Gold nanoclusters for efficient removal of organic pollutants at room temperature

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ABSTRACT

Nowadays, public concern and the enforcement of environmental regulations by governments have made it necessary to develop versatile materials capable of efficiently eliminating a wide range of organic pollutants from both indoor and outdoor emissions. These pollutants contribute to photochemical smog and ground-level ozone and have raised severe concern owing to probable short- and long-term adverse health effects. In order to completely remove said emissions, numerous air purification systems based on catalysts, photocatalysts, adsorbents or ozone-promoted oxidation have been developed. However, most of these technologies have a limited efficiency in removing several pollutants under ambient conditions.

In this context, Goldemar Solutions S.L. presents an innovative technology for the synthesis of gold nanocatalysts: Nanomaterials within the Subnanometer-Size Range. This discovery makes the gold nanocatalysts applicable for removing various harmful or undesirable compounds in sectors related to purification of air, providing the following potential uses thereof: i) complete removal of the cold-start emissions in automobile industry, ii) volatile organic compound (VOC) removal from indoor ambients or iii) air purification in enclosed environments such as submarines or aircrfats.

Keywords: air quality, catalytic oxidation, carbon monoxide, volatile organic compounds, gold nanocatalysts.

1 INTRODUCTION

Air pollutants are a major concern for human health and the environment. Indeed, public concern and the enforcement of environmental regulations by governments have opened a window of opportunity to develop novel materials capable of eliminating a wide range of air pollutants.

Currently, the vast majority of industrial catalysts for removing stationary VOCs and CO at room temperature are based on platinum group metals exhibiting excellent catalytic properties and comprising platinum, palladium, ruthenium, rhodium, osmium and iridium [1]. However, meeting the growing demand for such scarce metals in controlling several pollutant emissions is not sustainable.

Although, gold was formerly believed to be poorly active as a catalyst due to its electronic configuration, Haruta [2] discovered that gold nanoclusters, when supported on a porous support, present a high activity for CO oxidation at low temperatures. Since then, the interest in pioneering gold nanoclusters-based catalysts for the oxidation of different pollutants, including VOCs, has dramatically increased during the last 20 years.

Herein, we present a novel catalyst containing gold nanoclusters capable of eliminating huge amounts of organic pollutants at room temperature, even in the presence of moisture or other pollutants usually present in the feed gas. The application of this family of catalysts in air purification such as automotive emission control and low-temperature air purification, for different pollutants emitted in different sectors is presented on the basis of activity and stability tests thereof under simulated conditions of temperature, space velocity, and gas composition.

2 EXPERIMENTAL

2.1. Characterization of Goldemar's catalyst

As-prepared gold nanoclusters

The morphology of gold nanoclusters as-prepared is analyzed using Atomic Force Microscopy (AFM). The AFM measurements are carried out using a VEECO Dimension 3100 Atomic Force Microscopy operated in the tapping mode.

Stabilized gold nanoclusters

The morphology of the stabilized gold nanoclusters on different supports is determined by High Resolution Transmission Electronic Microscopy (HRTEM). The images are acquired using a JEOL JEM-2011 microscope operated at 200 kV.

2.2. Catalytic activity

Catalytic evaluation of Goldemar catalysts is performed in gas-flow conditions with different cases where the catalyst would be suitable for implementation. For carrying out catalytic testing, a MicroActivity Reference Setup (PID Eng&Tech) in a quartz microreactor (9.2 mm i.d.) is used.

The catalyst (0.1 g, sieve fraction 125-300 mm) is loaded between two layers of quartz wool and rested over a porous frit. Following, desired amounts of pollutants are introduced into the microreactor. Reaction conditions for

each experiment are described in the respective figures. The conversion degree of pollutants is determined by the analysis of reactants and products using Gas Chromatography (GC) coupled to Mass spectroscopy (MS), (Agilent 5975 GC/MSD) equipped with an HP-PlotU column. Carbon balance in all the conditions is close to 100%.

3 MATERIAL PROPERTIES

The presence of ultrasmall gold nanoclusters is demonstrated with the AFM image of Figure 1 (gold nanoclusters are the bright spots). It should be noticed that the formed nanoclusters are very homogeneous in size with a particle size distribution centered at 1.4 ± 0.5 nm.

The excellent stability of supported gold nanoclusters is confirmed in Figure 1 (b) by HRTEM images. Our material still consists of a large number of homogeneous gold nanoclusters, even, after being exposed to a thermal aging at 300ºC.

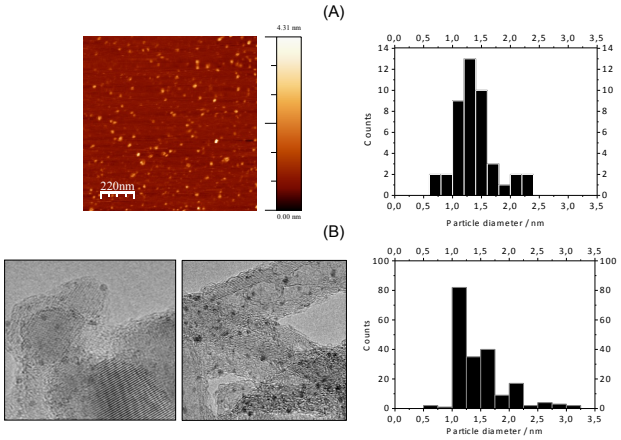

Figure 1: Morphology of Goldemar's catalyst. (A) AFM of aqueous solution containing gold nanoclusters and the resulting size distribution histogram (B) HRTEM of the material after being calcined when supported in TiO_2 or MWCNTs. The size distribution histogram has been measured for TiO_2 support.

Our patented technology permits, in a simple and economical manner, the assembly of a few gold atoms forming a specific configuration of clusters with 1.4 nm in particle size. Such a configuration displays extraordinary and unique catalytic properties for oxidizing toxic compounds under ambient conditions.

For the present case, gold nanoclusters have been supported on TiO_2 or Multiwalled Carbon Nanotubes (MWCTs). However, they can also be deposited on any other support such as zeolite, cerium oxide, activated carbon etc., which, in combination with our synthetic methods, provides flexibility of adjusting the reactivity of said catalysts according to the requirements of different applications.

4 PROMISSING APPLICATIONS FOR GOLDEMAR CATALYSTS IN SECTORS RELATED TO AIR PURIFICATION

4.1. Automotive emission control

Today, catalytic converters are used to convert harmful gases such as carbon monoxide (CO), hydrocarbons, and nitrogen oxides (NO and NO_2) produced by the motor vehicle engines into harmless ones. Catalytic converters provide an ideal and effective way to reduce environmental pollutants; however, they require a very high temperature to operate (usually above 300°C). While catalytic converters are very successful at collecting and eliminating 97% of the emissions, under typical urban driving conditions, 60% to 80% of all toxic emissions occur during the cold-start periods [3].

On the contrary to the existing solutions, ELBEGAST catalyst allows for complete mitigation of carbon monoxide and hydrocarbon emissions starting from the ignition of the engine, an exceptional improvement in the emission control technologies for the automotive industry.

Recent studies conducted in flow conditions (Figure 2) involving oxidation reactions of carbon monoxide (CO) and hydrocarbons (HC's) indicated that catalytic activity of gold nanoclusters, at gold loadings of as low as 2 milligram per gram of catalyst, is sufficient to oxidize vast amounts of said pollutants at room temperature without any evident signal of deactivation after being thermally aged up to 800 ºC or in the presence of moisture (a common inhibitor of catalysts).

Moreover, promising results for reduction of nitrogen oxides are also obtained with ELBEGAST catalyst and N_2O is not formed.

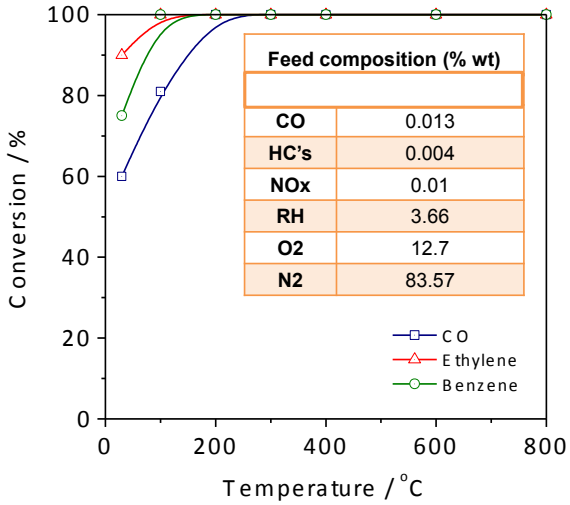

Figure 2: CO and hydrocarbon (ethylene and benzene conversion) conversion versus temperature curves after thermal aging of the catalyst at 800ºC for 5 hours. Contact time: 0.03 s, feed composition simulating automotive exhaust conditions, P=1 bar, time on stream at each temperature = 3 hours.

4.2. Low-Temperature air purification

Low-temperature oxidation of pollutants is becoming increasingly important in the context of cleaning air in both indoor and outdoor environments. The principal challenge of this application is to find a catalyst having a very high catalytic activity under ambient conditions and capable of dealing with streams containing large amounts of moisture. Accordingly, gold catalysts are demonstrated to be highly active and promoted by moisture for oxidation of many organic compounds [4].

Catalytic activity of Alberich catalyst for CO oxidation

The exclusive catalytic activity presented by Alberich catalyst is demonstrated in Figure 3a. As can be seen, complete oxidation of carbon monoxide under ambient conditions is possible in the presence or absence of water in the feed stream using only 100 mg of catalyst.

It should be noted that high catalytic activity remains constant for 20 hours (Figure 3b). Considering that one of the major technical issues of gold based catalyst technology is the deactivation thereof, observing no deactivation signal provides a superior feature.

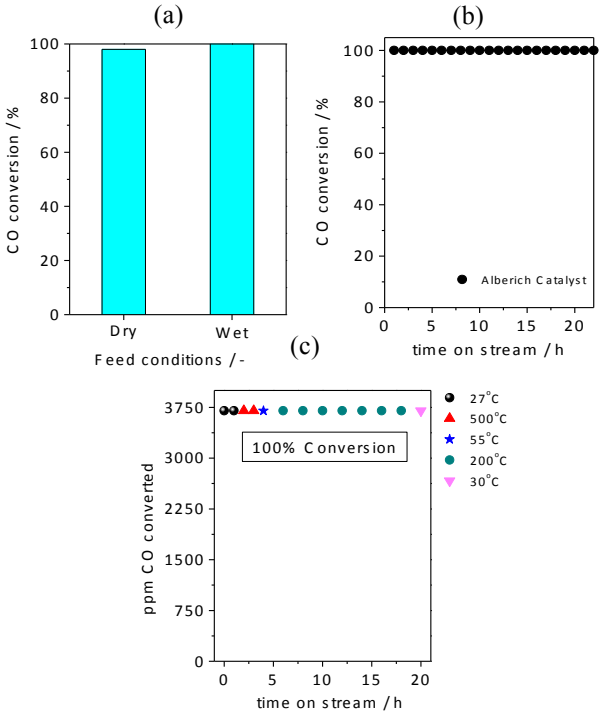

Figure 3: (a) CO conversion at room temperature in the absence and presence of moisture in the feed, R.H. = 95%, (b) Stability of Alberich catalyst under wet conditions, (c) Catalytic activity and thermal stability after exposing the catalyst at different tempretaures for 3 hours. Other conditions in all the tests: Other conditions: P=1 bar, contact time = 0.02s, 3700 ppm CO balanced in nitrogen.

Moreover, thermal stability tests performed at different temperatures, have proved that no alteration of the catalytic activity of gold nanoparticles for CO oxidation takes place, even when the catalyst is exposed to temperatures higher than the Tammann temperature of gold, 395ºC, (Figure 3c).

Finally, regenation of Alberich catalyst is possible, since its activity can be easily restored by a carbon burn-off at high temperatures.

Catalytic activity of Alberich catalyst for formaldehyde oxidation

The adverse effects of volatile organic compounds (VOCs) for human health are well recognized. These have been reported to be toxic and long term exposure thereto is potentially teratogen. For this reason, removing VOCs from indoor environments is a major social concern, which remains largely unsolved.

The versatility of our catalytic system for destroying several pollutants is confirmed in Figure 3. In this case, formaldehyde, used as molecule probe for VOCs removal, is completely converted to CO_2 and H_2O at room temperature. After 5 hours on stream, the catalyst remains stable and significantly, no noxious by-products are detected during the reaction.

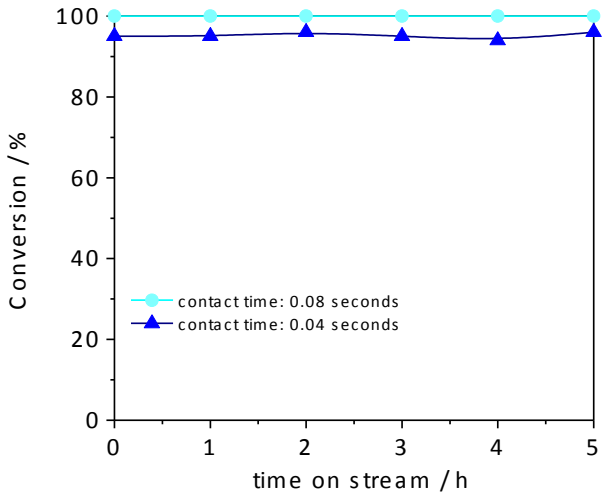

Figure 3: Formaldehyde conversion at room temperature at different contact times: 0.08s and 0.04s. Other conditions: 700 ppm of formaldehyde, P=1 bar, time on stream= 5 hours.

The ability of Alberich catalyst for low-temperature oxidation of carbon monoxide and formaldehyde at room temperature offers new opportunities for air purification applications such as removal of VOCs in flow conditions at domestic levels, enhancing respirators or other personal protective equipment (PPE) or purifiying air in closed ambients (submarines or airplanes).

5 CONCLUSIONS

Goldemar has developed a unique gold based catalyst with oxidation and reduction activity. To the best of our knowledge this the only catalyst with these characteristics in the market. The huge and stable catalytic activity of

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Goldemar catalysts towards the oxidation of CO and elimination of VOCs has been demonstrated simulating different flow conditions. Importantly, our catalyst activity starts at room temperature, which already presents a massive catalytic activity, up to temperatures in excess of 800 ºC. Furthermore, Goldemar catalysts can provide cost savings due to extremely small amount of gold used in the production of the catalyst.

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