

## **Experimental and Theoretical Study of CO Oxidation on PdAu Catalysts with NO**

### **Pulse Effects**

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### **Abstract:**

The effect of NO on CO oxidation was studied for Pt, Pd and PdAu catalysts. It was found that NO inhibits significantly the CO oxidation reactivity on both Pt and Pd catalysts. On PdAu catalyst, however, the presence of NO resulted in an enhancement of CO oxidation activity. In order to gain an atomistic understanding of this effect, density-functional-theory (DFT) calculations were performed on the adsorption and reaction properties of NO and CO on these metal surfaces. We have identified that the inhibition effects on Pt and Pd catalysts are due to stronger NO binding energy, and that the enhanced reactivity on PdAu is due to the reduced NO oxidation barrier on PdAu leading to NO<sub>2</sub> formation.

### **1. Introduction**

Noble metal catalysts, in particular platinum (Pt) and palladium (Pd), have been used traditionally in the automotive industry for pollution control. Gold (Au) on the other hand, has not been considered as an effective catalyst until the mid 1980s. The work from two laboratories during this period [1,2] have demonstrated a considerable potential to use gold as catalysts, particularly when prepared in the form of highly dispersed nanoparticles supported on metal oxides. Despite a rapid progress made in gold catalysis through both academic and industrial research, this field is relatively new compared to the research on platinum group metals (PGMs) for automotive pollution control. Specifically, industrial use of gold as automotive exhaust gas

catalyst is hindered by its instability under high temperature conditions. Due to the size dependence of melting temperature, the melting point of 2-nm diameter Au particles is estimated to be as low as 600K [3]. In contrast, Pd-Au alloy catalysts have attracted much interest for their high stability under severe conditions. Pd-Au catalysts are frequently used as catalysts, for example, for CO and hydrocarbon oxidation, synthesis of vinyl acetate monomer, hydrocarbon hydrogenation, cyclotrimerization of acetylene, or CCl<sub>2</sub>F<sub>2</sub> (CFC-12) hydrodechlorination [4-9]. Pd and Au are completely miscible as a solid solution, and Pd is generally considered the catalytic center while the influence of Au is explained through either “ensemble” or “ligand” effects [10-12]. “Ensemble effects” refer to changes in the catalytic properties of an ensemble of atoms on the PdAu surface when the chemical composition of the ensemble changes. As for the “ligand effect”, the addition of Au modifies the electronic properties of Pd atoms on the surface due to alloying. These changes lead to significant change of the catalytic activity on PdAu surface.

In this paper, we studied the effect of nitric oxide (NO) on the CO oxidation reaction on Pt, Pd, PdAu catalysts with pulse experiments in the temperature range from 50°C to 200°C. A step NO pulse of 375 ppm was introduced in the experimental system when CO oxidation attains steady state at a given temperature as we explain the details later. It was found that NO inhibits significantly the CO oxidation reactivity on Pt and Pd catalysts. On PdAu catalyst, however, the presence of NO resulted in an enhancement of CO oxidation activity. In order to gain an atomistic understanding of the NO effect on Pt, Pd and PdAu surfaces, we have performed density-functional-theory (DFT) calculations on the adsorption and reaction properties of NO and CO on these metal surfaces. Our simulation results indicate that in the temperature range we have experimentally studied, NO molecules readily compete with CO molecules for surface binding sites, and that the stronger NO binding leads to inhibition of CO oxidation on Pt and Pd. On PdAu surface, the NO oxidation barrier (0.84 eV) is significantly reduced compared to those on Pt and Pd (1.31 eV and 1.58 eV) leading to fast oxidation of adsorbed NO to NO<sub>2</sub>. NO<sub>2</sub> can promote CO oxidation through  $\text{CO} + \text{NO}_2 \rightarrow \text{CO}_2 + \text{NO}$  reaction. Our simulation results agree well with our experimental observations and support the hypothesis of NO promotion effect on PdAu catalysts.

## 2. Experimental Method

For the CO oxidation experiments, catalyst nanoparticles are prepared on alumina support using MI-386 (Rhodia,  $180 \text{ m}^2/\text{g}$ )  $\text{Al}_2\text{O}_3$ . Pd-Au (1.67 wt- % Pd, 2.0 wt- % Au) catalyst was prepared by reduction of  $\text{Pd}(\text{NO}_3)_2$  and  $\text{HAuCl}_4$  (Heraeus) in the presence of  $\text{N}_2\text{H}_4$ ,  $\text{NaBH}_4$  and  $\text{NaOH}$  (Sigma-Aldrich). Prepared samples were dried overnight in an oven at 393 K, calcined in air at 773 K for 2h with a heating rate of 8 K / min and then saved for reaction and characterization use. Pt (3 wt- %) catalyst was prepared by wet impregnation and Pd (3 wt- %) catalyst was prepared by ascorbic acid reduction.

The catalytic activity was determined in a fixed bed U-type quartz micro reactor. Sample (10mg of catalyst diluted by 90mg of  $\alpha$ -alumina) was supported with quartz wool. Powders are sieved between size of 0.15 and 0.18 mm to prevent pressure drop in the reactor bed. Gas analysis for CO and  $\text{CO}_2$  was performed by Agilent 3000A Micro GC using thermal conductivity detectors. CO was separated by molecular sieve column (10 m, 0.32 mm i.d.), and  $\text{CO}_2$  by plot Q column (5 m, 0.32 mm, i.d.). An Eco Physics CLD 822 cmh dual channel Chemiluminescence  $\text{NO}_x$  analyzer allowed the simultaneous detection of NO,  $\text{NO}_2$  and  $\text{NO}_x$ .

Total flow rate was  $200 \text{ ml min}^{-1}$ , corresponding to a GHSV of  $30\,000 \text{ h}^{-1}$ . The reactant concentrations, if they are present in the reaction, were 1000 ppm Carbon monoxide (CO), 10 vol % Oxygen ( $\text{O}_2$ ), 375 ppm Nitric Oxide (NO) in Helium as balance. In the NO pulse experiment, the procedure is repeated at different temperatures. At each isothermal temperature, a pulse of NO was introduced when steady state of CO oxidation activity was reached with just CO and  $\text{O}_2$ . The effect of NO can be directly measured as the CO oxidation changes when the NO pulse was introduced. For separate NO oxidation experiments, light off activity is compared between  $80^\circ\text{C}$  and  $350^\circ\text{C}$  with temperature ramp up rate of 10 K / min.

## 3. Computational Method

In order to model the NO competitive adsorption with CO, we calculated NO adsorption energies and NO oxidation barriers on Pt(111), Pd(111) and PdAu(111), respectively. We have used a  $p(2 \times 2)$  unit cell with 4 Pt atoms per layer. The metal slab consists of three layers, with

the bottom layer fixed at its crystallographic bulk lattice positions, and the rest of the atoms free to relax in all directions. A vacuum layer of 11 Å has been introduced to eliminate image interactions. Self-consistent DFT calculations were carried out with revised Perdew-Burke-Ernzerhof (RPBE) generalized gradient correction for the exchange-correlation functional, which has been shown to give accurate values for adsorption energies of many molecular species [13, 14]. The Vienna ab initio simulation package (VASP) was used for the calculations [15]. The Kohn-Sham single electron wave function was expanded by plane waves with an energy cutoff of 400 eV, and this cutoff energy gives a good convergence for both adsorption energies and activation barriers. A 4 × 4 × 1 k point mesh was used to sample the first Brillouin zone. The geometry optimization was terminated when the Hellmann-Feynman force on each atom was less than 0.05 eV / Å. The adsorption energy is calculated using the following equation:

$$\Delta E_{ads} = E_{total} - E_{sub} - E_{mol}$$

where  $E_{total}$ ,  $E_{sub}$ , and  $E_{mol}$  refer to the energies of the total system, the substrate, and the molecule, respectively.

NO oxidation activation barrier is calculated by locating the saddle point on metal surfaces by the dimer method [16]. The transition state is verified by subsequent frequency calculations diagonalizing the mass weighted second derivative force matrix.

#### 4. Results and discussion

NO pulse experiments were performed on Pt, Pd and PdAu catalyst. First the sample was exposed to CO and O<sub>2</sub> at a steady temperature for 15 min; NO was then introduced to the mixture. The results in Fig. 1 show that on Pt catalyst CO oxidation is significantly inhibited by NO. During the first isothermal CO oxidation at temperature (around 120°C) which starts around 300 min, the CO<sub>2</sub> concentration dropped from around 200 ppm to 50 ppm at 310 min when NO pulse was introduced. For the next fixed temperature (around 130°C) starting at 345 min, CO was totally converted to CO<sub>2</sub> (1000 ppm) before NO pulse. However, once the catalyst was exposed to NO at 355 min, CO<sub>2</sub> production was reduced down to below 200 ppm. This reduction was caused by the competitive adsorption of NO and CO. As summarized in the first row of Table I,

DFT calculations show that the strongest binding site (fcc, 1.53eV) for NO is stronger than that of CO (bridge 1.42eV) at zero coverage limit (ZCL) condition on Pt surface. This means that towards or near light off condition, where Pt surface was not fully saturated by CO adsorption, NO can compete with CO for adsorption sites effectively, and high NO coverage leads to a reduction in CO<sub>2</sub> oxidation reactivity. Figure 2 shows the CO oxidation experiment data on Pd catalyst with NO pulse at three isothermal oxidation conditions with similar inhibition effect by NO pulse. The DFT data in the 2<sup>nd</sup> row of Table I show that a similar explanation is applicable to Pd surface with stronger NO binding (hcp, 1.94 eV) than CO binding (hcp, 1.68 eV).

For the PdAu experiment (Fig. 3), the NO pulse shows qualitatively different effects on CO oxidation. At the first isothermal section (295 – 340 min at temperature of 120°C), the produced CO<sub>2</sub> is dropped less than 10% after the introduction of NO pulse at 305 min. On the other hand, for the third isothermal section (390 – 430 min with temperature 20°C higher), enhanced CO oxidation activity was observed with NO pulse, and CO<sub>2</sub> concentration is increased from 600 ppm to 800 ppm at 405 min. It is clear that Au is playing a role in changing surface chemistry for PdAu catalyst. Calculations of NO adsorption show that NO also competes with CO on PdAu similar to the adsorptions on Pt and Pd as shown on the 3<sup>rd</sup> row of Table I. Consequently, one may expect to see a similar NO inhibition effect on CO oxidation on PdAu surface in contradiction to the experimental data in Fig. 3.

This puzzling experimental observation on PdAu catalyst can be explained by the NO oxidation reaction on catalyst surfaces. Table II shows NO + O → NO<sub>2</sub> reaction energies on Pt, Pd, and PdAu surfaces. On Pt and Pd surfaces, the activation barrier are large (1.31 eV and 1.58 eV) and the reaction product is less stable than the reactants. Such energetic will effectively eliminate NO oxidation on Pt and Pd surfaces relative to CO oxidation reactions. However, a very low NO oxidation barrier on PdAu surface (0.84 eV as shown in Table II) indicates that adsorbed NO is easily converted to NO<sub>2</sub>, which is a strong oxidant and can readily react with CO at room temperature. This reduction in NO oxidation barrier is primarily due to the weakened oxygen binding to the PdAu surface, since the atomic oxygen sits a Pd-Au bridge site in the transition state (Fig. 5).

These different activation barriers are not in conflict with higher NO oxidation activity of Pt than PdAu (shown in Fig. 6) which was observed in a separate experiment. Mulla *et al.* [17] indicated in a Pt study that catalyst's oxygen uptake has an upper bound to keep the catalyst active. In other words, the formation of PtO at low temperature and in presence of strong oxidant NO<sub>2</sub> resulted in a less active catalyst. Pd catalyst, compared to Pt, is more susceptible to oxidation, and consequently it is less active for NO oxidation. Au, on the other hand, will be able to help maintain Pd in the reduced state through "ligand effect" so that PdAu becomes a better NO oxidation catalyst than Pd. Fig. 6 shows NO oxidation activity in the sequence from high to low activity: Pt > PdAu > Pd. In the NO pulse experiment, this sequence is changed due to the presence of CO. CO binds stronger on Pt than PdAu, and Pt has higher CO coverage than PdAu leading to less accessible sites for NO and O<sub>2</sub>. It is also shown in Fig. 6 that catalyst doesn't have significant activity until 200°C which is much higher than the studied temperature range in the NO pulse experiment. The enhanced NO oxidation activity in presence of CO especially for PdAu can be explained by weakened oxygen-metal bonds caused by the lateral interaction of O-CO. It was reported by Ovesson *et al.* [18] in a theoretical study that NO oxidation on metal is being inhibited (endothermic) by the strong oxygen-platinum bonds, and becomes exothermic only at about 0.25 ML O coverage at temperatures above 400K due to the lateral repulsive O-O and O-NO interactions. It is believed that coverage effect by CO can lower O-metal bond and activates NO oxidation reaction at lower temperature.

## 5. Summary

The effect of NO on CO oxidation was studied for Pt, Pd and PdAu catalysts with NO pulse experiments. DFT calculations are performed on the adsorption and reaction properties of NO and CO on these metal surfaces. DFT results explain the NO inhibition effect on CO oxidation by stronger NO binding energy than CO binding energy on Pt and Pd surface. The NO promotion effect on PdAu surface was explained by the reduced NO oxidation barrier on PdAu than those on Pt and Pd. The NO<sub>2</sub> produced on PdAu reacts with CO to increase carbon dioxide (CO<sub>2</sub>) production. The combined experimental and theoretical study of NO effect on CO oxidation on Pt,

Pd, and PdAu catalysts illustrates the explanatory and predictive power of computational modeling as well as providing the detailed insights on the underlying reaction mechanisms on catalyst surfaces.

		Top* (eV)	Bridge (eV)	Fcc (eV)	Hcp (eV)
Pt (111)	NO	-1.23	-1.39	-1.53	-1.35
	CO	-1.36	-1.42	-1.38	-1.38
Pd (111)	NO	-1.23	-1.66	-1.92	-1.94
	CO	-1.17	-1.54	-1.63	-1.68
PdAu (111) 1:1 ratio	NO	-1.10	-1.33	-1.32	-1.25
	CO	-1.03	-1.19	-1.20	-1.23

\* Please refer to figure 4 for the definition of the type of the sites.

Table I: Adsorption energies of NO under zero coverage limit on Pt(111), Pd(111) and PdAu(111), respectively.

	$\text{CO}^* + \text{O}^* \rightarrow (\text{CO}_2^*)$			$\text{NO}^* + \text{O}^* \rightarrow (\text{NO}_2^*)$		
	$E_{\text{act}}$ (eV)	Reactant (eV)	Product (eV)	$E_{\text{act}}$ (eV)	Reactant (eV)	Product (eV)
Pt (111)	1.07	-2.43	-3.13	1.31	-2.60	-1.92
Pd (111)	1.43	-2.72	-3.13	1.58	-3.02	-1.96
PdAu (111) 1:1 ratio	1.18	-1.63	-3.13	0.84	-1.53	-1.76

Table II: CO and NO oxidation barrier on Pt(111), Pd(111) and PdAu(111), respectively.

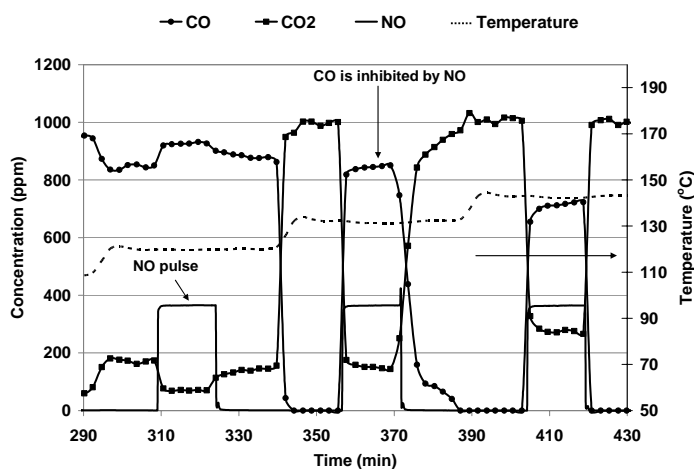


Figure 1: NO pulse experiment on 3 wt-% Pt catalyst at different temperatures. Three NO pulses are investigated under three isothermal conditions: 295-340 min at  $T \sim 120^\circ\text{C}$ , 340-390 min at  $T \sim 130^\circ\text{C}$ , and 390-430 min at  $T \sim 140^\circ\text{C}$ .

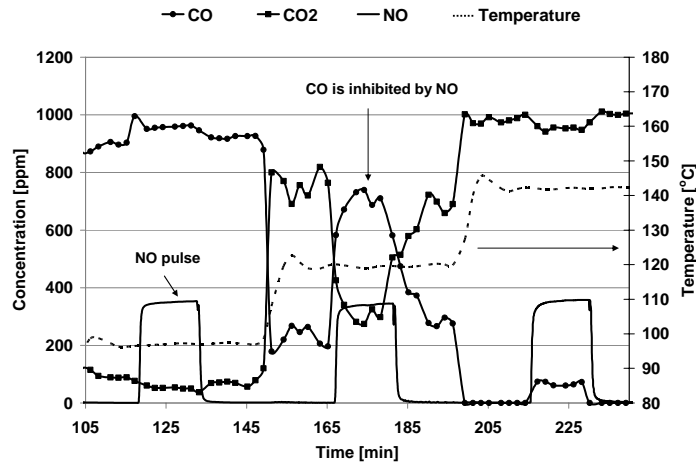


Figure 2: NO pulse experiment on 3 wt-% Pd catalyst at different temperatures. Three NO pulses are investigated under three isothermal conditions: 105-150 min at  $T \sim 95^\circ\text{C}$ , 160-200 min at  $T \sim 120^\circ\text{C}$ , and 205-245 min at  $T \sim 140^\circ\text{C}$ .

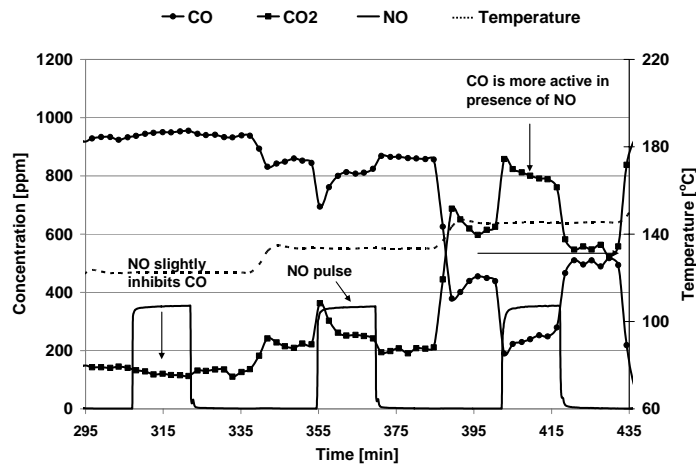


Figure 3: NO pulse experiment on 1.67 wt-% Pd, 2% wt-% Au catalyst at different temperatures. Three NO pulses are investigated under three isothermal conditions: 295-340 min at  $T \sim 125^\circ\text{C}$ , 340-390 min at  $T \sim 135^\circ\text{C}$ , and 390-435 min at  $T \sim 145^\circ\text{C}$ .

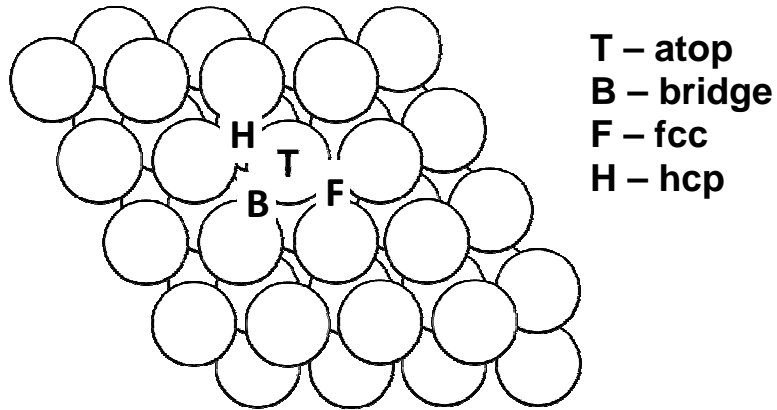


Figure 4: Different adsorption sites on a (111) surface.

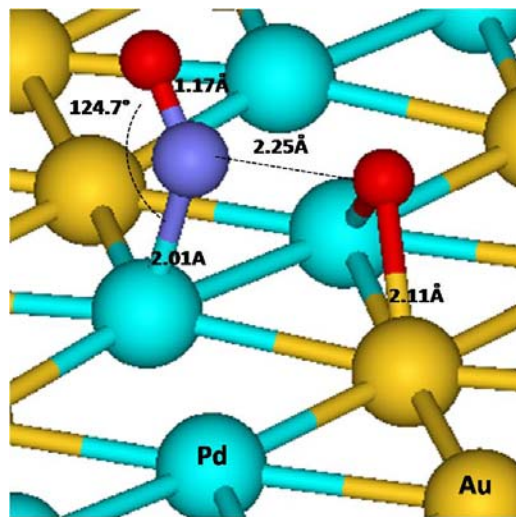


Figure 5: Transition state configuration for NO oxidation on PdAu(111) surface.

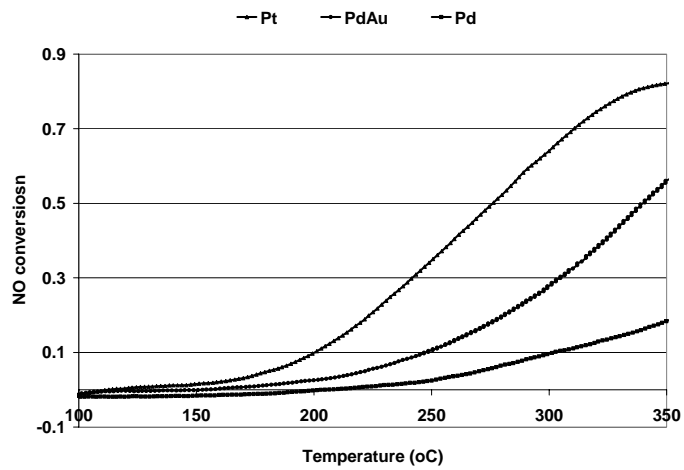


Figure 6: NO Oxidation comparisons for Pt, Pd and Pd-Au catalyst. 375 ppm NO, 10 vol % O<sub>2</sub>.

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