Article

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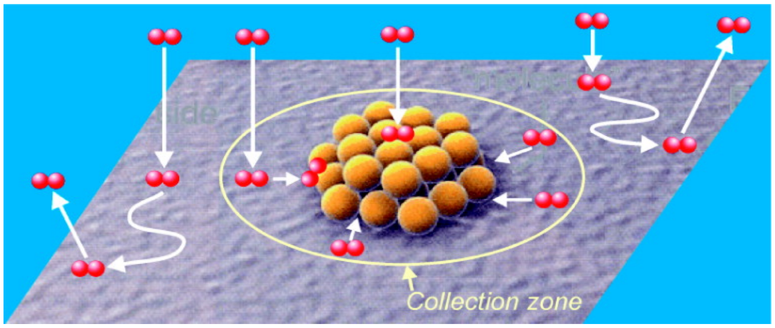

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Cluster Chemistry: Size-Dependent Reactivity Induced by Reverse Spill-Over

Martin A. Röttgen,[†] Stephane Abbet,[†] Ken Judai,[†] Jean-Marie Antonietti,[†]
Anke S. Wörz,[†,#] Matthias Arenz,*[,†] Claude R. Henry,[‡] and Ulrich Heiz[†]

Contribution from the Lehrstuhl für Physikalische Chemie I, Technische Universität München, Lichtenbergstrasse 4, 85748 Garching, Germany, and CRMCN-CNRS, Campus de Luminy Case 913, 13288 Marseille cedex 09, France

Received December 4, 2006; E-mail: Matthias.Arenz@mytum.de

Abstract: In the present work, the CO oxidation rate on size-selected Pd clusters supported on thin MgO films is investigated in pulsed molecular beam experiments. By varying the cluster coverage independent of the cluster size, we were able to change the ratio of direct and diffusion flux (reverse spill-over) of CO onto the cluster catalyst and thus probe the influence of reverse spill-over on the reaction rate for different cluster sizes (Pd_8 and Pd_{30}). The experimental results show that the change in reaction rate as a function of cluster coverage is different for Pd_8 and Pd_{30}. In order to explain these findings, the CO flux onto the clusters is modeled utilizing the collection zone model for the given experimental conditions. The results indicate that, for small clusters (Pd_8), the reaction probability of an impinging CO molecule is independent of whether it is supplied by diffusion or direct flux. By contrast, for larger clusters (Pd_{30}) a reduced reaction probability is found for CO supplied by reverse spill-over compared to CO supplied by direct flux.

Introduction

The evolution of the catalytic properties of oxide-supported transition metal clusters and nanoparticles with size depends on a variety of factors including the electronic structure, varying proportions of surface facets, and diffusion barriers of adsorbed species, as well as different coordinations of surface atoms. These properties vary dramatically with particle size, morphology, and particle−support interaction.[1,2] The support, however, also plays an active role in changing the reaction rate as it controls the supply of reactants to the reaction centers of the catalyst. In previous investigations it has been shown that physisorbed CO on an oxide substrate acts as a precursor state for chemisorption on supported metal particles.[3] As a consequence, the total flux, F_{tot}, of molecules onto a catalyst particle is the sum of the direct flux, F_{dir} (from the gas phase), and the diffusion flux, F_{diff}, from the support. It is the latter that is controlled by the support material properties. The diffusion of molecular species adsorbed on the support toward the catalyst particles is referred to reverse spill-over.[4]

Here we present coverage-dependent CO oxidation rates for size-selected Pd_8 and Pd_{30} clusters supported on thin MgO films. By changing the cluster coverage we were able to vary the ratio of direct and diffusion flux of CO onto the cluster catalyst and thus probe the influence of reverse spill-over on the reaction rate. With the use of the collection zone model, the diffusion flux, and thus the total flux of CO, is modeled, obtaining the reaction probability of an impinging CO molecule. Our results indicate that the influence of reverse spill-over on the reaction rate is different for small and larger clusters.

Experimental Section

The cluster model catalysts for the CO oxidation reaction were prepared by soft-landing Pd cluster cations, obtained via supersonic expansion of a cold laser-generated metal plasma onto a well-defined MgO(100) thin oxide film grown on a Mo(100) single crystal.[5] The support is prepared in situ for each experiment by evaporating magnesium in an $^{16}O_2$ background (Mg evaporation rate, 1−2 ML/min; O_2 background, 5×10^{-7} mbar).[6] The film was subsequently annealed to 840 K for 10 min. Auger electron spectroscopy (AES) measurements ensured one-to-one stoichiometry for magnesium and oxygen as well as the absence of any impurities. Typical film thicknesses of about 10 monolayers, as determined by AES peak intensities, were used.

Prior to deposition the cluster cations were mass-selected in a quadrupole mass spectrometer; the cluster coverage was determined by integrating the deposition current. In contrast to metal vapor deposition[3] this technique allows the independent variation of cluster coverage and cluster size. As discussed below, this is an important consideration in the analysis of the reaction probability for different reaction channels. Two different cluster coverages were studied for a given cluster size (Pd_8, Pd_{30}). The coverages for the respective cluster sizes were selected to provide an identical surface area of clusters on

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[†] Technische Universität München.

[‡] CRMCN-CNRS.

[#] Present address: CRMCN-CNRS, Campus de Luminy Case 913, 13288 Marseille cedex 09, France.

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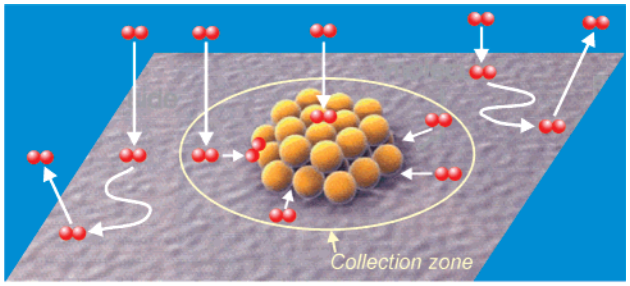

Figure 1. Collection zone model incorporates the diffusion flux toward a cluster beside the direct flux impinging directly from the gas phase. The amount of diffusive molecules reaching a cluster is defined through the collection zone, which depends on the mean diffusion length of the molecule on the support at the specific temperature and on the density of clusters.

the support. The substrate temperature during deposition was 90 K, and the cluster coverages were kept below 1% ML (1 ML = 2.25 × 10^{15} clusters/cm^2) in order to avoid cluster agglomeration. The catalytic action of the supported Pd_n ($n = 8, 30$) clusters was studied by means of pulsed molecular beams.[7] A constant background O_2 at a pressure of 5 × 10^{-7} mbar was used to ensure that the clusters were saturated with oxygen. A pulsed beam of CO was then used to initiate the catalytic cycle. After exposing the model catalysts to CO molecules by molecular beam pulses with a frequency of 0.1 Hz and a typical width of 100 ms (an effective pressure of 1 × 10^{-4} mbar at the surface), the obtained transients of the product CO_2 molecules were detected and averaged 30 times under isothermal conditions by an absolutely calibrated quadrupole mass spectrometer.[7] On the basis of the observed change of produced CO_2 molecules with time, the reactivity of the clusters can be expressed by maximum turn-over frequencies (TOFs), calculated by dividing the maximum of the CO_2 signal by the number of deposited Pd atoms. DFT calculations predict three-dimensional Pd cluster structures even for MgO-supported Pd_4.[8] However, as discussed in a previous paper, normalizing the reaction rate to the absolute number of cluster atoms is more appropriate as the number of exposed Pd sites is not exactly known.[9] For all transients the maximum intensity is reached shortly after opening the CO pulsed valve, at a constant partial pressure of oxygen. At this stage of the reaction, the reaction takes place in the high oxygen coverage regime, and therefore the CO adsorption is the rate-determining step. By calculating the TOFs, the evolution of the catalytic reactivity with temperature is obtained. Note that calculating the mean TOFs (CO_2 peak area divided by time and number of Pd atoms) leads to similar curve forms.

Collection Zone Model. The basic idea of the so-called collection zone model is displayed in Figure 1. In short, CO molecules impinging on the surface can either be (i) adsorbed directly on the catalyst particle (F_{dir}), (ii) reflected from or (iii) adsorbed in a physisorbed state on the MgO substrate. Molecules in a physisorbed state diffuse on the MgO substrate and may hit a cluster. Therefore, the total CO flux onto a cluster is $F_{\mathrm{tot}} = F_{\mathrm{dir}} + F_{\mathrm{diff}}$, i.e., two channels for chemisorption of CO molecules on the clusters have to be considered: the direct impact from the gas phase and the capture of diffusing particles physisorbed on the support. The direct flux is obtained from the calibrated flux of the pulsed valve. For calculating the diffusion flux, we used the collection zone model, which was first applied to isolated supported particles.[10,11] Here we used an extended version for an array of clusters by Henry and co-workers.[3,12] The model is based on three assumptions: (i) there is a regular array of interacting particles; (ii) the Pd clusters are perfect sinks for CO molecules diffusing on the substrate; (iii) a steady state is reached for the adsorption on the substrate. In previous experimental studies, it was shown that a regular cluster array is indeed a good first-order approximation for a random distribution as well as that CO desorption from supported Pd nanoparticles can be neglected.[3] For our experimental conditions here, steady-state conditions are not obvious. A close look, however, reveals that the lifetime of CO on MgO is much shorter (<1 ms at room temperature)[3] than the time span (>10 ms) where the maximal CO_2 production rates are observed.

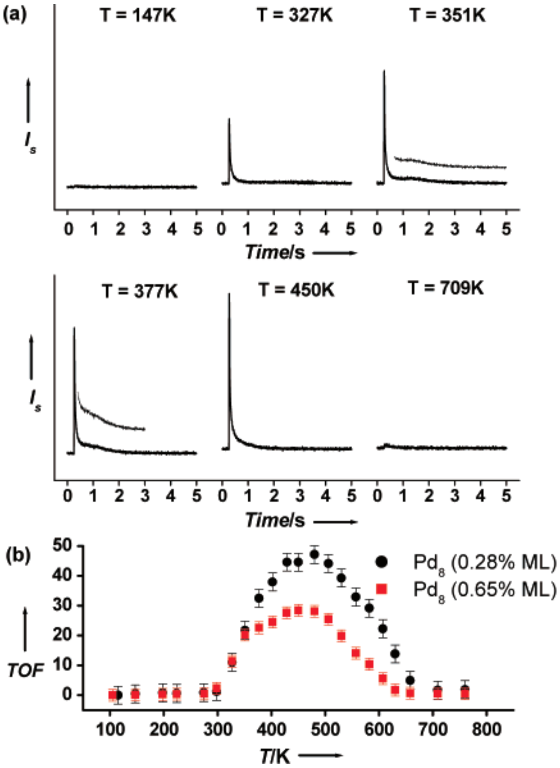

Figure 2. (a) CO_2 transients for representative temperatures obtained for Pd_8/MgO(100)/Mo(100) model catalysts. The insets represent the enlarged transients. (b) Evolution of the maximum turn-over frequencies (TOFs) as function of temperature. The TOFs are given in units of number of CO_2 molecules formed per cluster atom and second.

With the analytical solution of the diffusion flux given by the model, one defines a collection zone around each cluster, where all physisorbed molecules will become chemisorbed on the metal cluster. The width of this collection zone mainly depends on the mean diffusion length of the physisorbed molecules at the given temperature. For low temperatures and high cluster densities the collection zones may overlap, resulting in effective collection zones. The exact formulas and the kinetic parameters used in the calculations, e.g., adsorption and diffusion energies of CO on MgO, can be found in previous publications.[3,12,13] With the obtained values for F_{diff} and F_{tot}, we calculated the reaction probability (RP), given by RP = TOF/F_{tot}. For a detailed description of the collection zone model the interested reader is referred to refs 3, 4, and 14.

Results and Discussion

The averaged CO_2 transients obtained for Pd_8 (0.65% ML) are shown for selected temperatures in Figure 2a. Below 300 K no significant CO_2 evolution is observed. However, as the temperature is increased a CO_2 signal arises, reaches a maximum

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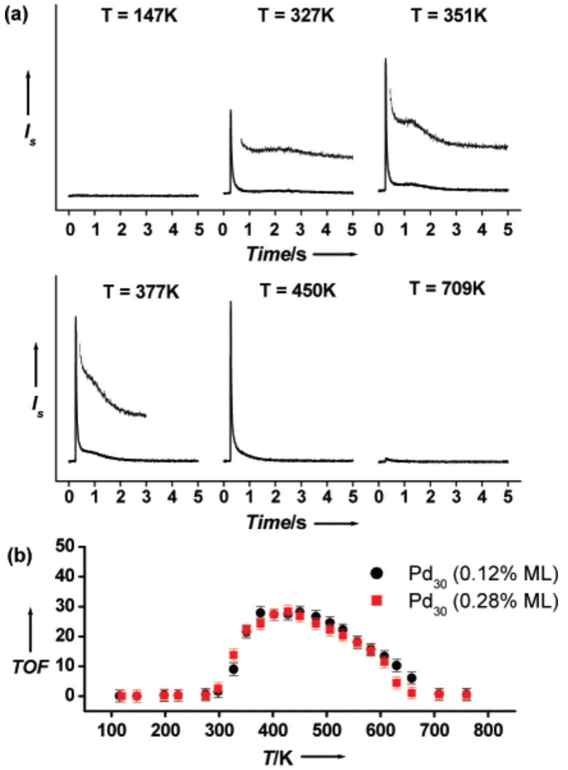

Figure 3. (a) CO_2 transients for representative temperatures obtained for Pd_{30}/MgO(100)/Mo(100) model catalysts. The insets represent the enlarged transients. (b) The evolution of the maximum turn-over frequencies (TOFs) as function of temperature.

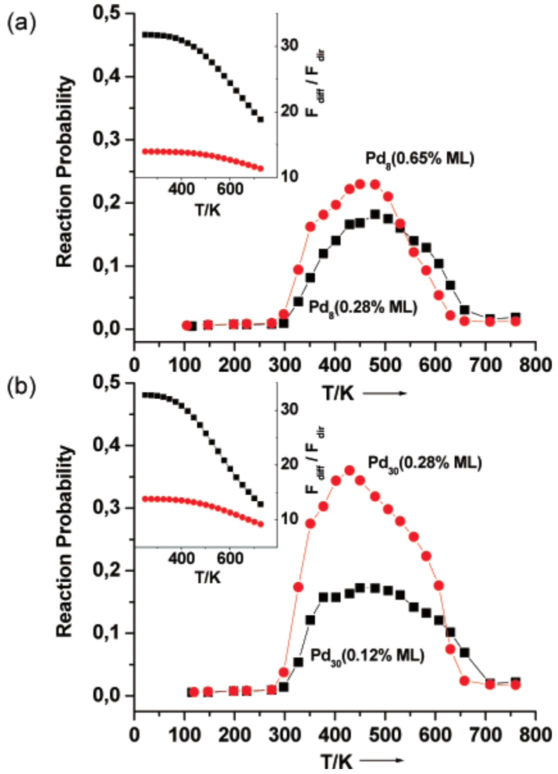

Figure 4. Reaction probabilities as function of temperature for different surface coverages of the Pd_8 (a) and Pd_{30} (b) clusters. The insets depict the calculated ratio of F_{diff}/F_{dir} as function of temperature.

(at around 450 K), before decreasing again at higher temperatures. At 709 K no further CO_2 production is observed. Interestingly, in addition to the main peak a small delayed contribution to the CO_2 formation is observed at 351 K between 1 and 2 s (see the enlarged transients in Figure 2a). The delay time decreases with increasing temperature until finally at 450 K the two features coalesce. Such an effect has been observed for non-mass-selected Pd clusters[7] and larger nanoparticles under similar (high CO mole fraction[15−17]) experimental conditions as well. The delayed CO_2 formation can be attributed to a CO coverage-dependent sticking coefficient of oxygen. That is, after the CO valve is closed the clusters are covered by CO and the oxygen sticking coefficient is minimized. Upon further reaction/CO desorption the oxygen sticking coefficient increases and thus accelerates the reaction. Consequently, a second maximum in the reaction rate is observed. It is noted that for temperatures in excess of the CO desorption temperature this feature disappears completely.

On the basis of the change of produced CO_2 molecules with time, the reactivity of the clusters is expressed by maximum TOFs, calculated by dividing the maximum of the CO_2 signal by the number of deposited Pd atoms. For all transients the maximum intensity is reached shortly after opening the CO pulsed valve, at a constant partial pressure of oxygen. By calculating the TOFs, the evolution of the catalytic reactivity with temperature is obtained (Figure 2b). Based on the ratio between F_{diff} and F_{dir} and the reaction mechanisms, we distinguish three different reaction regimes. The first regime spans a temperature range of 300 to ∼350 K and is followed by a second ranging up to ∼500 K. Above 500 K we distinguish a third temperature regime, where the TOFs start to decrease and eventually drop to zero. At such elevated temperatures cluster diffusion and agglomeration can no longer be excluded, and as a result, this region was not investigated further. At lower temperatures, however, the CO_2 signals exhibit no change in time (5 min acquisition time per CO_2 signal). Therefore, we exclude cluster agglomeration at these temperatures.

Between 300 and ∼350 K, the TOFs sharply increase, indicating that the reaction has started. Within this temperature range the TOFs are influenced only by the intrinsic properties of the specific cluster size (see Figures 2b and 3b),[18] since the total flux and thus the ratio of F_{diff}/F_{dir} is constant (insets in Figure 4). The catalytic action begins at approximately the same temperature, independent of the cluster size and coverage. The initial slope of the increasing reactivity is the same for identical cluster sizes. The CO_2 signal heights, in the form of an Arrhenius plot, give apparent activation energies for the Langmuir−Hinshelwood (LH) mechanism of the CO oxidation reaction for the two cluster sizes. For Pd_8 a value of 25.3 ± 2.5 kJ/mol for both cluster densities is obtained, compared to 36.5 ± 3.2 kJ/mol for the Pd_{30} model catalysts (0.12% ML and 0.28% ML). These values fit reasonably well with literature data obtained for Pd nanoparticles, particularly when it is noted that the substrates are different (see Table 1). For example, using molecular beam experiment under non-steady-state conditions, Stara et al.[19] reported 20 kJ/mol for 2.5 nm sized Pd nanopar-

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Table 1. Activation Energies of Selected Extended Pd and Cluster Systems

sample	E_{LH} [kJ/mol]	conditions	ref
Pd(111)	105 59	low O_2 coverage, $T > 500$ K high O_2 coverage, $T < 420$ K	24
Pd(111)	45−64	high O_2 coverage, $T < 500$ K	20
Pd (27 nm)[a]	32−45	high O_2 coverage, $T < 500$ K	19
Pd (5−6 nm)[b]	57 ± 8 62 ± 9	CO-rich regime, low temp O-rich regime, low temp	20
Pd (2.5 nm)[a]	19−20	high O_2 coverage, $T < 500$ K	19
Pd_{30}[c]	36 ± 3	O saturated, $T < 400$ K	
Pd_8[c]	25 ± 3	O saturated, $T < 400$ K	

[a] On Al_2O_3 thin film. [b] On Al_2O_3/NiAl(110). [c] On MgO(100)/Mo(100).

ticles supported on a Al_2O_3 support, whereas they reported higher activation energies for CO oxidation on larger (27 nm) Pd nanoparticles. In contrast Meusel et al.[20] observed no significant difference in the activation energy of CO oxidation on Pd nanoparticles and Pd(111). When the LH process is analyzed, a number of factors influence the activation barrier on extended Pd surfaces, like the activation and dissociation of the adsorbed oxygen as well as layer compression caused by adsorbing CO molecules,[16,21,22] which is a temperature-dependent process. For size-selected Pd clusters, however, no extended "CO adlayers" are formed. In contrast, the adsorption properties of CO molecules may be influenced by cooperative adsorption. Generally in this size region, the properties change in a nonlinear fashion with the cluster size,[18] making a direct comparison with data obtained on nanoparticles or single crystals difficult.

In the second regime (up to 500 K) the CO desorption becomes increasingly dominant in comparison to the LH activation process. In addition, the ratio between F_{diff} and F_{dir} is no longer constant implying the changing flux has an influence on the observed TOFs. In this region the highest reaction rates are measured. Most interestingly, the TOFs of the two different cluster sizes, Pd_8 and Pd_{30}, exhibit quite different variations from those achieved through changing of the cluster coverage, indicating a clear cluster size effect. That is, while the measured TOFs for the Pd_8 system in this temperature range clearly depend on the cluster coverage, the measured TOFs for the Pd_{30} system are almost independent of the coverage. More explicitly, the obtained TOFs for the Pd_8 system are ∼47 CO_2/Pd-atom•s at 480 K for 0.28% ML coverage and ∼28 CO_2/Pd-atom•s at 450 K for 0.65% ML, respectively. In comparison, the Pd_{30} system (Figure 3b) has a maximum TOF of approximately 28 CO_2/Pd-atom•s for both coverages (0.12% ML and 0.28% ML). At this point it is important to note that the ratio of F_{diff} and F_{dir} does not only depend on temperature but also on the cluster size and coverage.[1,3] As a consequence the observed TOFs will also be affected by these factors. Furthermore, the absolute turnover numbers strongly depend on the experimental conditions, e.g., the effective pressure of reactants on the surface. This becomes clear when comparing the TOFs obtained for the clusters to values of Pd nanoparticles supported on MgO(100) given in the literature.[15,23] For example, in molecular beam experiments TOFs of 0.12 are obtained for Pd particles in the range of 2.8−13 nm in diameter measured under steady-state conditions. However, at higher pressures (Pd nanoparticles supported on SiO_2) values of 20−2000 were measured. Therefore, care has to be taken when comparing TOFs obtained under different experimental conditions.

From a fundamental point of view, it is more appropriate to compare reaction probabilities (under identical conditions) rather than the different TOFs. The reaction probability (RP) is given by RP = TOF/F_{tot}, defining the probability of transforming an impinging CO molecule, delivered either by direct or by diffusion flux, into the product molecule CO_2. For its determination the total flux of CO molecules to the catalyst particle has to be calculated (see the Supporting Information). For this purpose we used the collection zone model.[3,10−12] The collection area depends on the mean diffusion length of the CO molecule on MgO as well as the cluster size and coverage. At low temperatures, small cluster sizes, and low cluster coverages the collection zone is maximal. Thus, by increasing temperature, cluster size, and/or cluster coverage, the collection zone will decrease. In the limit of overlapping adjacent collection zones, F_{tot} is calculated by F_{dir} and the so-called global sticking coefficient, obtained from the solution of the differential diffusion equation and the cluster surface cross section. For further details and the parameters used in the calculations see refs 3 and 12 and/or the Supporting Information.

Applying the collection zone model, we obtained reaction probabilities for the CO oxidation on Pd clusters, which are plotted in Figure 4. As for the TOFs, the reaction probabilities for CO oxidation on Pd_8 and Pd_{30} show a distinctively different behavior. This confirms that the reaction takes place in the high oxygen coverage regime (see above), and thus the CO adsorption determines the reaction rate. While for both coverages of Pd_8 the RP is approximately the same, for Pd_{30} it clearly depends on the cluster coverage. As mentioned before, the ratio of F_{diff}/F_{dir} is temperature dependent and it is higher for low cluster coverages (insets in Figure 4). As F_{dir} is constant, the diffusion flux, F_{diff}, increases with decreasing coverage. With this borne in mind, our results indicate that the reaction probability of Pd_8 is independent whether CO directly adsorbs on the cluster or whether it adsorbs by reverse spill-over. Thus, the activation energies on different reaction sites on Pd_8 (on the cluster or at the periphery) are identical or the diffusion of CO via the periphery onto the cluster is nonactivated. In contrast, the reaction probabilities of Pd_{30} are discriminated by the reverse spill-over and the conversion of CO to CO_2 is significantly less efficient if the CO molecules diffuse from the substrate instead of directly impinging from the gas phase onto the cluster. This observation can either be explained by a high barrier for CO diffusion onto the cluster or an enhanced activation energy for reaction on the periphery. These results indeed show for the first time the effect of the reverse spill-over on the reactivity to be cluster size dependent. It cannot be distinguished by the present experiments whether the reaction occurs on both the periphery and the cluster or on the cluster alone. Recently,

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however, Huber et al. performed DFT calculations for the CO oxidation on Pd_n ($n = 4-9$) clusters.[8] This work shows that magnesia-supported Pd clusters form crystalline Pd_xO_y clusters upon reaction with oxygen. When exposing the Pd_9O_y/MgO system to a single CO molecule indeed a low activation barrier was found for the interconversion of CO atop bonded CO to CO bonded to the cluster−support interface. However, for a detailed comparison of the experimental data to the theoretical calculations, activation barriers for the conversion of CO on larger clusters would be required.

In summary, presently the CO oxidation reaction is studied on size-selected Pd_n cluster model catalysts supported on thin MgO(100) films. By means of pulsed molecular CO beams the apparent activation energies for CO oxidation under CO-rich conditions were extracted for two cluster sizes, i.e., $n = 8$ and 30, with the one for Pd_8 being distinctly smaller. With the application of the collection zone model the differences in the coverage-dependent reaction probabilities observed for the two cluster sizes could be explained by a cluster-size-dependent efficiency of the reverse spill-over on the CO reaction. While for small clusters (Pd_8) the RP is identical for direct and diffusion flux of CO molecules, for larger clusters (Pd_{30}) the RP for the direct flux is higher than for the diffusion flux.

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Supporting Information Available: The parameters used in the collection zone model and the total CO fluxes calculated for the respective systems. This material is available free of charge via the Internet at http://pubs.acs.org

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