

## Low-Temperature Cluster Catalysis

Ken Judai,<sup>†</sup> Stéphane Abbet,<sup>†</sup> Anke S. Wörz,<sup>†</sup> Ulrich Heiz,<sup>\*,†</sup> and Claude R. Henry<sup>‡</sup>

Contribution from the University of Ulm, Institute of Surface Chemistry and Catalysis,  
Albert-Einstein-Allee 47, D-89069 Ulm, Germany, and CRMCN-CNRS,  
Campus de Luminy Case 913, 13288 Marseille Cedex 09

Received October 14, 2003; E-mail: ulrich.heiz@chemie.uni-ulm.de.

**Abstract:** Free and supported metal clusters reveal unique chemical and physical properties, which vary as a function of size as each cluster possesses a characteristic electron confinement. Several previous experimental results showed that the outcome of a given chemical reaction can be controlled by tuning the cluster size. However, none of the examples indicate that clusters prepared in the gas phase and then deposited on a support material are indeed catalytically active over several reaction cycles nor that their catalytic properties remain constant during such a catalytic process. In this work we report turn-over frequencies (TOF) for Pd<sub>n</sub> (n = 4, 8, 30) clusters using pulsed molecular beam experiments. The obtained results illustrate that the catalytic reactivity for the NO reduction by CO (CO + NO → 1/2N<sub>2</sub> + CO<sub>2</sub>) is indeed a function of cluster size and that the measured TOF remain constant at a given temperature. More interestingly, the temperature of maximal reactivity is at least 100 K lower than observed for palladium nanoparticles or single crystals. One reason for this surprising observation is the character of the binding sites of these small clusters: N<sub>2</sub> forms already at relatively low temperatures (400 and 450 K) and therefore poisoning by adsorbed nitrogen adatoms is prevented. Thus, small clusters not only open the possibility of tuning a catalytic process by changing cluster size, but also of catalyzing chemical reactions at low temperatures.

## Introduction

Heterogeneous catalysts most often consist of metal particles highly dispersed on oxide surfaces, where the metal center is the active site.<sup>1</sup> The oxides, however, not only serve as support material, but also can play an active role during a catalytic process. For instance, they are responsible for spill-over and reverse spill-over effects, they may change the properties of the metal particles by charge transfer or they may define the metal–support interface, where reactions often occur. Focusing on the metal part, two size regimes can be defined. First, heterogeneous catalysts can consist of metal particles with hundreds or thousands of atoms. For these sizes, size-dependent observations are most often explained by the changing morphology and the concomitant varying number of surface defects.<sup>2–4</sup> Second, the catalysts can be composed of small metal clusters<sup>5</sup> consisting of only a few or at most a few dozen atoms. This size range opens up fascinating opportunities for tuning the efficiency<sup>6,7</sup> and selectivity<sup>8</sup> of chemical and catalytic reactions at given temperatures by varying the cluster size.<sup>9</sup> Guiding

principles for understanding these size-dependent chemical properties are now emerging.<sup>10</sup> These are the unique dynamic structural fluxionality of clusters, distinct quantum size effects and characteristic cluster-support interactions.<sup>6,7</sup> Whether small clusters keep these unique properties during a catalytic process has not yet been shown experimentally. Here we report size-dependent turn-over frequencies (TOF) for the CO + NO catalytic reaction (NO + CO → CO<sub>2</sub> + 1/2N<sub>2</sub>) on small palladium clusters, showing that such small clusters indeed stay active during a catalytic process. Surprisingly, maximal reactivities are observed at temperatures 100 K below those observed for larger palladium particles<sup>11–13</sup> and bulk systems.<sup>11</sup> Information on the reaction mechanisms is obtained by comparing these results to earlier infrared and thermal desorption studies, revealing that at least 5 atoms are needed to initiate the catalytic oxidation of CO by NO and that a low and a high temperature mechanism exist where molecularly and dissociated NO is involved, respectively.

## Experimental Section

The cluster model catalysts were prepared by softlanding<sup>14–17</sup> (that is, deposition of the clusters without fragmentation and significant structural distortion)<sup>18</sup> size-selected cluster cations (singly charged)

<sup>†</sup> University of Ulm, Institute of Surface Chemistry and Catalysis.

<sup>‡</sup> CRMCN-CNRS.

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obtained via supersonic expansion of a cold laser-generated metal plasma onto well-defined oxide surfaces.<sup>19</sup> Deposition of less than 0.5% ML (1 ML =  $2.25 \times 10^{15}$  clusters/cm<sup>2</sup>) at a substrate temperature of 90 K ensures isolated clusters and prevents agglomeration.<sup>20</sup> By integrating the cluster current during deposition the densities are precisely known. For all model catalysts, the cluster density was scaled in order to cover similar surface areas. This precaution guarantees identical reverse spill-overs from the support material during the catalytic process, which means identical effective pressures of the reactant molecules on the clusters.<sup>21</sup> The magnesium oxide supports were prepared in situ by epitaxially growing thin films on a Mo(100) surface.<sup>22</sup> These films have bulklike properties as observed by low energy electron diffraction (LEED), electron energy loss spectroscopy (EELS), and ultraviolet photoelectron spectroscopy (UPS).<sup>23</sup> Under given experimental conditions (evaporation rate, oxygen background pressure, annealing temperature) a controlled density of oxygen vacancies (F-centers) on the surface is obtained, which is at least a factor of 5 larger than the cluster densities.<sup>24</sup> Monte Carlo simulations showed that under these conditions the clusters are efficiently trapped on F-centers and coalescence is prevented.<sup>20</sup> Binding energies of several eV ensure the cluster to be stable even at temperatures where the catalytic processes occur.<sup>6,17</sup> The catalytic properties were studied by pulsed molecular beams in a UHV chamber with a base pressure better than  $1 \times 10^{-10}$  mbar. To obtain turn-over frequencies for different cluster sizes the quadrupole mass spectrometer was calibrated for absolute particle numbers.<sup>25</sup> The obtained results are compared to temperature programmed reaction (TPR) and Fourier transform infrared (FTIR) studies.

## Results

The size-dependent cluster catalysis was studied by pulsed molecular beams. In these experiments a nitric oxide molecular pulse, produced by a newly designed, highly stable piezo valve, is injected onto the cluster catalysts and the product molecules CO<sub>2</sub> and N<sub>2</sub> are quantitatively detected by a mass spectrometer as a function of cluster size, temperature, and CO background pressure.<sup>25</sup> The catalytic formation of CO<sub>2</sub> on Pd<sub>30</sub> and Pd<sub>8</sub> is shown in Figures 1a/b for selected temperatures and for a constant CO partial pressure of  $5 \times 10^{-7}$  mbar and a NO effective pressure of  $1 \times 10^{-4}$  mbar. The effective pressure is defined as the average pressure at the location of the sample during the duration (fwhm: 100 ms) of the NO pulse. Pd<sub>8</sub> and Pd<sub>30</sub> show almost no catalytic reactivity up to about 390 K. For Pd<sub>30</sub>, maximal reactivity is observed at 420 K whereas Pd<sub>8</sub> is most reactive at 450 K. At higher temperatures the formation of CO<sub>2</sub> decreases. The CO<sub>2</sub> formation on both cluster sizes at temperature of maximal reactivity is stable even after hundreds of NO pulses, indicating that the clusters are stable at this temperature. The thermal stability of the cluster reactivity was

further studied by repeatedly measuring the temperature evolution of the CO<sub>2</sub> formation. Up to temperatures of 500 K, no change in the temperature-dependent reactivity pattern could be detected within the uncertainty of the experiment, whereas the reactivity almost disappeared for all temperatures after heating the sample up to 700 K. Thus, we attribute the measured reactivities up to about 500 K to the reactivity of the cluster size deposited on the MgO film.

Since the mass spectrometer is calibrated absolutely we extract from these data a catalytic activity averaged over a single pulse as a function of cluster size and temperature by integrating the CO<sub>2</sub> peaks and dividing the obtained numbers by the number of deposited atoms and the duration of the NO pulse. As we are not in steady-state conditions, we call it pseudo-turn-over frequency. The evolution of the pseudo-TOF as a function of temperature is shown in Figure 1c. These small clusters exhibit a size-dependent maximal catalytic reactivity with Pd<sub>8</sub> (maximal reactivity of 0.54 CO<sub>2</sub>/atom·sec at 450 K) being significantly more reactive than Pd<sub>30</sub> (maximal reactivity of 0.34 CO<sub>2</sub>/atom·sec at 420 K) whereas the latter reveal maximal reactivity at lower temperatures. For both cluster sizes, the catalytic reactivity was measured with increasing CO background pressure and as expected the reactivity is increasing (Figure 2).

## Discussion

These experiments showed for the first time that such small Pd<sub>n</sub> clusters are indeed catalytically active. They maintain their catalytic activity at least for a few hundreds of reaction cycles. From the obtained data, pseudo-turn over frequencies could be estimated. Compared to larger particles and single crystals these small Pd<sub>n</sub> clusters are reactive at considerably lower temperatures.<sup>11–13,27</sup> To better understand these findings, we review the reaction mechanisms of the oxidation of CO by NO on size-selected Pd<sub>4</sub>, Pd<sub>8</sub>, and Pd<sub>30</sub> on MgO thin films obtained by temperature programmed reaction (TPR) and Fourier transform infrared spectroscopy (FTIR) experiments.<sup>26</sup>

In summary, the oxidation of CO by NO is observed for clusters consisting of at least five atoms, e.g., Pd<sub>4</sub> is inert. Two different reaction mechanisms were reported for Pd<sub>n</sub> clusters with up to thirty atoms, where CO<sub>2</sub> is formed in a first reaction mechanism at around 150 K and in a second reaction mechanism CO<sub>2</sub> is formed at around 300 K (Figure 3a). FTIR studies indicate that at higher temperatures CO<sub>2</sub> is formed by a reaction mechanism where molecular adsorbed CO and atomic oxygen is involved. The adsorbed oxygen atom results from the dissociative adsorption of NO (NO → N<sub>ad</sub> + O<sub>ad</sub>). For clusters smaller than Pd<sub>20</sub> the NO dissociation is most efficient and thus no other reaction mechanism is observed. For larger clusters a second low temperature mechanism is proposed. An IR-band typically for 3-fold bound, molecularly adsorbed NO (1550 cm<sup>-1</sup>) points toward a reaction mechanism where the adsorbed CO is reacting directly with adsorbed NO via a Langmuir–Hinshelwood type reaction mechanism. For both reaction mechanisms the produced N<sub>2</sub> is desorbing in a temperature range between 300 and 500 K (Figure 3b). Interestingly, under NO-rich conditions (NO is exposed prior to CO) the reaction is almost inhibited.

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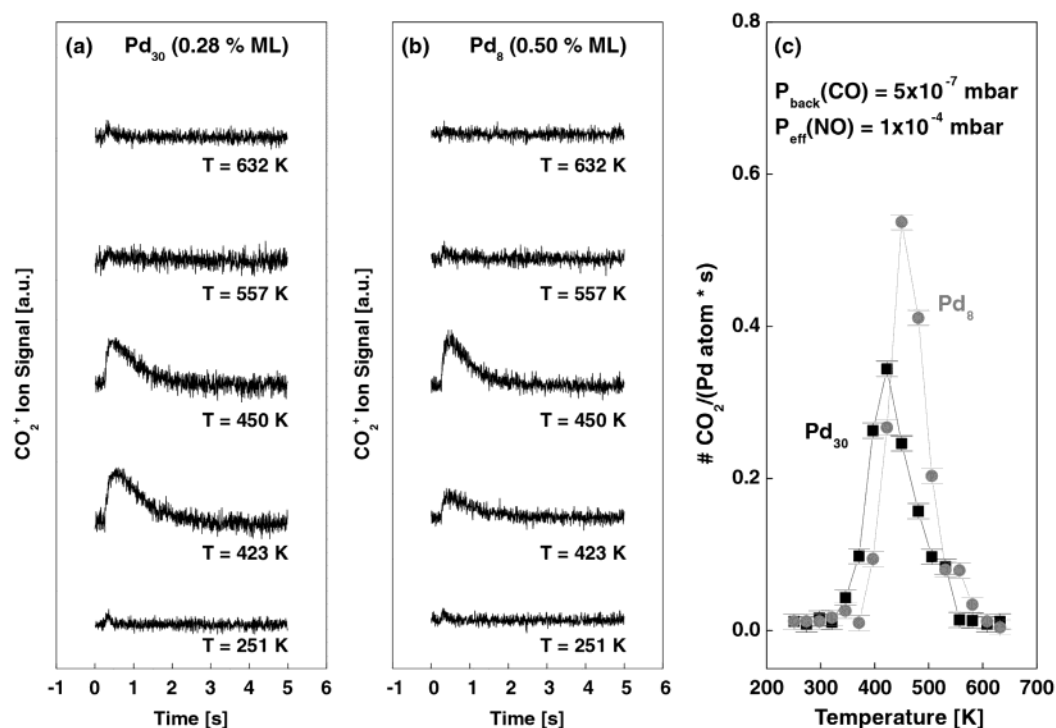
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**Figure 1.**  $\text{CO}_2$  formation measured for  $\text{Pd}_{30}$  (a) and  $\text{Pd}_8$  (b) at several temperatures. These  $\text{CO}_2$  transients were measured at an isotropic CO pressure of  $5 \times 10^{-7}$  mbar and an NO pulse with a width of 100 ms, resulting in an effective pressure of  $1 \times 10^{-4}$  mbar. From the calibrated integral of the  $\text{CO}_2$  peak and by dividing by the number of deposited atoms and the pulse width, the pseudo turn-over frequencies (TOF) at various temperatures are obtained. The evolution of the pseudo-TOF as function of temperature are shown in (c).  $\text{Pd}_8$  is more reactive, the temperature of maximal reactivity, however, is 30 K higher (Table 1).

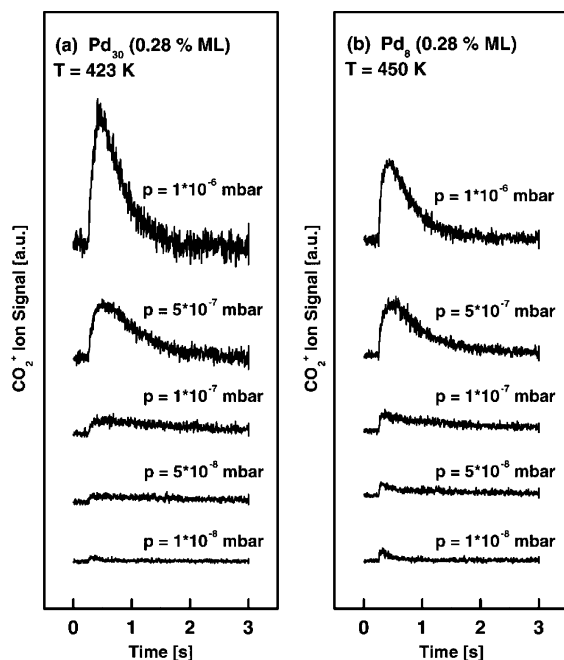
A distinct size dependency is also observed in the pulsed molecular beam experiments. In agreement with the TPR experiments,  $\text{Pd}_4$  is not reactive for the CO + NO reaction. Larger clusters readily produce  $\text{CO}_2$ . On one hand, the temperature of maximal  $\text{CO}_2$  formation is slightly lower for  $\text{Pd}_{30}$  (Figure 1a) than it is for  $\text{Pd}_8$  (Figure 1b), on the other hand, the maximum reactivity for  $\text{Pd}_8$  is higher by almost a factor of 2 (Figure 1c). In line with the TPR experiments, the reactivity is largely decreased under NO rich conditions as the clusters are poisoned by NO. This information is obtained by FTIR experiments where the IR-absorption band for CO is almost absent under these conditions.<sup>26</sup>

Before relating the size-dependent chemical and catalytic activity with intrinsic cluster properties (quantum size effects) one has to ensure that they cannot be explained by purely geometric effects related to the increased proportion of surface atoms with decreasing cluster size. As an example, a truncated octahedron of order 1 contains 38 atoms where the surface is composed of 32 atoms, representing 84% of the total number of atoms. In contrast, for  $\text{Pd}_8$  all atoms are on the surface. Thus, using these geometric arguments an increase in reactivity of only ~19% is expected for  $\text{Pd}_8$ , which is, however, significantly smaller than the one observed experimentally (~59%). Furthermore, the observed cluster reactivities are distinctly different compared to the reactivity of Pd nanoparticles<sup>11–13,28,29</sup> and single crystals.<sup>27,30</sup> Most importantly, the model catalysts consisting of small palladium clusters reach maximal reactivities at temperatures, which are 100 K lower than those for palladium particles with sizes of 2.5 nm and larger<sup>11–13</sup> (Table 1). Although the reaction temperatures depend on the partial pressures of the reactants in the experiments,<sup>33</sup> this interesting trend is also observed in the temperature programmed reaction (TPR) experi-

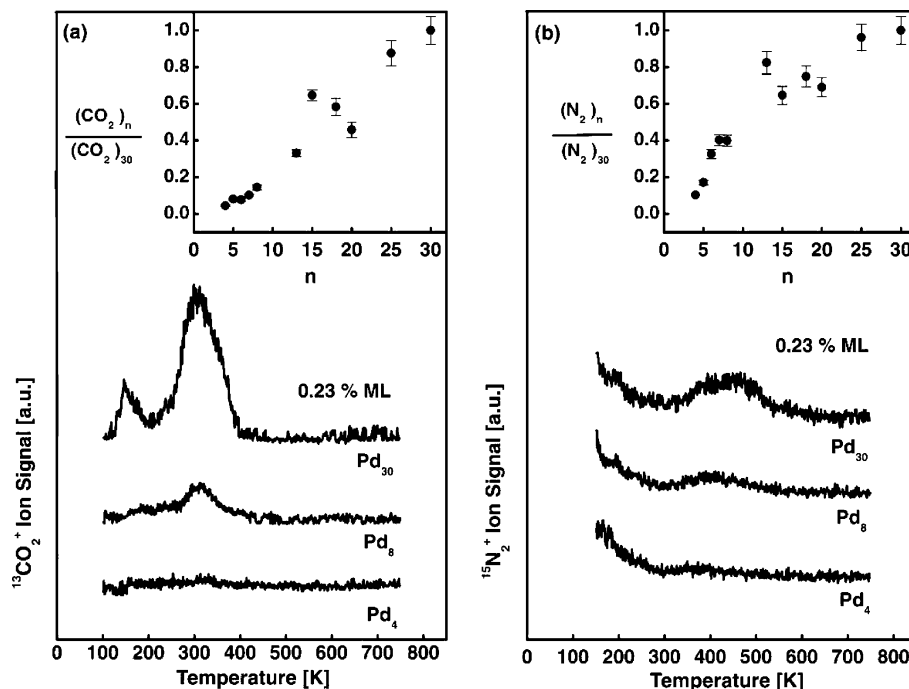
ments for these different systems. The reaction temperatures for the various systems and experimental conditions are summarized in Table 1. Possible origins are discussed in the following section. The TOF are strongly dependent on the experimental conditions and as the experiments reported here were carried out at NO pressures ( $10^{-4}$  mbar) between those of nanometer-sized Pd particles on  $\text{MgO}(100)$ <sup>12</sup> ( $6 \times 10^{-8}$  mbar) and those of nanometer-sized Pd particles on alumina<sup>11</sup> or Pd single crystals<sup>27</sup> (6 mbar) an accurate comparison is not possible. Nevertheless, we express the catalytic reactivity as the reaction probability (i.e., the conversion factor) with respect to the flux of NO. It is calculated by taking the ratio of the number of  $\text{CO}_2$  molecules produced in a single pulse per Pd atom and the number of NO in a beam pulse reaching a single Pd atom. The obtained values for the cluster model catalysts are in the range of  $10^{-4}$ . This reaction probability is about 4 orders of magnitude smaller than the one for nanoparticles on  $\text{MgO}(100)$  but 1 order of magnitude larger than for nanoparticles on alumina or Pd single crystals. Studies are under investigation where reaction probabilities for single crystals, nanoparticles and clusters are measured under identical experimental conditions.

Let us now compare in detail the results for  $\text{Pd}_{30}$  with those of single crystals and Pd nanoparticles in order to understand the low-temperature catalysis on clusters. On  $\text{Pd}_{30}$ , dinitrogen

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**Figure 2.**  $\text{CO}_2$  formation measured for  $\text{Pd}_{30}$  (a) and  $\text{Pd}_8$  (b) at 423 and 450 K, respectively. These  $\text{CO}_2$  transients were measured at varying isotropic CO pressures ( $1 \times 10^{-8}$  mbar –  $1 \times 10^{-6}$  mbar) and an NO pulse with a width of 100 ms, resulting in an effective pressure of  $1 \times 10^{-4}$  mbar. As expected the reactivity is increasing with CO pressure and saturation is not yet attained at these experimental conditions. In fact, it is known that a shallow reactivity maximum is reached at a mole fraction of the two reactants of 0.5.<sup>26</sup> This shows that at our experimental conditions we are far from the optimum. In addition, for  $\text{Pd}_{30}$  (Figure 2a) and  $\text{Pd}_8$  (Figure 2b) the fwhm of the  $\text{CO}_2$  transients is decreasing with increasing isotropic CO pressure. This can be understood by the competitive adsorption of the two reactants. When increasing the pressure of the less abundant reactant, in this case CO, the NO molecule is replaced more efficiently and the reaction can take place more rapidly. Thus, the reaction probability is increased leading to narrower transients. Interestingly,  $\text{Pd}_4$  shows no measurable catalytic reactivity under any of these experimental conditions.



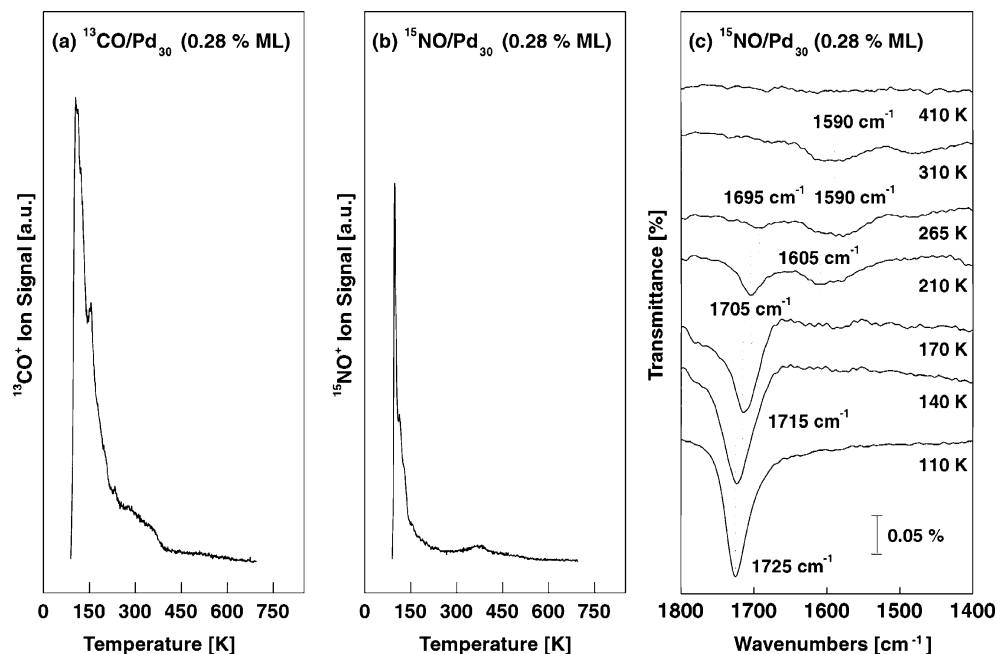
**Figure 3.** Formation of  $^{13}\text{CO}_2$  (a) and  $^{15}\text{N}_2$  (b) for  $\text{Pd}_4$ ,  $\text{Pd}_8$ , and  $\text{Pd}_{30}$  measured by a temperature programmed reaction (TPR) experiment. In these experiments, the cluster samples were first dosed at 90 K to 1 Langmuir (L)  $^{13}\text{CO}$  (Garba Gas, 99.37 vol.-%) subsequently to 1L  $^{15}\text{NO}$  (Aldrich Chemical Co., 98 atom-%). The reactivities for various clusters, expressed as the number of product molecules per cluster normalized to the formation on  $\text{Pd}_{30}$ , are shown in the insets. For these reactivities, only the main  $\text{CO}_2$  formation at around 300 K is considered.

**Table 1.** Reaction Temperatures for Maximal Formation of  $\text{CO}_2$  and  $\text{N}_2$  Measured in Single Cycle Temperature Programmed Reaction Experiments and Measured under Steady State Conditions or Using Pulsed Molecular Beams<sup>a</sup>

	$T_{\text{max TPR}}$ (K)		$T_{\text{max TOF}}$ (K)
	$\text{CO}_2$	$\text{N}_2$	$\text{CO}_2$
$\text{Pd}_8/\text{MgO}(100)/\text{Mo}(100)$	305	$\approx 400$	450
$\text{Pd}_{30}/\text{MgO}(100)/\text{Mo}(100)$	145, 300	$\approx 450$	420
$\text{Pd}/\text{MgO}(100)$			520 <sup>12,13</sup>
Pd particles 2.8 nm			
$\text{Pd}/\text{Al}_2\text{O}_3/\text{Ta}(110)$		500, 650 <sup>11</sup>	$> 650$ <sup>11</sup>
Pd particles 2.5 nm			
$\text{Pd}(111)$		450, 560 <sup>11</sup>	$> 650$ <sup>11</sup>
$\text{Pd}(100)$	480 <sup>31,32</sup>	500, 700 <sup>31,32</sup>	$> 650$ <sup>28</sup>
		480, 580 <sup>27, 28</sup>	

<sup>a</sup> In the case of two desorption peaks, both temperatures are given. Note that for both experimental schemes the cluster catalysts are most reactive at temperatures at least 100 K smaller than for single crystals or Pd nanoparticles.

is produced as a broad peak centered at around 450 K and  $\text{CO}_2$  gives rise to two sharper peaks at 300 and 145 K. On Pd nanoparticles supported on alumina or silica,<sup>28</sup> nitrogen recombination is observed at 500 and 680 K, which is 50 K to 230 K higher than for the cluster model catalysts. This behavior is similar to the one for open Pd surfaces such as  $\text{Pd}(100)$ <sup>27</sup> or  $\text{Pd}(320)$ <sup>30</sup> where a loosely bound nitrogen adspecies is involved for the formation of  $\text{N}_2$  at 500 K, whereas the  $\text{N}_2$  formation occurs via a strongly bound nitrogen adspecies at 600–700 K. Interestingly, the second mechanism takes place at temperatures much higher than the  $\text{CO}_2$  production (500 K).<sup>30</sup> This is the reason that at steady state conditions the strongly adsorbed nitrogen poisons the catalyst. In contrast, for  $\text{Pd}(111)$  the high temperature peak is almost absent and even disappears when the reactants are dosed at low temperature (as in the present experiments). The very small amount of the strongly bound nitrogen on  $\text{Pd}(111)$  is at the origin of the higher reactivity of



**Figure 4.** Thermal desorption spectra of  $^{13}\text{CO}$  (a) and  $^{15}\text{NO}$  (b) for  $\text{Pd}_{30}$ . The clusters were exposed at 90 K to the reactants and the sample was then linearly heated with a rate of 2 K/s. The low-temperature desorption around 120 K originates from the desorption of  $^{13}\text{CO}$  and  $^{15}\text{NO}$  from the MgO thin film. Also shown are the vibrational frequencies of  $^{15}\text{NO}$  adsorbed on  $\text{Pd}_{30}$  (c) as function of the annealing temperature. In these experiments, the sample was annealed to the indicated temperature and the spectra were then taken at 90 K. These temperature-dependent spectra contain the same information as coverage dependent experiments, with decreasing coverage as function of temperature.

this surface.<sup>11</sup> Interestingly, the behavior of  $\text{Pd}_{30}$  clusters is much more similar to that of a Pd(111) surface than it is to Pd particles in the nanometer size range. The similarity of the character of adsorption sites on these tiny clusters to those of Pd(111) is also manifested by the IR spectra of adsorbed NO. NO adsorbed on Pd(111) shows two bands near  $1560\text{ cm}^{-1}$  (main peak above RT) and  $1740\text{ cm}^{-1}$  (main peak below RT) corresponding to 3-fold and atop, respectively.<sup>34</sup> On  $\text{Pd}_{30}$  a strong absorption is observed at  $1725\text{ cm}^{-1}$  at low temperature while above RT an absorption band appears near  $1590\text{ cm}^{-1}$  as shown in Figure 4.

On Pd(100), NO gives only one absorption band that shifts from  $1630$  to  $1672\text{ cm}^{-1}$  when the temperature decreases from 500 to 100 K. When comparing the adsorption behavior and reactivity of  $\text{Pd}_{30}$  with Pd(111) further, distinct differences are, however, observed. First a very low-temperature  $\text{CO}_2$  peak at 145 K is observed on  $\text{Pd}_{30}$  but not on Pd(111). As shown before the corresponding reaction mechanism involves molecularly bound CO and NO. This mechanism is not relevant for the catalytic action observed by the pulsed molecular beam experiments as at such low temperature no  $\text{CO}_2$  is observed. Furthermore, desorption of CO and NO from the small clusters is observed at much lower temperatures as shown in Figure 4a/b in comparison to the Pd(111) surface ( $\text{Pd}_{30}$ :  $\sim 300\text{ K}$  for CO and  $370\text{ K}$  for NO). This may either indicate smaller intrinsic binding energies of these molecules with the cluster or higher local densities of the adsorbants where the larger repulsion leads to lower desorption temperatures. In addition, the energy of formation of  $\text{N}_2$  on the cluster is distinctly smaller than on extended surfaces and nanoparticles with crystalline facets. This may be due to a decreased interaction of atomic nitrogen atoms with the clusters and/or an increased dissociation probability of NO resulting in high local  $\text{N}_{\text{ad}}$  densities and a concomitant

strong repulsion favoring  $\text{N}_2$  formation. Thus for small clusters poisoning through  $\text{N}_{\text{ad}}$  is neutralized at distinctly lower temperatures in comparison to surfaces of bulk palladium.

## Conclusion

These results show that clusters consisting of only a few atoms are catalytically active at relatively low temperature and stay active during the process. A minimum cluster size of 5 atoms is needed for the catalytic reaction to take place. The catalytic properties of these small clusters are different than of nanoparticles or extended surfaces. With the mechanistic details obtained for the CO + NO reaction on small  $\text{Pd}_n$  ( $n \leq 30$ ), the catalytic process and the measured pseudo-TOF can be described as follows. Below 300 K very small amounts of  $\text{CO}_2$  are formed for  $\text{Pd}_{20-30}$  only and we describe this formation by a mechanism in which CO is directly oxidized by molecularly bonded NO. This mechanism is not efficient in the catalytic process. The formation of  $\text{CO}_2$  above 400 K is orders of magnitude larger and the corresponding reaction mechanism is described by the oxidation of CO by adsorbed oxygen atoms,  $\text{O}_{\text{ad}}$ , resulting from the dissociation of NO. This is the mechanism relevant in the catalytic process. The much reduced reaction temperatures for cluster materials in comparison to larger particles or single crystals may be on one hand explained by the fact that clusters consist almost exclusively of surface atoms. This means that oxygen cannot be accommodated in the bulk, which may largely reduce the activation energy for the formation of  $\text{CO}_2$ . On the other hand and more importantly, the formation of  $\text{N}_2$  on the cluster materials at low temperatures prevents poisoning of the model catalysts. Only when  $\text{N}_2$  is formed can the reaction cycles take place. The use of cluster-assembled materials in catalysis may open the possibility to tune the catalytic properties with cluster size. In this context, it is important that not only the activity can be changed but also the selectivity. In addition, the

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cluster catalysts are active at much lower temperature than the bulk analogues, which is an important issue for industrial applications. To compare absolute turn-over frequencies for various palladium catalysts work is in progress where the cluster model catalysts are compared with nanoparticles and extended surfaces at identical experimental conditions.

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