis.

served for HC oxidation. The dispersion of the sample following a Cl_2, 400°C treatment is more than twice that of the fresh catalyst and suggests that virtually all the platinum in the sample is involved in the reaction with Cl_2 and also that the oxidation product is well dispersed before its subsequent decomposition in H_2, 400°C. This observation is consistent with the conclusions of Foger and Jaeger (*9*) in their study of Cl_2 reactions with silica- and alumina-supported Pt. However, our results suggest little redispersion occurs in pure chlorine below 350°C, while Foger and Jaeger report the disappearance of Pt particles (via electron microscopy) in 10% Cl_2/N_2 after 4 h at 200°C.

Elemental and scanning electron microprobe analyses indicate no loss of Pt from the Cl_2, 400°C sample. Figure 4 compares the microprobe trace obtained on half-pellets of aged 0.1% Pt/alumina before and after the Cl_2, 400°C treatment. Macroscopic redistribution of Pt has not occurred to the extent that the overall profile of Pt on the pellet is changed. This observation implies that only a microscopic, or local, redispersion of Pt occurs over the surface of the support surrounding the initial particles of Pt. This process could involve a gas phase intermediate such as $PtCl_2$ as suggested by Foger and Jaeger (*9*) or a surface-bound, rapidly diffusing species produced at the alumina–platinum interface. Additional studies of the redispersion process in model Pt/alumina systems would be useful in determining the mechanism of Pt transport.

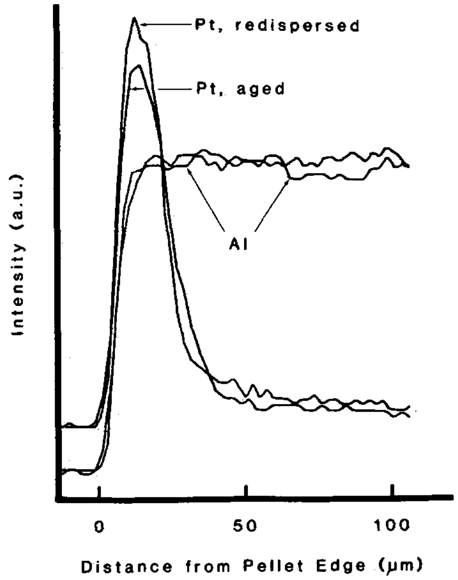

FIG. 4. Scanning electron microprobe traces of Pt and Al on half-pellets of aged 0.1% Pt/alumina before and after redispersion with Cl_2, 400°C. The Al scans mark the external edge (0 μm) of the pellets and have been superimposed. Also, the Al scans have been arbitrarily scaled to fit the same vertical scale as the Pt scans.

Qualitative TEM characterization of the fresh–aged–redispersed–reaged cycle on 0.1% Pt/alumina has been carried out. Figure 5 shows typical micrographs of the fresh (A) and aged (B) catalyst surface. The fresh catalyst has a Pt particle size of 2–5 nm which compares well with the 3.0 nm average particle size estimated from the dispersion (39%) measurement (*24*). Heating in air at 800°C for 4 h produces the aged catalyst with a particle size of 25–30 nm. This size range again compares favorably with that estimated from the dispersion (3%) measurement. Figure 6A shows a TEM micrograph of the redispersed catalyst that results from a Cl_2, 400°C treatment. Very few discrete particles are observed after this treatment, although dark smudge-like areas can be seen which appear ill-defined and thin. The lack of well-defined particles suggests that the metal is highly dispersed in particles much smaller than 2 nm (this size was readily observed on the fresh catalyst). This conclusion is supported by the dispersion measurement (86%) which indicates an average particle size of <1.5 nm. Subsequent aging of the redispersed sample produces a reaged catalyst which is similar to the original aged catalyst. Figure 6B shows a TEM micrograph of the Pt particles on this sample. The TEM results suggest a somewhat larger particle size, 40–75 nm, in the reaged catalyst, although the measured dispersions of aged and reaged catalysts are the same. Confirmation and quantification of this difference in particle size will require

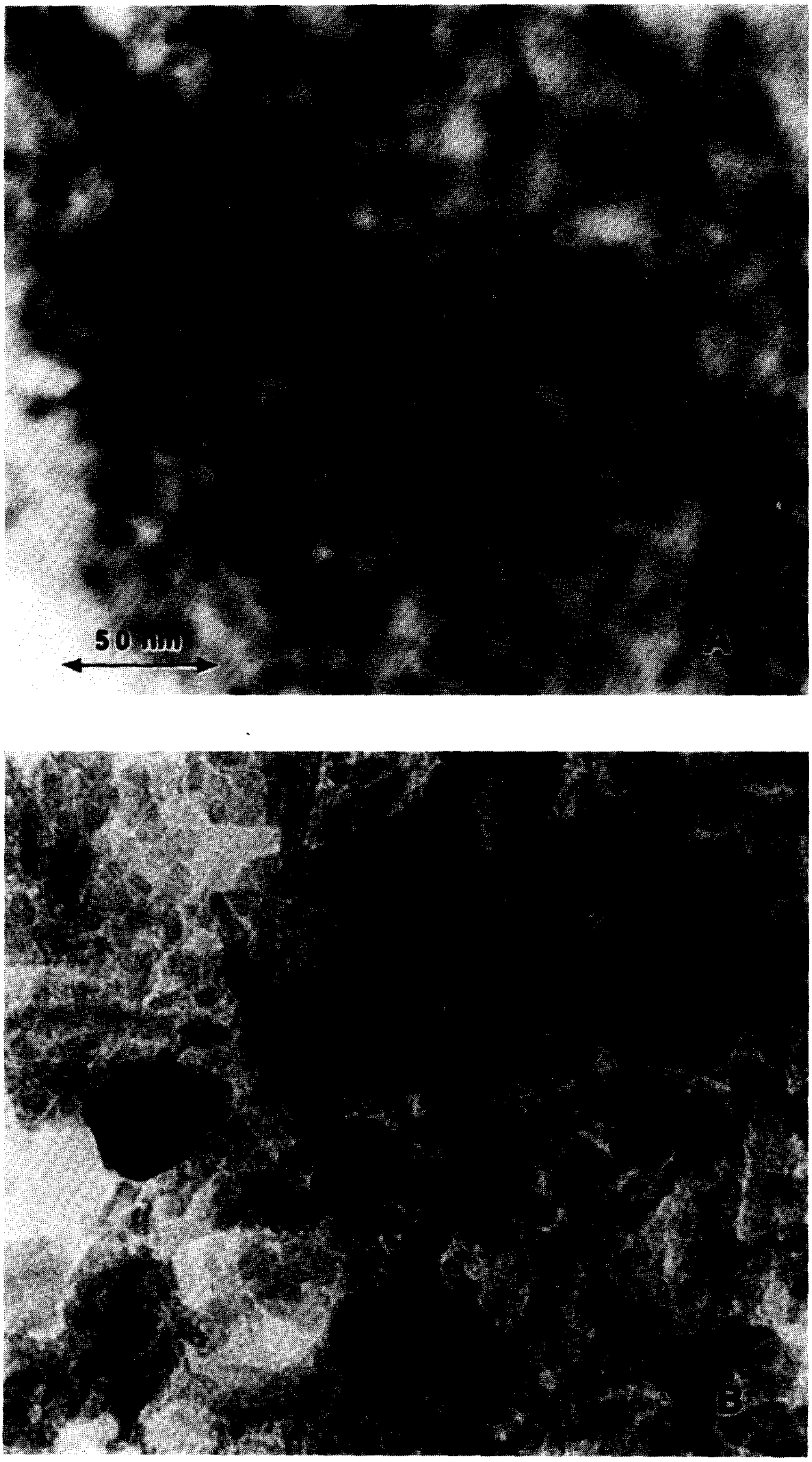

FIG. 5. Transmission electron micrographs of 0.1% Pt/alumina fresh (A) and aged (B), 800°C/4 h/air.

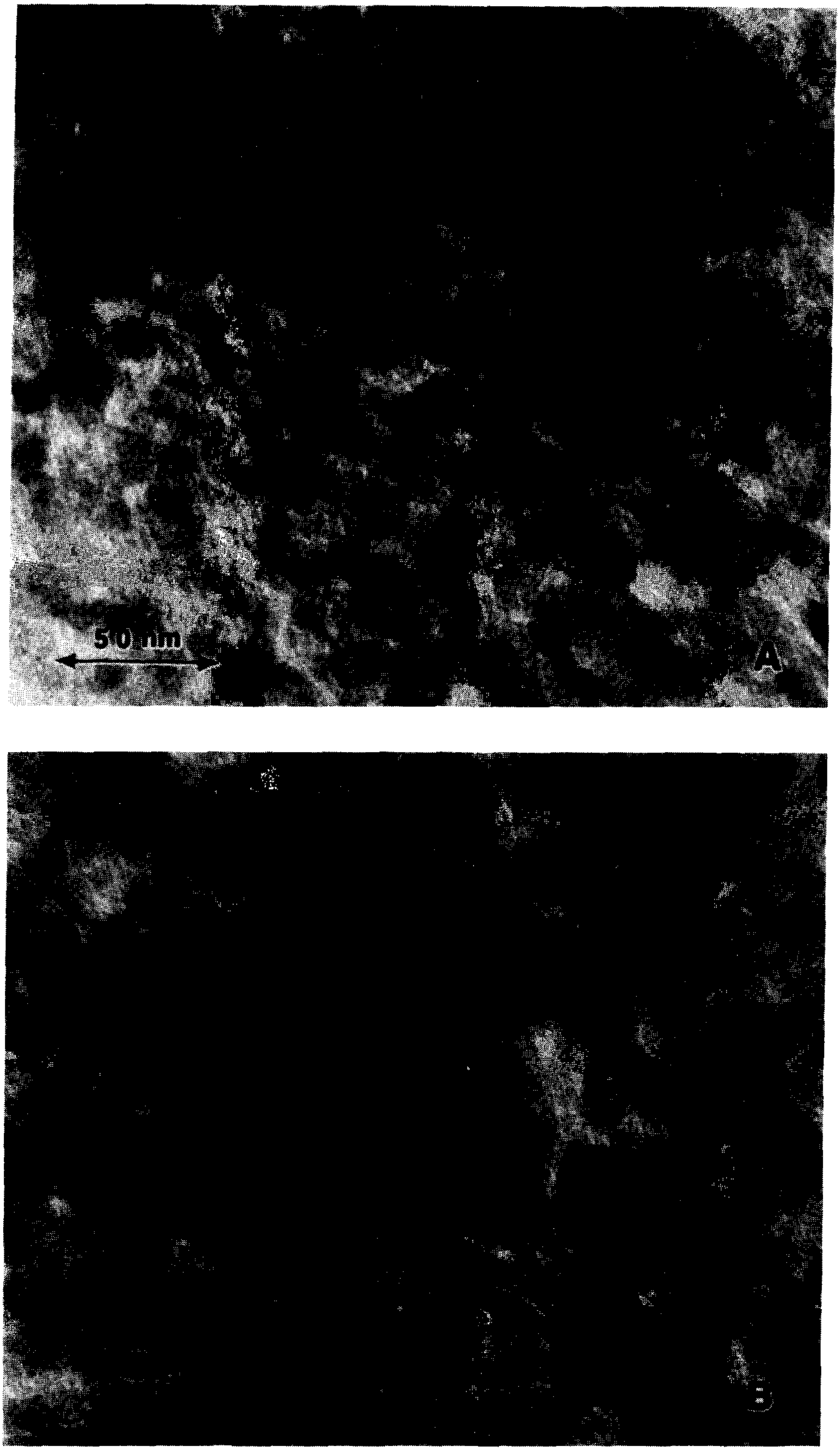

FIG. 6. Transmission electron micrographs of aged 0.1% Pt/alumina after redispersion (A) with Cl_2, 400°C. Subsequent reaging, 800°C/4 h/air, of the redispersed sample produced (B).

more extensive TEM particle size analysis. Differences in aged and reaged particle size distributions suggest that different aging mechanisms, or a different mix of more than one mechanism, occur for fresh and redispersed catalysts. The differences in aging characteristics may have a significant impact on redispersed catalyst thermal durability and should be studied further.

Some variations on the use of pure, flowing chlorine for the redispersion of 0.1% Pt/alumina have also been examined. For the experiments discussed above, a 10-g sample of catalyst was treated with wet chlorine at 60 ml/min for 30 min. This represents a Cl_2/Pt mole ratio of 1440 which is large compared to the stoichiometric requirements of either 1 or 2 for the formation of $PtCl_2$ or $PtCl_4$, respectively. Experiments with static chlorine atmospheres indicate that redispersion can be achieved at much lower Cl_2/Pt mole ratios. For example, a 10-g sample of aged 0.1% Pt/alumina, treated for 30 min with 100 ml of chlorine ($Cl_2/Pt = 80$) in a sealed tube at 450°C, was redispersed as effectively after 30 min of exposure as in the equivalent pure, flowing chlorine experiment (82% vs 78% dispersion, respectively).

The chlorine concentration dependence of the redispersion process was evaluated by exposing catalyst samples to flowing Cl_2/air mixtures. In these experiments, a 10-g sample of aged 0.1% Pt/alumina was treated at 450°C for 30 min in flowing air (50 ml/min). Chlorine (1.1–32.0 ml/min) was added to this constant air flow with a syringe pump to give various Cl_2/air mixtures. The range of mixtures examined was 2–39% (v/v) chlorine in air, representing a Cl_2/Pt mole ratio range of 26–1200 for the fixed exposure time of 30 min.

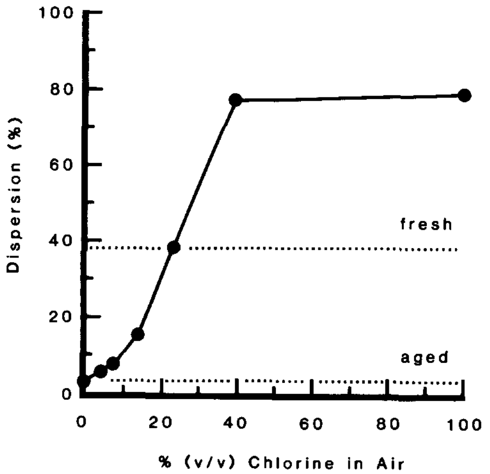

FIG. 7. The dispersion of aged 0.1% Pt/alumina as a function of chlorine concentration in air after a 30 min, 450°C treatment.

The results of these experiments, shown in Fig. 7, indicate that the degree of redispersion is fairly sensitive to chlorine concentration under the conditions of these experiments. The reason for this sensitivity is not readily apparent and could result from either thermodynamic or kinetic causes; additional experimentation will be required before this question can be addressed.

Other oxidants were briefly evaluated for their ability to redisperse aged 0.1% Pt/alumina. Several solution-based reagents were examined by impregnation followed with calcination. For example, aqueous solutions of chlorine (saturated in 0.1 *M* HCl), hydrogen peroxide (10% in 0.1 *M* HCl), hydrochloric acid (6 *M*) and aqua regia (3 : 1, concn HCl : concn HNO_3) were added to catalyst samples which were then heated in a tube furnace in air. Little or no redispersion was observed for any of these reagents even though all are capable of oxidizing bulk platinum. It appears that these solution oxidation agents require more time to attack supported Pt at elevated temperature than their evaporation/decomposition rates permit.

Other gaseous, halogen-containing strong oxidizing agents behave like chlorine. For example, there is a patent reference to the use of phosgene ($COCl_2$) as a redispersing agent for automotive oxidation catalysts (*14*). The ability of wet, gaseous bromine to redisperse aged 0.1% Pt/alumina is illustrated in Fig. 8. Bromine behaves in a manner similar to that of chlorine except that higher temperatures are required to achieve

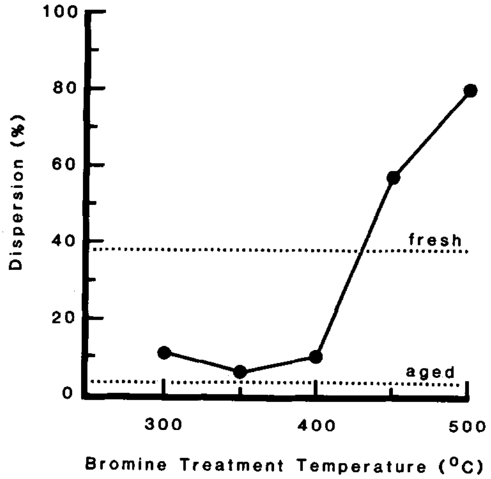

FIG. 8. The effect of gaseous bromine treatment temperature on the dispersion of aged 0.1% Pt/alumina.

a similar degree of redispersion. The redispersion mechanism is probably similar to that of chlorine, involving the formation of $PtBr_2$ followed by either gas phase or surface diffusion transport.

The results presented here basically agree with and supplement those of Foger and Jaeger (*9*). They proposed a mechanism for redispersion involving oxidation of the Pt particles to volatile $PtCl_2$ which subsequently readsorbs and undergoes further oxidation with Cl_2 to form an adsorbed Pt(IV) chloride. The overall mechanism clearly requires the oxidation of Pt crystallites and the subsequent transport of the oxidation product over relatively large distances. The nature of the transport species is not clear and, as noted earlier, could be an adsorbed, but surface mobile, species rather than gaseous $PtCl_2$.

The primary evidence for a non-gas phase species is the lack of change in the macroscopic Pt profile of the 0.1% Pt/alumina catalyst studied in this work. If a gaseous species was involved, then a detectable broadening of the Pt profile, along with some loss or redistribution of Pt through the catalyst bed, should be observed. Additional studies are needed to identify the nature of the transport mechanism in the Pt/alumina system.

II. Rh/Alumina

The Rh/alumina system was studied in a manner similar to that reported above for Pt/alumina. Hydrogen chemisorption was also used to estimate Rh dispersions after various redispersion treatments. There has been some disagreement in the literature (*25–33*) concerning the value of the H/Rh adsorption stoichiometry; values for H/Rh of 1.0–1.7 have been reported. Different procedures were used to determine H_2 adsorption (or desorption) by the various workers in this area, and all determine the value of irreversibly adsorbed H_2 differently. In particular, the evaluation of reversibly adsorbed hydrogen, which increases the observed H/Rh ratio, varies significantly. Some workers ignore reversible adsorption while others evaluate its contribution using a sample of blank support and thus ignore metal-catalyzed hydrogen spillover (*34*). These problems seem to be particularly troublesome in the study of highly dispersed Rh/alumina (*31–33*) containing Rh particles smaller than 1 nm (by TEM). Fortunately, several studies (*29–31*) of moderately dispersed Rh with particles larger than 1.5 nm indicate that particle size determinations with either TEM or hydrogen chemisorption (assuming H/Rh = 1.0) are in agreement, particularly when samples are pretreated in hydrogen at 450–500°C (*29–30*). The work reported here was conducted with a 0.08% Rh/alumina catalyst with a fresh particle size >2.0 nm determined by hydrogen chemisorption (assuming H/Rh = 1.0) following a 450°C hydrogen pretreatment. Smaller particle sizes were not observed in this study; thus the results should be free of complications associated with changes in H/Rh that may occur with smaller Rh particle sizes.

The fresh 0.08% Rh/alumina catalyst was treated for 4 h at 800°C in air to produce an aged catalyst for redispersion experiments. These conditions reduced the fresh catalyst

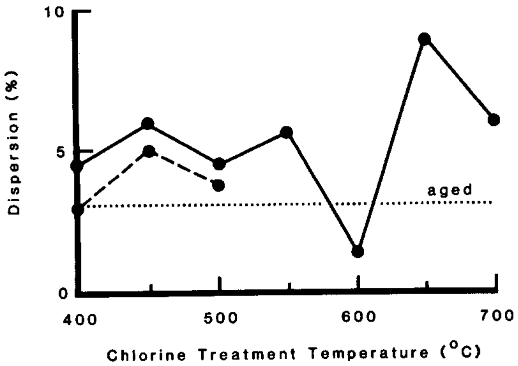

FIG. 9. The effect of chlorine treatment temperature on the dispersion of aged 0.08% Rh/alumina before (solid line) and after (dashed line) a 500°C, 5% H_2/N_2 pretreatment. The horizontal dashed line indicates the aged catalyst dispersion prior to these treatments.

dispersion from 57 to 3%. Treatment of the aged catalyst with chlorine over the 400–700°C range had little effect on its dispersion. This is illustrated by the solid line in Fig. 9. The lack of improvement could be due to several reasons. One possibility might be that a rhodium(III) oxide rather than rhodium metal is present on the air-aged catalyst. One would expect supported rhodium metal to react with chlorine somewhere in the 400–700°C temperature range (*36*), while a rhodium(III) oxide, e.g., Rh_2O_3, would be inert. Another possibility might be that a rhodium(III) chloride, e.g., $RhCl_3$, forms but crystallizes into bulk $RhCl_3$ rather than dispersing over the support. This is illustrated quite well in the work of Foger and Jaeger (*9*) in which bulk (on silica) or dispersed (on alumina) platinum chlorides form, apparently depending upon the degree of interaction between the oxidation product and the support. The affinity of the support for the oxidation product is likely to be the major driving force for the redispersion process. If bulk crystallization forces are stronger, then crystallization, rather than redispersion, should occur.

The first of these two possibilities was investigated by pretreating the aged 0.08% Rh/alumina catalyst with hydrogen in an attempt to reduce any oxide of rhodium present to the metallic state. After reduction, samples were treated with the normal chlorine treatment (see Experimental) sequence. The dashed line in Fig. 9 shows the effect of chlorine treatment temperature on the dispersion of catalyst samples which were pretreated at 500°C in 5% H_2/N_2 for 1 h. Such a pretreatment clearly had no real effect on the ability of a subsequent chlorination to redisperse the catalyst. However, higher hydrogen pretreatment temperatures have a much greater effect which is illustrated in Fig. 10. In this series of experiments, the pretreatment temperature was varied over the range 500–800°C while the chlorination conditions (500°C, 30 min) were held constant. Substantial redispersion results when the pretreatment temperature is ≥700°C. For example, a 700°C, 5% H_2/N_2 pretreatment gave an improvement in the dispersion from 3 to 37%. A control experiment in which the chlorination step was omitted following the 700°C, 5% H_2/N_2 pretreatment resulted in an increase in dispersion from 3 to 17%. Thus part of the im-

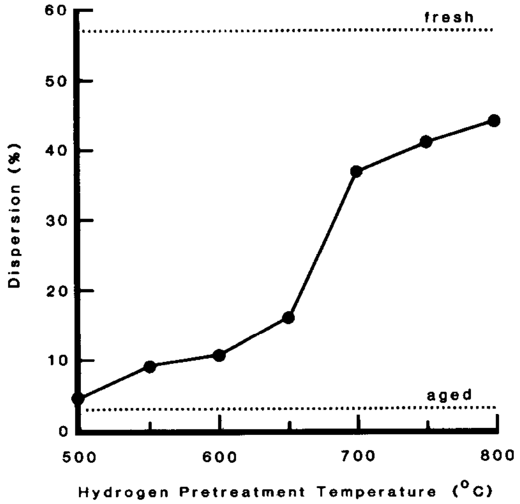

FIG. 10. The effect of the 5% H_2/N_2 pretreatment temperature on the dispersion of aged 0.08% Rh/alumina. The chlorination conditions were held constant at 30 min, 500°C. The horizontal dashed lines represent the fresh and aged dispersions of this catalyst.

provements indicated in Fig. 10 simply result from the pretreatment. The positive effects of such a high temperature pretreatment have been attributed by others (*28*, *36*) to the reduction of a difficult-to-reduce state of rhodium which is obtained by high temperature oxidation treatments. The redispersion results reported here lend some support to this hypothesis since oxidized forms of rhodium are not expected to react with chlorine as noted above. These results also suggest that a rhodium chloride phase will lead to rhodium redispersion if the chloride phase can be formed. The highest degree of redispersion was achieved following an 800°C, 5% H_2/N_2 pretreatment (3 to 44%). Thus, unlike the 0.1% Pt/alumina case, redisperison to fresh (or better than fresh) levels is not easily achieved for the aged Rh/alumina catalyst studied here even after extensive reduction.

Several of the samples used to develop the redispersion results given in Figs. 9 and 10 were also characterized in a laboratory reactor. In general, the shape of the CO, HC oxidation light-off curves of the 0.08% Rh/alumina samples are similar to those of fresh 0.1% Pt/alumina shown in Figs. 1 and 2, but shifted to lower temperatures. The 50% CO conversion temperatures for several 0.08% Rh/alumina samples are compared in Fig. 11A. The difference between fresh and aged samples is only 22°C, an amazingly small difference when compared with the 124°C difference between fresh and aged 0.1% Pt/alumina, Fig. 3. This observation is particularly difficult to understand since similar changes in dispersion are observed in both the Pt (39 to 3%) and Rh (57 to 3%) cases. Comparison of the other bars in Fig. 11A indicates that the best performance is obtained after a 700°C, 5% H_2/N_2 treatment, and that the performance level achieved is significantly better than fresh. All other treatments result in poorer performance, even though in some cases the dispersion is higher. The lack of correlation between the activity and the dispersion of these samples is illustrated in Fig. 11B and indicates that the performance of a Rh/alumina catalyst is more sensitive to factors other than dispersion which are controlled by reactor feedstream composition and temperature. The reactor data used to generate Figs. 11A and 11B were obtained from the last of a series of run-ups which represents the stable state of the catalyst for the reactor feedstream composition and operating temperature range. Generally, three to five run-ups were required to reach this stable state and the difference between the first and last run-up can be quite large. This is particularly true for the aged sample which had been treated in air at 800°C before reactor evaluation. This

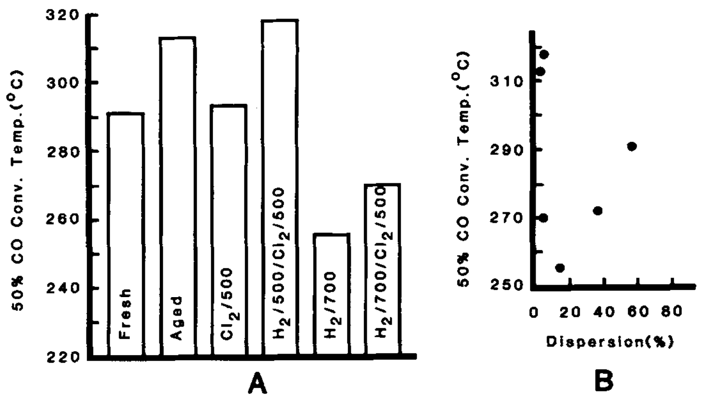

FIG. 11. The effect of several treatments on the 50% CO conversion temperature of 0.08% Rh/alumina (A) and the dependence of the 50% CO conversion temperature on catalyst dispersion (B).

sample exhibited 50% CO conversion temperatures of 410, 310, and 313°C in the first, second and third run-up, respectively. Samples which were reduced prior to reactor evaluation did not display such large shifts.

III. Bimetallic Pt–Rh/Alumina

The bimetallic Pt–Rh/alumina system was also examined in this work. This type of catalyst has wide application in automotive emission control systems and may display a number of potentially interesting interactions between metals (*37, 38*). The extent of alloy particle formation and the degree of surface enrichment that occurs on such particles should affect the way that Pt–Rh system behaves in its reactions with dispersing agents such as chlorine. An example of this sort of behavior was nicely demonstrated by Foger and Jaeger (*11*) in the Pt/Ir system. In that study, alloyed Pt/Ir and Pt were dispersed in chlorine but Ir was not.

Two types of Pt–Rh catalysts were selected for study. In both, the loading was fixed at 0.15% Pt–0.075% Rh which represents approximately equal amounts of both metals on an atom basis. One catalyst was prepared by co-impregnation of both metals (as chlorides) in a single step (referred to below as C–Pt/Rh) while the other was prepared by sequential impregnation of Rh followed by Pt with a calcination between impregnation steps (referred to below as S–Pt/Rh). The metals on the C–Pt/Rh sample should be well mixed on the atomic scale relative to the S–Pt/Rh sample, provided segregation into Pt metal and Rh oxide does not occur during calcination. Samples of each type of catalyst were subsequently aged for 4 h at 800°C in air, a treatment which is likely to cause segregation (*37*) into either discrete Pt and Rh oxide particles (on S–Pt/Rh) or Rh oxide-coated Pt particles (on C–Pt/Rh).

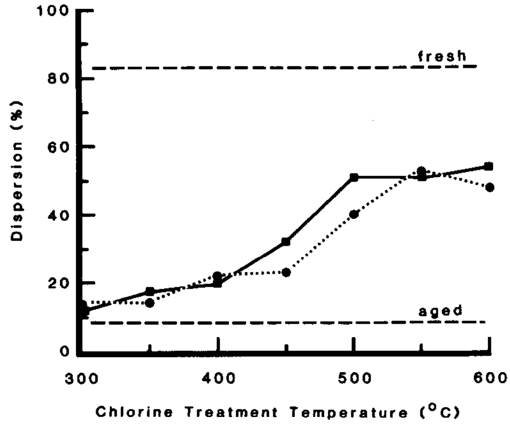

FIG. 12. The effect of chlorine treatment temperature on the dispersion of aged, co-impregnated (dashed line) and aged, sequentially impregnated (solid line) 0.15% Pt–0.075% Rh/alumina. The horizontal dashed lines indicate the fresh and aged dispersions of both types of catalyst.

The treatment of either of these aged catalysts with chlorine directly (no H_2 pretreatment, Fig. 12) results in partial redispersion in a manner similar to that for the Pt only case. Both types of catalysts have the same fresh and aged dispersions of 83 and 8%, respectively, and both respond to chlorine treatments similarly. Significant redispersion occurs in chlorine above 450°C, peaking at about 50% in both cases. This behavior is similar to that of Pt, which is nearly completely redispersed in this temperature range (Fig. 3), and unlike that of Rh, which is not redispersed (Fig. 10). The effects of 5% H_2/N_2 pretreatments (followed by Cl_2 at 500°C for 30 min) are shown in Fig. 13 and, as in the case of Rh alone, result in additional improvements in the dispersion of both types of catalysts to nearly fresh levels. Again, as was the case for Rh alone, a 700°C, 5% H_2/N_2 pretreatment without a subsequent chlorination gave an increase in dispersion from 8 to 17%.

The foregoing results indicate that both types of Pt–Rh catalysts behave in a manner which is intermediate between that of the monometallic constituents. This behavior could be rationalized equally well with either of two hypotheses involving (1) the presence of monometallic Pt and Rh (or Rh oxide), particles, or (2) the presence of particles with a distribution of composi-

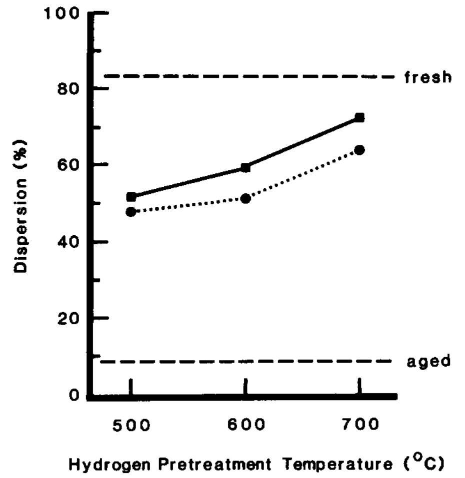

FIG. 13. The effect of hydrogen pretreatment temperature on the dispersion of aged, co-impregnated (dashed line) and aged, sequentially impregnated (solid line) 0.15% Pt–0.075% Rh/alumina. The chlorination conditions were held constant at 30 min, 500°C. The horizontal dashed lines represent the fresh and aged dispersions of both types of catalyst.

tions ranging between pure Pt and pure Rh (or Rh oxide). For case 1, the results can be perceived as the redispersion of about 80% of the Pt and none of the Rh in chlorine at 500°C (80% · $\frac{1}{2}$ + 8% · $\frac{1}{2}$ ≃ 44% of total metal dispersed) or the redispersion of about 80% of the Pt and about 45% of the Rh after pretreatment in 5% H_2/N_2 at 700°C (80% · $\frac{1}{2}$ + 45% · $\frac{1}{2}$ ≃ 63% of total metal dispersed). For case 2, only crystallites rich in Pt are dispersed in chlorine, while those rich in Rh required prior treatment in 5% H_2/N_2 at 700°C before they can be effectively attacked by chlorine. The determination of which hypothesis is correct will require detailed investigation by TEM. Such investigations should also reveal the difference, if any, between the two types of Pt/Rh catalysts in their fresh, aged and redispersed states.

The relationship between dispersion and CO oxidation activity for several of the S–Pt/Rh and C–Pt/Rh samples was also investigated. The shapes of the light-off curves for these catalysts from the standard laboratory reactor light-off test are similar to that of 0.1% Pt/alumina (Fig. 1) but shifted to lower temperature. Figure 14 compares the 50% CO conversion temperatures of the two types of Pt/Rh catalysts fresh, aged and after several treatments. The difference between fresh and aged catalysts is greater than that observed for Rh alone but smaller than that for Pt alone. For S–Pt/Rh, all the

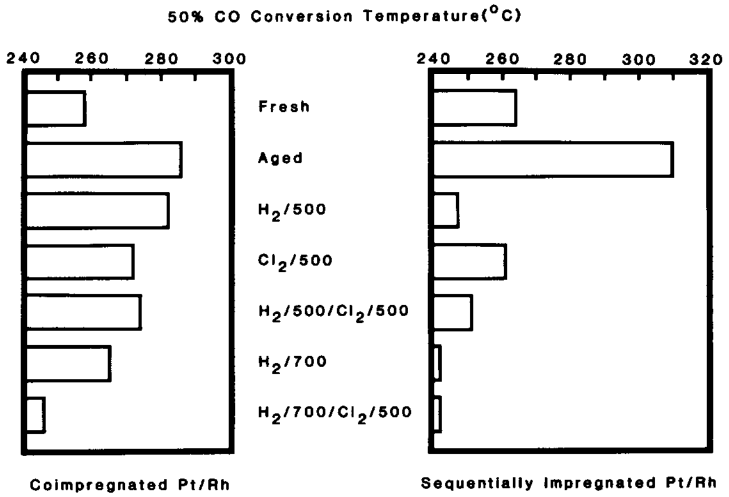

FIG. 14. The effect of several treatments on the 50% CO conversion temperature of S–Pt/Rh and C–Pt/Rh.

treatments shown in Fig. 14 produce catalysts with performances better than fresh while for C–Pt/Rh, only the H_2, 700°C/Cl_2, 500°C treatment produces a catalyst with activity better than fresh. As in the case of Rh alone, the 50% CO conversion temperature does not correlate with the dispersion of the sample. This is illustrated in Fig. 15 as a plot of activity (as 50% CO conversion temperature) of the samples from Fig. 14 versus their measured dispersion. There appears to be a weak trend toward improved performance as the dispersion increases, although the scatter of the data is quite large. This suggests that factors other than dispersion are more important in determining the activity of a Rh-containing catalyst. Again, as observed for Rh/alumina, significant shifts in the 50% CO conversion temperature occurred as the Pt/Rh samples equilibrated in the reactor feed. The aged samples which had been strongly heated in air displayed the largest shifts; initial 50% CO conversion temperatures shifted from 361 and 364°C to 286 and 310°C for C–Pt/Rh and S–Pt/Rh, respectively. Samples which had been strongly reduced tended to display lower initial 50% CO conversion temperatures which increased as the samples equilibrated in the feed. For example, the 700°C, H_2-treated C–Pt/Rh and S–Pt/Rh samples had initial 50% CO conversion temperatures of 215 and 220°C which increased to 265 and 242°C, respectively. These observations suggest that changes in oxidation state (or the morphological changes that occur with changes in oxidation state) have a larger impact on catalyst performance than changes in dispersion. Additional work is needed to understand how these changes affect catalyst structure and to associate particular catalyst structures with levels of catalytic performance. Progress in this area will require extensive use of analytical electron microscopy techniques.

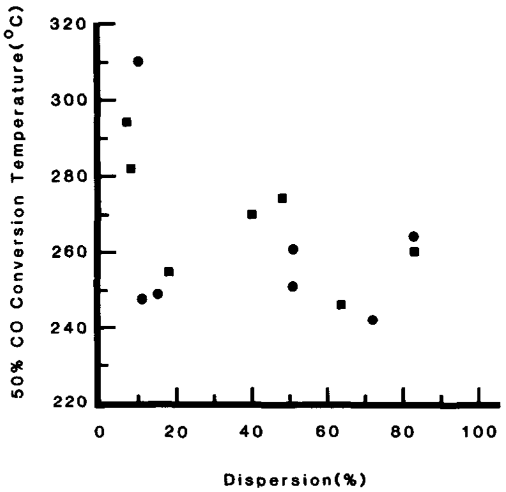

FIG. 15. The dependence of 50% CO conversion temperature on the dispersion of S–Pt/Rh (circles) and C–Pt/Rh (squares).

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