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A second CO adsorption state on palladium clusters supported on MgO(100)

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During the investigation of the oxidation of CO on palladium clusters supported on MgO(100) we have found two adsorption states of CO that are signified by largely different lifetimes. By comparing the relative amounts of CO adsorbed on these sites we suggest that the sites can be attributed to CO adsorbed on the facets and the edges of the palladium clusters, respectively.

Keywords: heterogeneous catalysis, clusters, CO oxidation, palladium

1. Introduction

We have investigated the oxidation of CO on palladium clusters supported on MgO(100) as a function of the palladium cluster size using molecular beam relaxation spectroscopy (MBRS). The experiments, including the preparation of the clean MgO(100) surfaces, were done in situ in an ultrahigh-vacuum (UHV) system with a base pressure of 2×10^{-8} Pa. The palladium clusters were produced by evaporation of palladium from a Knudsen cell onto freshly cleaved MgO(100) surfaces. The characterization of the palladium particles was done ex situ by transmission electron microscopy (TEM). The details of the experimental setup and the cluster preparation can be found elsewhere [1,2]. It has already been shown in an earlier communication that the shape of the clusters prepared by this procedure is well defined, i.e. surface of the clusters is entirely composed of (100) and (111) planes [4].

In the course of the investigations presented here it appeared, that the CO and CO_2 MBRS spectra can only be interpreted if we assume two different adsorption sites of the CO on the palladium clusters. This observation has some impact on the microscopic model of the CO oxidation on the palladium clusters. It implies that the mechanism of the reaction on clusters should differ significantly from that on close-packed (e.g. Pd(100), Pd(111)) single-crystal surfaces. So far it has been assumed in the literature that this particular reaction is not structure sensitive and shows no size effect [5,6].

2. Results

Fig. 1 shows CO_2 MBRS spectra for two different cluster sizes recorded at 433 K. The spectra were taken using a pulsed CO molecular beam of 2×10^{-5} Pa equivalent pressure and an isotropic O_2 pressure of 1.3×10^{-5} Pa. The CO pulse was started at the time

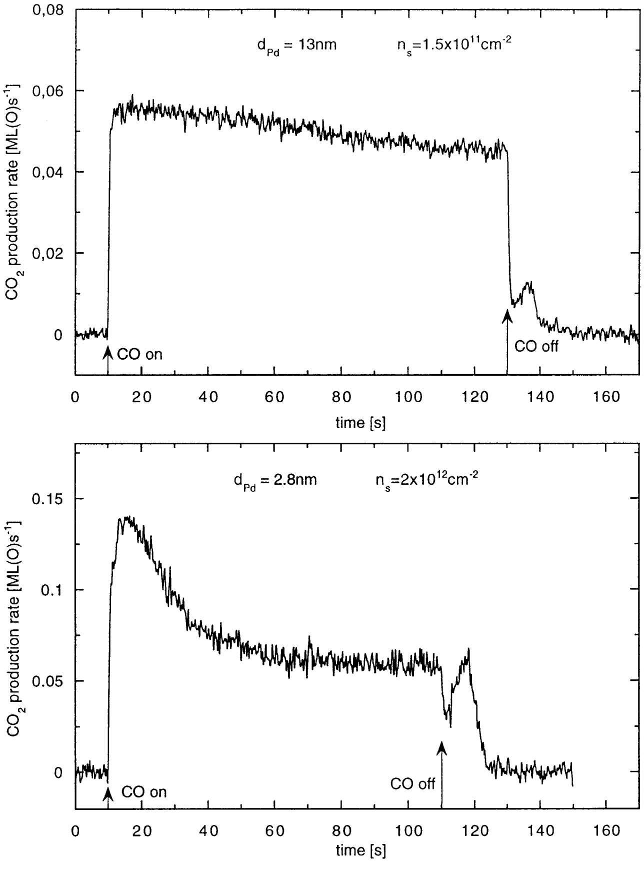

Fig. 1. The top graph shows the CO_2 MBRS spectrum for large palladium clusters (13 nm). The time at which the CO beam was opened is indicated by an arrow. The bottom graph shows the corresponding spectrum for small palladium clusters (2.8 nm). In both cases the temperature was 433 K and the oxygen pressure was 1.3×10^{-5} Pa. The equivalent pressure of the CO beam was 2×10^{-5} Pa.

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marked in the graph and was stopped after equilibrium had been reached. The oxygen exposure was started in such a manner, that the surface was always saturated by oxygen (we assume Θ_O(sat.) to be 0.25 ML as on extended surfaces) before opening the CO beam and was maintained constant even after the end of the CO pulse. The transient regime at the beginning of the CO_2 spectra originates from the high initial oxygen coverage, that causes the reaction to proceed under an excess of oxygen. The top graph corresponds to palladium clusters of 13 nm mean diameter and a particle density of 1.5×10^{-11} cm^{-2}, a size for which the adsorption energy of the CO equals that of CO on Pd(100) [7]. The bottom graph corresponds to palladium clusters of 2.8 nm mean diameter and a particle density of 2×10^{12} cm^{-2}. For clusters of this size a strong increase in the energy of adsorption of CO had been observed at low coverage as compared to large particles [7]. It appears that the two spectra show a very different behaviour of the CO_2 production rate. In particular, one can see a considerable CO_2 production after the end of the CO pulse for the small clusters. This feature is also visible in the spectrum of the large clusters but is less pronounced. A CO_2 production after the end of the CO pulse can only originate from CO that remains adsorbed on the surface of the palladium clusters. A spillover of CO from the substrate after the end of the CO pulse is excluded by the short lifetime of the CO on the MgO(100) surface [8]. Since the isotropic O_2 pressure is kept constant after the end of the CO pulse, the oxygen needed for the reaction will be supplied by adsorption of the oxygen. If we look at the duration of the CO_2 production after the end of the CO pulse, we find that it continues for about 10 s for the large clusters and 15 s for the small clusters. These durations increased when the temperature was decreased (fig. 2). This observation suggests that the residence time of the CO on the surface of the respective clusters must be at least in the order of this time. For CO on a Pd(100) surface the residence time is, however, only 0.2–0.3 s at this temperature [2]. Therefore, we conclude that we have found a CO adsorption state on palladium clusters that does not correspond to the well-known CO adsorption state on Pd(100) or Pd(111), respectively.

To see whether this adsorption state on the palladium clusters is just a modification of the single-crystal state or rather a new, so far unknown state we have recorded the CO MBRS spectra concurrently. In fig. 3 one can see a rapid decrease of the CO signal after the end of the CO pulse. The fall time of the signal is, however, finite. The CO equilibrium coverage under these reaction conditions is $\Theta_{CO} = 0.15$ ML. By fitting an exponential function,

$$n(t) = n_{eq} \exp[-t/\tau] , \qquad (1)$$

to the falling edge of the CO signal, we calculated the lifetime of the desorbing CO to be $\tau = 1.6$ s. Here $n(t)$ represents the CO signal and n_{eq} the equilibrium CO signal. Using a frequency factor of $\nu = 5 \times 10^{15}$ s^{-1} [2,3] this lifetime value yields, according to

$$E = RT \ln[\nu\tau] , \qquad (2)$$

a CO adsorption energy of $E = 132$ kJ mol^{-1}. This value is in good agreement with the value found for extended palladium surfaces and large clusters [7]. At low coverage ($\Theta_{CO} \approx 0.01$ ML) an energy of adsorption of 138 kJ mol^{-1} has been measured for clusters of 2.8 nm diameter [7] corresponding to a lifetime of 9 s. This value is in agreement with the lifetime of the strongly bound CO observed in the CO_2 MBRS spectra.

These observations suggest that the CO state with the short lifetime is the equivalent of the CO state on close-packed palladium single-crystal surfaces. It has not been observed in earlier CO MBRS experiments because they were always performed at low CO coverage where the long-lived CO state is populated exclusively. Because of these results we assign this state to CO adsorbed on the facets of the clusters. To clarify the nat-

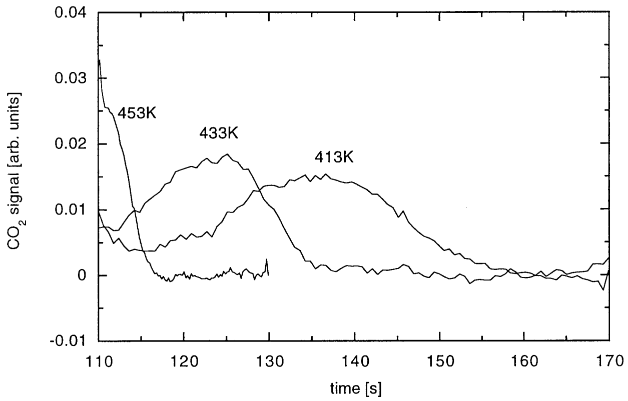

Fig. 2. Evolution of the CO_2 production after the end of the CO pulse for different temperatures and palladium clusters of 2.8 nm mean diameter. The O_2 and CO pressures were as in fig. 1. As the temperature decreases the time for which the CO_2 production continues increases.

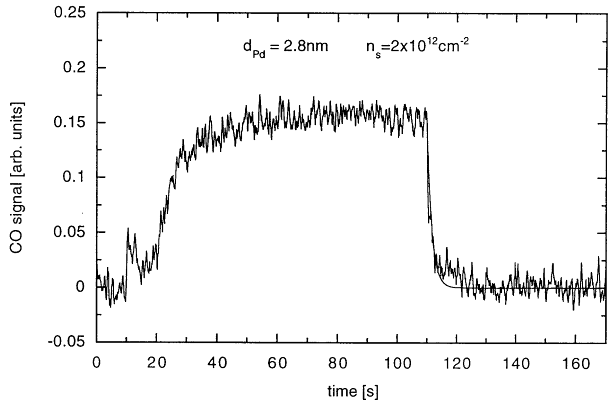

Fig. 3. CO MBRS spectrum for small palladium clusters (2.8 nm) during CO oxidation. The temperature was 433 K and the oxygen pressure was 6.7×10^{-6} Pa. The equivalent pressure of the CO beam was 2×10^{-5} Pa. The lower oxygen pressure facilitates the analysis of the falling edge of the spectrum due to a better signal to noise ratio.

ure of the long-lived CO adsorption state we inspect fig. 1 once again. Apparently the relative amount of long-lived CO increases as the cluster size decreases. Considering the increase of the ratio of edge to terrace sites with decreasing cluster size the relative increase of the long-lived CO state for small clusters can be explained by adsorption on edge sites.

The occurrence of two CO adsorption sites on palladium clusters is supported by recent in situ FTIR experiments [9]. Indeed, two adsorption lines corresponding to bridge and terminal bound CO were observed and correlated to facet and edge sites.

As already mentioned in the introduction, the existence of the two different CO adsorption sites must have an impact on the oxidation reaction. Xu and Yates have observed large differences between the reactivity of edge and terrace sites for the oxidation of CO on Pt(335) [10]. Therefore, the role of the edge sites during the CO oxidation on supported palladium clusters will be the subject of further investigations. A second fact that influences the reactivity of the (111) and (100) facets of the small clusters as compared to their single-crystal equivalents is their limit size. A change in the diffusion pattern of the reactants should be the result of the small area available. Since diffusion is one of the key processes for surface reactions this will also cause a change in the reactivity of these facets.

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