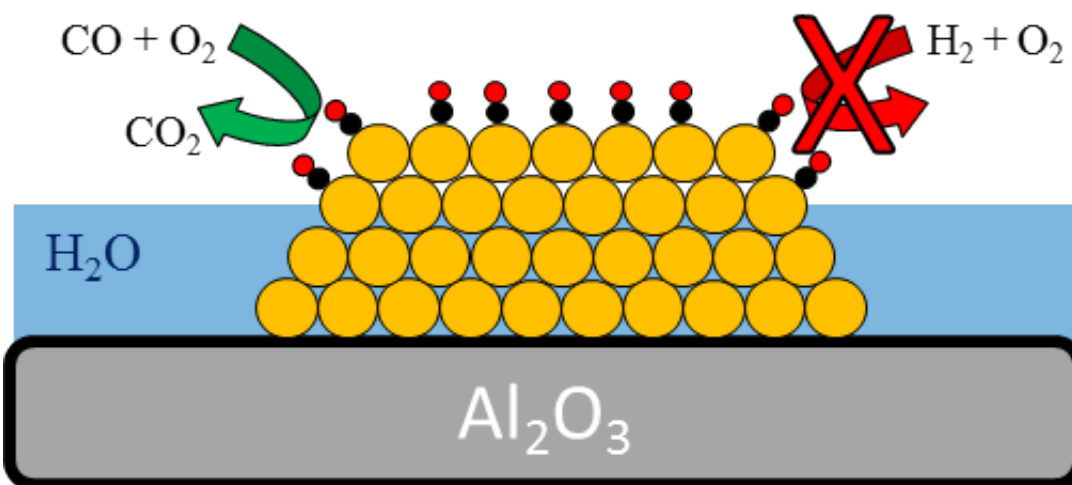


Tuning the gold nanoparticle catalyzed carbon monoxide PROX reaction to purify hydrogen gas

May 5 2016, by Heather Zeiger



Credit: Bert D. Chandler

(Phys.org)—A group of researchers from Trinity University in San Antonio and The Pennsylvania State University have developed a catalytic system using supported gold nanoparticles that surpasses industry standards by controlling space velocity of feed water, the monolayer coverage of water on the nanoparticle surface, and reaction temperature. Their work appears in *Nature Chemistry*.

Hydrogen gas is an important industrial product because hydrogen is used in several processes that have applications to everyday life. However, the processes used to make hydrogen also involve making a small amount of [carbon monoxide](#). Even a small amount of carbon monoxide can poison the metals used in fuel cell catalysts and the catalysts used in ammonia production. The predominant methods for getting rid of carbon monoxide, pressure-swing adsorption and methanation, are either expensive or end up consuming hydrogen in the process.

One of the more promising reactions for eliminating carbon monoxide without consuming hydrogen is the preferential oxidation of carbon monoxide with oxygen, or the PROX reaction. The PROX reaction involves the production of CO_2 through the oxidation of CO with O_2 ; however a competing reaction is oxidizing [hydrogen gas](#) to form water, which consumes some of the hydrogen product. The standard for this reaction is to reduce CO at the reactor outlet to 50ppm with an oxygen-to- CO_2 selectivity at least 50%. In the current research, Johnny Saavedra, Todd Whittaker, Zhifeng Chen, Christopher J. Pursell, Robert M. Rioux and Bert D. Chandler have called this the 50/50 goal.

Gold nanoparticles are known to be great oxidation catalysts for carbon monoxide but poor hydrogenation catalysts. Seemingly, gold nanoparticles would be an ideal catalyst for the PROX reaction. However, prior to the current research, there have been few examples of gold nanoparticle catalysts that achieve the 50/50 goal.

Previous research by Dr. Chandler's group elucidated CO oxidation reaction mechanism that operates at the metal-support interface. In particular, they found that the hydroxyl groups on the surface of the oxide support play an important role in anchoring water molecules. These anchored water molecules function as co-catalysts in the CO oxidation reaction, providing protons to help activate oxygen. According to

Chandler, "The fundamental work that we did to develop a better understanding of CO oxidation led directly to our rapid advances in the more practical PROX problem. This wasn't our initial goal, but it was a unique opportunity that we felt we had to pursue."

For the current study, Saavedra, et al. used gold nanoparticles on Al_2O_3 ($\text{Au}/\text{Al}_2\text{O}_3$) as the catalyst. They demonstrated that by controlling water pressure and the space velocity, or the flow rate normalized to the amount of [gold nanoparticles](#), the activity of the catalyst improved. Other groups' work generally did not include water and used much lower space velocities, which resulted in low activity and selectivity. However, Saavedra, et al. exceeded the 50/50 goal with space velocities that are one-to-two orders of magnitude larger than reported in the literature by carefully controlling the feed-water.

They tested their system at various water pressures and space velocities and found that the catalyst was relatively stable. It did not exhibit signs of degradation over a ten-hour period and remained selective for CO (rather than H_2) oxidation. They did, however, observe signs of degradation once water was removed from their system. Additionally, Saavedra, et al. found that while CO conversion increased as the space velocity decreased, O_2 selectivity did not change much, providing insight into the reaction mechanism. The two reactions seem to occur sequentially with CO reacting before H_2 .

The next step was to see how temperature affected the catalyst. For each temperature, they first tuned the space velocity so that the catalyst achieved 70% CO conversion with 30 Torr of water, and then decreased the water pressure. They found that as temperature increases, the water pressure range that yields the highest activity increases due to changes in the amount of adsorbed water.

This experiment, combined with direct water adsorption measurements,

revealed that at each temperature, the maximum activity occurs at about the same coverage of water on the Au/Al₂O₃ support. This added up to about one monolayer of water. More water than this diminishes the catalyst's activity. IR studies indicated that this is probably due to water blocking adsorption of CO on the Au nanoparticles. They also found that water enhances O₂ selectivity, which may be due to change in reaction kinetics.

Overall, with the right tuning of space velocity, [water](#) coverage and [reaction temperature](#), the CO-PROX reaction with an "unoptimized" Au nanoparticle catalyst can produce a very high conversion, leaving less than 10ppm of CO in H₂. Additionally O₂ selectively can be as high as 80%. This exceeds the 50/50 goal of 50 ppm CO and 50% O₂ conversion. The authors point out that their studies on understanding the mechanism behind the CO PROX reaction demonstrate that purification of H₂ in this manner is not necessarily a problem of catalyst optimization as much as reaction engineering.

More information: Johnny Saavedra et al. Controlling activity and selectivity using water in the Au-catalysed preferential oxidation of CO in H₂, *Nature Chemistry* (2016). [DOI: 10.1038/nchem.2494](https://doi.org/10.1038/nchem.2494)

Abstract

Industrial hydrogen production through methane steam reforming exceeds 50 million tons annually and accounts for 2–5% of global energy consumption. The hydrogen product, even after processing by the water–gas shift, still typically contains ~1% CO, which must be removed for many applications. Methanation ($\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$) is an effective solution to this problem, but consumes 5–15% of the generated hydrogen. The preferential oxidation (PROX) of CO with O₂ in hydrogen represents a more-efficient solution. Supported gold nanoparticles, with their high CO-oxidation activity and notoriously low hydrogenation activity, have long been examined as PROX catalysts, but

have shown disappointingly low activity and selectivity. Here we show that, under the proper conditions, a commercial Au/Al₂O₃ catalyst can remove CO to below 10 ppm and still maintain an O₂-to-CO₂ selectivity of 80–90%. The key to maximizing the catalyst activity and selectivity is to carefully control the feed-flow rate and maintain one to two monolayers of water (a key CO-oxidation co-catalyst) on the catalyst surface.

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Citation: Tuning the gold nanoparticle catalyzed carbon monoxide PROX reaction to purify hydrogen gas (2016, May 5) retrieved 20 March 2024 from <https://phys.org/news/2016-05-tuning-gold-nanoparticle-catalyzed-carbon.html>

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