

Room Temperature Hydrogen Oxidation and Anti-Poisoning Property of Ultra-Stable Gold Nanocatalyst for Passive Autocatalytic Recombiner System

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1. Introduction

As seen in the TMI accident in 1979 and the unfortunate Fukushima accident in 2011, in nuclear power plants (NPPs), the overheating of reactor core due to the loss or inability of the coolant causes the hydrogen to be generated by the oxidation reaction of Zircalloy, the cladding of fuel rod, by the water vapor at a high temperature of 1200 °C or more [1, 2]. As the generated hydrogen gas accumulate at the top of the air-filled reactor containment building, the hydrogen concentration within the reactor containment exceeds the lower flammability limit, 4.1%, in air. Eventually, in those two cases, the hydrogen-oxygen mixtures caused explosions, and in one of them, the containment building experienced a severe damage resulting in a massive leakage of radioactive materials. Since the two cases showed us the importance of fully passive hydrogen mitigation system against the unexpected severe accidents, and passive auto-catalytic recombiner (PAR) systems have been introduced in commercial nuclear power plants worldwide.

Currently available PAR systems adopt platinum group metal (PGM) catalysts to catalytically oxidize hydrogen. The PGM catalysts, however, have faced several challenges. One is that, in severe accidents, the catalysts should exhibit high catalytic activities at the initial stage where the temperature and the hydrogen concentration are still low [2], but the PGM catalysts cannot show high enough catalytic activities near room temperature. Of course, the catalysts also have to maintain their catalytic stability even at high temperatures with high concentration of hydrogen. Another is that, during the normal operation of NPP, the catalysts are continuously losing their activities as being adsorbed by airborne poisoning molecules, such as CO and volatile organic compounds (VOCs). Once they are adsorbed on the active sites of catalysts, the sites are blocked to be accessed by hydrogens in case of accident.

Thus, we introduce an alternative to the current PGM catalysts to overcome those challenges. Recently developed gold nanocatalyst in which the nanoparticles are fully confined by individual nanocages of mesoporous silica (Figure 1) shows unprecedentedly high catalytic activities at low temperatures for oxidation reactions of poisoning molecules as well as hydrogen. As the nanoparticles are immobilized by silica nanocages, the catalysts do not suffer from sintering up to very high temperatures.

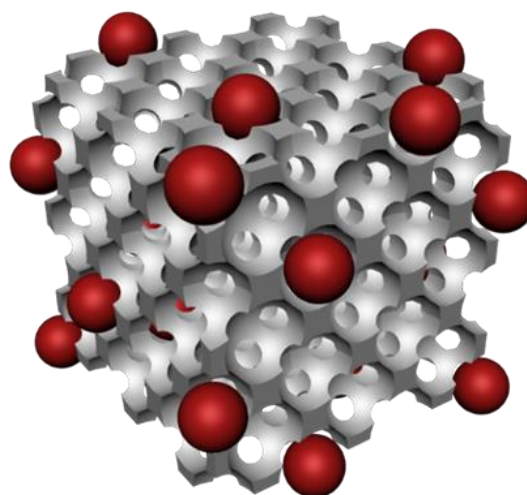


Figure 1. Schematic view of ultra-stable gold nanocatalysts individually confined in mesoporous silica matrix

2. Methods and Results

2.1. Synthesis of Catalysts

2.1.1. Synthesis of gold nanoparticles functionalized by PEG strands.

4 nm gold nanoparticles stabilized with oleylamine were synthesized by a known method [3] according to the following procedure. 60 ml of tetralin, 60 ml of oleylamine and 0.6 g of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ was stirred at room temperature for 10 minutes to prepare a solution. 6mmol of TBAB, 6ml of tetralin and 6ml of oleylamine were sonicated and rapidly added to the solution. The solution was further stirred at room temperature for 1 hour, ethanol was added, and the gold nanoparticles were precipitated by centrifugation. The product was redispersed in hexane and ethanol was added to centrifuge. The 4 nm gold nanoparticles were dispersed in 100 ml toluene.

The surface of 4 nm gold nanoparticles was functionalized with thiolated PEG by the following method. To gold nanoparticles dispersed in toluene, thiolated PEG was added. After stirring, hexane was added and centrifuged to precipitate PEG-functionalized gold nanoparticles. The collected particles was dried and dispersed in water and used in the next step.

2.1.2. Synthesis of gold nanoparticles embedded in mesoporous silica

The PEG-functionalized gold nanoparticles prepared in the previous step and Pluronic F127 were mixed and uniformly dispersed in aqueous HCl solution. To the solution, tetraethyl orthosilicate (TEOS) was added. The mixture was stirred for 15 minutes and maintained at room temperature without stirring for 40 hours. Then, the red precipitate was washed with water, dried, and then calcined at 450 °C under helium to remove the organic compounds.

2.2. Characterization of Catalysts

By observation of the synthesized nanostructure through a transmission electron microscope (TEM), it was confirmed that the gold nanoparticles were stably dispersed in the porous silica even after calcination at 450 °C, as shown in Figure 2. This shows that the catalyst is thermally very stable. The gold content in the catalyst was 5.56 wt% as determined by inductively coupled plasma-emission spectrometry (ICP-OES).

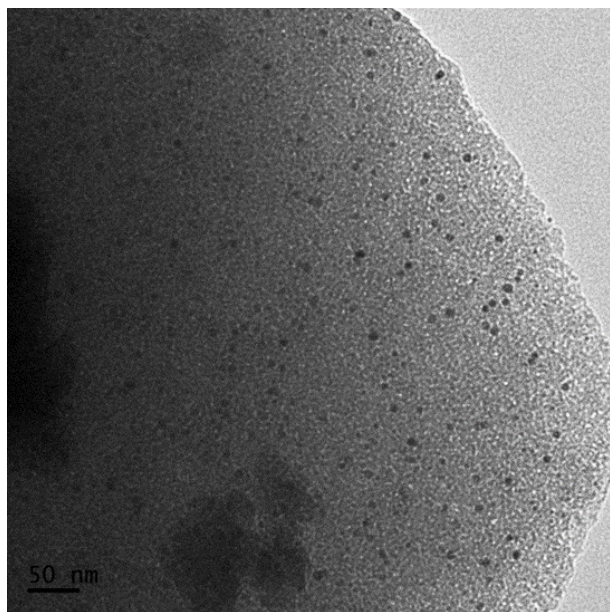


Figure 2. Transmission electron microscope image of gold nanoparticles dispersed in mesoporous silica nanocage

The pore structure of the catalyst was analyzed by argon adsorption method. The adsorption-desorption curve was obtained as shown in Figure 3(a), and the pore distribution was analyzed by the density functional theory (DFT) method as shown in Figure 3(b). The pore volume per unit mass of the catalyst was found to be 0.278 cc/g and the specific surface area was found to be about 916 m²/g, which is similar to that of general mesoporous silica materials synthesized by using Pluronic polymers.

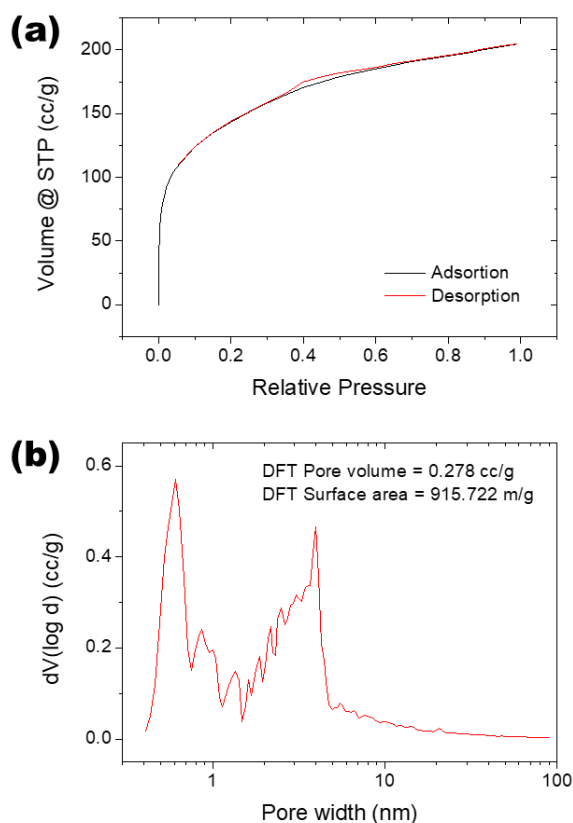


Figure 3. (a) Argon adsorption-desorption curves of the gold nanocatalyst in mesoporous silica (b) Pore volume distribution with respect to pore size

2.3. Catalytic Reaction

60 cc of air per minute and 1.7 cc of hydrogen per minute were mixed and passed through 100 mg of the catalyst, and the gas passed through was analyzed by gas chromatography (GC). Hydrogen was completely oxidized and removed at temperatures of 25 °C, 66 °C and 106 °C, respectively, as shown in Figure 4. It has higher activity than existing PGM catalysts from the room temperature, and can be usefully used for fully passive hydrogen mitigation system for NPPs.

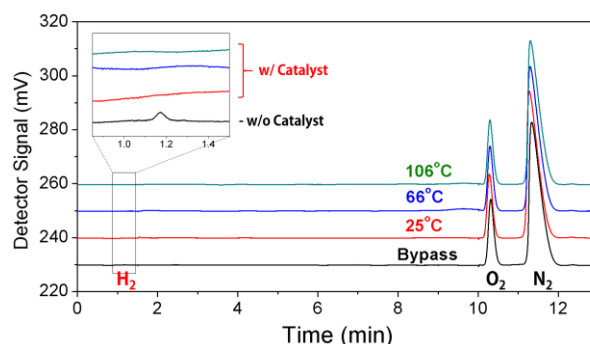


Figure 4. GC results of catalytic hydrogen oxidation using the gold nanocatalyst in porous silica nanocage

As a result of the carbon monoxide oxidation experiment using the catalyst at room temperature, the gas chromatogram as shown in Figure 5 was obtained. A gas containing 1% carbon monoxide and 20% oxygen was flowed into a 100 mg catalyst at a flow rate of 100 cc (STP) per minute, indicating that all of the carbon monoxide was fully converted to carbon dioxide. Carbon monoxide is a representative poisoning material to the PGM catalysts. The result implies that this newly developed catalyst can overcome the poisoning problem of current PAR systems, and provide a chance to build up a more reliable hydrogen mitigation system.

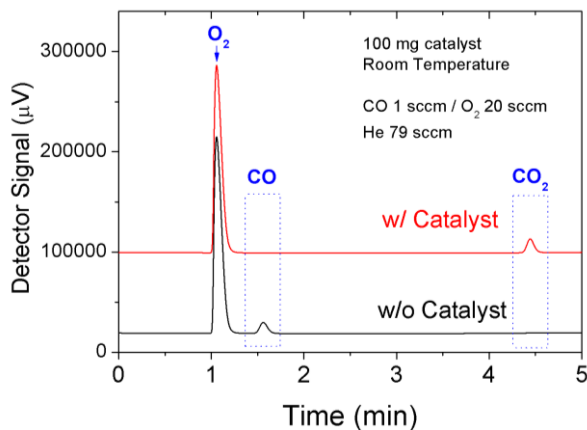


Figure 5. GC results of catalytic CO oxidation using the gold nanocatalyst in porous silica nanocage

3. Conclusions

An ultra-stable gold nanocatalyst structure of new concept is developed, and it shows exceptionally high catalytic activity from low temperatures. The new catalyst can be utilized in PAR system in NPPs, can provide a more reliable hydrogen mitigation system.

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