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THERMAL STABILITY OF PALLADIUM ON CERIA-DOPED ALUMINA

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Several palladium on alumina and ceria/alumina catalysts were prepared and oxidized in air between 400 and 1000°C. The metal dispersion was determined by hydrogen titration of adsorbed oxygen. Dispersions above 50% were maintained on 0.2% Pd/Al_2O_3 up to 900°C. Adding 5.0% ceria, or increasing the metal loading to 2.5%, greatly reduces the thermal stability of the palladium, such that the dispersion falls rapidly at 600°C. The rates of methane oxidation (moles of CO_2/g Pd h) at 250°C and 5% excess oxygen are nearly equal on 0.22–2.50% Pd/3.5–5.2% CeO_2/Al_2O_3, dispersion 14–42%, and 0.20–0.46% Pd/Al_2O_3, dispersion 59–86%, but are 10 to 20 times lower than the rate on 2.3% Pd/Al_2O_3, dispersion 11%. The lower rate of methane oxidation on ceria-promoted and highly dispersed palladium on alumina might be due to the conversion of the palladium into less active palladium oxide during reaction.

1. Introduction

Ceria is an important component of automobile emission control catalysts [1–3]. Under fuel rich conditions, it enhances the rate of carbon monoxide and hydrocarbon oxidation by catalyzing the water-gas shift reaction [1] and by providing lattice oxygen to react with the carbon monoxide and hydrocarbons [1,4,5]. Under lean conditions, the rare earth oxide may not have a beneficial effect. For example, Summers and Ausen [6] found that ceria decreases the rate of carbon monoxide oxidation over platinum. The magnitude of the decrease strongly depends on the catalyst pretreatment. When aged in air at 900°C, oxidation rates over $Pt/CeO_2/Al_2O_3$ catalysts fall precipitously. On the other hand, the activity of palladium and rhodium for carbon monoxide oxidation is relatively unaffected by the promoter [5–7]. The rate of alkane oxidation in excess air is strongly suppressed by adding ceria to platinum and palladium catalysts [2,8,9], but is enhanced by adding ceria to rhodium catalysts [8]. It is claimed that the ceria prevents the reaction of rhodium with alumina, thereby keeping the metal on the surface in an active form [8]. For platinum and palladium, the ceria is supposed to stabilize higher dispersions of the metals and promote their oxidation to metal oxides [2,8–11]. The metal oxides are believed to be poor catalysts for alkane oxidation.

The effect of ceria on the thermal stability of platinum and palladium was studied by Summers and Ausen [6]. They found that ceria did not keep platinum or palladium in a highly dispersed state during exposure to air at 900°C. For palladium, the dispersion after calcination decreased with increasing amounts of ceria. These results do not agree with the explanation given above for the lower rates of alkane oxidation on the promoted platinum and palladium catalysts.

The purpose of this paper is to explore further the effect of ceria on the thermal stability of palladium under oxidizing conditions. The oxygen, hydrogen and carbon monoxide adsorption capacities of ceria-promoted palladium on alumina have been measured after calcination in air at temperatures between 400 and 1000°C. On several of the samples, the palladium structure has been characterized by infrared spectroscopy of adsorbed carbon monoxide, and the activity for methane oxidation has been determined. These results are compared to analogous measurements made on unpromoted palladium on alumina catalysts [12].

2. Experimental

The alumina used in this study was flame-synthesized Degussa aluminum oxide "C", which had been calcined in air for 48 h at 1000°C (surface area 83 m^2/g). The ceria was deposited on the alumina by dissolving approximately 7.0 g $Ce(NO_3)_3 6H_2O$ in 1000 ml H_2O, adding 50.0 g Al_2O_3 to the solution, stirring the slurry for 2 h at 25°C, and slowly boiling off the liquid over 24 h. The alumina paste was removed from the beaker and placed in an oven at 125°C. It was stirred every 30 min until dry, then baked several more hours at 125°C. Next, the cerium nitrate-impregnated alumina was heated in air for 2 h at 400°C and for 24 h at 1000°C. Liquid nitrogen BET analysis showed that the surface area had not changed upon addition of ceria. Palladium was deposited on the alumina by ion exchange with H_2PdCl_4 and on the ceria/alumina by incipient wetness impregnation with H_2PdCl_4. After drying the samples at 125°C, they were calcined in air for 2 h at 400°C. Afterwards, the samples were stored in a desiccator. The amount of Ce and Pd deposited was determined by inductively coupled plasma emission spectroscopy.

Oxygen, hydrogen and carbon monoxide uptakes were measured each time after oxidizing the samples in air for 2 h at 100°C intervals from 400 to 1000°C. After each oxidation, the sample was reduced in 200 cm^3/min H_2 for 1 h at 300°C, evacuated to 1×10^{-6} Torr for 0.5 h at 300°C, and cooled in vacuum to 100°C. At 100°C, the capacities for oxygen adsorption and hydrogen titration of adsorbed oxygen were determined. Then, the sample was reduced at 300°C again, and the carbon monoxide adsorption capacity at 21°C was determined. Adsorption isotherms were recorded on a volumetric chemisorption apparatus at pressures between 10 and 100 Torr (1 Torr = 133 N/m2). The linear portion of the adsorption isotherm in the saturation region was back-extrapolated to zero pressure to give the amount taken up.

Infrared spectra of adsorbed carbon monoxide at saturation coverage were obtained on some of the samples. The procedure used is described elsewhere [12]. The spectra were recorded on a Digilab FTS-40 spectrometer with a DTGS detector of 8 cm^{-1} resolution and coadding 128 scans.

The rate of methane oxidation was determined in a differential conversion, fixed-bed microreactor. From 0.1 to 1 g of 32–60 mesh catalyst pellets was charged to a glass U-tube, 3 mm i.d. A thermocouple was placed just upstream of the pellets, and the tube was mounted in a flow system equipped with on-line gas chromatography. The concentrations of methane, oxygen and carbon dioxide were measured using a 1.83-m Carbosphere packed column held at 180°C and a thermal conductivity detector. Carbon dioxide was the only reaction product. The samples were reduced in 200 cm^3/min H_2 for 1 h at 300°C, then cooled in H_2 to 250°C. At 250°C, the sample was exposed to a 200 cm^3/min flow of 50 Torr CH_4, 110 Torr O_2 and 600 Torr He for 12 h to allow the reaction to achieve steady state. Then, the concentration of carbon dioxide exiting the reactor was measured as a function of total flow rate. The rate of methane oxidation was calculated from the slope of the straight line of CO_2 concentration versus inverse flow rate.

3. Results and discussion

Shown in fig. 1 are the dependencies of the oxygen, hydrogen and carbon monoxide uptakes on the oxidation temperature for 2.5% Pd/3.5% CeO_2/Al_2O_3. The uptakes are calculated by multiplying the moles of gas adsorbed by the adsorption stoichiometry and dividing by the total moles of palladium. The adsorption stoichiometries are assumed to be [13,14]:

$$\tfrac{1}{2}O_2 + Pd_s \rightarrow Pd\text{–}O_s$$

$$\tfrac{3}{2}H_2 + Pd\text{–}O_s \rightarrow Pd\text{–}H_s + H_2O$$

$$CO + Pd_s \rightarrow Pd\text{–}CO_s$$

The gas uptakes should be equivalent to the palladium dispersion provided that the ceria and alumina have no adsorption capacity and do not block adsorption sites on the metal. As can be seen in the fig. 1, the carbon monoxide and hydrogen uptakes are nearly equal. The average CO/3H ratio is 0.95 ± 0.25 for this sample. Chemisorption measurements made on two other samples, 0.85% Pd/5.0% CeO_2/Al_2O_3 and 0.22% Pd/5.2% CeO_2/Al_2O_3, yielded average CO/3H

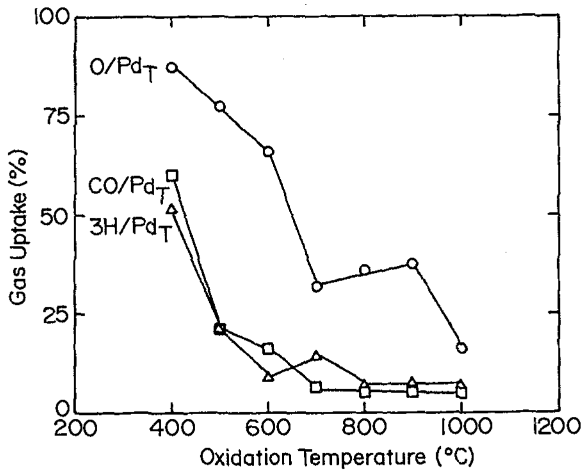

Fig. 1. The dependence of the oxygen, hydrogen and carbon monoxide uptakes on oxidation temperature for 2.5% Pd/3.5% CeO_2/Al_2O_3.

ratios of 0.70 ± 0.08 and 0.80 ± 0.13. The fact that the hydrogen and carbon monoxide uptakes remain close to unity over a wide range of metal loadings and oxidation temperatures suggests that these gases are titrating the exposed palladium atoms. This idea is strengthened by the infrared spectra which only show bands characteristic of carbon monoxide adsorption on palladium. No bands for carbon monoxide adsorption on alumina or ceria are detected. Furthermore, the ceria/alumina support does not adsorb significant amounts of oxygen, hydrogen or carbon monoxide.

Rieck and Bell [15] have examined the adsorption properties of ceria-doped palladium on silica. They found that hydrogen titration of adsorbed oxygen correctly measures the amount of metal exposed, but that the carbon monoxide adsorption is suppressed. In their study, $CO/3H = 0.61$. They concluded that after reduction, a partially reduced form of ceria migrates onto the metal particles and blocks some sites for carbon monoxide adsorption. Oxygen adsorption at 21°C reoxidizes the ceria, causing it to withdraw from the metal surface, and free up sites for subsequent hydrogen titration. In the present study, the carbon monoxide uptakes could be suppressed by ceria, since the CO/3H ratios range from 0.70 to 0.95. Based on the work of Rieck and Bell and the results reported here, it is concluded that hydrogen titration of adsorbed oxygen provides a reasonable estimate of the palladium dispersion of the ceria-doped catalysts.

The oxygen uptakes on 2.5% Pd/3.5% CeO_2/Al_2O_3 are far greater than the hydrogen and carbon monoxide uptakes. The excess oxygen adsorption is on the ceria that is reduced during the hydrogen treatment at 300°C. Several studies [4,15] have shown that precious metals catalyze the reduction of ceria at temperatures well below 300°C. Assuming that the ceria redox reaction is [4,9]

$$\tfrac{1}{2}Ce_2O_3 + \tfrac{1}{4}O_2 \rightleftharpoons CeO_2$$

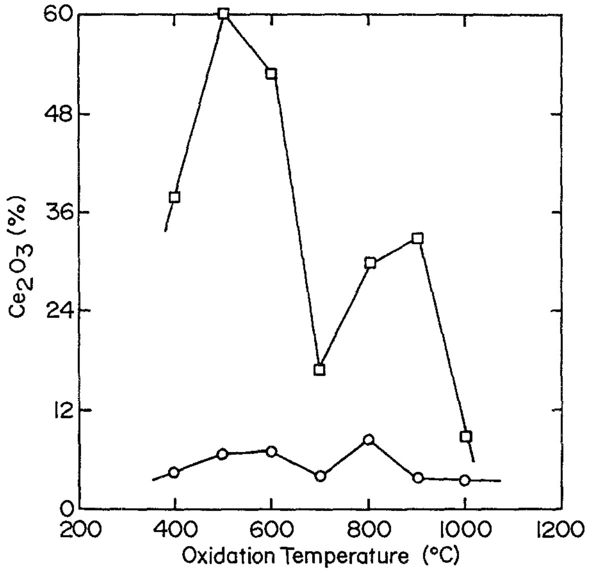

Fig. 2. The dependence of the percentage of ceria reduced on oxidation temperature for (○) 0.22% Pd/5.2% CeO_2/Al_2O_3 and (□) 2.5% Pd/3.5% CeO_2/Al_2O_3.

the following formula can be used to calculate the fraction of ceria reduced:

$$Ce_2O_3(\%) = (O - 3H)Pd_T/Ce_T$$

where O and $3H$ are the oxygen and hydrogen uptakes, Pd_T is the total palladium, and Ce_T is the total cerium. This quantity is plotted versus the oxidation temperature for 2.5% Pd/3.5% CeO_2/Al_2O_3 and 0.22% Pd/5.2% CeO_2/Al_2O_3 in fig. 2. These data show that the fraction of ceria reduced increases with the amount of palladium deposited. There is also a strong dependence of the Ce_2O_3% on the oxidation temperature. The ceria on alumina probably undergoes structural changes at different oxidation temperatures which affects the redox behavior [4].

The effect of the oxidation temperature on the dispersion of 0.2 and 2.5% Pd/Al_2O_3 catalysts with and without ceria is shown in fig. 3. The palladium dispersions have been determined by hydrogen titration of adsorbed oxygen. For the 2.5% Pd catalysts, the ceria does not alter the thermal stability of the palladium. The dispersions decrease rapidly as the samples are heated from 500 to 900°C, and obtain limiting values of about 5%. For the 0.2% Pd catalysts, the thermal stability is greatly reduced by the presence of ceria. After 700°C, the dispersion of 0.2% Pd/Al_2O_3 is 86%, while the dispersion of 0.22% Pd/5.2% CeO_2/Al_2O_3 is 42%. These results suggest that there are a small number of sites on the alumina support which bond tightly to the oxidized palladium at high temperatures. The ceria may preferentially cover these sites and thereby promote the agglomeration of the oxidized palladium. These results are consistent with the

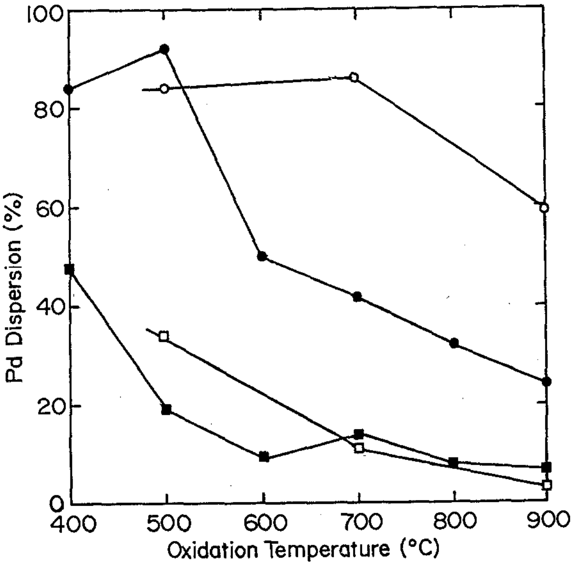

Fig. 3. The dependence of the palladium dispersion on oxidation temperature for (○) 0.2% Pd/Al_2O_3, (□) 2.3% Pd/Al_2O_3, (●) 0.22% Pd/5.2% CeO_2/Al_2O_3 and (■) 2.5% Pd/3.5% CeO_2/Al_2O_3.

study of Summers and Ausen [6]; they found that the dispersion of 0.05% Pd/Al_2O_3, oxidized at 900°C, was greatly reduced by adding ceria.

Infrared spectra for saturation coverages of carbon monoxide on 0.22% Pd/5.2% CeO_2/Al_2O_3, $D_{Pd} = 42\%$, and on 2.5% Pd/3.5% CeO_2/Al_2O_3, $D_{Pd} = 14\%$, are presented in fig. 4. The samples were oxidized at 700°C and reduced at 300°C prior to the experiment. Infrared measurements made on other $Pd/CeO_2/Al_2O_3$ catalysts produce the same results. Bands for carbon monoxide adsorbed on palladium are observed at 2080, 1995, 1955 and 1935 cm^{-1}. When the carbon monoxide coverage is reduced to a low value by heating to 250°C, the 2080 cm^{-1} peak shifts to 2030 cm^{-1}, and the peak below 2000 cm^{-1} shifts and splits into two broad bands at 1905 and 1850 cm^{-1}. The band above 2000 cm^{-1} is due to linearly bonded carbon monoxide on low coordination sites of the palladium crystallites, while the bands below 2000 cm^{-1} are due to bridge-bonded carbon monoxide on facets [14,16,17]. The infrared spectrum of the 0.22% Pd catalyst contains a much more intense band for linearly bonded carbon monoxide than the 2.5% Pd catalyst. This is because the small metal particles contain more low coordination sites than the large metal particles. The infrared spectra of the $Pd/CeO_2/Al_2O_3$ catalysts are exactly analogous to those of unpromoted Pd/Al_2O_3 catalysts. A careful examination of the spectra does not reveal any features indicative of an interaction of the ceria with the palladium surfaces. Nor are any bands evident for carbon monoxide adsorption on the support.

Shown in table 1 are the rates of methane oxidation measured on several palladium on alumina catalysts with and without ceria. The samples were

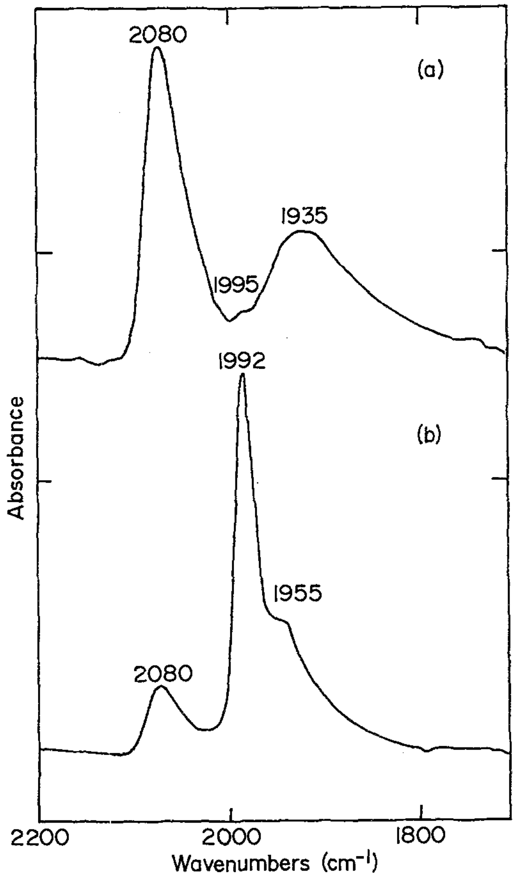

Fig. 4. Infrared spectra of saturation coverages of carbon monoxide at 21°C on (a) 0.22% Pd/5.2% CeO_2/Al_2O_3 and (b) 2.5% Pd/3.5% CeO_2/Al_2O_3. The samples were initially oxidized at 700°C.

Table 1
The effect of ceria on the rate of methane oxidation

Pd loading (%)	CeO_2 loading (%)	Initial Pd dispersion[a] (%)	Oxidation rate[b] (mole/g Pd h)
0.20	0.0	86	0.01
0.22	5.2	42	0.03
0.46	0.0	59	0.02
0.85	5.0	44	0.03
2.30	0.0	11	0.26
2.50	3.5	14	0.01

[a] Determined by hydrogen titration of adsorbed oxygen.

[b] Steady state rate at 250°C, 50 Torr methane, 110 Torr oxygen, balance helium and conversions below 0.5%.

oxidized at 700°C and reduced at 300°C prior to the experiment. Within the experimental error of the measurement, the rates are the same on all the samples except 2.3% Pd/Al_2O_3. The 2.3% Pd/Al_2O_3 exhibits a 10 to 20 times higher rate than the others. Hicks et al. [12] examined the effect of catalyst structure on the rate of methane oxidation over palladium on alumina. The palladium oxidizes during methane oxidation at temperatures above 200°C and in excess oxygen. The extent of palladium oxidation depends on the crystallite structure. Small crystallites are completely converted into palladium oxide. The palladium oxide spreads out over the alumina so that all the metal atoms are exposed and participate in catalysis. Conversely, large crystallites are converted into smaller ones with a surface covering of oxide. The rate of methane oxidation on the dispersed palladium oxide is much lower than the rate of methane oxidation on the crystallites. The results shown in table 1 for the unpromoted catalysts illustrate this trend. Separate experiments, reported in [12], found that 0.20 and 0.46% Pd/Al_2O_3 are completely oxidized under reaction conditions, while 2.3% Pd/Al_2O_3 is not.

The $Pd/CeO_2/Al_2O_3$ catalysts exhibit equally low rates of methane oxidation, irrespective of the initial metal dispersion. Several ideas can be put forth to explain this trend. The ceria could show an apparent inhibition of the reaction by adsorbing the carbon dioxide produced as carbonate. Rare earth oxides are known to form very stable carbonates [18]. However, this is not a likely possibility, because the reaction was run for 12 h prior to measuring the rate, and the amount of carbon dioxide generated was far in excess of the adsorption capacity of the ceria. A second possibility is that the ceria migrates onto the oxidized palladium under reaction conditions and blocks the sites for methane oxidation. A third possibility is that the ceria promotes the oxidation of the palladium, so that on all three $Pd/CeO_2/Al_2O_3$ catalysts, the palladium is dispersed over the support as palladium oxide. This would explain why the rate of methane oxidation per gram of Pd is the same on the $Pd/CeO_2/Al_2O_3$ catalysts and the low loading Pd/Al_2O_3 catalysts.

The last explanation given above is consistent with other studies of ceria-promoted precious metal catalysts. Yu Yao [8] observed a low rate of alkane oxidation over Pt and $Pd/CeO_2/Al_2O_3$. He attributed this to an interaction of the metal with ceria which converts the metal into a less active, oxidized state. Recently, Shyu et al. [9] characterized palladium on alumina catalysts doped with ceria by X-ray photoelectron spectroscopy. They found that the ceria promotes the oxidation of Pd to PdO, even on catalysts with high metal loadings and low dispersions. They observed that the rate of propane oxidation in excess oxygen falls upon addition of ceria, and ascribed this to the lower catalytic activity of palladium oxide. Although these prior studies are highly suggestive, more work should be done to characterize the effect of ceria on palladium under reaction conditions. In particular, in situ measurements need to be made of the palladium dispersion and oxidation state, and then correlated with alkane oxidation rates.

In summary, ceria improves the performance of emission control catalysts under fuel rich conditions by oxidizing carbon monoxide through the water-gas shift reaction, and also by providing lattice oxygen to oxidize carbon monoxide and hydrocarbons. Precious metals must be in close proximity to the ceria for it to have both water-gas shift activity [1] and oxygen storage capacity, i.e., to be reducible [4,15 and this work]. However, under fuel lean conditions, ceria promotes the agglomeration of platinum and palladium particles and may suppress alkane oxidation rates. In this case, it is better to keep the ceria away from the precious metals. The optimum formulation for automobile exhaust control may consist of mixtures of ceria-promoted and unpromoted metal on alumina catalysts. The distribution of Pt, Pd and Rh between the CeO_2/Al_2O_3 and Al_2O_3 supports must also have a large impact on performance [2].

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