Photochemistry of Methane on Pd/Al_2O_3 Model Catalysts: Control of Photochemistry on Transition Metal Surfaces**

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*Dedicated to Professor Manfred Baerns
on the occasion of his 65th birthday*

Nano-sized transition metal clusters, an important class of substances in catalysis, reveal many unique physical and chemical properties. These properties are strongly dependent on the size and the morphology of the clusters.[1–3] For example, the electronic structures of Pd clusters and the interaction with adsorbates such as carbon monoxide change drastically with cluster size.[4, 5] The size of clusters and, hence, their geometrical and electronic structures can be controlled by changing formation conditions such as metal deposition rates and surface temperature.[6] Thus, it is of great interest to know if surface (photo)reactions can be controlled by manipulating the electronic and geometrical structures of the metal clusters.

Owing to the importance of more effective use of natural gas, the thermal activation of methane C–H bonds has been studied extensively. Especially the conversion into methanol and other hydrocarbons is of great interest.[7] On the other hand, it has recently been discovered that methane physisorbed on Pt(111) and Pd(111) single-crystal surfaces is readily dissociated into methyl and hydrogen by irradiation with a 193-nm (6.42 eV) ArF excimer laser,[8–10] although gaseous methane absorbs light at wavelengths shorter than 145 nm (8.55 eV).[11] This strong shift of more than 2.1 eV is surprising in view of the low methane–surface interaction of around 230–250 meV. Controlled experiments showed that the electronic states of the metal surfaces play an important role in the photoexcitation of methane.[9, 12] In fact, photoreaction efficiency and photoinduced dynamics differ significantly as a result of differences in the surface electronic structures between Pt(111) and Pd(111).[10]

Is methane photodissociated also at transition metal clusters? If so, how does its photochemistry depend on the size of the clusters? These are questions we address here. By using a well-characterized model catalyst consisting of Pd clusters of various sizes deposited on a thin Al_2O_3 film epitaxially grown on NiAl(110) as support,[13–15] we have studied adsorption states and photoreactions (at $\lambda = 193$ nm) of methane and found that the photoreactions strongly depend on the cluster size.

The experiments were carried out in a stainless steel ultrahigh-vacuum (UHV) chamber equipped with facilities for spot profile analysis–low energy electron diffraction (SPA-LEED), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), X-ray Auger electron spectroscopy (XAES), and temperature-programmed desorption (TPD). The base pressure was kept below 5×10^{-11} mbar during the experiments.[16] A NiAl(110)-terminated single-crystal surface was cleaned by the conventional treatment. An epitaxial Al_2O_3 film of 5 Å thickness was obtained by oxidizing the cleaned crystal through exposure to 6×10^{-6} mbar of oxygen at 500 K and annealing at 1100 K. For the experiment the sample was cooled to 40 K with liquid helium. Laser irradiation was performed with a broad-band excimer laser ($\lambda = 193$ nm) with a laser fluence of 2.5 mJ cm^{-2} per pulse at a repetition rate of 4 Hz.

The Pd atoms were evaporated from a Pd rod in a commercial oven by electron bombardment. They were deposited onto the Al_2O_3 support at room temperature (300 K) to form Pd clusters with mainly (111) terraces.[15] The clusters used in this study have average diameters of 37 ± 16 Å (Pd film of 1.4 ± 0.3 Å deposited according to quartz microbalance measurements), 49 ± 10 Å (Pd film of 2.1 ± 0.4 Å), 65 ± 10 Å (Pd film of 3.5 ± 0.7 Å), and 73 ± 10 Å (Pd film of 7 ± 1.4 Å), as determined by SPA-LEED analysis.

Figure 1 shows the TPD results for deuterated methane (*m/z* 20, CD_4) from Pd clusters exposed to 0.5 L[17] CD_4 at 40 K. The numbers at the curves denote total Pd coverages. The peak temperature, at which the desorption rate is at a maximum, increases with cluster size (52 K for a film of 0.4 Å to 64 K for 7 Å); that is, the methane–cluster interaction becomes stronger as the clusters grow. The dashed curve corresponds to a TPD result for the Pd(111) single-crystal surface with 0.6 L CD_4.[18] The TPD profiles of the Pd clusters are broader than that of Pd(111) and have a long tail to higher temperatures. This may be attributed to cluster size

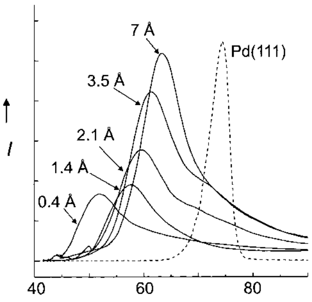

Figure 1. Series of CD_4 TPD spectra (*m/z* 20; solid curves) of Pd clusters of various sizes deposited on a thin Al_2O_3 film epitaxially grown on NiAl(110). The sample was exposed to 0.5 L CD_4 at 40 K. The desorption peaks are due to molecular desorption, $CD_4(ads) \rightarrow CD_4(g)$. The numbers denote the total Pd coverages as a measure of the cluster size (see text). The dashed curve corresponds to a TPD spectrum of a Pd(111) single-crystal surface after exposure to 0.6 L CD_4, and is depicted in a different scale. The heating rate for the clusters was 0.5 K s^{-1}, and 0.4 K s^{-1} for the Pd(111) single crystal.

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distributions and the inhomogeneity of the cluster surfaces in contrast to the well-ordered structure of the Pd(111) surface. However, no dissociative adsorption was observed for surfaces with Pd clusters.

Atoms and molecules with a closed shell, such as rare gases and methane, adsorb weakly on metal surfaces because of the dispersion force (van der Waals interaction) that is induced by dynamic response of bulk electrons to charge density fluctuations in an adsorbed molecule. It has been shown before that the electron population at the Fermi edge, which is mainly relevant for the interaction, drastically changes with cluster size in the size regime presented here.[4] The gradual increase in the peak temperature with the cluster size can be reasonably understood, since larger clusters contain more electrons available for the dynamic response.

Figure 2 shows the TPD results for CD_3H (m/z 19) measured after 193-nm ArF laser irradiation (1.5×10^{19} photons per cm^2) onto CD_4-precovered surfaces.[19] At around 140 K a new desorption peak, which is absent without laser irradiation, appears at 2.1, 3.5, and 7 Å Pd depositions. This peak is attributable to the recombinative desorption of methyl (CD_3) and hydrogen (H) from the surface;[20] that is, methane dissociates also at these Pd clusters. The hydrogen on the surface results from residual gas within the chamber and is due to the high sorptivity of palladium with respect to hydrogen adsorption. No other reaction products have been observed in the TPD after irradiation except for those from the recombinative desorption of $CD_3 + H/D$ and $H/D + H/D$.

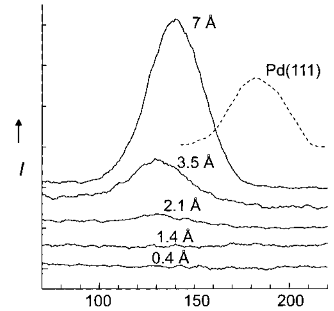

Figure 2. Series of CD_3H TPD spectra ($m/z = 19$; solid curves) of 0.5 L CD_4 precovered Pd clusters of various sizes after laser irradiation with 1.5×10^{19} photons per cm^2 at 193 nm. The desorption peaks are due to recombinative desorption, $CD_3(ads) + H(ads) \rightarrow CD_3H(g)$. The numbers denote the total Pd coverages as a measure of the cluster size (see text). The dashed curve corresponds to a TPD spectrum after irradiation of a Pd(111) single-crystal surface precovered with 1.1 L CD_4, and is depicted in a different scale. The heating rate for the clusters was 0.5 K s^{-1}, and 0.9 K s^{-1} for the Pd(111) single crystal.

Figure 3 a shows a plot of the CD_3H formation ratio β ($\beta = B/A_0$; B = integrated TPD peak areas of CD_3H after irradiation, A_0 = integrated TPD peak area of initially adsorbed CD_4 before irradiation) as a function of the total Pd coverage c. This plot shows that photodissociation is only observed when the cluster size exceeds a certain threshold (average cluster diameter between 37 and 49 Å). Beyond this point, the relative amount of photodissociated methane increases with increasing cluster size.

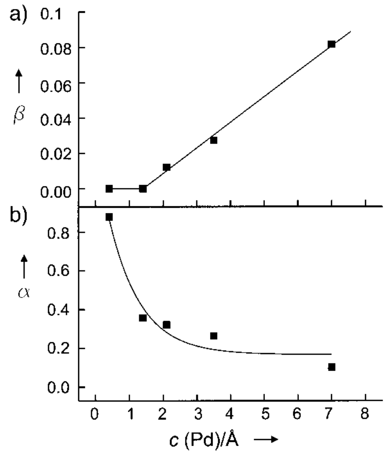

Figure 3. a) Plot of the CD_3H formation ratio β ($\beta = B/A_0$; B = integrated TPD peak areas of CD_3H after irradiation, A_0 = integrated TPD peak area of initially adsorbed CD_4 before irradiation) as a function of the total Pd coverage c; b) plot of the CD_4 depletion ratio α ($\alpha = 1 - A/A_0$; A_0 = integrated peak areas of CD_4 before irradiation, A = integrated peak areas of CD_4 after irradiation with 1.5×10^{19} photons per cm^2) as a function of the total Pd coverage. The total Pd coverages of 1.4, 2.1, 3.5, and 7 Å correspond to average cluster sizes of 37, 49, 65, and 73 Å, respectively, as determined by SPA-LEED analysis.

The coverage of methane is depleted by photodesorption as well as by photodissociation. Figure 3 b shows a plot of the CD_4 depletion ratio α ($\alpha = 1 - A/A_0$; A_0 = integrated peak areas of CD_4 before irradiation, A = integrated peak areas of CD_4 after irradiation with 1.5×10^{19} photons per cm^2) as a function of the total Pd coverage.[21] The depletion ratio of CD_4 decreases with increasing cluster size. The low depletion ratio for the larger clusters (≥ 40 Å) suggests the strong poisoning effect caused by methyl adsorbates that quench photoexcitation, as observed in single-crystal experiments.[22] The depletion ratio for the smaller clusters is mainly due to photodesorption, because no photodissociation could be observed. For rather small cluster sizes some laser-induced thermal desorption might be possible in view of the low desorption temperatures of methane for these clusters.

Why is methane that has been weakly adsorbed on the Pd clusters and the Pd(111) single crystal excited upon irradiation with 193-nm photons, when gaseous methane shows negligible absorbance? In contrast to numerous examples of surface photochemistry at metal surfaces, it has been confirmed by polarization-dependent cross-section measurements that methane on Pt(111) and Pd(111) surfaces is excited through a direct electronic transition localized within the adsorbate–substrate complex.[10] Since the strength of the interaction between methane and the Pd clusters is close to that with Pd(111), it would be appropriate to assume that the same excitation mechanism is applicable for the methane/Pd cluster system.

The excited state of the methane/Pd cluster system is likely a charge-transfer state, $CH_4^{\delta+} - M^{\delta-}$ (M: metal, $0 < \delta < 1$) according to ab initio calculations for CH_4/Pt_n[23] and CH_4/Pd_n clusters[24] ($n = 1-10$). Akinaga et al.[23, 24] calculated the excited states of the cluster levels at optimized configurations in the ground electronic state. The excited state responsible for dissociation to $CH_3 + H$ is formed from the mixing of the antibonding Rydberg state of methane (10 eV above the HOMO of methane in the gas phase) with unoccupied states of the metal. The excitation energy for photodissociation is reduced to about 7 eV with increasing number of metal atoms up to 10. The excitation energy depends strongly on the cluster size because electron redistribution over the metal atoms plays an important role in stabilizing this charge-transfer state.[23]

Another way to understand the excitation mechanism is given by recent slab local density approximation (LDA) calculations on CH_4/Pd(111). The equilibrium distance z between the Pd surface plane and the C nucleus is calculated to be 3 Å.[25] When complete charge transfer to the substrate is assumed in the excited state of methane, the image force stabilizes the excited state by 1.9 eV.[26] The ionization potential of physisorbed methane should then be reduced by 1.9 eV plus the work function of Pd(111). With a work function of 5.6 eV[27] and a gas-phase ionization potential of 12.6 eV,[28] the excitation energy for the complete charge transferred state is calculated to be 5.1 eV, which is accessible with a 6.4 eV photon. Within this model, the increased probability for methane photodissociation at larger clusters can be explained in terms of increased image force expected from the stronger interaction with methane.

In conclusion, adsorption states, photodissociation, and photodesorption of methane at $\lambda = 193$ nm on Pd clusters of various sizes on a thin epitaxial Al_2O_3 film show very pronounced size effects and remarkable differences to the behavior on Pd(111) single-crystal surfaces. These results strongly suggest that metal clusters of different sizes and shapes provide a unique way for controlling both photochemical and thermal reactions of hydrocarbons at metal surfaces.

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[17] 1 Langmuir (symbol L) corresponds to 1×10^{-6} s Torr = 1.33×10^{-6} s mbar.

[18] At this exposure, a $(\sqrt{3}\times\sqrt{3})R30^\circ$ LEED pattern of CD_4 is formed on Pd(111).[10]

[19] The typical irradiation condition was 2.5 mJ cm^{-2} per pulse at 4 Hz and at normal incidence to the surface.

[20] We observed m/z 19 (CD_3H) instead of m/z 20 (CD_4) to avoid spurious desorption signals from parts other than the sample surface. Owing to the high sorptivity of palladium with respect to hydrogen adsorption, residual H_2 in the UHV chamber dissociatively adsorbs on Pd clusters to form hydrogen adsorbates during experiment even at pressures below 10^{-10} mbar. However, this enables the background-free measurement of the recombinative reaction $CD_3(ads) + H(ads) \rightarrow CD_3H(g)$.

[21] This figure shows the branching ratio between methane which has reacted and that which has not after the methane depletion is terminated.

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Synthesis, Characterization, and Crystal Structure of Cyclotrisilene: A Three-Membered Ring Compound with a Si=Si Double Bond**

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The synthesis of several compounds with double bonds involving silicon or germanium has been accomplished[1] following the discovery of $Mes_2Si{=}SiMes_2$ (Mes = 2,4,6-trimethylphenyl)[2] and $(Me_3Si)_2Si{=}C(OSiMe_3)Ad$ (Ad = 1-ada-

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