Nanotubes as Catalysts

Gold-Nanotube Membranes for the Oxidation of CO at Gas–Water Interfaces[**]

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An exciting discovery in the area of heterogeneous catalysis is the observation that nanoparticles of gold on high-surface-area supports exhibit high activity for oxidation of CO with O_2 ($CO + 1/2\,O_2 \rightarrow CO_2$) at room temperature.[1,2] This discovery is of particular relevance for the production of fuel-cell-grade hydrogen, since carbon monoxide must be removed from hydrogen streams generated by catalytic reforming of hydrocarbons.[3] The origins for the unique catalytic properties of supported gold catalysts are still unresolved. These properties have been related to changes in the electronic properties, the presence of defect sites, and the existence of strain for metallic gold nanoparticles.[4–8] Unique catalytic properties have also been related to the presence of sites associated with the catalyst support, such as cationic gold species, and sites at gold–support interfaces.[9,10]

Here we show that it is possible to study the catalytic properties of metallic gold, without interference from a catalyst support, by using nanotubes of gold in polycarbonate membranes. These nanotubes exhibit catalytic activity for the oxidation of carbon monoxide by O_2 at room temperature, and this activity is enhanced by liquid water, promoted by increasing the pH of the solution, and increased using H_2O_2 as the oxidizing agent. The rate can also be increased by depositing KOH within these nanotubes. These rates are comparable with those found in heterogeneous catalysis studies with gold nanoparticles on oxide supports, which suggests that the high activity of these latter catalysts may be related to the promotional effect of hydroxyl groups.

Gold nanotubes of uniform size were prepared via a template-synthesis method by electroless deposition of gold[11] within the pores of a 10-μm-thick, track-etched polycarbonate membrane containing 220-nm-diameter pores.[12] All surfaces of the template membrane were first sensitized with a Sn^{II} salt, activated by formation of a metallic Ag layer, followed by electroless deposition of gold for a period of 2 h. The gold nanotubes were cleaned with a 25% HNO_3 solution for 15 h.[13] Hydrophobic or hydrophilic self-assembled monolayers were formed on gold nanotubes by rinsing the samples in ethanol for 20 min, followed by immersion for 17 h in solutions of ethanol containing $HS(CH_2)_{15}CH_3$ or $HS(CH_2)_{15}COOH$, respectively.[14]

Gold nanotubes embedded within the pores of the polycarbonate template membranes were exposed by reactive ion etching (RIE) using an oxygen plasma to selectively etch approximately 2.3 μm of polycarbonate, leaving the gold nanotubes intact.[15] Figure 1 shows images from field-emission scanning electron microscopy (SEM) of the top surface of a template membrane after electroless deposition of gold followed by RIE. The images in Figure 1 reveal a high level of surface roughness; the length scale is ≈53 nm.

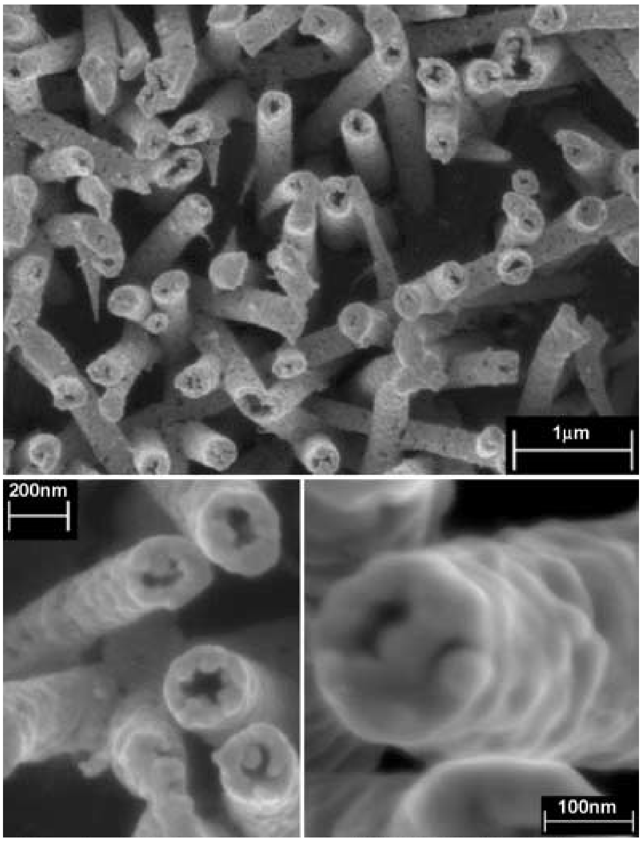

Figure 1. Field-emission SEM images of gold nanotubes at different magnifications. Micrographs were taken on the etched side of the membrane.

The membrane reactor used to study CO oxidation over gold nanotubes is shown schematically in Figure 2.[12] Table 1 shows results for the rate of CO oxidation by O_2 at 300 K and 1 bar total pressure for a $CO{:}O_2$ ratio of 1:1. The rate of CO_2 production is low in the absence of water, but it is increased by about 50% in the presence of water vapor at a pressure of 30 mbar (the vapor pressure of water at 298 K). The rate is significantly higher (by a factor of 10) when the $CO{:}O_2$ gas stream saturated with water-vapor at 298 K is passed over a gold membrane that had been previously in contact with

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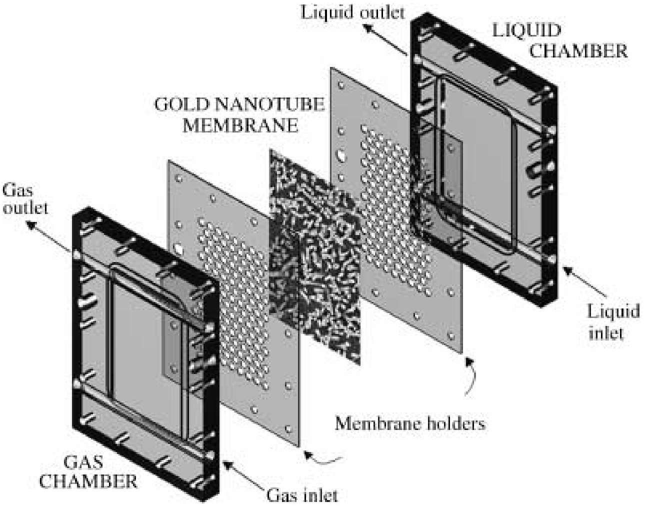

Figure 2. Diagram of the membrane reactor used to study CO oxidation on gold nanotubes positioned at the interface between two reaction chambers.

Table 1: Rate of CO_2 production for combinations of gas and liquid streams. Data collected using a gold membrane treated by RIE, with the etched side of the membrane facing the gas chamber.

Gas chamber[a]	Membrane	Liquid chamber[b]	CO_2 rate[c]
$CO:O_2$	Au	None	3
$CO:O_2$ H_2O (30 mbar)	Au[d]	None	30
$CO:O_2$ H_2O (30 mbar)	Au/KOH[d]	None	77
$CO:O_2$	Au	H_2O	47
$CO:O_2$	Au	H_2O (pH 13)	230
CO[e]	Au	H_2O (0.5 % H_2O_2)	590

[a] Total gas flow rate = 100 $cm^3\,min^{-1}$ (STP); $CO:O_2$ ratio = 1:1. [b] Liquid flow rate = 2 $cm^3\,min^{-1}$. [c] In units of μmol of CO_2 per gram of Au per minute. [d] Liquid water or KOH solution filled inside gold nanotubes. [e] Total gas flow rate = 100 $cm^3\,min^{-1}$ (STP); CO:He ratio = 1:1.

liquid water,[12] which suggests that liquid water within the gold nanotubes is responsible for the observed enhancement in the rate of CO oxidation. Indeed, a high rate of CO oxidation is achieved when the membrane containing the gold nanotubes is positioned at the interface between a $CO:O_2$ gas stream and a stream of flowing liquid water. Furthermore, the rate of CO oxidation by O_2 in the presence of liquid water is increased further (by a factor of 5) when the pH value of the solution is increased to 13. High rates of CO oxidation over the gold nanotubes were also achieved by bringing a gas stream containing CO (balanced with He to CO/He = 1) on one side of the membrane into contact with an aqueous solution containing 0.5 wt % H_2O_2 on the other side ($CO + H_2O_2 \rightarrow CO_2 + H_2O$).

The promotional effect of liquid water at high pH values on the rate of CO oxidation by O_2 can also be achieved by depositing KOH within the gold nanotubes, by first bringing gold nanotubes into contact with an aqueous solution containing KOH (0.1M). As seen in Table 1, when the membrane containing the gold nanotubes is subsequently exposed to a gas stream containing CO and O_2 saturated with water vapor at 298 K, the rate of CO oxidation is about three times higher than for the original gold membrane. Thus by using gold nanotubes that have been filled with an aqueous KOH solution and using a gas stream saturated with water vapor, high rates of CO oxidation over a long reaction time (> 40 h) were observed, with a slow decline of the rate due to a possible loss of the liquid water from the nanotubes. In this way, by taking advantage of water within gold nanotubes, it is possible to achieve high rates of CO oxidation on metallic gold without the need for a continuous flow of liquid water over the sample at high pH values.

It has recently been shown that the energetics for water dissociation and the activation energy barrier for this process are more favorable on Pt surfaces in liquid versus gas phases, and negatively charged hydroxyl groups formed by the heterolytic dissociation of liquid water may be reactive intermediates for the oxidation of CO to CO_2.[16] This behavior is apparently operative on gold surfaces as well, since we detect the formation of small amounts (0.5 μmol min^{-1} per g of gold) of H_2 when gold nanotubes are brought into contact with gaseous CO on one side of the membrane and liquid water on the other side, which leads to water-gas shift at room temperature ($CO + H_2O \rightleftarrows CO_2 + H_2$). Negatively charged hydroxyl groups may also be supplied to the metal surface by increasing the pH value of the solution. While the details of the mechanism for CO oxidation by O_2 over gold are still not fully understood, it appears that one of the key steps is the activation of O_2.[8,17–19] We suggest that the presence of hydroxyl groups facilitates the interaction of CO with O_2, thus leading to the formation of CO_2 and peroxyl species, since we have observed the formation of small amounts (1.5 μmol min^{-1} per g of gold) of hydrogen peroxide in the liquid phase during oxidation of CO by O_2 on gold nanotubes in the presence of liquid water. In addition, gold is an effective metal for the catalytic synthesis of hydrogen peroxide from hydrogen and oxygen.[20] Finally, we note that the higher catalytic activity for the oxidation of CO by H_2O_2 compared to oxidation by O_2 in liquid water may be related to the weaker O–O bond in the former oxidizing agent.

The participation of hydroxyl groups in the oxidation of CO by O_2 is in accordance with results from studies of catalysts consisting of gold supported on high-surface-area oxide supports. Previous studies have found that the rate of CO oxidation by O_2 is strongly influenced by the nature of the catalyst support, which suggests the importance of catalytic sites at the gold–support interface.[21,22] Furthermore, the rate of CO oxidation by O_2 is enhanced by the presence of water vapor[23–26] and by treatment of the catalyst in water-containing atmospheres.[27,28] Findings such as these have led researchers to suggest that CO oxidation is promoted by hydroxyl groups associated with cationic gold species on the support or associated with the support itself. Our results provide strong evidence for the role of hydroxyl groups in promoting the rate of CO oxidation by O_2 on gold, and these hydroxyl groups need not only be associated with the support but may be supplied by liquid water, especially at high pH values.

It is noteworthy that the rates of CO oxidation by O_2 measured for gold nanotubes in the presence of liquid water at high pH values are comparable to those rates measured in heterogeneous catalysis reactions using gold nanoparticles on oxide supports. The BET surface area of the gold-nanotube membrane used in our reaction studies is $5.2\,m^2g^{-1}$ of gold (8×12 cm sheet containing 0.19 g of gold). Assuming a site density of 10^{15} sites$\,cm^{-2}$ for a gold surface, we thus estimate that the turnover frequency for CO oxidation by O_2 in liquid water at high pH values is about $0.04\,s^{-1}$. Indeed, the turnover frequency for CO oxidation on supported gold catalysts typically ranges from 0.01 to $0.5\,s^{-1}$.[21,23]

Finally, we note that placing nanotubes in a membrane reactor offers a unique opportunity to study reactions at gas–liquid interfaces, since the gas and liquid reactants may access the active sites by counterdiffusion from opposite ends of the nanotubes. Transport can be controlled by placing the catalytic membrane between additional membranes containing gold nanotubes that have been functionalized with self-assembled monolayers of hydrophobic and hydrophilic thiols, as demonstrated previously for molecular filtrations.[11] Table 2 presents results for the oxidation of CO by H_2O_2 for cases where the gold nanotubes were placed between such hydrophilic and/or hydrophobic membranes, which were themselves inactive for CO oxidation under all experimental conditions of this study. It can be seen that only small effects are caused by placing a hydrophilic membrane between the gold nanotubes and the liquid water (entries 2 and 3), and by placing a hydrophobic membrane between the gold nanotubes and the gas phase (entries 2 and 6). However, a strong inhibiting effect on the rate of CO oxidation is caused by placing a hydrophobic membrane between the gold nanotubes and the liquid water (entries 1 and 5), which hinders the transport of liquid water to the reactive interface. Also, the rate of CO oxidation is inhibited by placing a hydrophilic membrane between the gold nanotubes and the gas phase (entries 1 and 4), which hinders the transport of gaseous species through liquid-filled nanotubes that are positioned between the gas phase and the reactive interface. It should be noted by comparing the rates in Tables 1 and 2 that higher rates of CO oxidation are achieved by the RIE treatment, which exposes the gold nanotubes from the polycarbonate membrane at the gold–gas interface.

Table 2: Rate of CO_2 production for combinations of hydrophobic and/or hydrophilic membranes surrounding a gold nanotube membrane. Data collected using a gold membrane without RIE.

Entry	Gas–Au membrane	Au–liquid membrane	CO_2 rate[a,b]
1	Hydrophilic	Hydrophobic	9
2	Hydrophobic	Hydrophilic	84
3	None	Hydrophilic	130
4	Hydrophilic	None	10
5	None	Hydrophobic	7
6	Hydrophobic	None	79
7	None	None	150

[a] Total gas flow rate = $100\,cm^3min^{-1}$ (STP); CO:He ratio = 1:1. Liquid flow rate = $2\,cm^3min^{-1}$; 0.5 wt% H_2O_2. [b] Rate is given in units of µmol of CO_2 per gram of Au per minute.

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