$CO + O_2$ and CO + NO Reactions over Pd/Al₂O₃ Catalysts

D. R. Rainer,[†] M. Koranne,[‡] S. M. Vesecky,[§] and D. W. Goodman^{*,†}

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, W. R. Grace and Co., Washington Research Center, Columbia, Maryland 21044, and Monsanto Company, 800 N. Lindbergh Blvd., St. Louis, Missouri 63167

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The kinetics of the CO + NO and CO + O_2 reactions have been studied over several different Pd/Al₂O₃ powder catalysts covering a wide range of average Pd particle sizes. The structure-insensitive nature of the CO + O_2 reaction over Pd has been exploited to determine the relative dispersions in several Pd/Al₂O₃ powder catalysts by measuring the rate of that reaction and normalizing against surface area. This method, assuming particles of hemispherical shape, yields average particle sizes that are consistent with observations using TEM. For the CO + NO reaction over the same catalysts, a pronounced structure sensitivity is evident that results in higher reaction activities over larger Pd particles. Differences between CO oxidation rates for the CO + O_2 reaction prior and subsequent to exposure to the CO + NO reaction are suggestive of the formation of an inhibiting, site-blocking species during the latter reaction. These results are discussed with reference to surface science and kinetics studies over single crystal and model planar Al₂O₃ supported Pd catalysts which have indicated that the structure-sensitive formation and stabilization of an inactive atomic N species plays a significant role in determining the reaction activity over a particular crystal plane or particle size.

1. Introduction

Due to the important implications for automobile emissions control, the CO⁺ O_2^{1-9} and CO + NO¹⁰⁻¹⁹ reactions have been extensively studied over a variety of transition and noble metals. In particular, Rh, Pt, and Pd have received a great deal of attention due to their successes as three-way catalysts (for the simultaneous reduction of NO and the oxidation of CO and unburnt hydrocarbons) in commercial automotive catalytic converters. There has been a substantial effort to elucidate the basic reaction pathways and catalytic characteristics of these systems to facilitate their improved design. While Rh has typically been perceived as the critical component in these multimetal catalysts, due largely to its enhanced selectivity for the complete reduction of NO,20 there has recently been an impetus to develop a Pd only catalyst suitable for use in commercial converters. Several factors account for this. Continuous improvement in gasoline formulation has marginalized the negative impact of the inferior resistance to Pb and S poisoning displayed by Pd relative to the other metals. Additionally, Pd has demonstrated excellent characteristics for hydrocarbon oxidation²¹ and a resistance to sintering at elevated temperatures. Factoring in the greater availability (and hence cheaper cost) of Pd relative to Rh²⁰ makes the desire for a Pd only catalyst very understandable. Here we examine the catalytic properties for the CO + NO reaction over several Pdonly catalysts and show how the parallel study of the $CO + O_2$ reaction over the same catalysts complement these efforts.

The CO oxidation reaction has generated considerable interest, not only due to its importance in terms of emissions control but also because its relative simplicity makes it an ideal, tractable heterogeneous catalysis problem. The reaction mechanism over noble metals has been described by a Langmuir–Hinshelwood model where molecularly adsorbed CO reacts with atomic oxygen on the surface, desorbing CO₂. Because CO adsorbs more strongly on the surface than molecular O₂, the surface of the catalyst is predominantly populated with adsorbed CO under reaction conditions, which inhibits the dissociative adsorption of oxygen. Thus, the rate-limiting step under typical conditions is believed to be the desorption of CO. This is consistent with the negative first-order dependence on CO concentration and positive first-order dependence on O₂ concentration generally observed for the reaction except at ratios far from stoichiometric.^{2,6–8}

Another important aspect of the CO/O₂ reaction is its structure insensitivity at and near stoichiometric reaction conditions; excellent agreement in the rate of the reaction over Pd single crystal and supported Pd/SiO₂ catalysts has been observed,¹ as well as over a range of particle sizes in supported catalysts.² This particular characteristic of the reaction was very significant for the CO + NO studies over Pd/Al₂O₃ powder catalysts described in this work, as it allowed the various powder catalyst dispersions to be estimated using the CO oxidation rate as a measure of Pd surface area.

The following mechanism for the CO + NO reaction has been proposed for Rh:¹²

$$CO_{(g)} \rightleftharpoons CO_{(a)}$$
$$NO_{(g)} \rightleftharpoons NO_{(a)}$$
$$NO_{(a)} \rightleftharpoons N_{(a)} + O_{(a)}$$
$$NO_{(a)} + N_{(a)} \rightleftharpoons N_2O_{(g)}$$
$$N_{(a)} + N_{(a)} \rightleftharpoons N_{2(g)}$$
$$CO_{(a)} + O_{(a)} \rightleftharpoons CO_{2(g)}$$

The fast step in this process is the scavenging of atomic $O_{(a)}$ by $CO_{(a)}$ to desorb CO_2 .

The present study of the CO + NO reaction over Pd/Al_2O_3 catalysts reveals a pronounced particle size dependence comparable to that observed over supported Rh,¹⁰ with larger particles displaying significantly enhanced specific activities

^{*} To whom correspondence should be addressed.

[†] Texas A & M University.

[‡] W. R. Grace and Co.

[§] Monsanto Co.

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Figure 1. TEM images of the four different Pd/Al₂O₃ powder catalysts used in the kinetics studies. The α -Al₂O₃ is a low surface area support (~5 m²/g) relative to the γ -Al₂O₃ (~155 m²/g), resulting in much larger particles at a similar Pd loading.

relative to smaller ones. This structure dependence is discussed in relation to UHV experiments over planar model supported Pd/Al₂O₃/Ta(110) catalysts that indicate an enhanced activity for atomic nitrogen formation and stabilization on smaller Pd particles. Additionally, a brief discussion of the CO + O₂ reaction over the powder Pd/Al₂O₃ catalysts is presented that emphasizes the utility of this structure-insensitive reaction for dispersion measurement.

2. Experimental Section

The CO + O₂ and CO + NO reactions over Pd/Al₂O₃ powders were performed in a conventional atmospheric flow

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reactor. The microreactor itself consists of a vertical, hollow quartz tube ~ 15 cm long, with an inner diameter of ~ 5 mm along half the length of the inlet side, and tapering down to ~ 1 mm, housed in a ceramic heating furnace. The catalyst resides on a plug of glass wool packed in at the constriction point. This design accelerates the removal of the product gas eluting from the catalyst bed, minimizing the exposure time to the heated region after the catalytic reaction has occurred. The temperature was monitored by a type "K" thermocouple junction residing just above (\sim 1 mm) the catalyst bed, coupled to the electronic furnace control. The flow rates of the reactant gases were controlled by Brooks Model 5850 mass flow controllers. Mixtures of 5% CO, NO, and O₂ diluted in He (Matheson, 99.995%) were passed through the quartz microreactor at typical flow rates of 68 cm³/min. The product gases were analyzed using a Varian Model 3400 gas chromatograph with a column from HayeSep (Model DB, $1/_8$ in. \times 30 ft).

Four different Pd/Al₂O₃ powder catalysts were prepared using a standard incipient wetness impregnation technique from a Pd nitrosyl nitrate solution. Three different loadings of Pd were added to a γ -Al₂O₃ powder (surface area ~155 m²/g) in weight percentages of 0.1, 1.0, and 5.0%. These amounts were chosen to obtain three catalysts exhibiting distinctly different average particle sizes for kinetics comparisons for the CO + NO reaction. Additionally, a low surface area α -Al₂O₃ powder (surface area ~5 m²/g) was loaded with 2% Pd in order to obtain a very low-dispersed catalyst with a large average particle size. The catalyst was dried in air for ~16 h at 80 °C, ground into a powder, and reduced in flowing pure hydrogen for 4 h at 700 K.

The micrograph images of the catalyst were acquired using a JEOL JEM 2010 model transmission electron microscope (TEM) at a beam voltage of 2 kV, achieving a maximum magnification of $400\ 000 \times$.

The planar model supported catalysts used in the temperature programmed desorption (TPD) experiments were obtained by vapor depositing Pd onto a previously prepared Al₂O₃ thin film supported on a Ta(110) substrate in ultrahigh vacuum (UHV). The UHV system was of a type previously described in the literature,^{22,23} equipped for Auger electron spectroscopy (AES), infrared reflection—absorption spectroscopy (IRAS), and TPD. The Pd was evaporated from a source comprised of a high-purity Pd wire tightly wrapped around a resistively heated Ta filament. The preparation of the Al₂O₃ thin film has been described previously.^{24,25} The sample temperature was monitored using a type "C" thermocouple junction spot-welded to the edge of the single-crystal substrate, and the TPD experiments were carried out with a linear heating rate of 5 K/s.

3. Results and Discussion

3.1. CO + O₂ Reaction. The CO oxidation reaction was performed on each of the four different Pd/Al_2O_3 powder catalysts in the flow reaction mode. The primary purpose of these experiments was to determine the Pd dispersion of each catalyst for reference in the CO + NO reaction study. Because the reaction is structure insensitive, the total surface area of the supported Pd will be proportional to the rate of the reaction.

Each catalyst was subjected to TEM study to determine the approximate size distribution. Figure 1 contains a representative TEM image from each catalyst. For the lowest loading (0.1%), very few particles can be detected in the images and none larger than approximately 20 Å.

The CO oxidation rate was determined for all four catalysts in units of mol/(g of Pd s) at 460 K. For the 0.1% catalyst the turnover frequency (TOF) was then calculated assuming 100%



Figure 2. Arrhenius plot for the $CO + O_2$ reaction over the 0.1% Pd/ γ -Al₂O₃ catalyst.

TABLE 1:	$CO + O_2$	Reaction	Rate	Data	and	Dispersion
Estimates						

	rate at 450 K (TOF)	dispersion based on $CO + O_2$ rate (7%)	approx avg particle size based on dispersion (Å)	E _a (kcal/mol)
0.1% Pd/ γ -Al ₂ O _{3^a}	0.013	100 ^f	<30 ^g	30.1
1.0% Pd/ γ -Al ₂ O ₃ ^{<i>a</i>}	е	19.2	60	29.3
5.0% Pd/ γ -Al ₂ O _{3^a}	е	8.9	125	31.3
2.0% Pd/α-Al ₂ O ₃ ^a	е	0.9	1200	30.7
5.0% Pd/SiO ₂ ^b [3]	0.031			24.6
Pd(110) ^c [1]	0.03			26.0-33.1
Pd(100) ^d [9]	0.04			27.0

 a 4.4 Torr of CO, 2.3 Torr of O₂. b 9.8 Torr of CO, 4.9 Torr of O₂. c 16 Torr of CO, 8 Torr of O₂. d 1 Torr of CO, 0.5 Torr of O₂. e Rates normalized against 0.1% Pd/ γ -Al₂O₃ catalyst. f Assumed. g From TEM images.

dispersion. Since the reaction has been shown to be structure insensitive,^{1,2} the turnover frequencies (molecules reacted per site per second), TOF, were assumed to be equal for each catalyst. The rates of the remaining three catalysts were then normalized against the 0.1% catalyst to yield the dispersion of each. This approach to metal surface area measurement for supported Rh catalysts has yielded results consistent with those acquired by H₂ chemisorption titration techniques.¹⁰

There is some degree of error inherent in this approach; based on a simple model for spherical (or hemispherical) particles, the dispersion for 20 Å Pd particles is approximately 50%. If all the particles in the 0.1% catalyst were 20 Å in diameter, the dispersion assumption would be off by only a factor of 2. This should be the upper limit of the error introduced by this assumption since no particles larger than \sim 20 Å were imaged. Furthermore, no error is introduced into the relative dispersions between the four catalysts since they are all based on the same assumption of 100% dispersion for the lightly loaded catalyst. The average particle sizes as determined from this method were compared with TEM micrographs of each catalyst. While it is difficult to get a statistically meaningful size distribution from the TEM data due to the large range of particle sizes involved, the two methods appear to be qualitatively consistent.

CO oxidation was carried out over these catalysts in the temperature range from 450 to 480 K at a total pressure of 1 atm. The partial pressure of CO and O_2 were 4.4 and 2.3 Torr, respectively, diluted in a He carrier gas. No significant catalyst deactivation was observed for this reaction; steady state was reached very quickly in all cases. The Arrhenius plot for the 0.1% catalyst is presented in Figure 2. Table 1 displays the TOF at 450 K for the 0.1% catalyst, the dispersion and



Figure 3. Partial pressure dependence in each reactant for the CO + O_2 reaction over the 1.0% Pd/ γ -Al₂O₃ catalyst at 460 K.

approximate average particle size for each catalyst based on the oxidation rate normalized against the 0.1% loading, the E_a for the reaction over each catalyst, and some literature values for Pd single crystals and other supported Pd catalysts for comparison. The excellent agreement in the TOF's for the CO oxidation rate with literature values for supported and single crystal Pd catalysts (within a factor of 2–3) indicate the validity of this approach for dispersion determination.

The activities for the CO + O₂ reaction over the 1.0% Pd/ γ -Al₂O₃ catalyst at 460 K as a function of partial pressure in each reactant are presented in Figure 3. The reaction is found to be approximately negative first order in CO and positive first order in O₂, in agreement with other studies^{3,4} and consistent with the mechanism that identifies CO desorption as the ratelimiting step.

3.2. CO + NO Reaction. The CO + NO reaction was carried out over each of the four catalysts in the temperature range 540-580 K, with partial pressures of 4.5 and 5.2 Torr in CO and NO, respectively. Upon initiation of the reaction, a period of sharp deactivation was observed over which the activity decreased by a factor of 5 or more. After approximately 8 h, steady state was reached with only very nominal decreases in the activity observed as a function of time. All the data presented here were obtained at steady state.

Figure 4 shows the Arrhenius plots for each catalyst. The TOF frequencies are for CO conversion and are based on the dispersions determined for each catalyst by the CO oxidation reaction. Arrhenius plots for NO reduction, presented in Figure 5, consistently display TOF's about 60% higher than for CO oxidation and yield very similar E_a 's. Clearly, a particle size dependence exists for this reaction, with a concomitant increase in the activity with increasing average particle size. The largest particles, those in the 2% Pd/ α -Al₂O₃ catalyst, display a dramatic activity enhancement (~30×) over the particles in the 1% and 0.1% loaded catalyst. A similar particle size dependence for supported Rh catalysts has been observed by Oh and Eickel, who have reported a 45-fold increase in the activity for the largest particles relative to the smallest in an average particle diameter range from ~10 to 700 Å.¹⁰

The deactivation that occurs upon initiation of the reaction before steady state is reached could represent particle sintering, resulting in decreased Pd surface area or possibly the buildup on the surface of certain inhibiting species until some equilibrium is reached. Particle sintering seems unlikely as the catalyst has been exposed to much harsher temperature conditions during



Figure 4. Arrhenius plots for CO_2 formation for the CO + NO reaction over four Pd/Al₂O₃ powders at the indicated partial pressures (1 atm total pressure with He diluent).



Figure 5. Arrhenius plots for NO reduction for the CO + NO reaction over four Pd/Al₂O₃ powders at the indicated partial pressures (1 atm total pressure with He diluent).

initial reduction than it experiences in the CO + NO run. Additionally, comparisons of TEM images of reacted and unreacted catalysts reveal no qualitative changes in the particle size distributions, although, again, precise particle size distributions over wide ranges of particle sizes are sometimes difficult to obtain by TEM. The nature of this deactivation was investigated by performing the CO + O₂ reaction over the 5% catalyst both before and after the CO + NO reaction was run and then comparing the rates.

Figure 6 shows the CO oxidation rate for the CO + O_2 reaction as a function of time on stream (TOS) for a 5% Pd catalyst over which the CO + NO reaction has previously been carried out. The initial rate after CO + NO reaction exposure decreases relative to the rate over the fresh catalyst by a factor of ~6. As the TOS for the CO + O_2 reaction increases, the CO oxidation activity increases until it plateaus at about half the original value at around 400 min. This is suggestive of the presence of an inhibiting site blocking surface species (or more than one) that is (are) deposited during the CO + NO reaction and then reacted off to some degree during the subsequent CO + O_2 reaction. That only half of the original CO + O_2 activity is recovered implies either the presence of a poison that cannot



Figure 6. Effect of exposure to the CO + NO reaction on the rate for the CO + O_2 reaction over the 5% Pd/ γ -Al₂O₃ catalyst. The horizontal line at the top marks the CO + O_2 reaction rate at 460 K before exposure to the CO + NO reaction at 560 K for 1 day, and the scatter plot data is the CO + O_2 rate after CO + NO exposure. Time on stream refers to CO + O_2 exposure, not CO + NO exposure.

be easily removed in this way or that some sintering is responsible. Again, the latter seems unlikely based on the harsh reduction conditions to which the catalyst has been exposed.

An identical experiment was conducted on the 1% Pd/Al₂O₃ catalyst. The $CO + O_2$ oxidation rate for the catalyst used for the CO + NO reaction was \sim 35% of the rate observed on the fresh catalyst. At $CO + O_2$ TOS's up to 1200 min, this rate did not change appreciably. While it is unclear why this catalyst did not exhibit the same regenerative behavior for the CO oxidation reaction, this experiment does demonstrate that the differences observed in the rates for the 5% and 1% loaded catalysts are not simply the result of a differing degree of sintering during the reaction. In fact, immediately following the CO + NO reaction, the $CO + O_2$ oxidation rate is decreased more on the 5% relative to the fresh catalyst than on the 1%, indicating that the 6-fold enhancement in the CO + NO rate for the 5% relative to the 1% is not due to a higher degree of sintering among the smaller particles during the CO + NOreaction.

Regarding the identity of the poison(s), there are several candidates. Small supported Pd particles have been shown to be active for CO dissociation under certain conditions.²⁷⁻³⁰ An inactive carbon species could well play the role of a site blocker, and this would be consistent with the observed activity trend, with the smaller particles subject to the most severe carbon poisoning. Another consideration is the possibility of the presence of an inactive adsorbed atomic nitrogen species that is created and/or stabilized on undercoordinated defect sites. Such a species has been proposed by Oh and Eickel to explain the structure sensitivity as a function of particle size observed for supported Rh catalysts and also differences in the activity and E_a observed between single crystals and powders.¹⁰ For Pd, based on comparisons with model catalyst systems, there does indeed seem to be some indication that an inactive form of adsorbed nitrogen plays an important role in determining the activity of a catalyst for the CO + NO reaction.

Kinetics and UHV surface analysis studies on Pd single crystals and planar model supported $Pd/Al_2O_3/Ta(110)$ catalysts have correlated the activity for the CO + NO reaction with the formation of inactive atomic nitrogen.^{19,31} A particle size dependence similar to that observed for the Pd/Al_2O_3 powders has been recorded for the model particles, although not as





Figure 7. TPD monitoring (a) ${}^{15}N_2$ desorption and (b) ${}^{15}N_2O$ desorption over several different Pd coverages with the indicated average particle sizes in a Pd/Al₂O₃/Ta(110) catalyst after exposure to ${}^{15}NO$ at 550 K.

pronounced as in the powder catalysts, and the single-crystal studies have indicated that close-packed Pd surfaces are more active than open ones. CO + NO TPD data and postreaction XPS have shown that the less active surfaces display higher coverages of atomic N under reaction conditions.

This is illustrated in Figure 7, which shows TPD data for ¹⁵NO adsorbed on several different Pd loadings in the Pd/Al₂O₃/ Ta(110) model catalyst corresponding to the indicated average particle sizes. The desorption spectra for N_(a) recombination is presented in Figure 7a; two features are evident. The higher temperature desorption peak occurs above 600 K, higher than the reaction temperatures employed in these experiments, which suggests that the species giving rise to this feature is inactive under these conditions. The ratio of the high-temperature feature to the low-temperature feature is increasing with decreasing particle size, consistent with the idea of having an enhancement for the formation of the stable nitrogen species on the smaller particles. Similar results have been recorded for the single crystals. The Pd(100) surface, which is ~ 5 times less active than the (111) plane, displays a significantly higher ratio of the higher temperature to the lower temperature N2 recombination feature in a similar TPD experiment; additionally, coadsorption of CO does not appreciably alter these results.¹⁹

Another indicator of an increased $N_{(a)}$ coverage on the smaller particles is the absence of ${}^{15}N_2O$ in the TPD spectra, evident in Figure 7b. For the smallest particles studied in the 1.1 equivalent monolayer (ML) loading, ${}^{15}N_2O$ desorption is beneath the detection limit, suggestive of a relatively low coverage of molecularly adsorbed ${}^{15}NO$ on the surface. Conversely, the largest particles in the 22 ML Pd coverage display significant activity for N₂O production. Similar results have been reported for NO adsorbed on Pd/ α -Al₂O₃³² and Pd/SiO₂/Mo(110) model catalysts of the type described here.³³

The reaction orders for CO and NO were determined for the 5% loaded catalysts. Plots for activity vs partial pressure for each reactant are presented in Figure 8. The data reveal a positive one-half-order dependence on NO concentration and a negative first-order dependence in CO under the conditions described. Similar findings have been reported for Pd single crystals, although the degree of CO inhibition is not as pronounced.¹⁹

The temperature-dependent selectivities between the reaction pathways for N_2 and N_2O formation for each catalyst are presented in Figure 9. No clear correlation between selectivity



Figure 8. Partial pressure dependence in each reactant for the CO + NO reaction over the 5% Pd/γ -Al₂O₃ catalyst at 550K.



Figure 9. Selectivity for N_2 formation vs temperature for the CO + NO reaction over each powder catalyst.

and particle size is evident. At 550 K there is no significant difference in selectivity among the catalysts. As the reaction temperature is increased, the selectivity for N₂ formation decreases for the 1% and 5% loaded catalyst, but does not change appreciably for the other two catalysts. The change is not large; the highest N₂ selectivity observed for any system was 43% and the lowest 28%.

 N_2 selectivity has also been found to be independent of particle size for supported Rh catalysts. The reaction has been observed to favor N_2O formation at low temperatures (75% N_2O at 450 K) and N_2 formation at higher temperatures (100% N_2 at 550 K). 10,34,35

4. Conclusions

The structurally insensitive nature of the $CO + O_2$ reaction over Pd has been exploited to determine the relative dispersions in several Pd/Al₂O₃ powder catalysts by measuring the rate of the reaction. This method, assuming particles of hemispherical shape, yields average particle sizes that are consistent with observations using TEM. For the CO + NO reaction over the same catalysts, a pronounced structure sensitivity is evident that results in higher activities over larger Pd particles, comparable to that previously observed for supported Rh catalysts. While the origin of this particle size dependence has not been entirely clarified, there has been some indication from model catalyst studies that the preferred formation and stabilization of an inactive atomic nitrogen species on the smaller particles, with their higher step/edge defect densities, plays a role in determining the reaction rates. The activity loss for the $CO + O_2$ reaction after the catalyst has been exposed to the CO + NO reaction, and subsequent recovery with increasing time-on-stream is consistent with the formation of an inhibiting species on the surface that is formed during the latter reaction and is removed by the former.

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