Highly efficient low temperature catalytic processes based on durable gold catalysts

K. Guillois[1], A. Tuel[1], P. Laveille[2], J.-M. Basset[2], C. Petit[3], V. Caps[3]*

[1]*IRCELYON (Institut de recherches sur la catalyse et l'environnement de Lyon), University of Lyon / CNRS UMR 5256, 2 Avenue Albert Einstein, 69626 Villeurbanne Cedex, France*
[2]*KAUST Catalysis Center, 4700 King Abdullah University of Science and Technology, Thuwal 23955 – 6900, Kingdom of Saudi Arabia*
[3]*ICPEES (Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé), Université de Strasbourg / ECPM / CNRS UMR 7515, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France*
**corresponding author:caps@unistra.fr*

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 methylcyclohexane (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_2 and Au/Al_2O_3 catalysts [1].

Materials and Methods

1.5 wt.% Au/TiO_2 and 1.5 wt.% Au/Al_2O_3 catalysts were prepared by the direct anionic exchange method, followed by calcination at 300°C for 4 h [1]. 0.73 wt.% $Au/SiO_{2\text{-}R972}$ was obtained by $NaBH_4$ reduction of $AuPPh_3Cl$ 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_2 / 44% H_2 / 43.5% N_2/ 9% He gas mixture, was then introduced at a total flow rate of 192 mL min^{-1} and split between the 16 reactors (12 mL min^{-1}/reactor, with a deviation of less than 2%, 1 atm, GHSV ~ 18,000 h^{-1}). After being activated by ramping at 0.25° min^{-1} 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 $SiO_{2\text{-}R972}$ support remains stable even after 12 month-storage (**Figure 1a**): average sizes of 2.9 ± 1.2 and 2.8 ± 1.0 nm are indeed found on the as-synthesized and 12 month old $Au/SiO_{2\text{-}R972}$ catalyst, respectively. Structural stability is also maintained at 80°C under the oxidizing conditions of the liquid phase tS/MCH co-oxidation (**Figure 1a**), after which the average size is found at 3.1 ± 1.2 nm.
Furthermore, $Au/SiO_{2\text{-}R972}$ displays enhanced durability in PROX (**Figure 1b**), even at the lower temperatures at which H_2 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_2 and 72% for Au/Al_2O_3.

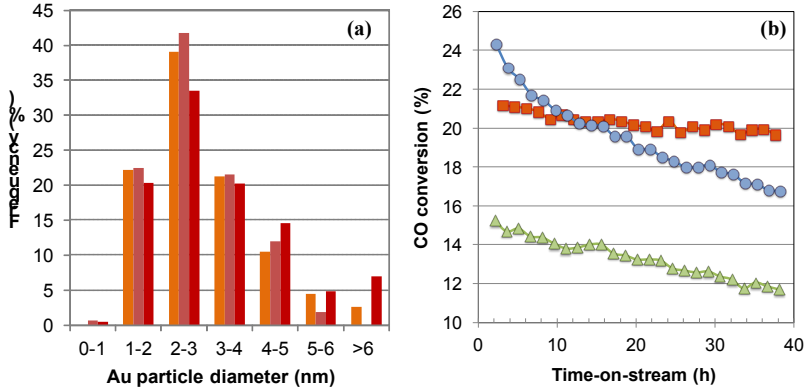

Figure 1. **(a)** Gold particle size distribution in $Au/SiO_{2\text{-}R972}$ as-synthesized (■), after 1 year in air/dark/22°C (■), after 96 h in aerobic *tS*/MCH co-oxidation at 80°C [5] (■)
(b) Stability vs. time-on-stream of $Au/SiO_{2\text{-}R972}$ (■) Au/TiO_2 (●) and Au/Al_2O_3 (▲) in the PROX reaction at 50°C

Significance

The OH-free support makes Au NP structurally stable and the catalyst surface less reactive towards CO_2, which results in a more durable catalyst for low temperature processes.

References

1. Ivanova, S.; Petit, C.; Pitchon, V.; Caps, V. *ChemCatChem* **2010**, *2*, 556.
2. Guillois, K.; Mangematin, S.; Tuel, A.; Caps, V. *Catalysis Today* **2013**, *203*, 111.
3. Costello, C. K.; Kung, M. C.; Oh, H.-S.; Wang Y.; Kung, H. H. *Applied Catalysis A*, **2002**, *232*, 159.
4. Corti, C. W.; Holliday R. J.; Thompson, D. T. *Topics in Catalysis*, **2007**, *44*, 331.
5. Guillois, K.; Burel, L.; Tuel, A.; Caps, V. *Applied Catalysis A* **2012**, *415-416*, 1.