CO Oxidation on Nanotowers formed from Au/CeO$_2$ Multilayers

Zheng Zhou*, Howard Saltsburg, Maria Flytzani-Stephanopoulos,
*Department of Chemical and Biological Engineering, Tufts University,
Medford, Massachusetts 02155 (USA)*
zheng.zhou@tufts.edu

Introduction

The high activity of supported Au nanoparticles for the catalytic CO oxidation has been described extensively and discussed in terms of the role of the gold particle size and that of the atoms at the periphery of the interface between Au and supports [1-3]. The interaction of a metal particle supported on an oxide was considered by Frost who proposed that the oxygen vacancy concentration in the metal oxide increases at the metal/metal oxide interfacial sites due to the junction effect [4]. However, there is no direct evidence showing that the periphery of the interface between metal and support is the locus of active sites for the CO oxidation reaction in the Au/CeO$_2$ system.

This work focuses on investigating the role of the interface in CO oxidation, using a multilayered structure of Au/CeO$_2$ (also called Au/CeO$_2$ nanotowers). This structure allows one to control quantitatively the following three variables: the total surface area of Au/CeO$_2$, the interfacial length, and the thickness of each Au layer. Zuburtikudis et al. have shown that such a nanotower structure with the edge dimension in nanometer scale reproduced the size effects observed with conventional nanoscale particles [5]. A strong dependence on interface length for CO oxidation on Ir/Al$_2$O$_3$ nanotowers was observed by Chaplin using this approach [6]. In this work, such a structure was adapted to Au/CeO$_2$ catalyst, which allows the three variables to change independently and, thus, enables the evaluation of the role of each variable separately.

Materials and Methods

Au/CeO$_2$ alternating nanolayers were prepared by photolithography and vapor deposition. Photolithography using a contact mask reproduced an array of 10 micrometer square openings on each three-inch diameter silicon wafer. The total number of openings on each wafer is approximately 11 million. Au and CeO$_2$ were deposited alternatively from perpendicular sources into the openings and formed the layered structure. In this work, a set of five-bilayer Au/CeO$_2$ nanotower samples were prepared in such a way that the thickness of each Au or CeO$_2$ layer was kept to 4nm (as indicated by the crystal monitor). SiO$_2$ layers were deposited between Au and CeO$_2$ to vary the interface number from 5 to 9. A cap-layer of 20nm SiO$_2$ was used in all preparations so that only the side surface was accessible to the reactants. Finally, the lift-off step removed the photo resist and left a clean side surface for the reaction. Samples were prepared at the Microsystems Technology Laboratories (MTL) of MIT. The activity tests of CO oxidation were conducted in a recycle reactor. CO and O$_2$ were introduced to the reactor with a pulse injection after the sample was stabilized at the desired temperature in He. The initial reaction rate was calculated from the concentration curve recorded by an on-line mass spectrometer.

Results and Discussion

The multilayer films were a little wavy, but are conformal as shown in the TEM picture of a cross-sectional view of Au/CeO$_2$ multilayer (Fig.1(a)). A clear interface was formed between Au and CeO$_2$, which can be taken as a straight line. No activity for CO oxidation was observed under the test conditions when the Au and CeO$_2$ films were totally disconnected by inserting SiO$_2$ layers. The CO oxidation rates along the interfaces were studied quantitatively. A set of five bi-layer Au /CeO$_2$, with the same surface area, but different Au-CeO$_2$ interface lengths was tested. The number of Au-CeO$_2$ interfaces was varied from 5 to 9 by inserting SiO$_2$ layers. As shown in Fig. 1(b), the oxidation rate taken from the fresh samples increased linearly with the number of Au/CeO$_2$ interfaces, which indicates that activity derives from the interaction of the two phases. When the reaction rate was normalized by the interfacial length, it was found that the rate was three orders of magnitude higher than on conventional supported Au catalysts found in the literature [7]. The difference may be caused by over-estimation in calculating the interface length in the two structures. However, there is evidence that the CeO$_2$ layer in the nanotower structure is polycrystalline and highly defective, which could be responsible for the higher activity when contacted with gold. Further studies of the deposited films and the local structure of Au/CeO$_2$ interfaces are underway to understand the deactivation of this catalyst. In preparing the nanotower structure, a continuous film is needed to simulate the particle size in the same range. Therefore, the layer thickness cannot be < 2nm, which limits the application to studying the activity of gold particles bigger than 2 nm.

Fig. 1: (a) Cross-sectional view of multilayer Au/CeO$_2$ films. Sample was prepared as described in ref [8]; **(b)** CO production rate as a function of number of interfaces. CO production rate was calculated based on nanotowers on one wafer because on each wafer, the total surface area of Au/CeO$_2$ is the same. Rates were measured at 160 ^{o}C, with a molar gas ratio of CO:O$_2$:He = 1:2:97.
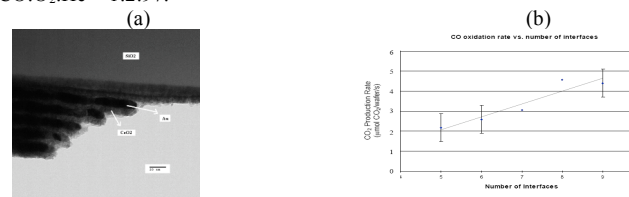
Significance

This work has produced a structure in which the interfacial length of Au and CeO$_2$ is controlled while keeping the same surface area of both the Au and CeO$_2$ layers. The CO oxidation reaction rate scales with the interfacial length.

References
1. Haruta M. *et al.*, *J. Catal.* 144, 175 (1993).
2. Valden M., Lai X., Goodman D. W., *science* 281, 1647 (1998).
3. Lopez N. *et al.*, *J. Catal.* 223, 232 (2004).
4. Frost J. C., *Nature* 334, 577 (1988).
5. Zuburtikudis I., Saltsburg H., *Science* 258, 1337 (1992).
6. Chaplin M., PhD dissertation, University of Rochester, 1997.
7. Liu W., Flytzani-Stephanopoulos M., *J. Catal.* 153, 304 (1995).
8. Walck S. D., McCaffrey J. P., *Thin Solid Films* 308-309, 399 (1997).