

## The effect of particle size on nitric oxide decomposition and reaction with carbon monoxide on palladium catalysts

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The effect of palladium particle size on its catalytic activity was investigated by the decomposition of chemisorbed nitric oxide and the reaction of nitric oxide with carbon monoxide in flow conditions. Palladium particles (30–500 Å) were prepared on silica thin films (100 Å) which were supported on a Mo(110) surface. The reactivity of the supported palladium varied with the metal particle size. On large palladium particles, nitric oxide (NO) reacts to form nitrous oxide (N<sub>2</sub>O), dinitrogen (N<sub>2</sub>) and atomic oxygen during temperature-programmed reaction, whereas on small particles (< 50 Å), nitrous oxide is not formed. Similarly, reactions of NO with CO on large particles, in flow conditions produce N<sub>2</sub>O, N<sub>2</sub> and CO<sub>2</sub>, whereas N<sub>2</sub>O is not produced on small particles. In addition, more extensive NO decomposition is observed on the smaller particles.

**Keywords:** NO decomposition; CO; palladium particles; Mo(110)

The effect of metal particle size on catalytic properties has been the focus of extensive work for several decades (see, for example, ref. [1]). As the dimension of a metal particle approaches the nanometer range, its properties can be expected to deviate from those of the bulk due to variations in electronic structure and to changes in the nature of the surface adsorption sites. In this letter, we show that reactions of nitric oxide on supported palladium depend upon the metal particle size. We believe this to be the first report that addresses the reactivity of nitric oxide as a function of palladium particle size. The reactions of nitric oxide on palladium are of considerable interest, largely motivated by efforts to develop better catalysts for control of air pollutants (see, for example, ref. [2]). In this study, it is found that on large palladium particles, nitric oxide (NO) reacts to form nitrous oxide (N<sub>2</sub>O), dinitrogen (N<sub>2</sub>) and atomic oxygen during temperature-programmed reaction, whereas on small particles (< 50 Å), nitrous oxide is not formed. Similarly, reaction of NO with CO on large particles produce N<sub>2</sub>O, N<sub>2</sub> and CO<sub>2</sub>, whereas N<sub>2</sub>O is not produced on small particles.

Experiments were carried out in an ultrahigh vacuum chamber equipped with a quadrupole mass, Auger electron and FTIR spectrometers, and a turbomolecular pump [3]. Palladium was evaporated onto silica thin films ( $\sim 100$  Å) which were supported on a Mo(110) substrate [4]. The size of the palladium particles was determined with STM, AFM and chemisorption methods. Particles in the range of 30–500 Å can be readily prepared by evaporating controlled amounts of palladium and subsequently annealing to 900 K [5]. The surface structure of the palladium catalysts was probed with infrared reflection-absorption spectroscopy (IRAS) of chemisorbed carbon monoxide. As shown in fig. 1, large particles consist primarily of (111) and (100) facets based on a comparison of the IRAS spectra for CO on supported palladium with CO on Pd(111) and Pd(100). On the smaller particles, more CO is adsorbed on the atop sites ( $2110\text{ cm}^{-1}$ ) than on the bridging sites ( $\sim 1990$  and  $1880\text{ cm}^{-1}$ ), which is consistent with there being more edge/defect sites on the small particles [5].

The effect of palladium particle size on the catalytic properties was investigated utilizing the decomposition of chemisorbed NO (fig. 2) and reactions of NO with CO in flowing conditions (fig. 3).  $^{15}\text{NO}$  was used in order to differentiate  $\text{N}_2$  from CO and  $\text{N}_2\text{O}$  from  $\text{CO}_2$  with mass spectrometry. During temperature-programmed

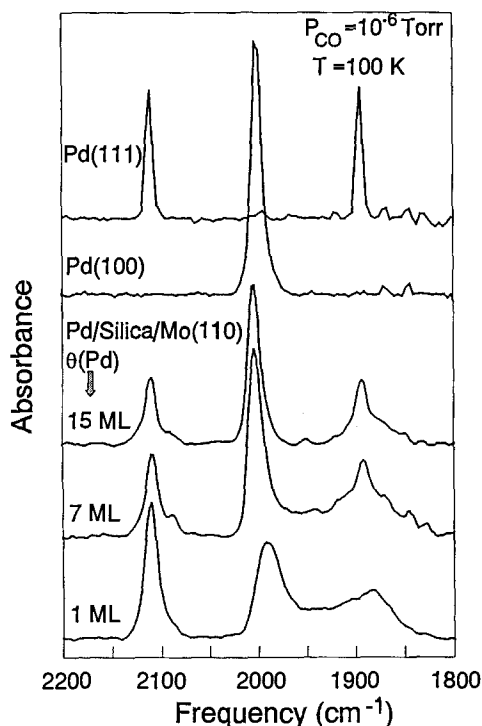


Fig. 1. A comparison of infrared reflection-absorption spectra of CO on Pd(111), Pd(100) and silica-supported palladium surfaces. The spectra were collected at 100 K with a CO pressure of  $1 \times 10^{-6}$  Torr.

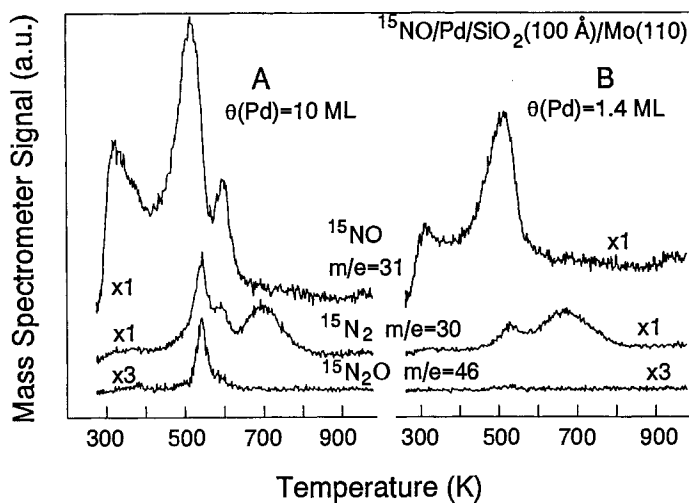


Fig. 2. Temperature-programmed reaction spectra for  $^{15}\text{NO}$  on model silica-supported palladium catalysts.  $^{15}\text{NO}$  was adsorbed at 290 K to saturation. The palladium coverages were (A) 10 monolayer, corresponding to a particle size of  $\sim 250$  Å, and (B) 1.4 monolayer, corresponding to  $\sim 55$  Å [4].

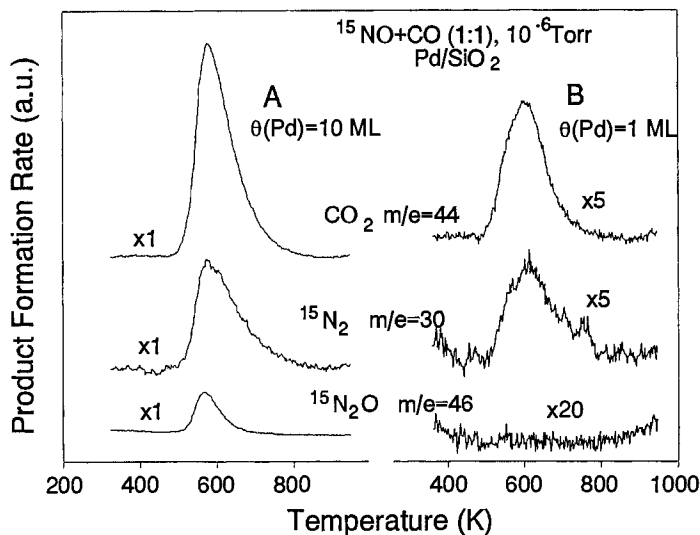


Fig. 3.  $\text{CO} + ^{15}\text{NO}$  reaction rates as a function of temperature for small and large particle Pd catalysts. The gas phase pressure was  $1 \times 10^{-6}$  Torr with equimolar CO and  $^{15}\text{NO}$ . The product formation rate was monitored via mass spectrometry. The palladium particle sizes correspond to  $\sim 250$  Å (A) and  $\sim 45$  Å (B).

reaction on the large particles following a saturation  $^{15}\text{NO}$  exposure,  $^{15}\text{NO}$  desorbs in three peaks centered at 315, 515 and 595 K;  $^{15}\text{N}_2$  is produced in peaks at 545, 595 and 690 K; and  $^{15}\text{N}_2\text{O}$  is evolved in a peak at 545 K (fig. 2A). The 545 K  $\text{N}_2$  peak is attributed to the fragmentation of  $\text{N}_2\text{O}$ . On small palladium particles ( $< 50 \text{ \AA}$ ),  $^{15}\text{N}_2\text{O}$  is not produced;  $^{15}\text{NO}$  desorbs in two peaks at 310 and 515 K, and  $\text{N}_2$  is evolved at 530 and 670 K (fig. 2B). The relative yield of  $\text{N}_2$  with respect to  $^{15}\text{NO}$  desorption (above 400 K) decreases as the particle size grows (from  $\sim 50\%$  for  $30 \text{ \AA}$  to  $\sim 20\%$  for  $250 \text{ \AA}$  particles), suggesting less NO decomposition on the larger particles. In addition, the formation of  $\text{N}_2\text{O}$  on the larger particles correlates with the appearance of the NO desorption peak at 595 K. There is no detectable  $\text{O}_2$  evolution below 1000 K for all sizes of palladium particles. However,  $\text{O}_2$  desorption is observed in a peak at  $\sim 1250 \text{ K}$ , concurrent with the desorption of palladium. Therefore, the oxygen from nitric oxide decomposition is apparently dissolved into the bulk of the palladium particles.

The reaction of CO with NO under flowing conditions further demonstrates a particle size effect (fig. 3). The relative rate of product evolution was monitored with a quadrupole mass spectrometer during reaction with flowing  $^{15}\text{NO}$  and CO (1 : 1) at  $1 \times 10^{-6}$  Torr. The reaction rate increases with the catalyst temperature, reaching a maximum at  $\sim 580 \text{ K}$ , then declines. On the large palladium particles (fig. 3A), the maximum rate of  $^{15}\text{N}_2\text{O}$  evolution is 570 K, 10 K lower than the maxima for both  $\text{CO}_2$  and  $\text{N}_2$  production. On the small particles ( $< 50 \text{ \AA}$ ),  $^{15}\text{N}_2\text{O}$  is not produced during the steady-state reaction of a 1 : 1 mixture of  $^{15}\text{NO}$  and CO (fig. 3B).  $\text{N}_2$  is produced by NO dissociation and atomic nitrogen recombination, and  $\text{CO}_2$  is produced from the oxidation of carbon monoxide. There is a temperature ( $\sim 580 \text{ K}$ ) at which the product formation rate is maximized, since the residence time for CO and NO decreases with temperature whereas the reaction rates increase with temperature.

Both the decomposition of NO and the reaction of NO with CO show that the reaction channel for  $\text{N}_2\text{O}$  formation is not available on the small particles ( $< 50 \text{ \AA}$ ). The  $\text{N}_2\text{O}$  formation requires the simultaneous presence of adsorbed NO and atomic nitrogen at sufficient coverages. The temperature programmed reaction spectra of fig. 2 show that the dissociation of NO occurs along the trailing edge of the main NO desorption peak at 515 K. The formation of  $\text{N}_2\text{O}$  correlates with the appearance of the NO desorption peak at 595 K. The higher adsorption energy of the 595 K state increases the NO surface residence time and thus enhances the probability of  $\text{N}_2\text{O}$  formation by NO combination with atomic nitrogen. It is noted that on extended single crystal surfaces,  $\text{N}_2\text{O}$  is also formed during the decomposition of NO [6–8]. However, the decomposition of NO and the formation of  $\text{N}_2\text{O}$  correlate with the presence of step/defect (low-coordination) sites on the single crystal surfaces [6–9]. Accordingly then, it is likely that there are surface sites with low coordination and varying reactivities on the large particles and extended surfaces. On the perfect (111) and (100) facets, NO desorbs at  $< 520 \text{ K}$  [8,9], whereas on particles with a variety of low-coordinated sites, NO can be decomposed to

atomic nitrogen and oxygen on some sites, or can be more strongly adsorbed (595 K desorption state) on other sites. The presence of both sites on the large Pd particles, a strong adsorption site for NO and a second that promotes decomposition, provides a mechanism for the formation of N<sub>2</sub>O. The absence of the N<sub>2</sub>O on the small palladium particles, on the other hand, can be explained by the lack of the high temperature NO adsorption state (595 K) which is, in turn, related to the reactivity of the surface sites. The surface of the small particles is more reactive as indicated by the increased amount of NO dissociation ( $\sim 50\%$  for 30 Å and  $\sim 20\%$  for 250 Å particles), so that all NO molecules on the low-coordinated sites are likely decomposed to atomic oxygen and nitrogen at lower temperatures. The presence of atomic oxygen and nitrogen in the near surface region will likely further decrease the NO adsorption energy.

In conclusion, NO dissociation and reaction with CO on model silica-supported palladium catalysts depend strongly on the metal particle size. The smaller palladium particles exhibit higher activities for NO dissociation, but lower activities for N<sub>2</sub>O formation, compared to the larger particles. This size effect consists of electronic and geometric contributions, and will be the subject of further investigations.

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