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Low-Concentration Supported Precious Metal Catalysts Prepared by Thermal Transport

INTRODUCTION

Previous work from this laboratory (*1*) has shown that the active catalytic components on the support surface exist in two forms: bulk-like particulates and highly dispersed atoms or highly dispersed oxides (ions). Since the active components can be present in different chemical or valency states, they will possess different catalytic properties. For example, the oxidation of CO or hydrocarbons over precious metals supported on Al_2O_3 with or without other additives will follow different reaction kinetics depending on the degree of dispersion and oxidation state of the precious metal (*2*). During heat treatment or reactions, particularly at elevated temperatures, the dispersed atoms or ions at high concentrations may aggregate to form particulates while at low concentrations the particulates can disperse and spread over the support surface. The dependence of such interphase transformation on the nature of the support or on the environmental conditions has been the subject of several studies (*3–8*). The effect of the support additives, such as rare-earth oxides used in many automotive catalysts, has received less attention.

The study of the individual phases and their transformation is difficult because in conventional catalysts, such as automobile catalysts, the two phases usually coexist in unknown proportions. Neither the initial nor the final state of the catalyst surface after a reaction can be easily assessed. Furthermore, the catalysts prepared by impregnation can be inhomogenous due to uneven wetting, adsorption, entrapment of the solution, etc. Residual anion species such as chloride add to the complexity of the system.

In this study, the thermal transport from bulk phase to the dispersed phase is examined using a simple model system. That is, the precious metal was thermally transported from a metal sheet to an Al_2O_3 support surface by heating together in air. The catalytic activity of the Al_2O_3 powder after such treatment was evaluated by a standard reaction, the oxidation of CO. The metal concentration on such catalysts is very low and it is highly dispersed. The effect of the support additives, CeO_2, temperature, and conditions of preparation on the metal transport, and the catalytic activity have been examined and compared with those of comparable composition prepared by the impregnation method.

Some practical implications of this study are given at the end of this paper.

EXPERIMENTAL SECTION

Catalyst preparation. Al_2O_3 powder (Catapal, Conoco Chemical Co.) was dehydrated at 250°C for 16 h and calcined at 800°C in an alumina crucible for 20 h before being used for the preparation of *all* the catalysts used in this study.

The CeO_2 was added to the alumina by conventional incipient impregnation with solutions containing the desired amount of cerium nitrate. The impregnated aluminas were dried under an IR lamp, and the nitrate decomposed at 250 to 350°C, followed by calcination in a muffle furnace at 800°C for at least 4 h. The concentration of the CeO_2 was calculated from the concen-

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tration and the amount of the salt solution and the weight of the Al_2O_3 powder used. It was checked by the total weight gain.

For impregnated catalysts, the precious metal component was added to the alumina powder, with or without CeO_2, by incipient impregnation with H_2PtCl_6, $PdCl_2$, or $Rh(NO_3)_3$ solutions of the appropriate concentration. The same drying and calcination procedures as described above were used.

Pt, Pd, and Rh sheets 0.001 in. thick were purchased from Alfa Chemical Co. They were washed with dilute HNO_3, distilled water, and acetone, dried, and heated in air to 800°C prior to use. A thin layer of the Al_2O_3 powder with or without CeO_2 was spread over the bottom of a flat-bottom α-alumina dish, and the metal sheet was placed over the powder and in contact with it. The dish was then covered with an α-alumina top and heated in air in a muffle furnace at the desired temperature for a specified time. In a few cases, the metal sheet was kept from direct contact with the powder by three α-alumina spacers. The sheet was removed at the end of the heating period and the powder was gently mixed and used for the determination of catalytic activity and for neutron activation analysis.

Determination of catalytic activity. The rate of CO oxidation was determined using a set of standard inlet conditions: stoichiometric concentration (0.67% of CO and 0.33% of O_2) in He at atmospheric pressure, and a specific flow rate of 1000 ml [NTP]/min g catalyst.

The Pt concentration was determined by neutron activation analysis performed at the Phoenix Nuclear Reactor of the University of Michigan. The analytical accuracy at the low concentrations involved is estimated to be ±10% of the true value.

RESULTS

The oxidation of CO over the Pt, Rh, and Pd catalysts prepared by thermal transport from the thin noble metal sheets to Al_2O_3 without ceria is similar in its character to that observed over the comparable catalysts prepared by impregnation (*2, 12*), namely: (1) a short activation in O_2-free He at 450°C or in the reaction atmosphere at 450°C is required for maximum activity and (2) no significant reduction of the catalyst nor a change in its activity was observed after treatment with 1% CO at 450°C.

For all of the catalysts containing CeO_2 a strong Pt–CeO_2 and Rh–CeO_2 interaction was observed as manifested by deactivation in an oxidizing atmosphere and a sharp increase in activity after reduction (*2, 12*). This was not found for the case of Pd supported on CeO_2/Al_2O_3.

The reaction rates were found to be 0 to positive fractional order with respect to CO and O_2 over both the oxidized and reduced catalysts for all combinations of metals and supports. This type of kinetic behavior has been associated with a highly dispersed noble metal phase particularly in the presence of CeO_2 (*2*). A comparison of the oxidation of CO over the Pt and Rh catalysts with or without ceria to that observed over catalysts prepared by impregnation is given in Table 1. In this table, only the highest activity achievable for each catalyst, expressed as the *lowest* temperature for 50% reaction over the reduced (450°C) catalysts, is given. A direct comparison can only be made in the case of Pt since no analyses are available for the Pd and Rh catalysts prepared by thermal treatment.

The activity of the catalysts after reduction at 450°C as a function of the preparation temperature in the presence of the thin noble metal sheets is shown in Fig. 1. The duration of heating was 4 h at each temperature. Only for the catalysts containing Pt was the concentration determined by neutron activation and is shown (in ppm) next to the corresponding activity points. For the case where there was no ceria present in the support, the transfer of Pt reaches a constant value of about 40 ppm and is independent of the temperature in the range of 700–900°C. A nearly constant

TABLE 1

Comparison of CO Oxidation by Noble Metal Catalysts Prepared by Thermal Transfer and by Impregnation

Catalyst wt% CeO_2	PPM noble metal	Method of preparation	T°C 50% for CO oxidation[a] *after* indicated thermal transfer temp. and reduction at 450°C with 1% CO		
			800°C	900°C	1000°C
0	125 Pt	Impregnation[b]	325	361	396
0	~40 Pt	Thermal transfer	359	360	393
8.7	250 Pt	Impregnation	148		
8.7	135 Pt	Impregnation	166	177	179
9.0	222 Pt	Thermal treatment	131		
9.0	426 Pt	Thermal treatment		131	
9.0	? Pt	Thermal treatment			165
0	140 Pd	Impregnation	260	260	256
0	? Pd	Thermal transfer	466	347	306
5.9	140 Pd	Impregnation	208	211	222
9.0	? Pd	Thermal transfer	457	338	293
0	133 Rh	Impregnation	269		
0	? Rh	Thermal transfer	>500	401	380
5.9	135 Rh	Impregnation	224	336	406
9.0	? Rh	Thermal transfer	500	167	245

[a] Standard CO oxidation test as described in text. Temp:–50% conv.

[b] Impregnation with noble metal nitrate solutions to incipient wetness; dried with IR lamp; decomposed 250–350°C; calcined in air for 4 h at 800°C.

activity was also observed for these catalysts. Although the concentrations of Pd and Rh were not determined, the activity results indicate that while below 800°C the transfer of Pd and Rh may be lower than that of Pt, the catalysts become more active when the transfer is done at higher temperatures. The Pd and Rh catalysts prepared by thermal transfer at 1000°C are equal or more active than the corresponding Pt–Al_2O_3 catalyst made at 1000°C. The activity of Rh–Al_2O_3 catalysts is maintained even after a preparation temperature of 1000°C where dissolution of Rh ion into the Al_2O_3 is expected (*9*). Apparently the rate of thermal transfer of Rh from the sheet is faster than the rate of dissolution.

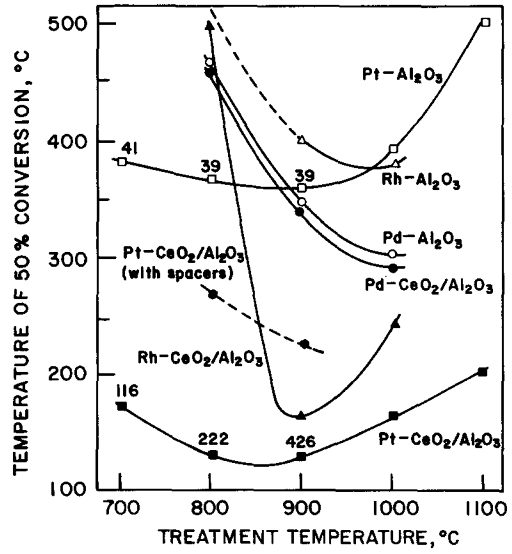

FIG. 1. Temperature of 50% conversion in the oxidation of CO over precious metal catalysts supported on Al_2O_3 or CeO_2/Al_2O_3 as a function of preparation temperature. Catalysts reduced at 450°C.

A strong enhancement in Pt concentration and in catalytic activity is observed in the presence of CeO_2. While the analytical determination of Pt by neutron activation in the presence of relatively large amounts of Ce is difficult due to interference, nevertheless the increase in Pt transfer with preparation temperatures below 900°C is clearly shown. The transfer of Pt, albeit to a lesser degree, was also observed when the Pt sheet was separated from the powder with spacers. We have taken this as evidence (although not irrefutable) that the transfer of noble metal from the sheet to the alumina does not necessarily involve contact surface diffusion.

As in the case of pure Al_2O_3, the transfer of Pd to CeO_2/Al_2O_3 is very small at 800°C and increases sharply with temperature. The transfer of Pd, as inferred from the activity results may not be affected by the presence of CeO_2 in agreement with the weak Pd–CeO_2 interaction observed over the impregnated Pd catalysts *(12)*.

In the case of Rh, the deposition of Rh on CeO_2/Al_2O_3 by thermal transfer increases sharply as the temperature increases from 800 to 900°C. The enhancement of the activity and, presumably the transfer of Rh, with the addition of CeO_2 is so large that the activity of the 900°C sample is almost as large as that of the Pt catalysts. Further increases in preparation temperature result in less active catalysts.

These results show that in the presence of bulk-phase precious metals and air, the thermal transfer from the bulk phase to the rest of the support surface could be important in maintaining the activity in high temperature application, particularly for the Rh-containing catalysts. The presence of ceria not only can stabilize the metals in the dispersed phase (*2*) but probably is important in enhancing the transport kinetics involved.

The effect of ceria concentration. The activities of Pt and Pd catalysts prepared by heating the metal sheets with Al_2O_3 powder coated with varying amounts of CeO_2 at 800°C for 6 h are shown in Fig. 2. The numbers next to the points represent the Pt concentration (in ppm) determined by neutron activation analysis. Bearing in mind the experimental error of the activation analysis at the low levels of metals, the trend in Pt concentration and activity is at least qualitatively as expected: the large increase in activity of the Pt and only slight increases in Pd with an increase in CeO_2 concentration similar to that which has been observed for the impregnated catalyst *(12)*.

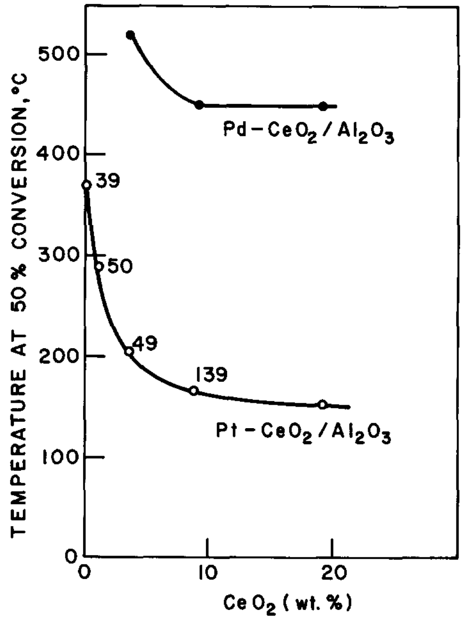

FIG. 2. Temperature of 50% conversion in the oxidation of CO as a function of ceria content prepared at 800°C for 6 h. Catalysts reduced at 450°C.

Metal migration between supports. It was important to ascertain whether the precious metal deposited on the Al_2O_3 or CeO_2 can migrate from one support to the other in the temperature range studied. For this purpose two samples were studied where in each case the metal was deposited either on alumina or on ceria and then diluted with the other support and heated.

In the first case, pure CeO_2 powder, preheated at 800°C and with a surface area of 10 m^2/g, was heated in air in contact with Pt sheets at 800°C. This catalyst was mixed with 9 times by weight of Al_2O_3 powder by grinding. The sequential conversion curves of this mixture are shown in Fig. 3. The

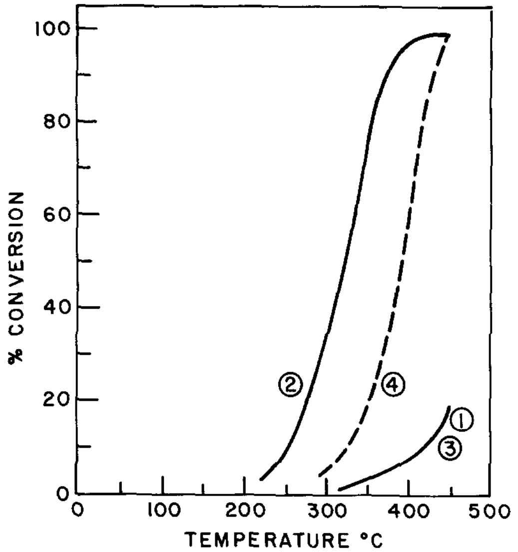

FIG. 3. CO oxidation over a mixture of 1 part thermally prepared Pt–CeO_2, and 9 parts Al_2O_3. (1) Fresh mixture, (2) after reduction, (3) after calcination in air at 800°C, and (4) after rereduction.

inactive state of the fresh mixture, curve 1, and the sharp increase in activity after reduction, curve 2, for Pt–Ce catalysts are shown. The same sample after heating in air at 800°C for 5 h again results in a relatively inactive catalyst, curve 3. After another reduction treatment, the activity increases but is not fully recovered. This suggests that some of the Pt has been transferred from CeO_2 to the Al_2O_3 surface even though the affinity of Al_2O_3 for Pt is lower than that of CeO_2.

In the second sample, an equal weight of CeO_2/Al_2O_3 and a Pt/Al_2O_3 catalyst containing 250 ppm of Pt prepared by impregnation, both preheated at 800°C, were mixed by grinding (Fig. 4). The initial conversion curves 1 and 2 are those typical of Pt/Al_2O_3. After heating at 800°C in air for 1 h, the inactive form, curve 3, and the activation after reduction, curve 4, are typical for catalysts of Pt on CeO_2. Thus, the Pt on Al_2O_3, even at such a low concentration and dispersed state, can migrate from the Al_2O_3 surface to the ceria sites.

CONCLUDING REMARKS

The described results clearly show that in air the precious metals can be thermally transported from the bulk metallic phase to the Al_2O_3 surface at the temperatures studied. The presence of CeO_2 greatly enhances the transfer from the bulk Pt and Rh to the support surface, but has much less effect in the case of Pd. A strong interaction between the oxides of Pt or Rh and CeO_2 is perhaps the driving force for such a transfer. The Pt catalysts prepared by this method are comparable in activity to those of similar concentration prepared by the impregnation method. It was also shown that thermal transport takes place between different supports which may cause dynamic redistribution of the noble metals between these supports when used as catalysts in oxidizing conditions at high temperatures.

The thermal transport from the bulk metal to Al_2O_3 or $Al_2O_3 \cdot CeO_2$ is observed only during preparation in air and not in vacuo or under a reducing atmosphere in hydrogen. Therefore, it is plausible to sup-

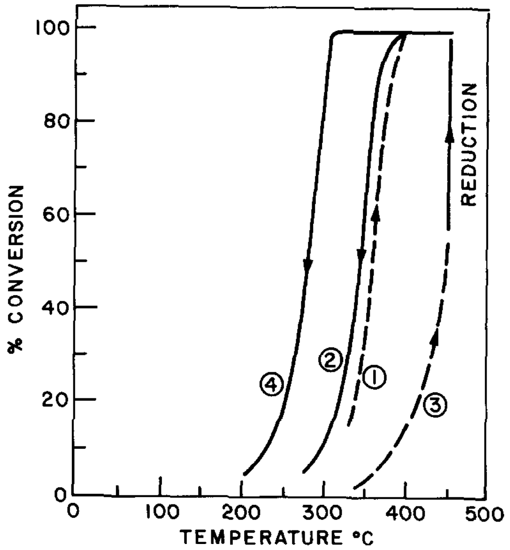

FIG. 4. CO oxidation over a mixture of 1 part of impregnated Pt/Al_2O_3 (250 ppm) and 1 part $CeO_2(19\%)/Al_2O_3$. (1) Fresh mixture, (2) after reduction, (3) after calcination at 800°C, and (4) after rereduction.

pose that it is the gaseous, volatile oxides of the precious metals that are involved in the process. The large difference in the ease of transport at 800°C (Pt $\gg$ Rh and Pd) and the sharp increase in transport of Pd and Rh at $\geq$900°C can perhap be best rationalized by the difference in the stability of the corresponding oxides at these temperatures (*10*).

It is worth mentioning that, as seen in Fig. 2, the sharp increase in catalytic activity associated with the thermal migration of the noble metal to the ceria-containing support is noted at low-ceria contents where it is predominantly present in the dispersed state (*11*). In this range the Pt content does not change much and is similar to that found for pure Al_2O_3 but the activity changes rapidly. The Pt content increases when the bulk CeO_2 phase appears but the activity remains a constant for the reaction conditions used. These results together with the reducibility of surface Ce (*12*) indicate a very complex interaction between Pt (and Rh) with surface Ce resulting in enhancement in the specific catalytic activity. Whether redox reactions of Ce actually contribute to the overall CO oxidation activity deserves further study.

Finally, the results of this study, in addition to suggesting a rather exotic way of preparing noble metal catalysts, are of practical importance in two ways. The first is that when alumina or in particular alumina–rare earth oxide catalyst supports are prepared by calcination in Pt or Pt–Rh crucibles in air above 700°C, the supports will be contaminated by noble metals. One could extrapolate this conclusion to the area of laboratory preparation of ceramic sensors where the resultant activity and selectivity may be influenced by the composition of the vessel used for calcination. The second is concerned with automotive catalysts in which the noble metals are intentionally separated from one another by the method of impregnating each noble metal onto its own support (pellet or powder) which are then mixed to form the final catalyst. When used under high temperature oxidizing conditions there may be unwanted mixing of the noble metals.

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