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In Situ Electron Microscopy Studies of Palladium Supported on Al_2O_3, SiO_2, and ZrO_2 in Oxygen

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Controlled atmosphere electron microscopy (CAEM) has been used to observe and compare directly the behavior of palladium particles supported on γ-alumina, silica and zirconia, when heated in the presence of oxygen. Palladium is converted to PdO on all three supports at temperatures in excess of 325°C and undergoes a wetting and spreading action to form thin flat crystallites. At temperatures above 750°C a significant fraction of the PdO disproportionates to form metallic Pd, which subsequently undergoes a rapid interaction with both alumina and silica at 800°C to form compounds that probably consist of mixtures of the respective oxides; however, the precise composition of these species cannot be determined. It is suggested that this phenomenon is responsible for deactivation of these catalyst systems at high temperatures. This type of interaction was not observed when zirconia-supported palladium specimens were treated under the same conditions. In this case, the support appeared to stabilize the formation of PdO up to 900°C. It is significant that on all supports a fraction of the palladium remains in the form of PdO up to the highest temperatures even though bulk thermodynamics predict that it should all be in the metallic state. © 1995 Academic Press, Inc.

INTRODUCTION

Over the past 5 years a considerable amount of research effort has been devoted to the study of oxide-supported palladium systems. This work has been stimulated by the realization that this metal exhibits exceptional catalytic activity for the oxidation of methane (1). The efficiency of such combustion reactions is a critical aspect in a number of processes where the attainment of stringent emission control standards is necessary for continued operation. While the majority of investigations have focused on the behavior of the palladium/γ-alumina–oxygen system (2–10), there has been a growing awareness that modified alumina (11–13) and in particular zirconia can provide improved stability for the active palladium species at high temperatures (10, 14–16).

As with most supported metal catalysts, palladium systems are susceptible to various forms of deactivation and the temperature range where such phenomena are encountered is dictated to a large degree by the nature of the interaction with the support media (3, 12, 13, 17, 18). Recent studies have shown that the presence of H_2S in the methane feed tends to poison the catalytic combustion activity of palladium (19, 20). The extent of this action, however, was found to be more severe on a silica than on an alumina support. This difference was attributed to the ability of the latter oxide to trap the sulfate groups, the sulfur species generated under oxidizing conditions. Silica was unable to perform this function and as a consequence, the sulfate groups were selectively adsorbed on the sulfaces of the metal particles (19).

Other workers (6) have demonstrated that the chemical nature of the palladium precursor salt can have an adverse effect on catalyst performance. In this regard, chloride-containing salts of the metal dispersed on γ-alumina were found to produce catalysts for methane oxidation inferior to those derived from nitrate sources. Possible causes cited for this behavior included undesirable reactions of the halide species with either the metal or support components.

In the absence of either chemical poisons or the potential for carbon deposition, particle sintering becomes the major mode by which supported metal systems undergo deactivation (21). One of the key factors in determining the contribution of sintering to the overall deactivation process is the nature and strength of the metal–support interaction (22). The studies of Ruckenstein and co-workers (21), who have used transmission electron microscopy to observe the postreaction appearance of supported metal particles following treatment in oxygen or hydrogen at increasing temperatures, have provided valuable information with regard to the morphological transformations that occur in such systems. These workers examined the behavior of palladium particles supported on thin films of γ-alumina following treatment in oxygen, hydrogen, and alternating cycles of these gases (23–25). They reported that the metal particles underwent some extraordinary changes in morphology as the specimens were treated at progressively higher temperatures in oxygen (23). At temperatures up

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to 750°C it was claimed that the crystallites were present as PdO and that in such circumstances a strong interaction was established with the oxide support, which resulted in a spreading action. It was argued that this condition contributed to the eventual rupture and fragmentation of the crystallites. When the reaction temperature was increased to about 900°C, PdO was converted to the metallic state, and the crystallites were found to have undergone a significant increase in size and acquired a dense faceted form.

Lieske and Volter (26) studied the change in the chemical state of palladium particles supported on γ-alumina as a function of oxygen treatment using temperature-programmed reduction (TPR) and complemented these experiments with particle size measurements as determined by oxygen chemisorption. The conclusions of this investigation were in many respects consistent with those reached from the earlier electron microscopy studies, with the exception being that these workers invoked the participation of a two-dimensional PdO surface complex in the crystallite redispersion process.

Chen and Schmidt (27) used an electron microscopy approach similar to that described above to investigate the behavior of palladium on silica in reactive environments. They found that when 1.5-nm-thick palladium films deposited on thin sections of silica were heated in 1 atm air, then PdO was formed at 300°C. Continued heating up to 700°C produced little change in either the size or morphology of the metal oxide particles, which remained as relatively thin platelets of about 5.0 nm average width. Decomposition of PdO to the metallic state commenced at 740°C and was complete after heating to 850°C. Examination of specimens that had been treated at this temperature showed that the particles had increased in size to about 70 nm and had acquired well-defined hexagonal shapes.

In the current investigation we have used controlled atmosphere electron microscopy (CAEM) to observe and compare directly the behavior of palladium particles supported on thin films of γ-alumina, silica, and zirconia, when heated in the presence of oxygen. In a separate series of experiments the chemical state of the particles has been determined at various stages of the reaction via the use of *in situ* electron diffraction measurements.

EXPERIMENTAL

The experiments reported here were carried out in a modified JEOL 200CX TEM electron microscope (28). This instrument is equipped with a custom-designed environmental cell, which accommodates a heating stage. With this arrangement it is possible to continuously observe changes in the appearance of a specimen as it undergoes reaction in a gas at temperatures up to 1000°C. The dynamic events occurring during the reaction are captured on videotape and replayed later for detailed analysis. We estimate that the point-to-point resolution achieved on the TV monitor is of the order of 0.4 nm under sufficiently stable conditions. A recent development with the technique is the capability of performing *in situ* electron diffraction analysis of supported small particles to establish the chemical state of the reacting specimen (29).

Transmission specimens of model catalyst systems consisting of palladium dispersed on thin films of various oxides were made according to the following procedures. A 40-nm-thick nonporous film of γ-alumina was prepared by anodizing thin aluminum foils in 3 wt% tartaric acid solution (30) and annealed at 600°C in air for 20 h. After reaction the aluminum foil was dissolved in saturated mercuric chloride solution, and the remaining thin sections of γ-alumina were floated off from solution, washed in distilled water, and finally picked up on an electron microscope grid. Silica films of similar thickness were prepared by vacuum deposition of a 50/50 SiO_2/Si mixture onto a Pyrex slide, previously coated with a film of detergent. The resulting silica film was scored into small squares, released from the slide by careful immersion in water, washed, and mounted on a grid. Prior to use these films were heated in oxygen at 600°C for 2.0 h to ensure complete conversion to silica. Films of zirconia of about 35 nm thickness were produced by sputtering from a high-purity zirconium target in an oxygen environment onto sodium chloride crystals. The salt was subsequently dissolved away in water leaving the thin oxide sections floating on the surface. These specimens were washed to remove all traces of salt and then picked up on electron microscope grids.

Palladium was introduced onto these oxide films by vacuum evaporation of spectrographically pure metal wire from a cleaned tungsten filament at a residual pressure of about 10^{-6} Torr. The amount of metal and distance separating the filament from the specimen was selected so as to produce a known coverage on the support. In most cases this was fixed at about a monolayer; however, heavier loadings were used in some experiments. The oxygen used in this work was obtained from Alphagaz Co. with a stated purity of 99.999% and was used without further purification.

RESULTS

a. Palladium/γ-Alumina–Oxygen

When palladium/alumina specimens were heated in the presence of 0.2-Torr oxygen, nucleation of the evaporated metal film into particles of ~2.5 nm diameter was achieved at 150°C. As the temperature was progressively increased to 250°C it was apparent that the electron density of the particles had decreased appreciably, probably as a result of the conversion of metallic palladium to the oxide, PdO. At 350°C a dramatic change in the morphological charac-

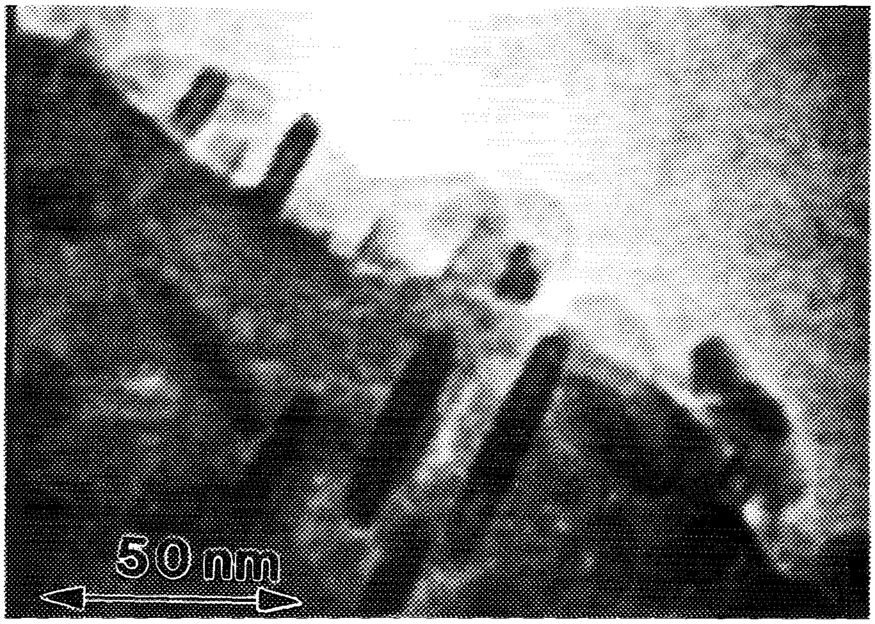

FIG. 1. Electron micrograph of the needle-like structures formed from the interaction of Pd and γ-alumina in oxygen at 840°C.

teristics of the particles was observed as they proceeded to undergo a wetting and spreading action on the support. It was significant that the temperature where this transformation took place was close to the Tammann temperature of PdO (~320°C), a condition under which the surface atoms in the solid are believed to exhibit mobility.

As the temperature was gradually raised to 650°C the spreading action of particles on the support intensified to such a degree that it was almost impossible to detect the existence of individual particles and this condition appeared to persist until the temperature was raised to 800°C. At this stage, the spread PdO phase was observed to undergo a change in structure resulting in the reformation of numerous small dense particles. The presence of these new entities was, however, short lived as they rapidly started to transform into needle-like shapes, about 20 nm in length and 2.5 nm in width. The growth of these needle-like structures was accompanied by the formation of pits in the alumina support indicating that there was a direct link between these two processes, which involved the chemical interaction of palladium and aluminum species. A survey of the alumina support edges revealed that needles and thin hexagonal-shaped platelets were also being formed preferentially at these regions. Examples of these unusual growth structures are presented in the micrographs, Figs. 1 and 2, which were taken from the video display of the reaction at 840°C. The sequence of micrographs, Figs. 3A–3D, shows the growth of needle-like structures over a period of 1.5 min produced on the alumina film at 840°C. It is conceivable that the needles are actually platelets formed at an angle to the support surface. Continuous observations of the reaction revealed that the platelets retained the shape of their leading edge, indicating that growth occurred by transport of material from the solid rather than by gas-phase deposition. Reactions were followed up to 900°C, at which stage the average size of platelets was of the order of 60 nm. It was also clear that at this temperature there was virtually no evidence for the presence of discrete metal crystallites. A schematic representation of the observed pattern of behavior of the palladium/alumina–oxygen system as the temperature is increased from 150 to over 800°C is given in Fig. 4a.

When these specimens were subsequently allowed to cool in the presence of oxygen to room temperature there was a major change in their appearance. Most of the needle and platelet structures were observed to shrink in size and eventually restructure into much smaller dense hexagonal-shaped crystallites, about 15 nm in size, with characteristics similar to those reported by Chen and Ruckenstein (23) from postreaction examination of palladium/alumina specimens that had been heated in oxygen at 920°C. The present observations suggest that these structures consist of a metastable palladium–aluminum–oxygen phase, the existence of which would not be apparent from a postreaction examination. In a further set of experiments previously reacted specimens were reheated in oxygen and the identical pattern of behavior to that of a fresh specimen was once again observed when the temperature was increased to 800°C, suggesting that the restructuring process was reversible in nature.

A separate series of experiments was conducted to identify any spurious effects resulting from interactions of the electron beam with the reacting specimens. These studies were carried out in light of the concerns raised by Heinemann and Poppa (31), who reported that at high-electron dosages and under high-vacuum conditions, γ-alumina

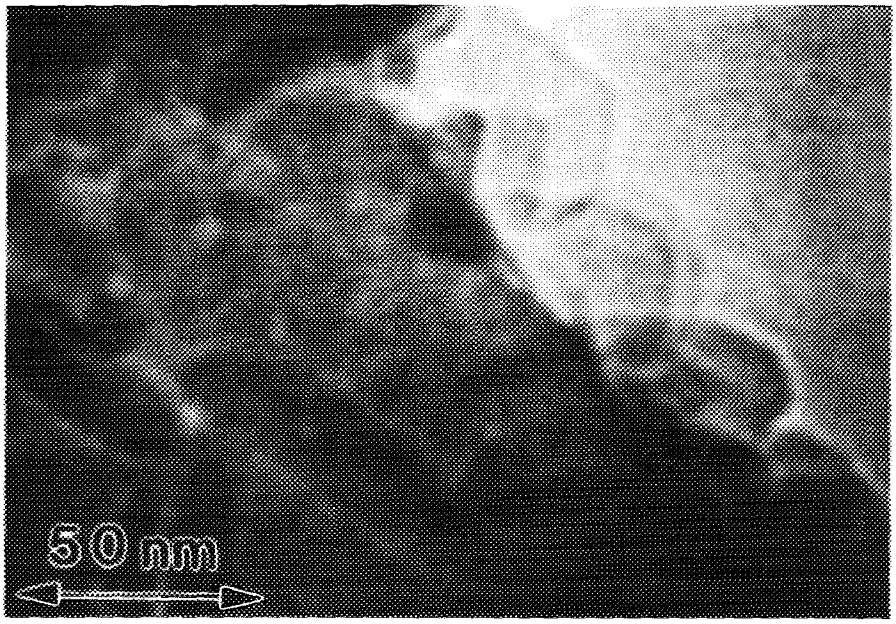

FIG. 2. Electron micrograph of platelet structures produced at the same time as the needles.

films underwent recrystallization to form α-alumina ostensibly at room temperature, a transition that normally occurs at >1000°C. When palladium was present on the oxide support the metal was observed to spread over the entire surface in the form of a thin film. In the current investigation these extreme electron beam conditions were carefully avoided by use of an image intensifier attached to the TV camera, which enables one to still observe the specimen while working with very low-intensity radiation. Indeed, when specimens were examined during reaction on an intermittent basis they exhibited the same pattern of behavior as that found when the specimen was exposed to the electron beam in a continuous fashion. We are therefore of the opinion that under the present experimental conditions the electron beam did not exert any adverse effects on the reactivity of the system.

From subsequent detailed analysis of palladium/alumina specimens containing a heavier metal loading (about five monolayers) it was possible to obtain particle size distributions of the metal oxide crystallites on the support at temperatures over the range 315 to 825°C. The data, which are based on measurements of at least 2000 particles at each temperature, are presented in Fig. 5, from which it can be seen that the average particle size remains relatively constant over the range 315 to 600°C, but exhibits a sharp increase as the temperature is gradually raised to 825°C.

In a complementary set of experiments the microscope was operated in the diffraction mode and patterns recorded at various stages of the reaction in an attempt to establish the identity of the chemical species present as the temperature was gradually increased. These measurements were performed on palladium/alumina specimens containing either 1 or 5 monolayers (ML) of the metal. The results of these experiments, which are presented in Tables 1 to 5, indicate that as the specimens were heated, PdO became the stable phase at temperatures up to around 750°C; however, at intermediate temperatures the spread condition of the oxide particles resulted in a very weak pattern. For the samples containing a monolayer of deposited metal, the transformation of PdO to Pd did not occur until the temperature was raised to above 750°C. In contrast, with the samples prepared with a heavier metal coverage it was evident that a fraction of the PdO was converted to Pd at temperatures as low as 560°C. As the temperature was progressively raised to 800°C all specimens exhibited a similar pattern of behavior with the metallic phase undergoing an interaction with the support to form either a mixed oxide or an intermetallic compound. Since diffraction data are not available for the mixed oxides it is not possible to determine the exact chemical nature of these species. It was significant that at 880°C, a condition under which bulk thermodynamics predict that Pd metal should be the stable phase, there was an indication that a small amount of PdO was still present on the alumina surface, Table 4. On cooling to room temperature, the analysis showed a complex pattern of behavior, in addition to the existence of compounds containing both Pd and Al species; Pd and PdO were also found to be present.

b. Palladium/Silica–Oxygen

These experiments were all carried out on silica films containing a monolayer of deposited palladium. When the specimens were reacted in 0.2 Torr oxygen very tiny particles of about 1.0 nm diameter were observed to form on the surface at 150°C. As the temperature was gradually

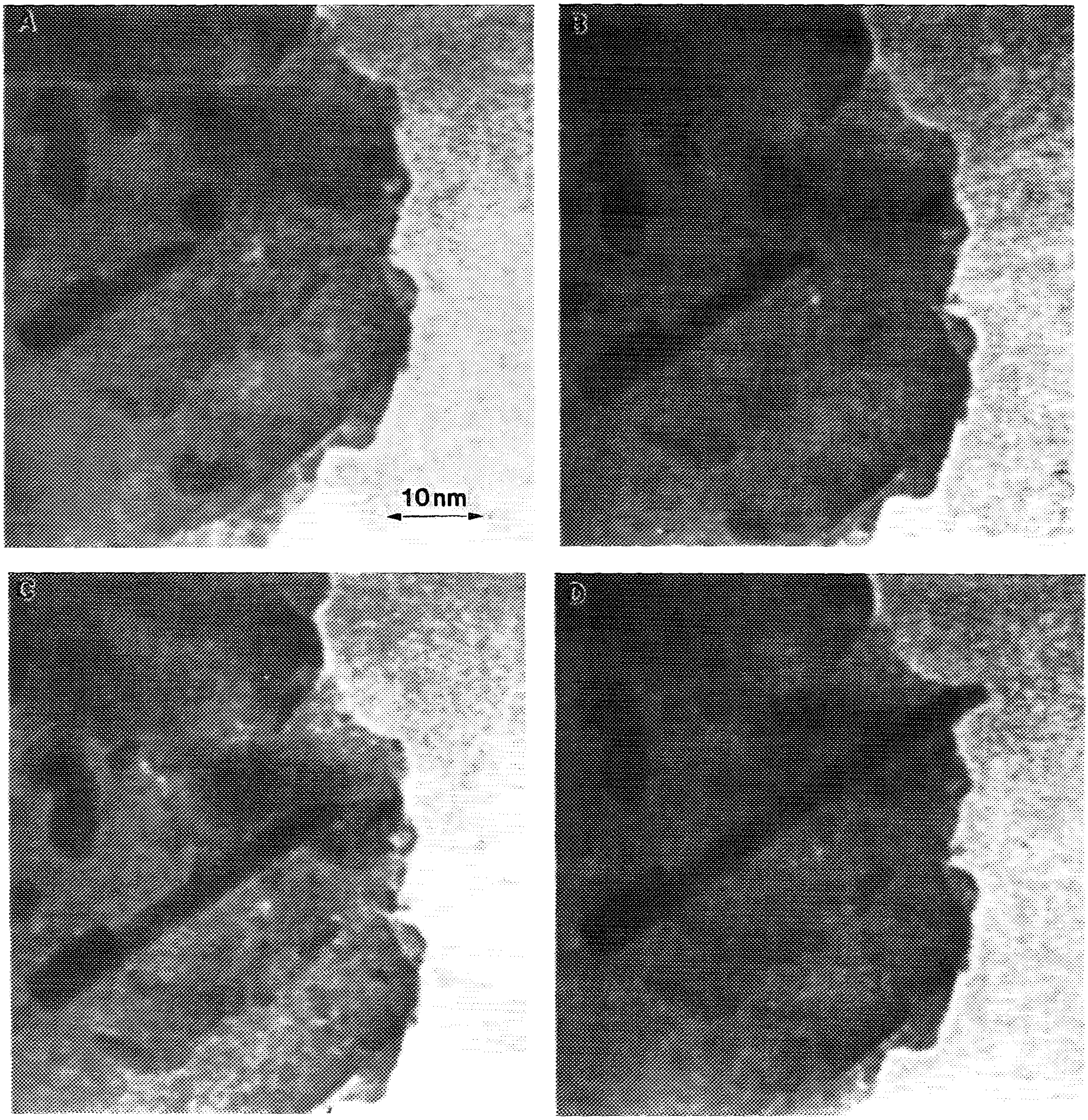

FIG. 3. Sequence of micrographs taken from the video record showing the growth of needle-like structures produced from the interaction between palladium and alumina in oxygen at 840°C over a period of 1.5 min.

raised from 350 to 650°C the particles exhibited an increase in size, reaching an average width of 2.0 nm; however, it was not possible to ascertain any details regarding their morphological characteristics since their electron density was very close to that of the silica support. At this stage of the reaction palladium was probably present as PdO and due to the creation of a strong oxide–oxide interaction the particles were in a spread state. The rate of particle growth increased significantly as the temperature reached 750°C and after holding at this level for 10 min the average

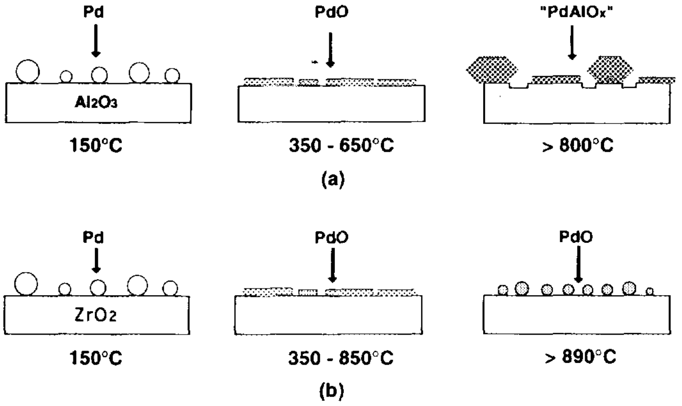

FIG. 4. Schematic representation of the behavior of palladium particles supported on (a) γ-alumina and (b) zirconia, as the respective systems are heated in the presence of oxygen from 150 to over 800°C.

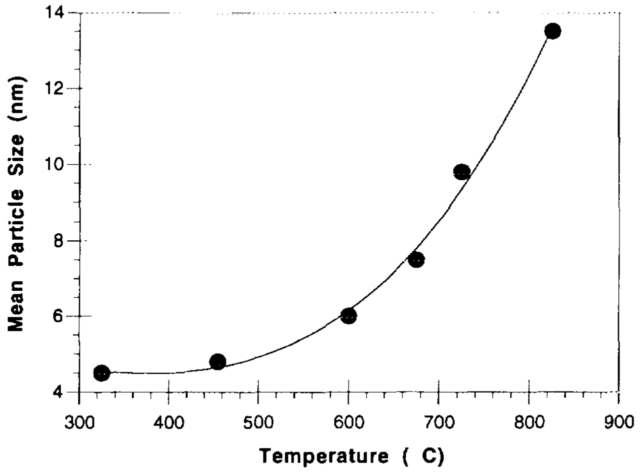

FIG. 5. Average particle size as a function of reaction temperature for the palladium/alumina-oxygen system.

TABLE 1

Electron Diffraction Analysis of Palladium (1 ML)/Alumina in O_2 at 725°C

Measured *d*-spacings (nm)	*d*-spacings (nm)		
	Al_2O_3	Pd	PdO
0.1494	0.1491		
0.1636	0.1652		
0.1779	0.1778		
0.2134	0.2140		0.2152
0.2333	0.2337		
0.2426	0.2451		0.2644
0.2624			
0.4413	0.4474		

TABLE 2

Electron Diffraction Analysis of Palladium (5 ML)/Alumina in O_2 at 560°C

Measured *d*-spacings (nm)	*d*-spacings (nm)		
	Al_2O_3	Pd	PdO
0.1374	0.1370	0.1375	0.1361
0.1946	0.1938	0.1945	—
0.2225	0.2237		—
0.2363	0.2337		—
0.2720	0.2740		–
0.4442	0.4474		—

size was 5.0 nm. A detailed examination of the particle structures showed that they were highly faceted and relatively thin, and furthermore the thickness was uniform across a given crystallite, characteristics generally associated with a "pill-box" morphology.

At 800°C the appearance of the specimen changed dramatically as the faceted crystallites transformed into needle-like structures in a manner similar to that observed with the palladium/γ-alumina-oxygen system. On raising the temperature to 850°C the rate at which this process occurred increased to such an extent that the whole surface was covered with needles and large platelets up to 80 nm in width. It was also apparent at this temperature that small dense particles were beginning to emerge between the larger structures. In many regards the appearance of palladium/silica specimens undergoing reaction in oxygen at 850°C resembled that of the previous system under the same conditions.

On completion of the initial heating step, specimens were continuously observed during cooling and after a period of about 5 min at room temperature the needle and platelet structures were observed to decrease in size and

TABLE 3

Electron Diffraction Analysis of Palladium (5 ML)/Alumina in O_2 at 725°C

Measured *d*-spacings (nm)	*d*-spacings (nm)		
	Al_2O_3	Pd	PdO
0.1378	0.1370	0.1375	1361
0.1498	0.1491	—	—
0.1958	0.1938	0.1945	—
0.2233	0.2237		—
0.2363	0.2337		—
0.2715	0.2740		—
0.4430	0.4474		—

TABLE 4

Electron Diffraction Analysis of Palladium (5 ML)/Alumina in O_2 at 880°C

Measured *d*-spacings (nm)	*d*-spacings (nm)					
	Al_2O_3	Pd	PdO	Al_3Pd_2	Al_3Pd	$Al_xPd_yO_z$
0.1483	0.1491	—	0.1463	0.1491	0.1480	?
0.1924	0.1938	0.1945	—	0.1952	0.1899	?
0.2230	0.2237	0.2246	—	—	0.2251	?
0.2338	0.2337	—	—	—	0.2366	?
0.2422	0.2451	—	—	—	0.2394	?
0.2614	0.2583	—	0.2644	0.2583	0.2579	?
0.2704	0.2740	—	0.2668	—	0.2711	?
0.3053	—	—	0.3043	—	—	?
0.3544	—	—	—	—	0.3539	?
0.4430	0.4474	—	—	—	—	?

reform into relatively large globular particles, which did not appear to exhibit any preferred orientation or location with respect to the support medium. If the system was reheated in oxygen then these particles started to undergo a wetting and spreading action on the silica at ~325°C, which culminated in the transformation of the globular particles into larger thin faceted crystallites. The appearance of the surface remained relatively unchanged until the temperature was raised to 770°C, and at this point the thin crystallites, which were probably in the form of PdO, ruptured and rearranged into smaller dense particles. On continued heating to 800°C these freshly created particles underwent reaction with the support and transformed into needle and large platelet structures. The sequence of events accompanying the heating and cooling cycles were quite reproducible and also occurred in experiments where the electron beam was switched off during most of the heating period.

c. Palladium/Zirconia–Oxygen

At low temperatures the behavior of palladium/zirconia specimens exposed to 0.2 Torr oxygen mirrored that of the previous two systems; nucleation of the evaporated metal film into small particles occurred at ~150°C and upon raising the temperature to 350°C the particles were observed to undergo a spreading action on the support. This latter transformation was so rapid that after a short period of time it was no longer possible to discern the presence of individual particles, and instead the surface of the zirconia was covered by an interconnected network of small diffuse islands. On continued heating to 575°C these structures underwent fragmentation and this process was followed by the development of numerous small faceted crystallites, ranging from 2 to 6 nm in width. These freshly created particles were so thin that it was possible to observe features of the underlying support through them.

No further modifications in the appearance of the speci-

TABLE 5

Electron Diffraction Analysis of Palladium (5 ML)/Alumina in O_2 at Room Temperature after Heating to 900°C

Measured *d*-spacings (nm)	*d*-spacings (nm)					
	Al_2O_3	Pd	PdO	Al_3Pd_2	Al_3Pd	$Al_xPd_yO_z$
0.1364	0.1370	0.1375	0.1361	0.1380	0.1364	?
0.1487	0.1491	—	—	0.1491	0.1480	?
0.1927	0.1938	0.1945	—	0.1952	0.1899	?
0.2210	0.2237	—	—	—	—	?
0.2316	0.2337	—	—	—	0.2300	?
0.2398	—	—	—	—	0.2394	?
0.2590	0.2583	—	—	0.2583	0.2579	?
0.2704	0.2740	—	0.2668	—	0.2711	?
0.3511	0.3466	—	—	—	0.3539	?
0.4429	0.4474	—	—	—	—	?

TABLE 6

Electron Diffraction Analysis of Palladium (5 ML)/Zirconia in O_2 at 575°C

Measured *d*-spacings (nm)	*d*-spacings (nm) ZrO_2	Pd	PdO
0.1277	0.1223	—	0.1222
0.1436	0.1432	—	—
0.1500	0.1510	—	0.1522
0.1758	0.1780		—
0.2010	0.2020		0.2006
0.2485	0.2488		—
0.2866	0.2839		—

men were seen until the temperature was increased to 890°C, at which point the particles started to exhibit a distinct change in morphology from the thin flat structure to that of very dense smaller crystallites, ~0.5 nm in diameter. The rate of this transformation increased appreciably as the temperature was further increased to over 900° and after about a period of 30 min at 925°C these particles had grown to between 1.0 and 2.5 nm in size. The observed pattern of behavior in this high-temperature range was quite different than that seen with either of the previous palladium/oxide support systems. In this case the particles appeared to maintain their integrity and there was no indications of any unusual interactions with the support. The transformations in particle morphology observed in this system are presented in the schematic diagram, Fig. 4b. A comparison of this sequence of events with that depicted in Fig. 4a allows one to see the distinct differences in behavior of palladium particles supported on alumina and zirconia.

The results of *in situ* electron diffraction studies performed on this system are presented in Tables 6 to 8. Inspection of these data indicates that once palladium was converted to PdO, even when the temperature was raised to 900°C the particles remained in this chemical state. Specimens were generally held at the maximum temperature for a period of about 30 min. It is significant that this condition was found to persist on specimens containing an initial palladium loading of 5 ML.

TABLE 7

Electron Diffraction Analysis of Palladium (5 ML)/Zirconia in O_2 at 815°C

Measured *d*-spacings (nm)	*d*-spacings (nm) ZrO_2	Pd	PdO
0.1227	0.1223	—	0.1222
0.1436	0.1432	—	—
0.1503	0.1510	—	0.1522
0.1760	0.1780		—
0.2028	0.2020		0.2006
0.2503	0.2541		—
0.2883	0.2839		—

TABLE 8

Electron Diffraction Analysis of Palladium (5 ML)/Zirconia in O_2 at 900°C

Measured *d*-spacings (nm)	*d*-spacings (nm) ZrO_2	Pd	PdO
0.1229	0.1223	—	0.1222
0.1331	0.1329	—	0.1334
0.1436	0.1432	—	—
0.1500	0.1510		0.1522
0.1758	0.1780		—
0.2028	0.2020		0.2006
0.2479	0.2488		—
0.2890	0.2839		—

DISCUSSION

Comparison of the behavior of palladium on the three support media during reaction in 0.2 Torr oxygen shows that the systems share many common features. At temperatures greater than 325°C and less than 800°C electron diffraction analysis shows that palladium is present predominantly in the form of PdO. In all cases the PdO particles exhibit a strong tendency to undergo a wetting and spreading action on the oxide supports, a feature generally associated with the creation of a strong metal oxide–support interaction. As a consequence, the particles acquire a morphology consisting of relatively thin flat structures. Although the strength of the interaction may vary according to the nature of the oxide support, it is clear that in all these systems particle sintering does not occur to any appreciable extent over the range 350 to 700°C.

Baldwin and Burch (3) suggested that for the γ-alumina-supported palladium catalyst the activation step is associated with reconstruction of the PdO particles. Other workers (7, 9) extended this concept and argued that the active catalytic entity, PdO, was present on the support surface at temperatures in excess of 350°C in a highly dispersed form. It was also claimed that the higher catalytic activity for methane combustion observed under these conditions was directly related to the reaction rate of the surface oxygen species associated with the PdO phase higher than those chemisorbed on Pd. While the results of the present investigation do not resolve the questions relating to the mechanistic features of the catalytic methane combustion

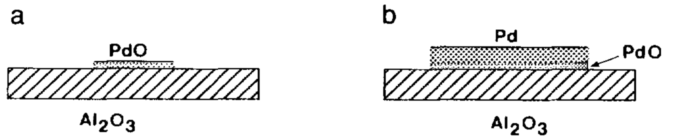

FIG. 6. Schematic representation of the effect of initial metal loading on the possible morphological and chemical changes existing at the interface between palladium and alumina as the specimens are heated to 560°C in oxygen.

reaction they do provide direct evidence that PdO is formed under similar reaction conditions and that the metal oxide undergoes a morphological transformation on all three oxide supports at about 350°C.

In situ electron diffraction analysis of palladium particles supported on γ-alumina and zirconia in 0.2 Torr oxygen reveals some unique insights into the chemical changes that occur as these systems are progressively heated from 20 to 900°C. The finding that with specimens containing an initial monolayer coverage of metal, PdO is stable at temperatures of up to 750°C under the prevailing low pressure oxygen conditions is inconsistent with the predictions of bulk thermodynamics. At 0.2 Torr of oxygen, thermodynamic calculations indicate that the transition of PdO to Pd should take place at about 570°C (32, 33). The failure to detect the presence of Pd on specimens initially containing a monolayer coverage of metal at this temperature may be due to the fact that such particles are very thin and consequently difficult to detect in the diffraction pattern. A further possibility is that the PdO phase is stabilized when in intimate contact with certain oxides. This condition would arise from the establishment of a strong chemical interaction with the support, which causes the PdO to spread in the form of a thin, flat particle, as shown schematically in Fig. 6a. In this context it is interesting to find that data obtained from X-ray absorption near-edge structure (XANES) by Davoli *et al.* (34) provide evidence that the local structure of PdO supported on either silica or γ-alumina was significantly different than that of bulk PdO. These observations were rationalized according to the notion that a strong interaction existed between the two components of the catalyst. In other related work, Bayer and Wiedemann (35) made a comprehensive investigation of the interaction of palladium powder with oxygen at various pressures and reported that the temperature for the dissociation of PdO was sensitive to a number of factors including the grain size of the metal, the heating rate, and the atmosphere. Examination of the electron diffraction data shows, however, that with specimens containing an initial heavy metal loading there is some evidence for the formation of Pd at 560°C. In these circumstances it is possible that the region of the particle in contact with the support remains in the PdO state, whereas the remaining metal atoms in the particle will gradually undergo disproportionation to create a mixed Pd/PdO crystallite, as illustrated in Fig. 6b.

Major differences in the appearance of specimens were observed when the three systems were heated to temperatures in excess of 800°C, conditions under which bulk PdO is expected to be converted into metallic palladium. *In situ* electron diffraction examination of the alumina-supported specimens showed the contrary to bulk thermodynamic predictions, some of the palladium remained in the oxide state even at ~900°C. On the other hand, metallic species generated from the disproportionation of the major fraction of PdO underwent a rapid chemical interaction with both alumina and silica supports to form needle-like and platelet structures. Direct observations of this process clearly demonstrated that both the support and metallic components were involved in the growth of these unusual structures, many of which appeared to decompose during cooling to lower temperatures. It should be stressed that this type of behavior might not be observed by a conventional postreaction transmission electron microscopy examination. Unfortunately, it was not possible to identify the chemical composition of these mixed metal phases with any degree of certainty since crystallographic data of mixed aluminum–palladium oxides are not available. It is possible to match some of the spacings to the intermetallics, Al_3Pd and Al_3Pd_2, and such compounds could be localized at the interface and isolated from the gaseous environment. The formation of such intermetallics under oxidizing conditions must, however, be regarded as somewhat inconclusive.

Although this unusual reaction has not been reported previously for oxide-supported palladium systems, in a number of studies the formation of analogous structures has been detected in reactions that involve the heating of other noble metals on alumina supports to temperatures in excess of 800°C. Baker *et al.* (36) using the CAEM technique to study the sintering characteristics of platinum on alumina in oxygen observed spectacular transitions in the appearance of the specimens at temperatures in excess of 800°C. The metal particles initially spread on the alumina to form diffuse islands and then quite suddenly reconstructed to produce well-defined dense shapes. Sprys and Mencik (37) found a similar effect when platinum/alumina specimens were heated within the electron microscope by the use of intense electron beams to generate heat and characterized the structures formed under these conditions as the intermetallic compound, Pt_3Al, from electron diffraction analysis. More recently several articles have dealt with the problem encountered with high-temperature interactions between rhodium and the γ-alumina support in automotive catalyst exhaust systems (38–40). The loss of catalytic activity of this system during NO reduction has been attributed to the formation of a strong interaction between the two components, which results in the diffusion of rhodium into the oxide. Yao *et al.* (38) reported that this form of deactivation was not found when the noble metal was supported on either zirconia or α-alumina.

In the model developed by Farrauto *et al.* (7) to explain the observed deactivation of palladium/alumina catalysts during high-temperature methane combustion reactions, sintering of metal particles was considered to be the critical factor. If one now compares their mechanism with the observations made by *in situ* electron microscopy it becomes apparent that both studies share many common features and the only major point of disagreement revolves around the chemical identity of the deactivated state.

Finally, one of the most important features to emerge from this investigation is the finding that the zirconia-supported palladium system does not exhibit the same type of high-temperature chemical interaction as that displayed with the other oxide supports. Mercera *et al.* (41) reported that the thermal stability of zirconia could be enhanced following the introduction of certain other oxides into the system. It is therefore not unreasonable to expect that PdO will also perform this function on zirconia and as a result also achieve an increase in its own thermal stability over that found with either γ-alumina or silica. Indeed, other workers (42) found that in PdO/ZrO_2 catalysts derived from a $PdZr_3$ precursor the noble metal oxide did not decompose to the metallic state until temperatures of about 900°C and even under these conditions there was evidence that this transformation was not complete.

Although the wetting behavior or strength of the interaction of metal oxides with nonreacting metals is not an easily predictable property, a somewhat more fundamental approach to the understanding of the root causes for the relative thermal stability of the PdO/ZrO_2 system may be obtained from a consideration of the optical dielectric constant (ε_∞) of the respective oxides. Indeed, it has been found that there is a strong correlation between the dielectric function and electronic polarization. Stoneham and Tasker (43, 44) have used this rationale to develop a classification of the wetting characteristics of certain metals on a variety of oxide supports. In their treatment they found that metals tend to exhibit a strong wetting action on oxides with high ε_∞. We believe it is possible to extend their arguments to include the behavior of small PdO particles supported on this same set of oxides. In this regard it would be expected that the noble metal oxide particles would form a relatively stronger and more stable interaction with ZrO_2, ε_∞ of 4.75, than with either Al_2O_3 (2.9) or SiO_2 (2.4).

SUMMARY

Controlled atmosphere electron microscopy studies have demonstrated that while palladium particles supported on alumina, silica, or zirconia exhibit similar growth characteristics at temperatures below about 800°C when heated in the presence of oxygen, major differences are observed in the respective patterns of behavior at higher temperatures. *In situ* electron diffraction measurements indicate that as the temperature was raised to 325°C then on all supports palladium is in the form of PdO. Under these conditions a strong interaction is established with the oxide supports, which results in a wetting and spreading action of the PdO to form very thin flat structures.

On continued heating to 750°C the majority of the PdO crystallites on both γ-alumina and silica were converted to the metallic phase. The temperature at which this transformation occurred appeared to be dependent to a large extent on the initial coverage of the metal on the support; with a 5-ML coverage the formation of metal was detected at 560°C. In contrast, when palladium was supported on zirconia then even at 900°C disproportionation of PdO to the metallic state was not observed to any significant degree, a condition that persisted on samples containing a heavier initial metal loading.

At temperatures above 800°C metallic species present on either γ-alumina or silica were found to undergo a rapid interaction with these supports to produce large crystalline platelet structures consisting of a mixture of both solid components. At this stage it is not possible to identify the chemical state of these materials since crystallographic data for mixed aluminum–palladium oxides or the silicon–palladium analogs are not available. It was interesting to find that upon cooling of these specimens to room temperature there was a tendency for these unusual structures to decompose, indicating that they were metastable in nature.

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