FINAL REPORT
Complete Oxidation of Methane on Palladium Catalysts
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This is the final report for grant DE-FG02-00ER15026. It summarizes all the accomplishments in 8 sections.

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RESEARCH ACCOMPLISHMENTS ON CURRENT GRANT (Jan. 2000 to Jul. 2003)

1 - Adaptations on Existing Unit and Construction of New Unit

We adapted one of our existing UHV-high pressure systems to allow for the measurement of rates at conditions relevant to combustion at high temperature. It consisted of converting a batch reactor into a continuous well-mixed reactor, introducing a bank of mass flow controllers, routing a fraction of the gas to impinge directly on the sample to avoid mass transport limitations, and a sample heating system based on an IR lamp to relieve the heating stress from the electrical heating system. This system will continue to be used for measurement of kinetics on single crystals.

Figure 1 shows our new chamber constructed for this project during the past 2 years. It is used for the preparation of samples by metal evaporation, characterization by surface science techniques, scanning tunneling microscopy (STM), and high pressure (1 atm) and temperature (900 K) treatments.

Fig. 1-Ultrahigh vacuum chamber used for preparation, characterization, and reaction studies.

The ultrahigh vacuum three-chamber is mounted on four air legs to allow for vibration-free operation of the STM. The first chamber is an analytical chamber equipped with a mass spectrometer for temperature programmed desorption (TPD)

experiments, low energy electron diffraction (LEED), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), sputtering, and metal deposition. The metal deposition unit has two deposition guns and a film thickness monitor. The second chamber is an atomic resolution scanning tunneling microscope STM (RHK, model UHV 300) and the third is a custom-built reaction chamber. The sample can be transferred among the chambers in a motorized stage. In the analyzer chamber the sample is heated by electron bombardment and in the reaction cell it is heated by an IR lamp. With this setup we can prepare clusters by evaporation, characterize them, and carry out reactions at pressures up to 1 bar.

The utilization of a UHV system allows control on sample preparation. For example, for clusters deposited by evaporation, the substrate needs to be pristine to avoid influence of contamination on cluster nucleation [1]. During analysis, the presence of contaminants (adsorbed species) on the surface and on the microscope tip prevents atomic resolution images to be achieved.

2 - Turnover Rate and Reaction Orders for the Complete Oxidation of Methane on a Palladium Foil in Excess Dioxygen. Monteiro, R.S., D. Zemlyanov, J.M. Storey and F.H. Ribeiro, J. Catal., 2001. 199(2): p. 291-301.

The turnover rate and reaction orders for the combustion of methane in excess oxygen over Pd foils were in agreement with literature results reported for supported catalysts. The rate equation was $r = k[\text{CH}_4]^{0.7}[\text{O}_2]^{0.2}[\text{H}_2\text{O}]^{-0.9}$ (Fig.2). The turnover rate on the Pd foil was $59 \times 10^{-2} \text{ s}^{-1}$ at 550K, 160 Torr of O_2 , 16 Torr of CH_4 , 1 Torr H_2O , and N_2

balance to 800 Torr, with the number of active sites defined as the number of surface Pd atoms calculated from the initial geometric area of the foil. This rate is three times higher than the highest value reported in the literature for supported catalysts. The surface area of the foil, measured by isotopic

Fig. 2. The reaction order dependence for Pd foil on methane (2-32 Torr CH_4 , 160 Torr O_2 , N_2 to balance 800 Torr), oxygen (80-240 Torr O_2 , 16 Torr CH_4 , N_2 to balance 800 Torr) and water (0.5-8 Torr H_2O , 16 Torr CH_4 , 160 Torr O_2 , N_2 to balance 800 Torr).

exchange of surface oxygen with $^{18}\text{O}_2$, increased by a factor of approximately two after reaction. The main species observed on the surface after reaction by XPS was PdO. Sample activation during reaction was not observed. The reaction was carried out in a batch reactor at 598 K and atmospheric pressure with characterization before and after reaction by X-ray and Auger spectroscopies and temperature programmed desorption.

3 - Surface area increase on Pd foils after oxidation in excess methane. Monteiro, R.S., D. Zemlyanov, J.M. Storey and F.H. Ribeiro *J. Catal.*, 2001. 201(1): p. 37-45.

An increase in the PdO surface area by a factor of about 20 was observed after treatment of Pd foils in excess methane at 598 K (Fig. 3). The surface area was increased as the O_2 partial pressure in the activation treatment was decreased. The activated foil was probed by the reaction of complete oxidation of methane in excess O_2 . The rate was proportional to the PdO surface area and thus the turnover rate per unit of PdO area was the same as for the untreated foil. Critical for this assessment was the determination of the PdO surface area measured by exchange of surface oxygen with $^{18}\text{O}_2$. The PdO surface area decreased by interaction with water when the sample was cooled. After treatment of the foil in excess methane, PdO but not Pd was identified by X-ray photoelectron spectroscopy, and carbon deposits from methane were identified on the surface and in the bulk by temperature programmed desorption.

Fig. 3. SEM images for (A) clean Pd foil, (B) Pd foil after reaction in excess O_2 (598 K, 160 Torr O_2 , 16 Torr CH_4 , N_2 balance to 800 Torr, for 170 min), and (C) Pd foil after activation treatment (598 K, 16-4 Torr O_2 , 160 Torr CH_4 , N_2 balance to 800 Torr, for 60 min).

4 - UV Raman spectroscopic study of hydrogen bonding in gibbsite and bayerite between 93 and 453 K. Rzhetskii, A.M. and F.H. Ribeiro, *Journal of Raman Spectroscopy*, 2001. 32(11): p. 923-928.

Raman spectra of bayerite and gibbsite (hydrargillite) were measured at the temperatures of 453 K, 295 K, and 93 K as well as after H-D exchange at 423 K with gaseous D_2O . Spectra in the O-H stretching vibration region were recorded with the use of ultraviolet laser excitation, which avoided the fluorescence problem typical for these materials. Lowering the temperature led to a spectral resolution improvement with additional bands resolved in the $\nu(\text{OH})$ spectrum of bayerite. It was established that the

positions of the Raman bands are sensitive to the temperature of the sample. A spectral criterion based on different shift of band positions with temperature was proposed as a method to distinguish between structural OH groups forming H-bonds between hydroxide layers or in the same plane of the layer. It was found that the highest frequency band at 3655 cm^{-1} in the spectrum of bayerite does not participate in H-bonding. A one-to-one correspondence between Raman spectra recorded in $\nu(\text{OH})$ and $\nu(\text{OD})$ regions upon partial H-D exchange with D_2O is evidence that the multiplicity of spectral bands are caused by different O-H...O distances in the hydroxide lattice rather than by vibrational coupling of H-bonded hydroxyls.

Figure 4. *In situ* Raman spectrum of bayerite at room temperature after partial H-D-exchange at 423 K with D_2O . The spectrum for the O-D stretching region is enclosed by a rectangle in the bottom of the figure and also shown in an enlarged version.

5 - Coverage of Palladium Catalysts by Oxidized Silicon During Complete Oxidation of Methane, Guanghui Zhu, Ken-ichiro Fujimoto, Dmitri Yu. Zemlyanov, Abhaya K. Datye, Fabio H. Ribeiro, To be submitted to the Journal of Catalysis.

The interaction between silica and palladium during the complete oxidation of methane was investigated on a polycrystalline palladium foil and on supported model palladium catalysts. During methane oxidation, oxidized silicon covered the palladium oxide surface as observed by TEM on silica-supported catalysts and by XPS on palladium foil. The migration of oxidized silicon deactivated the catalysts by blocking the active sites for methane oxidation. Reduction of silica-supported catalysts by hydrogen at 923 K also resulted on migration of oxidized silicon species. Depth profiling on the deactivated

palladium foil revealed that oxidized silicon resided on the outmost layers of the palladium particle surface.

Fig. 5 TEM of reduced Pd/SiO₂ after chemisorption. Reduction in pure H₂ at 923 K for 2 h.

Fig. 6 I_{Si}/I_{Pd} change as function of time-on-sputtering (I_{Si} : XPS signal intensity of Si 2s; I_{Pd} : XPS signal intensity of Pd 3d)

6 - Kinetics of Methane Oxidation under lean conditions over Pd and PdO, Guanghui Zhu, Dmitri Yu. Zemlyanov, Fabio H. Ribeiro, to be submitted to the Journal of Catalysis

Catalytic combustion for power generation is operated from high temperature, when Pd is stable phase, to low temperature, when PdO is stable phase. Obtaining the reaction mechanism, especially reaction orders and activation energy at various temperatures, is necessary to predict the catalyst performance and to facilitate the combustion system design.

A unit was built to study the kinetics on model catalysts at various temperatures without heat and mass transfer limitations. This system allowed kinetic studies in both CSTR and batch mode. At high temperature, data was collected in CSTR mode to avoid total conversion of methane; at low temperature, data was collected in batch mode to get detectable concentration of CO₂. Two gas circulation pumps and an adjustable valve were employed to increase the gas flow rate at high temperature just enough to avoid mass transfer limitation at the lowest heating power. The experiments were carried out on a polycrystalline palladium foil with geometric surface area of about 0.5 cm². The palladium foil was heated up resistively at low temperature (<350°C). When high

temperature ($>350^{\circ}\text{C}$) was needed, an IR lamp was employed to supplement the foil heating through a glass window in the reactor.

The reaction mechanism changed with temperature and the palladium chemical state. The reaction orders for CH_4 , O_2 and H_2O were 0.7, 0.2, -0.9 at 325°C , 0.6, 0.0, 0.0 at 590°C , and 0.7, 0.0, 0.0 at 700°C . The stable phase on these experiments was PdO at 325°C and 590°C , and Pd at 700°C , which was measured by XPS analysis after reaction. The activation energy is 125 kJ mol^{-1} at the temperature range of $295\text{--}355^{\circ}\text{C}$, 26 kJ mol^{-1} at $510\text{--}600^{\circ}\text{C}$ and 118 kJ mol^{-1} at $660\text{--}730^{\circ}\text{C}$. Note that the thermodynamically stable phase is PdO for the first two temperature regions and Pd for the last temperature region. Surface area of palladium oxide was measured by $^{18}\text{O}_2$ exchange, and the surface area of palladium was calculated based on atom density on the Pd foil of $1.27 \times 10^{19}\text{ m}^{-2}$. When the sample was heated above the decomposition temperature of PdO and decomposed to Pd, the turnover rate decreased from 1.57 s^{-1} to 0.50 s^{-1} , considering the surface area change. The lower overall rate on Pd was attributed to a combination of surface area reduction and a different reaction mechanism.

Fig. 7 - Reaction orders as a function of temperature.

7- An Explanation for the Hysteresis on the Oxidation of Methane, Guanghui Zhu, Dmitri Yu. Zemlyanov, Fabio H. Ribeiro, to be submitted to Catalysis Letters

Hysteresis in catalytic methane combustion affects the performance of the combustion system because of a lower catalyst activity after PdO is transformed to Pd. The phenomenon was reported in the literature, but the cause of this phenomenon is not well understood.

During catalytic methane combustion in a lean fuel mixture, when the sample is heated above the decomposition temperature of PdO and decomposed to Pd, the rate decreases substantially (Fig. 8). We attribute the lower rate to a combination of surface area reduction and a different reaction mechanism. When the reaction temperature was subsequently decreased to allow for the formation of PdO, the sample showed hysteresis

in catalytic conversion. The reactivity was regained (and PdO formed) only when the reaction temperature was decreased substantially below the point where PdO should be formed (as predicted by thermodynamics).

By introducing a lean fuel mixture after heating a clean palladium metal foil in N_2 to the temperature where hysteresis occurred, the catalyst had the same low activity as when hysteresis occurred. In another experiment, if the sample is heated to the reaction temperature in an O_2 containing mixture the foil can be readily oxidized. Those results indicate that hysteresis is caused by the inability to oxidize the catalyst and occur only if the starting chemical state of palladium is metal at that temperature, and has no connection with the previous temperature history. The surface can be oxidized only if the proper concentration of oxygen on the surface is achieved, which is a combination of temperature and O_2 partial pressure.

To increase the catalyst activity when hysteresis occurred, a rich fuel mixture was introduced into the reactor for 1 hour before switching to a lean fuel mixture. The nominal turnover rate after rich treatment was 6 to 10 times higher than the one obtained before rich treatment without considering surface area change, while the surface was still palladium metal after rich treatment. Subsequent lean reaction at $325^\circ C$ gave 12 times turnover rate of the lean reaction started with a clean foil, which indicated that the foil after rich treatment had 12 times the surface area of the clean foil. The surface area increase can explain the turnover change after rich treatment. This major surface rearrangement shows again that the cause for hysteresis is related only to a critical concentration of oxygen on the surface that triggers the oxidation.

Figure 8. Hysteresis in catalytic methane combustion. Sample was heated in reactants mixture (0.77 Torr O_2 , 0.15 Torr CH_4 and inert gases (N_2 and He) balance to atmospheric pressure) from room temperature to $730^\circ C$ and then cooled down. Each point represents steady state methane conversion at corresponding temperature. From thermodynamics, PdO decomposes to Pd at $615^\circ C$ in 0.77 Torr O_2 .

8- Structure of Pd(111) after oxidation in O₂, Jinyi Han, Dmitri Yu. Zemlyanov, Fabio H. Ribeiro, to be submitted to the Journal of Catalysis.

Oxidation of Pd(111) in pure oxygen was carried out in a high-pressure reaction chamber and the effects of oxygen pressure, reaction time and reaction temperature were characterized thereafter with low energy electron diffraction (LEED), temperature programmed desorption (TPD) and scanning tunneling microscopy (STM). Clean Pd(111) surface showed a structure with smooth terraces separated by mono-atomic steps (step height 0.226nm) (Fig. 9a and 9b).

Fig.9 Clean Pd(111) surface.
(a) LEED pattern. (80eV)
(b) STM image.

Initial exposure of Pd(111) to 1 torr O₂ at 600K for 10min resulted in the formation of hollowed surface structure with small islands and peninsulas, which could be explained by the diffusion of oxygen atoms into bulk phase and the ejection of Pd atoms (Fig. 10). Small size clusters (1-2nm) were observed to nucleate and grow after exposure of Pd(111) to higher pressure of O₂ between 10 and 25 torr at 600K. As adjacent clusters grew together, distorted regions due to lattice mis-match were formed and created a porous structure with small gap about 0.5-1nm between individual clusters (Fig. 11). Comparison of the surface roughness in these conditions which was between 0.04-0.22nm with that of clean Pd(111) surface which was around 0.01nm suggested that Pd(111) surface became apparently rough after the oxidation in high pressure of oxygen. Intensive oxidation of Pd(111) in 50torr and 100torr pure O₂ at 600K for 10min resulted in the growth of semi-spherical particles (5-10nm in diameter) and further aggregation into large agglomerates to minimize the surface tension (Fig. 12 and Fig. 13). The surface of Pd(111) became more irregular compared with that in 10-25 torr with the measured roughness in the range of 0.75-2.51nm, which was 4-11 times of the step height.

Fig. 10 Exposure Pd(111) to 1 torr O_2 at 600K for 10min. Oxygen coverage 2.03ML.

Fig. 11 Exposure Pd(111) to 10 torr O_2 at 600K for 10min. Oxygen coverage 4.46ML.

Fig. 12 Exposure Pd(111) to 50 torr O_2 at 600K for 10min. Oxygen coverage 6.66ML.

Fig. 13 Exposure Pd(111) to 50 torr O_2 at 600K for 10min. Three dimension view.

Surface morphology of Pd(111) could also be modified by increasing the reaction temperature or extending the reaction time. Similar porous surface structure was observed after exposure of Pd(111) to 1 torr O_2 at 820K for 10min (Fig. 14) and large aggregation structures were detected on Pd(111) surface after oxidation in 12.5 torr at 600K for 60min (Fig. 15).

Fig. 14 Exposure Pd(111) to 1 torr O_2 at 820K for 10min. Oxygen coverage 146.82ML.

Fig. 15 Exposure Pd(111) to 12.5 torr O_2 at 600K for 60min.

As revealed in all STM images, the Pd(111) oxidation process caused a surface roughening process with nucleation and growth of clusters, particles and agglomerates. The increase in surface area could be related to the expansion of Pd lattice structure by oxygen penetration into the bulk phase after reaching surface saturation. The surface area change with oxidation pressure is shown in Fig. 16.

Fig. 16 Surface area increases with oxidation pressure