

# Durable PROX catalyst based on gold particles and hydrophobic silica

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## Introduction

One of the specificities of gold catalysts is their activity at low temperature in oxidation reactions. As a result, supported gold nanoparticles (Au NP) are particularly suited to environmental applications and catalytic processes involving temperatures below 100°C, such as the ultimate purification step of hydrogen feeding proton-exchange membrane fuel cells (PEM-FC), namely preferential oxidation of CO in hydrogen-rich streams (PROX) [1]. In addition, their peculiar reactivity towards molecular oxygen, hydroperoxides and radicals makes them highly selective in useful synthetic transformations, such as the aerobic epoxidation of stilbene (tS) with methyleyclohexane (MCH) [2].

While durability in the liquid phase is not an issue, oxide-supported gold catalysts have been shown to suffer from acute deactivation in low temperature gas phase oxidation [3], which has been identified as the major hurdle towards commercialization so far [4].

In this communication, we will show that, in addition to being more selective, recently developed hydrophobic gold catalysts [5], exhibit superior durability in the PROX reaction, as compared with benchmark Au/TiO<sub>2</sub> and Au/Al<sub>2</sub>O<sub>3</sub> catalysts [1].

## Materials and Methods

1.5 wt.% Au/TiO<sub>2</sub> and 1.5 wt.% Au/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by the direct anionic exchange method, followed by calcination at 300°C for 4 h [1]. 0.73 wt.% Au/SiO<sub>2-R972</sub> was obtained by NaBH<sub>4</sub> reduction of AuPPh<sub>3</sub>Cl in ethanol in the presence of the methyl-terminated Aerosil silica R972 from Evonik Industries, followed by activation for 2 h at 200°C in vacuum [5]. All catalysts exhibit similar particle size distributions centered at about 3.0 ± 0.4 nm (TEM analysis).

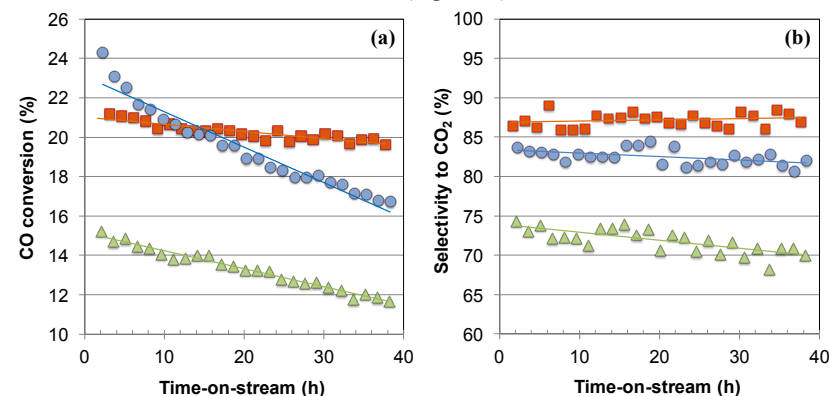
PROX was performed in a high-throughput Flowrence set-up from Avantium, equipped with 16 parallel fixed-bed stainless steel reactors (i.d. 2 mm). Each reactor was loaded with 50 mg of a mixture containing various amounts of the catalyst powder (0.8 – 1.6 μmol of gold), in order to achieve a variety of conversion levels, and a γ-alumina diluent. The 1.9% CO / 1.6% O<sub>2</sub> / 44% H<sub>2</sub> / 43.5% N<sub>2</sub> / 9% He gas mixture, was then introduced at a total flow rate of 192 mL min<sup>-1</sup> and split between the 16 reactors (12 mL min<sup>-1</sup>/reactor, with a deviation of less than 2%, 1 atm, GHSV ~ 18,000 h<sup>-1</sup>). After being activated by ramping at 0.25° min<sup>-1</sup> from 40 to 280°C and then down to 150°C, the catalysts were held at various temperature (150, 100 and 50°C) for over 30 h. CO conversions were determined on the basis

of on-line Varian 490 micro-GC analysis, using external calibration.

## Results and Discussion

While Au NP dispersed over alumina systematically grow from 3.4 nm on average to ca. 6.0 nm upon storing the catalyst for 10 months at ambient temperature (ca. 22°C), the size of the gold particles dispersed over the hydrophobic SiO<sub>2-R972</sub> support remains stable even after 12 month-storage: average sizes of 2.9 ± 1.2 and 2.8 ± 1.0 nm are indeed found on the as-synthesized and 12 month old Au/SiO<sub>2-R972</sub> catalyst, respectively. Structural stability is also maintained at 80°C under the oxidizing conditions of the liquid phase tS/MCH co-oxidation, after which the average size is found at 3.1 ± 1.2 nm.

Furthermore, Au/SiO<sub>2-R972</sub> displays enhanced durability in PROX (**Figure 1a**), even at the lower temperatures at which H<sub>2</sub> cleaning of the carbonate-contaminated surface is inefficient [3]. This is obtained at the superior selectivity towards CO of 88%, as compared with 82% for Au/TiO<sub>2</sub> and 72% for Au/Al<sub>2</sub>O<sub>3</sub> (**Figure 1b**).



**Figure 1.** Stability vs. time-on-stream (**a**) and selectivity towards CO<sub>2</sub> (**b**) observed over Au/SiO<sub>2-R972</sub> (■) Au/TiO<sub>2</sub> (●) and Au/Al<sub>2</sub>O<sub>3</sub> (▲) in the PROX reaction at 50°C

## Significance

The OH-free support makes Au NP structurally stable and the catalyst surface less reactive towards CO<sub>2</sub>. On this hydrophobic surface, oxygen activation proceeds via a hydrogen-only mediated pathway (as opposed to a support-mediated pathway), which results in a more stable and more selective low temperature PROX catalyst.

## References

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