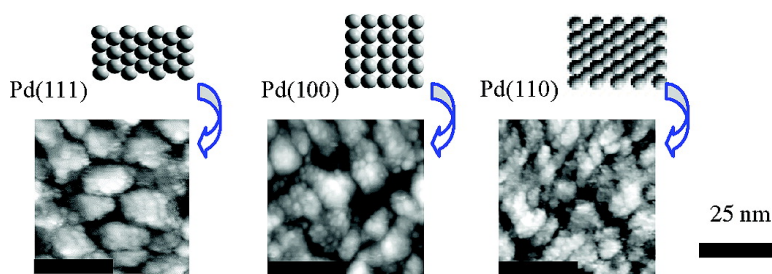Communication

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The Turnover Rate for the Catalytic Combustion of Methane over Palladium Is Not Sensitive to the Structure of the Catalyst

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We present the kinetics for the catalytic combustion of methane on palladium in its metal and oxide forms, both of which are of practical interest. The results show that the rate is not dependent on the structure of the catalyst but is strictly proportional to the total surface area. The data provide benchmark kinetics for this reaction. Methane is the "greener" of the fossil fuels. It has the highest hydrogen-to-carbon ratio of all hydrocarbons and thus will produce the highest amount of energy per CO_2 formed when burned. Also, many of the large reserves of natural gas, which are composed mainly of methane, have very small amounts of sulfur and nitrogen compounds. Thus, when natural gas is burned the emission gases will contain correspondingly low concentrations of SO_x and NO_x formed from S and N compounds. For the production of energy, the best way to burn methane is through a catalytic combustor because much less than 1 ppm of NO_x is generated thermally in the process.[1] Catalysts are also needed as an abatement device in technologies that use methane as a fuel since some of it will slip through the system unburned: methane is a potent greenhouse gas. Palladium will be the metal of choice in practical catalytic applications because it has the highest rate per unit of metal surface area.[2]

Catalytic rates per unit of active area provide the quantitative measure to allow for comparison of catalysts. One difficulty in this quantification is that the rates may be dependent not only on the surface area but also on the particular structure of the active site, which would then have to be defined for each sample. Thus, to specify the rate of reaction, one needs to find if the reaction is sensitive to the structure of the catalyst. The fact that a practical industrial catalyst is composed of nanometer-sized clusters formed by a combination of single crystals surfaces provides a way to investigate this structure sensitivity; comparing the rates on a set of large single-crystal surfaces that make up the clusters can identify whether the rates depend on the structure of the surface. For example, the structure sensitivity for the synthesis of ammonia from N_2 and H_2 over Fe catalysts was confirmed directly by showing that the rate on the open Fe(111) face is a factor of at least 500 higher than on the more densely packed Fe(110) face.[3] In addition, the rate per unit area on the Fe(111) face matches the rate on the best industrial catalyst.[4] These facts show that the active site is composed of Fe(111) faces.[5] Another example is the structure sensitivity of the water−gas shift reaction verified on Cu(111) and Cu(110) surfaces.[6] To prove that a reaction is not sensitive to the structure of the catalyst can be challenging since it has to be shown that the rate is not dependent on any particular structure. The procedure described above using large single crystals can still be used. For a fcc metal such as Pd, measuring and comparing the rates on the dense (111) and (100) faces, which make up the faces of most of the clusters in a supported catalyst, and on the more open (110) face is one strategy. If the reaction is sensitive to the

structure, the different geometry on the surfaces should affect the rates. In addition to the different geometries exposed by the single crystals there may be low coordination sites that may be kinetically important. The contribution of these sites can be tested by measuring the rates on catalysts composed of particles in the range 1−10 nm, which is the range where the number of sites with a given coordination changes with size most rapidly. If the reaction kinetics is the same on the single crystals and on clusters of critical size, one can safely, but not with absolute certainty, label the reaction as insensitive to the structure of the catalyst. Examples of this combination of approaches to study structure sensitivity are the oxidation of CO on Pd[7,8] and hydrogenation of CO on Ni.[9] This is the approach we will be using. The question of structure sensitivity on methane combustion does not have a unanimous answer. Cullis and Willatt[10] found that the reaction is independent of particle size; Baldwin and Burch[11] found a change in TOR of 2 orders of magnitude on a series of catalysts with no correlation between particle size and TOR; Hicks et al.[12] found that the TOR is higher for larger Pd particles; Garbowski et al.[13] stated that the reaction is structure-sensitive by observing from TEM analysis that some of the less packed planes ((100), (110)) are more active than the more packed one (111), but Ribeiro et al.[14] found that the rates were similar on supported Pd catalysts with particles in the range 1−10 nm and which were prepared with different supports and different precursors. More recently, Fujimoto et al.[15] on Pd/ZrO_2 and Müller et al.[16] on Pd−Zr alloys found a "weak" (factor of 3−9) structure sensitivity as the particle size varied from 4 to 10 nm.

The experimental procedure is detailed in the Supporting Information. Before we present the data, we should point out that an added complication to establishing the structure sensitivity in the oxidation of methane is that bulk Pd can be in the metal or oxide state depending on how temperature and O_2 pressure affect the equilibrium $Pd + {}^1/_2O_2 = PdO$. Thus, the kinetics on metal and oxide states is shown below for each case. To test the structure sensitivity of the rate on the oxides, the same procedure of measuring rates on large single crystals described above could be used except that single crystals of PdO with different orientations cannot be prepared by the standard cutting and polishing techniques. Our approach is to use metal single crystals with the most common faces present on a metal particle and then measure the rates after they oxidize. We expect that the same type of oxide structures would be formed on a supported catalyst.

The kinetic data for Pd in the metallic state are presented in Table 1. The foil is composed mainly of the most stable (111) planes with defects created by grain boundaries and steps, thus simulating low coordination sites. The similar kinetic parameters on all surfaces in Table 1 imply that the reaction is not sensitive to the structure of the catalyst. This may be surprising at first but under the reaction conditions employed in our studies, the surface is mostly covered by adsorbed oxygen, creating an oxidized surface where nonuniformities are overwhelmed by stronger oxygen−oxygen interac-

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Table 1. Kinetic Parameters on Palladium Metal Model Catalysts[a]

| | TOR | E_a | reaction orders | | |
catalyst	(s^{-1})	(kJ mol^{-1})	CH$_4$	O$_2$	H$_2$O
Pd(111)	2.8 ± 0.1	140 ± 10	0.7 ± 0.1	−0.1 ± 0.1	0.05 ± 0.04
Pd(100)	2.5 ± 0.3	130 ± 15	0.9 ± 0.2	0.01 ± 0.06	0.07 ± 0.04
Pd(110)	2.7 ± 0.3	150 ± 10	0.9 ± 0.1	−0.1 ± 0.1	0.00 ± 0.03
Pd foil	1.4 ± 0.1	125 ± 20	0.7 ± 0.1	−0.1 ± 0.2	0.05 ± 0.08

[a] TOR at 973 K, 2.3 Torr O$_2$, 0.46 Torr CH$_4$, and 0.05 Torr H$_2$O.

Table 2. Kinetic Parameters on Palladium Oxide Model Catalysts[a]

| catalyst before oxidation | relative surface area | TOR (s^{-1}) | E_a (kJ mol^{-1}) | reaction orders | | |
				CH$_4$	O$_2$	H$_2$O
Pd(111)	2.6 ± 0.6	2.8−2.9	140 ± 20	0.8 ± 0.2	−0.1 ± 0.2	−0.9 ± 0.1
Pd(100)	2.1 ± 0.1	5.0−5.3	125 ± 15	0.8 ± 0.1	0.1 ± 0.2	−1.0 ± 0.2
Pd(110)	1.9 ± 0.2	1.2−1.4	160 ± 20	0.7 ± 0.2	0.2 ± 0.3	−1.0 ± 0.2
Pd foil[17]	2.2	2.5	125	0.7	0.2	−0.9

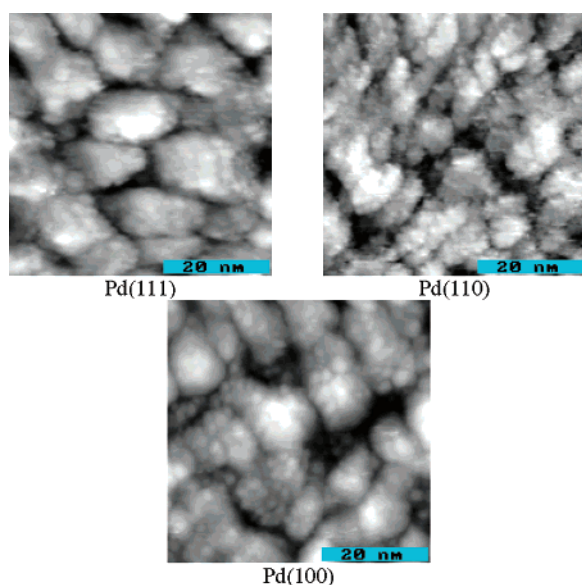[a] TOR at 598 K, 160 Torr O$_2$, 16 Torr CH$_4$, and 1 Torr H$_2$O.

Figure 1. STM images of Pd single crystals after CH$_4$ oxidation in 16 Torr CH$_4$, 160 Torr O$_2$, 624 Torr N$_2$ at 600 K for 60 min. U_{bias} = 0.7 V, I_{tunnel} = 0.5 nA. The scale bar denotes 20 nm.

tions; the incoming methane interacts with a uniform surface covered by oxygen. The rates on large single crystals could not be compared in this case with the rates on supported catalysts because the magnitude of the rate is too high to allow for measurement on the supported catalysts without the influence of heat and mass transport limitations.

The kinetic data for the case where Pd is oxidized to bulk PdO are presented in Table 2. The same surfaces employed in Table 1 are also used here but they are oxidized to PdO about 25 layers deep. The oxide does not grow epitaxially on the single crystals, as the unit cells are not commensurable. The consequence is that the oxidized surfaces form amorphous and similar "cauliflower-like" structures as illustrated in Figure 1. The relative surface area is defined as the ratio of area after reaction to the clean metal area. All kinetic parameters are again similar on the catalysts tested. Reaction data for the oxidized state of Pd is available for supported catalysts in the critical range of 1−10 nm Pd crystallite size (Table 3). The turnover rate for the supported catalysts varied modestly within this critical range, with a higher variation among studies by different groups. Comparison between model and supported catalysts shows that the orders of reaction, apparent activation

Table 3. Comparison of Turnover Rate with Literature Values

| catalyst | particle size (nm) | activation energy[a] (kJ mol^{-1}) | reaction order | | | TOR[b] (s^{-1}) |
			CH$_4$	O$_2$	H$_2$O	
Pd black[17]	10	135	0.7	0.1	−0.8	0.5[c]
Pd/Si−Al$_2$O$_3$[14]	2.6−6.2	170−184	−	−	−1.0	0.1[d]
Pd/Al$_2$O$_3$[14]	49−134	150	−	−	−	0.07−0.16[d]
Pd/ZrO$_2$[14]	4.3−81	170	−	−	−	0.1−0.7[d]
Pd/ZrO$_2$[15]	3−9	185	1.1	0.1	−1.0	0.5−3.0[d]
Pd/ZrO$_2$[18]	5.5−12.5	−	−	−	−	0.3[d]

[a] Assuming reaction order for water is −1, the activation energy was corrected for the water inhibition effect. [b] TOR calculated at 598 K, 16 Torr CH$_4$, 1 Torr H$_2$O, and N$_2$ balance to 800 Torr. [c] Number of sites measured from BET surface area (47 m^2 g^{-1}). [d] For plug flow reactor, partial pressures for reactants and products are the average of values for inlet and outlet concentration.

energy, and turnover rates are similar. The turnover rates are lower on the supported samples in Table 3 than on the single crystals in Table 2, which can indicate the existence of the effect of impurities or interaction with the support on the supported samples. The structure insensitivity in this case is caused by an amorphous growth of oxide illustrated in Figure 1, which is independent of the underlying structure.

In summary, by using large single-crystal model catalysts we have shown that the reaction of combustion of methane over Pd is not sensitive to the structure of the catalyst. This finding implies that industrial catalysts should be prepared to maximize the Pd surface area without consideration of the cluster shape. Because we used model catalysts that allowed for (1) precise measurement of surface area, (2) control of the surface purity, and (3) absence of support to introduce a metal−support interaction, the kinetics presented can be used as benchmark values for Pd in the metal (high temperature) and oxide states.

Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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