

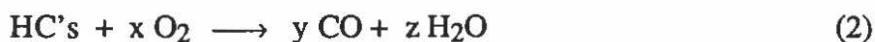
## Operation of Three-Way Catalysts in the Control of Automobile Exhaust Gas Composition

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Increasing public concern about air pollution has fueled legislation demanding ever tighter control of automobile emissions. Auto emissions are controlled by more thorough combustion within the auto engine itself and through the use of catalytic converters. These catalytic converters remove CO, unreacted hydrocarbons (HC's), and NO<sub>x</sub> from the auto exhaust stream by catalyzing the following reactions:

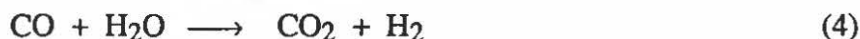


As catalytic converters came to be widely used in automobiles in the mid-1970's, noble metal catalysts, mainly Pt or Pd supported on alumina, were used to oxidize carbon monoxide and HC's. These catalysts had to be able to withstand the high temperatures (300-900 °C) of automobile exhaust and operate under both oxidizing and reducing conditions without loss of activity. Although the oxidizing Pt catalysts were very efficient in removing CO and HC from automobile exhaust, they were inefficient in the removal of NO<sub>x</sub>. Therefore, in less than five years following the introduction, the Pt (or Pd) catalysts gave way to a newer type of catalyst, the three-way catalyst (TWC) [1-2, 21].

Three-way catalysts derive their name from the fact that they effectively catalyze reactions that remove CO, HC, and NO<sub>x</sub> from the exhaust stream. In order for the catalyst to function properly, the ratio of reducing and oxidizing reactants is kept near stoichiometry by maintaining an air/fuel ratio of about 14.7 [1]. Under these conditions NO is reduced at the same time that CO, HC, and H<sub>2</sub> are oxidized. Typical modern TWC's contain Rh, Pt, and CeO<sub>2</sub> on a high surface area alumina support which is then pelletized or coated on ceramic honeycomb monoliths inside the catalytic converter (Figure 1) [2].

After more than a decade of use, a complete picture of the mechanism of action for the three-way catalysts is still missing; however, there is a growing body of data that gives useful insight into the complex nature of TWC's.

One way of simplifying the study of TWC's is to examine adsorption and model reactions on single crystals of Pt, Pd, or Rh. There already exists an overwhelming amount of data concerned with this topic [7-8,16-19]. Although this information is potentially useful, one has to be cautious about applying single crystal results to an operating TWC [23]. There is often a significant amount of metal-support interaction in TWC's [3-5,13,20], which may enhance the differences between the single crystal and the highly dispersed forms of the noble metals. For instance, rhodium oxides have such strong interactions with alumina that under high temperature oxidizing conditions Rh will diffuse into the alumina unless stabilized with ceria (CeO<sub>2</sub>). The addition of ceria to TWC's produces several other effects. Ceria also promotes the water-gas shift reaction (equation 4) on Rh catalysts [24] and provides oxygen storage, where oxygen can migrate from ceria to Rh under reducing conditions [25].



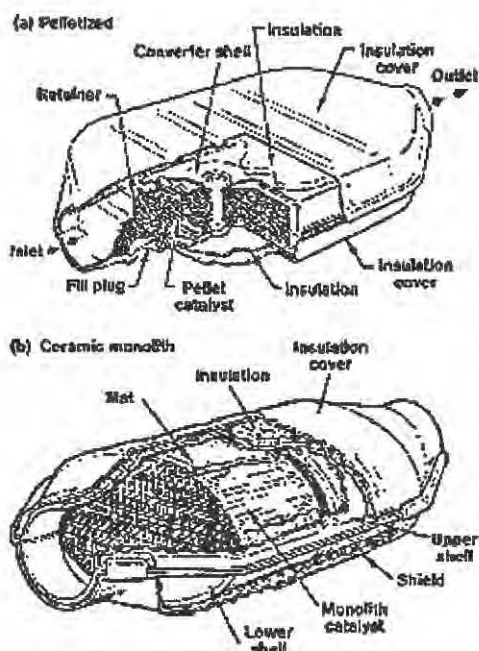


Figure 1. Drawing of Pelletized and Monolithic Catalytic Converters

It appears that certain reactions, especially those involving NO, are quite structure sensitive and complex [6]. Indeed reactions involving NO, particularly on Rh, are often complicated by the fact that NO can adsorb molecularly or dissociatively [1,7,8]. Electron energy loss spectroscopy studies of Rh(111) have shown that NO adsorbs dissociatively at low coverages, while at higher coverages, NO adsorbs molecularly on Rh(111) [16]. Unlike NO, CO predominantly adsorbs molecularly on the noble metals; however, several different Rh-CO species can form, such as  $\text{Rh}(\text{CO})_2$ , Rh-CO, and  $\text{Rh}_2\text{CO}$  [14]. The number of surface species is even greater because there is also  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , Pb, and  $\text{SO}_2$  in the exhaust gas, which can also adsorb and compete with NO and CO [22].

Many different intermediates can be formed from the catalyzed reactions of the adsorbed species. For example, isonitryls [9] and dinitrosyls [10] have been identified on supported noble metal catalysts during the reduction of NO by CO. For the isocyanates, however, it has been shown that they mainly reside on the support and not actually on the noble metal, where NO reduction occurs [11].

In addition to the advances made over the last twenty years, there has been progress in finding alternative, cheaper catalysts that do not contain rhodium. One such catalyst is a palladium-only catalyst being developed by AlliedSignal [12]. Unfortunately, these new catalysts still have some problems (e. g. S poisoning), and it may be several years before they are commercially viable.

## References

1. Recent Review: Shelef, M.; Graham, G. W., "Why Rhodium in Automotive Three-Way Catalysts?," *Catal. Rev.-Sci. Eng.* **1994**, *36*(3), 433-457.

2. Taylor, Kathleen C., "Catalysts in Cars," *CHEMTECH* September 1990, 551-555.
3. Yao, H. C., et al., "Surface Interactions in the System Rh/Al<sub>2</sub>O<sub>3</sub>," *J. of Catal.* 1977, 50, 407-418.
4. Yao, H. C., et al., "Metal-Support Interaction in Automotive Exhaust Catalysts: Rh-Washcoat Interaction", *J. of Catal.* 1980, 61, 547-550.
5. Arai, H.; Tominaga, H., "An Infrared Study of Nitric Oxide Adsorbed on Rhodium-Alumina Catalyst", *J. of Catal.* 1976, 43, 131-142.
6. Oh, S.; Eickel, C., "Influence of Metal Particle Size and Support on the Catalytic Properties of Supported Rhodium: CO-O<sub>2</sub> and CO-NO Reactions," *J. of Catal.* 1991, 128, 526-536.
7. Wolf, R. M., et al., "Dissociation of nitric oxide and reaction with hydrogen on Rh(111) and various stepped Rh(111) surfaces," *Surf. Sci.* 1991, 246, 135-140.
8. Schwartz, S. B., et al., "NO + CO Reaction on Rh(111): Steady-State Rates and Adsorbate Coverages," *J. Phys. Chem.* 1988, 92, 389-395.
9. Unland, M., "Isocyanate Intermediates in the Reaction of NO and CO Over Noble Metal Catalysts," *J. of Catal.* 1973, 31, 459-465.
10. Liang, J., et al., "FT-IR Study of Nitric Oxide Chemisorbed on Rh/Al<sub>2</sub>O<sub>3</sub>," *J. Phys. Chem.* 1985, 89, 5840-5845.
11. Dalla Betta, R. A.; Shelef, M., "Isocyanates from the reaction of NO and CO on supported noble-metal catalysts," *J. of Mol. Cat.*, 1975/76, 1, 431-434.
12. Summers, J. C.; Williamson, W. B., "Palladium-Only Catalysts for Closed-Loop Control," Environmental Catalysis: ACS Symposium Series: Denver, CO; March 28-April 2, 1994, 94-113.
13. Cho, Byong K., "Chemical Modification of Catalyst Support for Enhancement of Transient Catalytic Activity: Nitric Oxide Reduction by Carbon Monoxide over Rhodium," *J. of Catal.* 1991, 131, 74-87.
14. Solymosi, F.; Bansagi, T.; Novak, E., "Effect of NO on the CO-Induced Disruption of Rhodium Crystallites," *J. of Catal.* 1988, 112, 183-193.
15. Hendricksen, D.; Eisenberg, R., "The Role of Water in the Rhodium(I) Catalyzed Reduction of Nitric Oxide by Carbon Monoxide: An Isotope Labeling Study," *J. Am. Chem. Soc.* 1976, 98, 4662-4664.
16. Root, T. W., et al., "Electron energy loss characterization of NO on Rh(111): I. NO Coordination and Dissociation," *J. Chem. Phys.* 1986, 85(8), 4679-4686.
17. Root, T. W., et al. "Electron energy loss characterization of NO on Rh(111): II. Coadsorption with Oxygen and CO," *J. Chem. Phys.* 1986, 85(8), 4687-4695.
18. Bowker, M., et al., "NO Adsorption on Rh(110)", *Surf. Sci.* 1991, 257, 33-40.

19. Wickham, D. T., et al., "Adsorption of Nitrogen Dioxide and Nitric Oxide on Pd(111)," *Surf. Sci.* **1991**, *243*, 83-95.
20. Nunan, J., et al., "Physiochemical Properties of Ce-Containing Three-Way Catalysts and the Effect of Ce on Catalyst Activity," *J. of Catal.* **1992**, *133*, 309-324.
21. Kummer, J. T., "Use of Noble Metals in Automobile Exhaust Catalysts," *J. Phys. Chem.* **1986**, *90*, 4747-4752.
22. Oh, S.; Carpenter, J., "Role of NO in Inhibiting CO Oxidation over Alumina-Supported Rhodium," *J. of Catal.* **1986**, *101*, 114-122.
23. Oh, S., et al., "Comparative Kinetic Studies of CO-O<sub>2</sub> and CO-NO Reactions over Single Crystal and Supported Rhodium Catalysts," *J. of Catal.* **1986**, *100*, 360-376.
24. Shido, T.; Iwasawa, Y., "Reactant-Promoted Reaction Mechanism for Water-Gas Shift Reaction on Rh-Doped CeO<sub>2</sub>," *J. of Catal.* **1993**, *141*, 71-81.
25. Zafiris, G. S.; Gorte, R. J., "Evidence for Low-Temperature Oxygen Migration from Ceria to Rh," *J. of Catal.* **1993**, *139*, 562-567.