Journal of Catalysis **187,** 275–284 (1999)
Article ID jcat.1999.2545, available online at http://www.idealibrary.com on IDEAL®

TEM Study of the Microstructural Modifications of an Alumina-Supported Palladium Combustion Catalyst

Maxim Lyubovsky,* Lisa Pfefferle,*[,1] Abhaya Datye,†[,2] Jaime Bravo,† and Travis Nelson†

*Department of Chemical Engineering, Yale University, New Haven, Connecticut 06520; and †Department of Chemical and Nuclear Engineering and Center for Microengineered Materials, University of New Mexico, Albuquerque, New Mexico 87131

Received July 17, 1998; revised April 23, 1999; accepted May 4, 1999

An α-alumina-supported Pd catalyst was studied for the catalytic combustion of methane. Changes in catalyst activity due to variations in the oxygen partial pressure were correlated with corresponding changes in the catalyst oxidation state, particle size, and morphology. At a temperature of 1070 K, the apparent catalyst activity increased with time under the reaction conditions where decomposition of the PdO phase occurs. The formation of large, faceted crystallites of metallic Pd, 200–300 nm in size, was observed by TEM during this process. The increase in activity with increasing particle size is counterintuitive and suggests that metallic Pd surfaces formed under reaction conditions are highly reactive. Since the activation energy for methane oxidation over Pd metal is greater than that over PdO, our results can only be explained by an increase in the pre-exponential factor for this reaction on metal surfaces. To gain insight into the changes in morphology, a model Pd/α-alumina catalyst was subjected to similar thermal treatments. It was found that decomposition of PdO leads to the formation of large Pd metal particles. Upon cooling, these Pd particles re-oxidize by the formation of rough polycrystalline PdO particles rather than by the formation of uniform layers of Pd oxide on the Pd metal. Our observations suggest a mechanism to explain the phenomenon of Pd catalyst activation observed in our previous research and by other research groups.

Key Words: **catalytic combustion of methane; Pd/PdO phase transformation; TEM.**

INTRODUCTION

Palladium is considered to be the most active catalyst for complete methane oxidation. With today's stricter restrictions on pollution for gas turbines and for automotive exhaust, considerable effort is being directed at the development of effective and stable catalytic combustion systems. Numerical modeling demonstrates a significant decrease in exhaust NO_x levels when combustion is stabilized on the catalyst wall. In such models, the catalyst is usually considered having a constant activity independent of the reaction conditions. The Pd-based catalyst system, however, has a complicated behavior, which is highly dependent on the reaction conditions (1). It is now widely accepted that a Pd-based catalyst supported on alumina can readily undergo oxidation/reduction transformations during the heterogeneous methane oxidation. These transformations can lead to rapid changes in apparent catalyst activity. In gas turbine applications where the surface temperature can be coupled with the reaction rate, such changes in the activity can lead to uncontrollable reaction oscillations, overheating or extinguishing of the reaction.

The change in the oxidation state of the active metal phase is accompanied by restructuring between the tetragonal bulk oxide, PdO, and the fcc metallic Pd crystal lattice. Unusual effects in the catalytic activity related to this transition were found by several groups of investigators (2–5). In our previous work (6), we observed a sharp tenfold increase in the reaction rate after *in situ* reduction of the catalyst by hydrogen. When the reaction temperature was kept near the Pd/PdO transition equilibrium, the catalyst activity increased when the oxygen partial pressure in the gas mixture was lowered (7). In Ref. (8) as well as in the work of Farrauto *et al.* (2) and McCarty (3), in contrast to the activation observed after reduction, the phenomenon of catalyst activation during the reactor cooling cycle was observed. These experimental results suggest that the oxidation state of the catalyst, metal–support interactions, and catalyst particle morphology are interdependent parameters, which strongly influence the activity of the catalyst. Therefore, understanding of the effect of Pd oxidation/reduction on the catalyst particle size, state, and morphology is important.

In previous work, Chen and Ruckenstein (9–11) used transmission electron microscopy (TEM) to study the effect of high-temperature treatment by oxygen and by hydrogen on the particle size of a γ-alumina-supported Pd catalyst. They found that, in an atmosphere of oxygen at temperatures up to 925 K, conditions under which the PdO phase is stable, cracks and pits appeared on the surface of the crystallites during Pd oxidation. At temperatures above 1175 K

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[1] E-mail: pfefferle@biomed.yale.edu.
[2] E-mail: datye@unm.edu.

0021-9517/99 $30.00

in pure oxygen, and above 1025 K in air, the catalyst was converted to the metallic state, forming much larger, dense, faceted crystallites. No pits and cavities were observed after the high-temperature treatment.

Chen and Schmidt investigated particle size changes for silica-supported pure Pd and Pt and their alloys during treatment in air, hydrogen, and nitrogen at different temperatures (12). They found that PdO particles retained the shape of thin platelets and a particle size of about 5 nm from 600 K, when the oxide was formed, to 1000 K, when they decomposed. After the oxide decomposition was completed at 1100 K, the catalyst particle size increased to approximately 70 nm, and the particles acquired a well-defined hexagonal shape. The authors also noted that the particle size increase was much more rapid when the catalyst was treated in air rather than in pure nitrogen.

Garbowski *et al.* (13) studied the activity of γ-alumina-supported Pd toward methane oxidation at temperatures between 473 and 873 K and reaction mixtures consisting of 1% methane and 4% (oxidizing conditions) or 1% (reducing conditions) oxygen in nitrogen. They found that after aging took place at 873 K for 14 h, the catalyst activity substantially increased under both reducing and oxidizing conditions. The authors argue that, after hydrogen reduction at 773 K, the Pd/Al_2O_3 sample exhibits Pd(111) surfaces which form epitaxially on the Al_2O_3(222) surfaces due to similar spacing and symmetry.

Rodriguez *et al.* (14) used a controlled atmosphere electron microscope to observe the behavior of Pd particles supported on γ-alumina, silica, and zirconia, when heated in oxygen. For alumina- and silica-supported catalysts, they found that a significant fraction of the oxide transformed into metallic Pd and underwent a rapid interaction with the support at temperatures above 1000 K. Zirconia was found to stabilize the oxidized PdO phase up to 1175 K.

In this work, our objective was to correlate the activity of an α-alumina-supported Pd catalyst with changes in particle size and morphology during the catalyzed methane oxidation reaction. The reactions were performed in a thin film reactor where Pd metal particles were deposited on plates of α-alumina (6). The reactants pass at high linear velocities through a thin slit over the α-alumina plate positioned in a clam-shell reactor. The reactor can be opened to quickly drop the plate into a cooling bath, allowing rapid quenching of the catalyst to make *ex situ* observations of catalyst morphology. This reactor type is well suited to obtain kinetic data free of transport limitations. In previous work, conversion as a function of flow rate was used to evaluate possible mixing effects, and a parameter range was chosen to permit measurement of intrinsic kinetics (6). Unfortunately, with these thin alumina plates, only indirect methods such as XPS, XRD, and diffuse reflectance spectroscopy can be used to infer morphology. Therefore, we used two types of model catalysts to derive information on particle morphology. First, a thin film of an alumina sol was deposited on Au TEM grids, on which Pd was deposited. Several TEM grids were glued on the same α-alumina plate used for reaction studies and removed at different times on stream for examination *ex situ* by TEM. The second type of model support was Pd supported on an α-alumina powder. This Pd/Al_2O_3 powder catalyst was subjected to similar thermal treatments and examined by TEM. By using these two types of model catalysts, we can gain confidence that the morphology is representative of the working Pd/α-alumina plate catalyst, and meaningful correlations can be made between the kinetic data and particle size and morphology of the Pd phases.

EXPERIMENTAL

As described above, the first model catalyst used in this study was Pd supported on a thin film of γ-alumina. The alumina layer was deposited onto gold TEM grids by dipping them into a Vista alumina sol solution, drying for about 1 h at 373 K and calcining at 773 K overnight. The resulting film was approximately 100-nm thick. These model samples were attached to standard α-alumina plates similar to those used in our previous studies of methane oxidation (6, 7). The plates had zero porosity and surface roughness on the order of 1 μm. Pd was loaded onto the plates and onto the alumina-covered TEM grid from the same $Pd(NO_3)_2$ solution. A drop of the solution was placed on the grid preheated to 400 K so that it dried instantly. The metal was fixed on the support by heating the sample in the furnace air to 800 K for 10 min and the procedure repeated until the desired coverage was reached. The average Pd coverage was 3–5 nm as measured by the X-ray microprobe technique (6). The area of the sample accessible to the gas mixture was equal to 5 cm^2, which gives the total amount of the catalyst available for reaction on the order of 10^{-5} g.

The α-alumina plate with the attached grids was then placed into the reactor cell and exposed to different reaction conditions as described below. The sketch of the reactor cell is shown in Fig. 1. The sample plate is placed into the titanium holder such that the gas mixture could flow in a thin gap over the catalytic surface. This provides high linear flow rates and contact times between 0.05 and 0.2 s. Because a very small amount of the catalyst was placed into the reactor, low levels of methane conversion could be maintained, even at high temperatures. The measured activation energies were comparable to those reported in the literature, suggesting that the reactor was operating in a kinetic regime. The plate and the holder were pressed between two electric heaters. The temperature controller, which adjusts the power supplied to the heaters, was regulated by a thermocouple located on the back of the plate. The catalyst sample in the reactor has good thermal contact with the wall of the reactor. This allows temperature control of the catalyst surface independently of the reaction

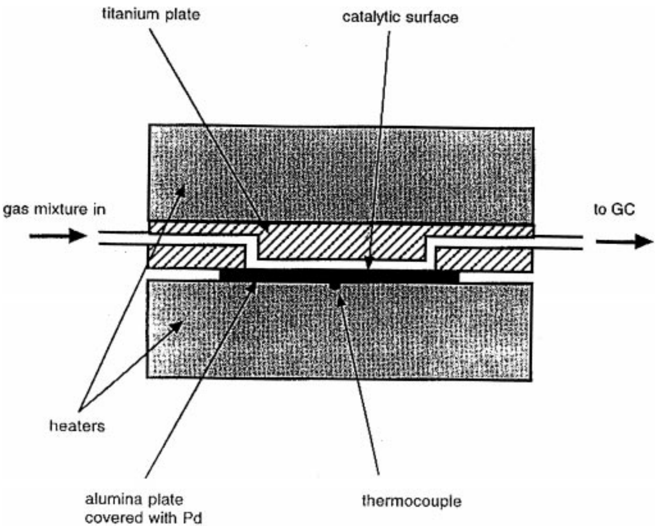

FIG. 1. Schematic diagram of the experimental reactor cell.

rate, by using external electric power. Isothermal measurements could therefore be performed. The design of the reactor also allows rapid release of the plate from the hot reactor so that it could be dropped into liquid nitrogen. This allowed cooling of the catalyst in approximately 10 s. Our previous study (6) showed that this time was much shorter than the characteristic time for Pd phase transformations.

In the beginning of each experimental run, several TEM grids were attached to the plate and covered with Pd. At a particular point during the run, the plate would be taken out of the reactor and quenched. One grid would be taken from the assembly for further TEM investigation, the rest would be replaced into the reactor, and the experimental run would continue to the next point of interest where the next grid would be taken off. Therefore, in the experiments described below, each grid has been subjected to the whole sequence of conditions described for the previous grids.

In a parallel study, a second type of model catalyst was used. The 5 wt% Pd/α-alumina catalyst was prepared to provide access to high-resolution TEM (HRTEM) measurements. A Sumitomo AKP-50 α-alumina powder was used as the support and Pd(acac)$_2$ was used as the precursor. After impregnation, the catalyst was calcined in air at 773 K, reduced in H_2 at 873 K for 2 h, and then subjected to an oxidation in air at 773 K before being used for this set of experiments. These studies were performed at a total pressure of 630 Torr (atmospheric pressure in Albuquerque). The first experiment involved heating in a thermogravimetric analyzer (TGA) in flowing air with a heating rate of 5 K/min to 1245 K and then cooling to room temperature in air also at 10 K/min (15). The sample used for the TGA (thermogravimetric analysis) experiment could not be rapidly quenched; hence, an alternate procedure was used for preparing samples for *ex situ* TEM examination. Aliquots of this catalyst were heated to selected temperatures in an alumina crucible kept in a tube furnace and quenched by dropping the sample in liquid nitrogen. These quenched samples were examined in a JEOL 2010 TEM with a 1.9-Å-point resolution to observe the changes in particle structure after oxidation and to distinguish Pd and PdO regions on the surface. In previous work (15, 16), we have confirmed that the quenching step is rapid enough that a metallic sample removed at $T > 1173$ K and dropped in liquid N_2 shows no detectable surface oxide by XPS.

RESULTS

In the experiment shown in Fig. 2, the catalyst plate with attached TEM grids was set into the reactor and preheated to ~1000 K in flowing air. Such a pretreatment procedure produces an initial catalyst in the form of PdO as confirmed by XRD and electron diffraction. Subsequently, 2% methane was introduced and the temperature was increased to 1070 K and allowed to stabilize. Methane conversion vs time for this experimental run is shown in Fig. 2. CO_2 was the only product, and no CO was detected at any point during this experimental run. After approximately 20 h on stream, during which time the catalyst activity slightly increased, the plate was released from the reactor and quenched. The arrows in the figure show the points when the sample was quenched for TEM analysis. Once a TEM grid was removed from the plate, the rest of the sample was reintroduced into the reactor and preheated to 1000 K in flowing air. The same reactant mixture flow was set through the reactor, and the reactor temperature was increased back to 1070 K. After measurements on the second step

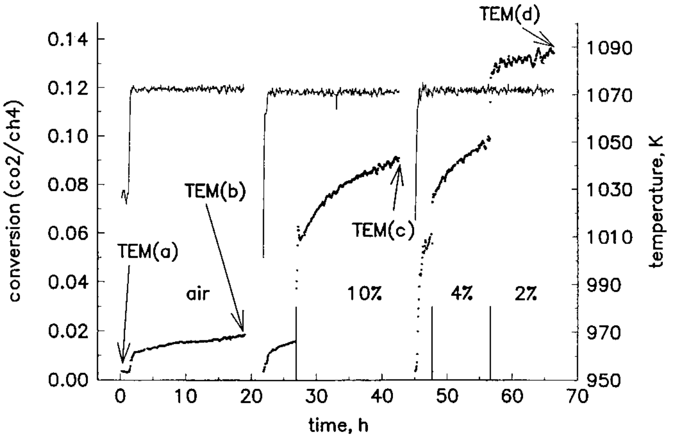

FIG. 2. Methane conversion to CO_2 over the alumina-supported Pd catalyst. 2% methane in the mixture, varying oxygen, balance of nitrogen; 1 atm pressure. Numbers in the graph show the oxygen concentration. Arrows indicate where the process was interrupted and the TEM samples taken from the alumina plate. Vertical lines indicate where the oxygen concentration was decreased stepwise.

were started, it was found that the initial conversion was similar to that seen at the start of this experiment. The conversion then increased and in approximately 5 h reached the same level as that before the interruption.

After 27 h on stream (vertical line in the graph), the oxygen concentration in the gas mixture was decreased in one step to 10%, with nitrogen substituted for oxygen to maintain a constant flow rate. There was a sharp increase in catalyst activity, followed by a gradual increase over the next 15 h. The rate of increase of conversion is much faster than that seen when the reaction was performed using air.

After 42 h, the sample was quenched and another TEM grid was removed from the alumina plate. The plate was then reinstalled into the reactor and preheated in the flow of 10% O_2 in nitrogen (without methane). When the reactor temperature reached 1020 K, 2% methane was added to the mixture and conversion measurements were started while the reactor temperature was increased back to 1070 K. The catalyst activity again was found to have decreased due to the interruption, but it increased rapidly under reaction conditions. After 48 h on stream (second vertical line), the oxygen concentration in the reaction mixture was further reduced to 4% (stoichiometric). Catalyst activity increased during this treatment at approximately the same rate as with 10% oxygen. After 57 h on stream (third vertical line), the oxygen concentration was decreased to 2%. A rapid initial increase in the catalyst activity occurred followed by an almost constant activity over the next 10 h. The overall methane conversion at this point was 14%, but even under these conditions, we do not expect the reaction kinetics to be influenced by diffusion limitations. At the end of the run, the catalyst was quenched and the last TEM grid was removed from the plate.

The TEM micrograph of the fresh sample after calcination in air at 825 K, before the reaction treatment, is shown in Fig. 3a. The catalyst is in the oxidized crystalline PdO state after this pretreatment, which was also confirmed by UV–visible spectroscopy (6), with a particle size on the order of 5–10 nm. The TEM image obtained after the reaction in the methane–air mixture is shown in Fig. 3b. At this point the particle size had increased to approximately 20–30 nm. The next TEM image, after reaction in 10% O_2, is shown in Fig. 3c. Only large particles in the 100- to 150-nm size range were found in this sample. Most of the particles appear rounded and lack any pronounced faceting, but some have characteristic triangular shapes, which suggest that particle restructuring may have occurred during the reaction. The electron diffraction patterns from the sample in Fig. 3c confirm that the catalyst particles are in the metallic Pd state. The TEM image obtained at the end of this experiment, after reaction in a mixture with 2% oxygen, is shown in Fig. 3d. The Pd particles at this point have grown even larger and are now on the order of 200–300 nm. Most of the particles have restructured into the faceted crystallites.

Parallel to the combustion reactivity experiments described above, the model 5% Pd/α-alumina powder catalyst was heated in air in a TGA to study the phase transformations. Figure 4 shows the changes in weight as a function of temperature. A sharp drop in weight is seen as the catalyst is heated beyond about 973 K. This drop in weight is caused by the transformation of PdO into Pd metal. The sample was heated up to 1248 K to ensure complete transformation to Pd metal. Upon cooling of the sample, there was no immediate weight gain, and the sample had to be cooled below 973 K before any oxidation occurred. The behavior seen here is similar to that reported previously by Farrauto *et al.* (2). The only significant difference lies in the temperature at which re-oxidation occurs. On γ-alumina, which was used as a support by Farrauto *et al.* (2), the sample had to be cooled below 923 K before any oxidation was seen.

To obtain samples for *ex situ* TEM analysis, the same temperature cycle was repeated, but using a larger tube furnace. Approximately 0.5 g of catalyst sample was placed in an alumina boat and heated to different temperatures following the cycle in Fig. 4. The heating rate was 5 K/min and the atmosphere was laboratory air. After the specified temperature was reached, the sample was quickly withdrawn and dropped into a beaker containing liquid nitrogen. TEM images of samples quenched at 673 and 1173 K on the ramp-up cycle are shown in Figs. 5 and 6. The sample shown in Fig. 7 was quenched at 823 K during the cool down.

As seen in Fig. 5, the sample contains particles of PdO which are much larger than those seen in Fig. 3a. The larger particle size is a result of the prior history of this sample (reduction at 873 K in H_2 followed by oxidation at 773 K). The PdO is polycrystalline, as can be inferred from the contrast from the low-magnification view. The higher magnification image shows that the PdO surfaces are smooth. Heating to 1173 K transforms the PdO to Pd, accompanied by a growth in particle size (Fig. 6). Several of the Pd metal particles exhibit pronounced facets that are characteristic of low-index planes in fcc crystals. However, only particles oriented along their low-index zone axes will appear faceted in TEM images. Since the particles are randomly oriented, those particles which are not oriented along a zone axis will generally appear rounded and devoid of facets. Therefore, it is quite likely that a larger fraction of these metal particles could have low-index facets. A previous study of Pt/SiO_2 has shown that tilting the sample to bring particles in alignment with the electron beam improves visibility of surface facets (17). Finally, we show in Fig. 7 the sample that was quenched after heating to 1173 K, holding at that temperature for 30 min and then cooling to 823 K (Fig. 7). It can be seen that the particles are now again composed of polycrystalline PdO. The contrast of the particle in Fig. 7 is unusual and is suggestive of a patchy surface oxide phase. Formation of these patches may hinder further oxidation, possibly due to voids that may be formed by migration of

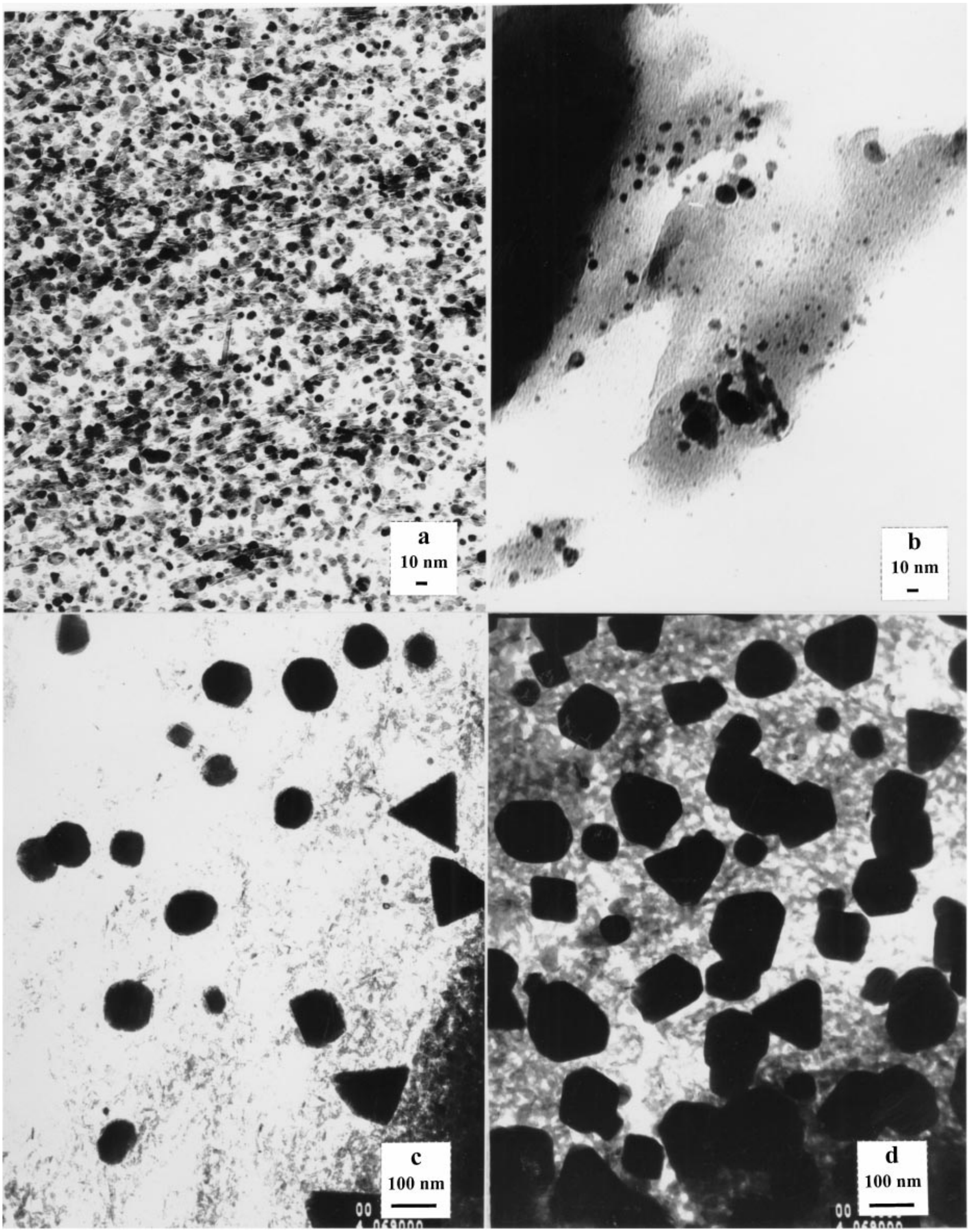

FIG. 3. Micrographs of the TEM samples obtained using the procedure shown in Fig. 2: (a) before the reaction, impregnation with $Pd(NO_3)_2$ solution, and calcination at 820 K overnight; (b) 20-h treatment at 1070 K and 2% methane in air following treatment (a); (c) 15-h treatment at 1070 K and 2% methane in 10% oxygen/nitrogen balance following treatment (b); (d) 10-h treatment at 1070 K and 2% methane in 2% oxygen/nitrogen balance following treatment (c).

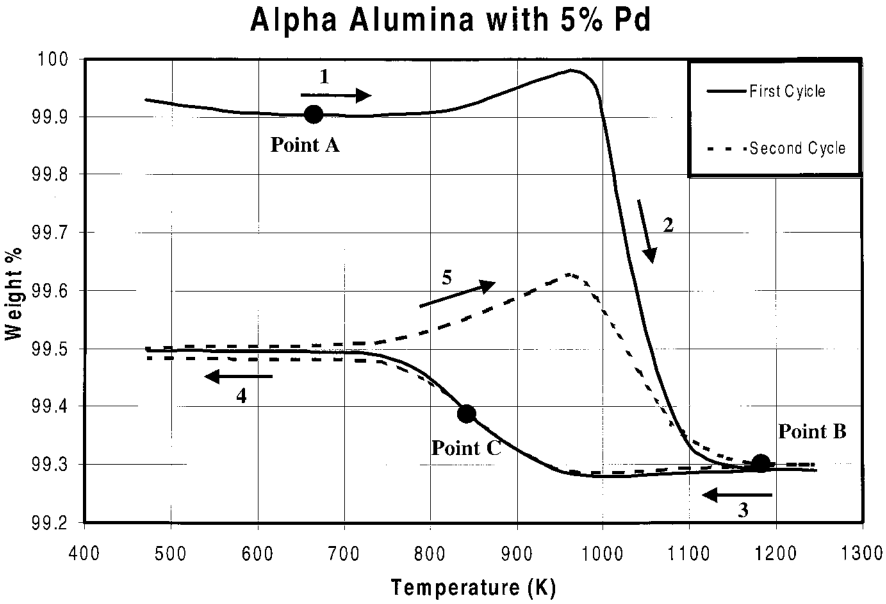

FIG. 4. TGA analysis of 5% Pd/α-alumina. The numbered arrows indicate the direction of the heating cycle. The labeled points (A, B, and C) indicate where a sample was quenched and studied by TEM.

Pd cations to the surface where they get oxidized. Hence, further oxidation resumes in another part of the particle where oxide nucleation has commenced. This gives rise to a complex internal structure as evident in Fig. 7a. The outline of the particle also shows a rough surface compared to the comparatively smoother surface on the PdO particle in Fig. 5a. A higher magnification view in Fig. 7b confirms that the internal structure is composed of domains of crystalline PdO. The complex internal microstructure must be a consequence of the rapid oxidation that occurs at high temperature during cool down.

DISCUSSION

The experimental procedure shown in Fig. 2 is similar to that used in our previous work (7). There, we observed that at temperatures below 1046 K and an oxygen partial pressure of 0.21 atm, catalyst activity decreased with time, while at higher temperature (or lower oxygen pressures at this temperature) the activity increased with time. The particular temperature at which the catalyst activity dependence on time changed sign depended on the oxygen partial pressure. We attributed this behavior to the change in the

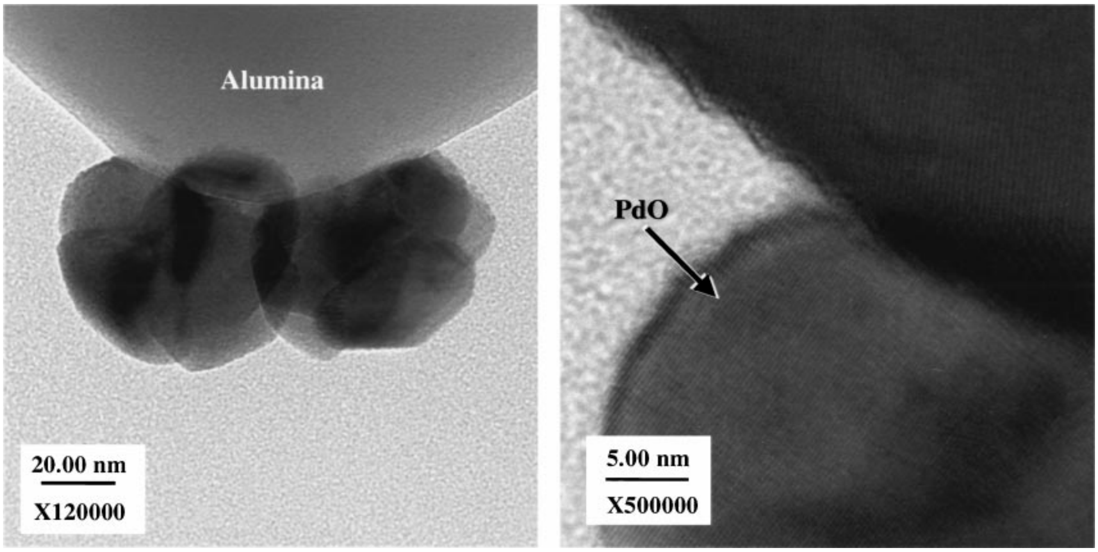

FIG. 5. TEM micrographs of 5% Pd/α-alumina. The sample was heated in air to 673 K at a ramp rate of 5 K/min and quenched.

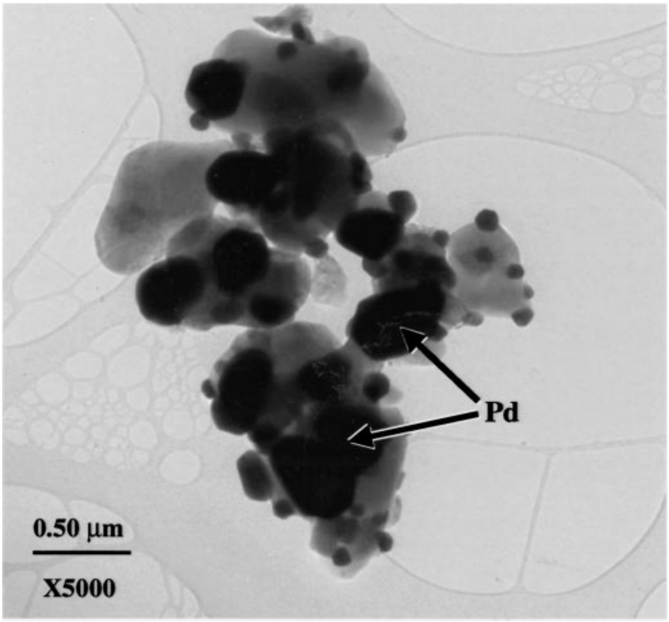

FIG. 6. TEM micrograph of 5% Pd/α-alumina. The sample was heated in air to 1173 K at a ramp rate of 5 K/min and quenched.

catalyst oxidation state. At lower temperatures and higher oxygen partial pressures, the oxidized PdO state of the catalyst is stable, while at higher temperatures and lower oxygen pressures the metallic Pd state is stable. The temperature at which Pd becomes thermodynamically favored over PdO depends on the oxygen pressure. At a total pressure of 1 atm, the transition temperature is 1046 K with 21% O_2, 1019 K with 10% O_2, and going down to 961 K at 2% O_2. Therefore, since our experiment was performed at 1070 K, we should be in a regime where Pd metal is favored over the oxide PdO.

In our experiment, the catalyst activity was found to increase with time at the beginning of the run. After the experiment was interrupted and the sample was quenched (to take the first TEM grid off the plate), the catalyst was found to have lost its initial activity and it took some time to regain the activity the catalyst had prior to interruption of the run. This suggests that quenching and the preheating in air (approximately 3 h from room temperature to 1000 K) changed the state of the catalyst and brought it to a state of lower activity. We attribute this to the re-oxidation of the catalyst during the preheating in air, and restoration of catalyst activity as the metallic state is reached after exposure to reaction conditions. In the next step of this experiment, the oxygen partial pressure was lowered to 10%, which resulted in a rapid increase in activity followed by a gradual increase in activity that continued for over 15 h. During this period, all reaction conditions were kept constant. Likewise, the conversion continued to increase when oxygen content was further reduced to 4%. Only after reaching an oxygen content of 2% did we see the catalyst activity level off at 14% conversion, after an initial rapid increase. As we show below, there are three factors that lead to the observed changes in catalyst reactivity: transformation of PdO → Pd, the negative order of reaction in P_{oxygen} on metallic Pd, and a gradual reconstruction of the Pd metal surfaces into their most active form.

First, let us consider the phase transformation between PdO and Pd. Pd oxidation is a reversible solid state reaction $2PdO \leftrightarrow 2Pd + O_2$ with the thermodynamic parameters $\Delta H^\circ_{1050\,\mathrm{K}} = 25.7$ kcal/mol and $\Delta S^\circ_{1050\,\mathrm{K}} = 22.3$ cal/(mol K) (18). While the transition temperature at which Pd becomes

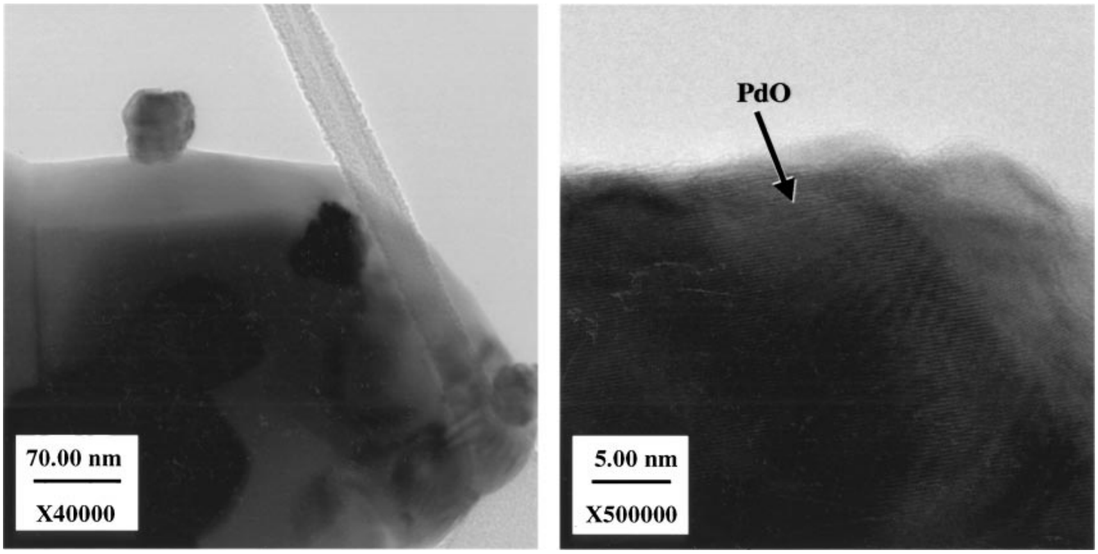

FIG. 7. TEM micrograph of 5% Pd/α-alumina. The sample was heated in air to 1173 K at a ramp rate of 5 K/min and cooled to 823 K at the same ramp rate. After reaching 823 K, the sample was quenched.

favored over PdO is well defined, the transformation is slow since it involves diffusive processes within the particle. As seen from the TGA data, it must take approximately 10 min at 1070 K for complete transformation from PdO → Pd. The rapid increase in activity seen in our experiment in air as well as in 10% O_2 after the interruption in the reaction must both be associated with the formation of metallic Pd. There is also a rapid increase in activity when the oxygen pressure was dropped in a stepwise fashion from air to 10%, 4%, and 2% oxygen. This sharp increase we feel is a result of the inhibition effect of oxygen on methane combustion on metallic Pd. A reaction order of zero with respect to oxygen over PdO has been found by us and others (19) for fuel lean conditions. Over the metallic Pd phase, however, this changes to negative order for fuel lean conditions. Early in the step with 10% oxygen, the surface is likely largely converted to metallic Pd. At this temperature, only minutes are required for this conversion. Therefore, the sharp increase in activity occurring at the step change in oxygen concentration must arise from the negative reaction order in oxygen.

In addition to the two rapid activity changes described above, there is a third effect, a gradual increase in activity over 15 h seen most clearly during the reaction in 10% oxygen. TEM observations of the catalyst samples after reaction in air followed by progressively lower oxygen content shown in Fig. 3 provide clues to the progressive restructuring of the catalyst over time that may lead to the observed increase in activity. The micrograph of the catalyst after the first reaction step in air (Fig. 3b) shows that the particle size was of the order of 20–30 nm, a significant increase over the particle size before the start of the reaction (5–10 nm). At this stage, it can also be seen that particles retain their spherical shape and do not have any defined surface orientation. At the next step, with 10% oxygen in the mixture, the rate of activity increase was much higher and was accompanied by a further increase in particle size, which now was of the order of 50–150 nm (Fig. 3c). Most particles observed at this stage still retained their spherical shapes, suggesting that they are randomly oriented and there is no preferred surface facet exposed. However, some particles (two particles seen on the right edge of the micrograph) do show pronounced triangular shapes, suggesting the formation of low-index facets during this stage of the reaction. Another observation from this micrograph is the coalescence of neighboring particles (as seen on the left side of the micrograph in Fig. 3c). Therefore, surface migration and agglomeration of the smaller particles may be contributing to particle growth.

Finally, at the end of the experimental run, when the oxygen concentration in the gas mixture was lowered to 2%, the reaction rate, after an initial rapid increase, leveled off at a conversion of 14%. The TEM micrograph of the sample at the end of this treatment is shown in Fig. 3d. The particle size had now increased to 100–200 nm, and the crystallites had acquired more regular shapes. In addition to triangular particles, we also see other shapes including some hexagonal particles. With the decrease in oxygen pressure, decomposition of PdO leads to the formation of a metallic Pd surface. This appears to cause a large increase in particle mobility over the alumina support, leading to increased agglomeration, which was observed during the reaction with 10% oxygen in the mixture (Fig. 3c). The further slow increase in conversion appears to be due to crystallite faceting which produces low-index Pd surfaces.

The phenomenon of catalyst particle size increase during the reduction is similar to that observed by Chen and Schmidt (12) for Pd supported on silica. These authors found that, in air, the particle size remained small (10–20 nm) at temperatures below 1000 K, i.e., under conditions where the PdO phase was stable. Above this temperature, the formation of large Pd crystallites was observed, and at 1125 K only Pd particles 150–200 nm in size with triangular and hexagonal shapes were present. A similar effect was observed by Chen and Ruckenstein (9–11) who observed the formation of large, dense, faceted Pd crystallites on γ-alumina at temperatures above 1175 K in pure oxygen, and above 1025 K in air.

In a recent work, Rupprechter *et al.* used HRTEM to study the morphology of Rh nanoparticles supported on amorphous alumina films (20). The authors observed that a significant fraction of Rh crystallites had triangular or pseudopentagonal shapes, which were similar to the particle shapes seen in Fig. 3d in this paper. Analysis of these model Rh samples made by the authors demonstrated that the triangular-shaped particles were half-tetrahedra with a (011) base plane and three (111) side faces. Pseudopentagonal particles were pyramids with a (001) base and one (111) and four (110) side faces. Because Pd and Rh metals have a similar fcc lattice structure, we suggest that triangular and hexagonal Pd crystallites seen in Figs. 3c and 3d exhibit Pd(111) and Pd(110) facets.

The results reported here seem apparently counterintuitive. The catalyst becomes more active while the catalyst dispersion decreases ten-fold or more. In our previous work (6), we found that the pre-exponential factor (A) in the expression for the reaction rate was higher for methane oxidation over metallic Pd than over the oxide, and the extent of water poisoning was not as significant. This difference in the A factor was compensated by the higher activation energy for the reaction over the metal compared with the oxide. In the experiments reported here, surfaces with initially random crystallographic orientations appear to restructure into low-index facets. As the reconstruction of the Pd crystallites progresses, there are further increases in the catalyst activity, implying therefore further increases in the pre-exponential factor.

There is theoretical support for a significantly higher pre-exponential factor for metallic low-index Pd surfaces when compared to PdO. Broclawik *et al.* (21, 22) carried out several theoretical studies of the activation of methane on PdO and Pd using density functional methods. They identified two stable adsorption complexes on PdO requiring moderate activation energy (24.5 kcal/mol). The product of C–H bond scission was found to be stable; however, it lies on the singlet potential energy surface whereas the entrance channel and all intermediates lie on the triplet surface. The singlet–triplet crossing is expected to occur in the vicinity of the transition state which can strongly affect the efficiency of the process, leading to a low A factor.

An alternative explanation has been proposed by Iglesia (23), who suggested that the rate-limiting step is methane activation on oxygen vacancies in the PdO lattice. The reaction is approximately negative first order in water concentration and zero order in oxygen, suggesting that water is blocking the active sites. True oxygen "vacancies" may not be present due to oxygen diffusion from the bulk and possible crystal shear effects. In any case, the oxygen vacancy concentration would be extremely low, leading to a low apparent A factor. Burch *et al.*, on the other hand (24), propose that the decomposition of palladium hydroxide and breaking the surface OH bond are the rate-limiting steps for methane activation over PdO. In their experiments, the initial activity for a very dry methane/air mixture over dry PdO/Al_2O_3 is significantly higher than for catalysts previously exposed to reaction mixtures. The implication here is that a large portion of the surface is unavailable due to the stable surface hydroxide formed, leading again to a low pre-exponential factor in the kinetic expression. The near-negative first-order dependence of methane oxidation on water has also been shown to bias the apparent activation energy measured (25). A similar strong inhibiting effect of water vapor has not been observed on metallic Pd surfaces at high temperatures, where the mechanism is consistent with competitive adsorption of methane and oxygen on the metal (O being strongly bound). This mechanism correctly predicts the negative oxygen order as well as the high activation energy (approximately 45 kcal/mol) that we (26) and others have observed. The further increase in the A factor as the low-index surfaces are formed suggests a structure sensitivity for methane adsorption as a function of the crystal plane.

The oxidation process studied in the TGA experiments also provides insight into the activity increase seen on metallic Pd catalysts when they are cooled from high temperatures. The TEM images in Fig. 7 are not consistent with the growth of a surface oxide on a shrinking metal core. Rather, a complex microstructure is observed with domains of oxide that are randomly oriented. Some patches of oxide appear to be present over low-contrast regions that are suggestive of voids caused by metal ion diffusion. The mechanism of oxidation is not very clear and seems to depend on oxidation temperature. However, what is clear is that the oxide formed on cooling shows a high degree of roughness on the microscale. We suggest that the enhanced activity seen during cool down (e.g., (2), (3), (8)) is related to the nature of the oxide formed under these conditions.

CONCLUSIONS

The activity of Pd/α-alumina was studied for the oxidation of methane at atmospheric pressure. The reactivity was correlated with the morphology of the metal and oxide particles in these catalysts. Since we were unable to directly image the metal particles on the α-alumina plates used for catalytic reactions, two model catalysts were used to infer morphology changes. For α-alumina-supported Pd catalysts, we found that the particle size of PdO is of the order of 5–10 nm when the catalyst is prepared from $Pd(NO_3)_2$ followed by calcination. When methane oxidation was carried out under conditions that favor decomposition of PdO to Pd (1070 K with 2% methane in air), a gradual increase in methane oxidation activity was observed. Decreasing the oxygen pressure after the catalyst was in the reduced Pd state led to a further increase in activity that coincided with the step changes in oxygen concentration. The initial rapid increase in observed activity was related to the negative order in oxygen during reaction under lean conditions on metallic Pd. As the reaction continued, the mobility of the metallic Pd caused a gradual increase in the metal particle size. Surprisingly, the increase in particle size led to a further increase in activity, not a decrease as one would expect based on the loss of active-phase surface area. TEM observations at the end of this run showed faceted metal particles exposing low-index planes. We therefore conclude that the catalyst must be restructuring slowly under reaction conditions to expose low-index surfaces that are apparently more reactive. These results suggest that methane oxidation over metallic Pd is structure sensitive and is favored over low-index metal surfaces.

The reduction/oxidation study on model α-alumina-supported Pd showed that oxidation during cooling in air from high temperatures did not occur via a shrinking core mechanism. The oxide formed under these conditions shows significant roughening, which may explain the reactivation of the metal catalyst during cool down.

ACKNOWLEDGMENTS

We are grateful for financial support from the U.S. Department of Energy and from the State of Connecticut. The work was performed using the electron microscopy facility at the University of New Mexico which is supported by the Earth and Planetary Sciences department, NASA, NSF, and the State of New Mexico. We thank the reviewers of this manuscript for their helpful suggestions.

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