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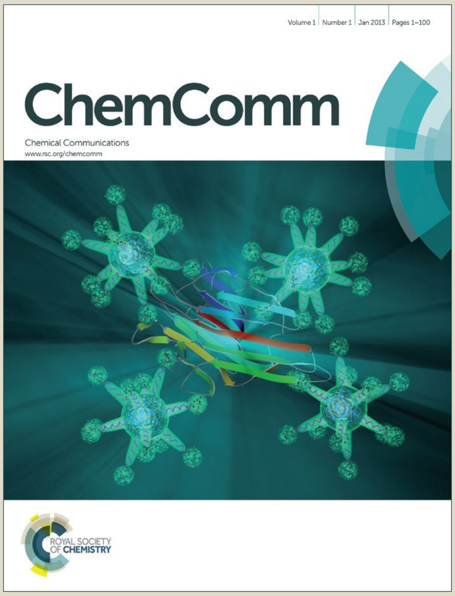

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COMMUNICATION

Durable PROX catalyst based on gold nanoparticles and hydrophobic silica

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3 nm gold nanoparticles obtained by direct chemical reduction of $AuPPh_3Cl$ in the presence of hydrophobic silica are highly active over a prolonged period of time for low temperature CO oxidation in the presence of hydrogen.

The still unmatched catalytic activity of gold nanoparticles (Au NP) for low temperature CO oxidation was discovered over 20 years ago.[1,2] This major breakthrough uncovered a large field of potential applications in oxidation catalysis and industrial processes.[3] However, the viability of many of these applications is hindered by the low stability of gold catalysts under reaction conditions.[4-7] Oxide-supported gold nanoparticles indeed suffer from acute sensitiveness to carbon dioxide and water.[8] The main source of irreversible deactivation in structure-sensitive reactions such as CO oxidation is the growth of gold particles[9] beyond the critical diameter for activity (ca. 5 nm).[10] Another cause of deactivation is the formation of poisoning carbonate-type surface species.[11,12]

Most approaches aiming at producing more stable gold catalysts[13] have focused so far on enhancing the thermal stability of gold nanoparticles against sintering[14] by increasing the so-called "strength of gold-support interaction", in e.g. Au/Al_2O_3,[15,16] Au/metal-phosphates,[17] core-shell and yolk-shell nanocomposites,[18] Au/multi-layered oxides[19] and SiO_2-modified Au/TiO_2 catalysts.[20,21] However, stability of these materials is obtained in most cases at the expense of activity, due both to the lower gold surface available on the larger particles (ca. 15 nm) required for the specific encapsulation methods[18] and to the confinement of the Au-support interface active site.[22]

We have thus considered another option, which consists in shutting down the sites for deactivation by neutralizing the oxygen functions of the support. Both previously mentioned deactivation phenomena (particle growth and carbonate formation), are indeed known to involve the sites at the gold-support interface, namely surface oxygen and hydroxyls groups provided by the support.[23-25] Hence, OH-free gold catalysts should be more durable than the existing ones. The challenge was to produce catalytically active Au NP over hydrophobic surfaces.

This was recently achieved by the direct chemical reduction of triphenylphosphine gold chloride inside an ethanol suspension of the methyl-terminated Aerosil R972 silica from Evonik Industries.[26] The 2.9 ± 1.2 nm gold particles (2.8 ± 1.0 nm after 12 months, Fig. 1) generated on the surface of this commercially available support by this straight-forward, one-pot method (followed by vacuum treatment at 200°C) proved highly active in the methylcyclohexane-mediated aerobic epoxidation of *trans*-stilbene, due to the enhanced dispersion of the hydrophobic catalytic particles within the apolar liquid reaction medium.[27]

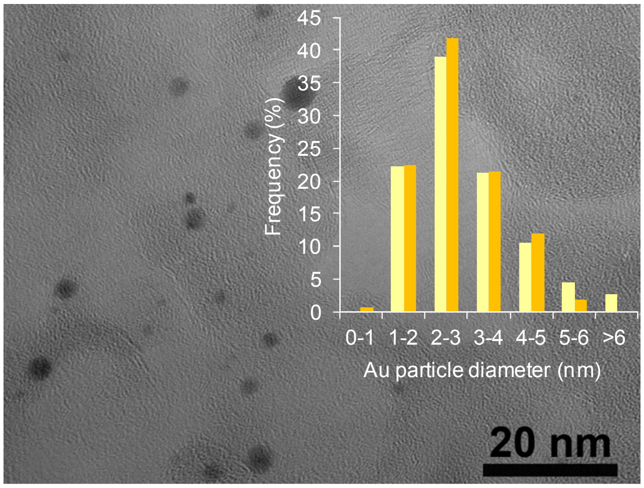

Fig. 1 Transmission electron micrograph (TEM) of $Au/SiO_{2\text{-}R972}$. Insert: distribution of gold particle sizes of the as-synthesized (🟨) and 12 month old (🟧) catalyst

Here, we report for the first time, that this $Au/SiO_{2\text{-}R972}$ hydrophobic gold catalyst exhibits extended durability in the preferential oxidation of CO in hydrogen-rich feeds (PROX) and that this is achieved at a level of activity which is similar to that of the Au/TiO_2-catalyzed CO oxidation benchmark.

The comparative study of the catalytic properties of $Au/SiO_{2\text{-}R972}$, Au/TiO_2 and Au/Al_2O_3 (both prepared by the direct anionic exchange method[15,16,28]), in the preferential oxidation of CO in hydrogen rich feeds (PROX) is performed at atmospheric pressure using a high-throughput Flowrence® from Avantium. Flowrence® is equipped with 16 parallel fixed-bed stainless steel reactors (i.d. 2 mm), as previously described.[29] Each reactor is loaded with 50 mg of a mixture containing the catalyst powder and a γ-alumina diluent. In a typical experiment, the catalytic bed contains 0.8 μmol of gold, which correspond to 3.8 to 7.6 mg of the catalyst depending on the gold loading of the material (from 0.73 wt.% in $Au/SiO_{2\text{-}R972}$ to 1.5 wt.% in Au/TiO_2 and Au/Al_2O_3). The 1.6±0.3% CO / 1.4±0.2% O_2 / 41±3% H_2 gas mixture in

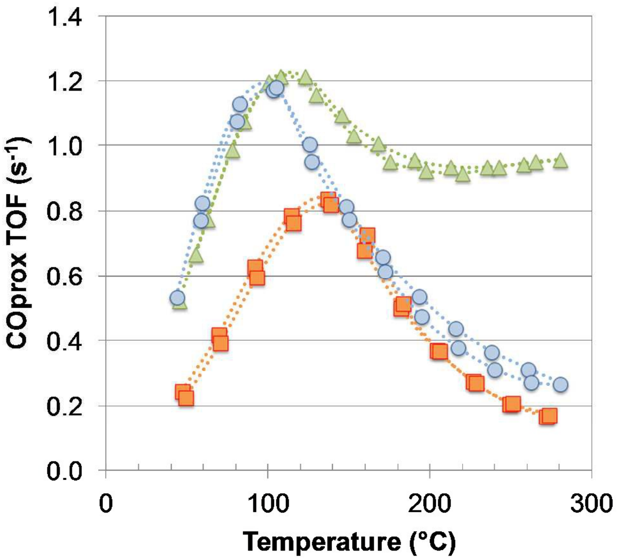

Fig. 2: Turnover frequencies observed in a stabilized cycle under PROX conditions (heating up and down to 280°C) over Au/$SiO_{2\text{-}R972}$ (■) Au/TiO_2 (●) and Au/Al_2O_3 (▲)

N_2/He is then introduced at a total flow rate of 192 mL/min and split between the 16 reactors (12 mL min^{-1}/reactor, with a deviation of less than 2%, GHSV ~ 18,000 h^{-1}). The products are analyzed by on-line Varian 490 micro-GC equipped with 2 MS5A (He-internal standard, H_2, O_2, CO) and 1 PPQ (CO_2) columns. Light-off curves are obtained by ramping the catalyst, under CO / O_2 / H_2 gas mixture, at 0.25° min^{-1} from 40 to 280°C. A PROX cycle refers to the catalytic response of a material obtained upon heating to 280°C and cooling down to 40°C at the constant rate of 0.25° min^{-1}. Durability tests were subsequently performed by holding the catalyst at a given temperature (50°C) for an extended period of time (38 h). Stability is also evaluated after subsequently submitting the catalysts to CO oxidation (1.9% CO / 1.6% O_2 in N_2/He) for 38 h at 150, 100 and 50°C. Turnover frequencies (TOF, s^{-1}) are defined as the number of mole of reactant converted per number of mole of surface gold atom per second. It takes into account gold dispersions of 0.43 for all catalysts, as calculated[28] from the average size determined by TEM (3 nm) of the pseudo-cuboctahedral particles. Selectivity to CO_2 is defined as the percentage of mole of oxygen consumed in the formation of CO_2.

Fig. 2 shows that the catalytic behaviour of Au/$SiO_{2\text{-}R972}$ under PROX light-off conditions is similar to those of Au/TiO_2 and Au/Al_2O_3: the rate of CO oxidation increases with increasing temperature until reaching a maximum value at the temperature at which all oxygen present in the feed is consumed. The conversion of CO subsequently decreases as the temperature is further increased, due to competition for the available oxygen between CO and H_2, which is in favour of H_2 at these temperatures.[30] Nevertheless, the maximum CO conversion is achieved at higher temperature on Au/$SiO_{2\text{-}R972}$ (138°C), as compared with Au/TiO_2 (100°C) and Au/Al_2O_3 (110°C). Besides, at temperatures below 138°C, the intrinsic activity of Au/$SiO_{2\text{-}R972}$ is lower than that observed over Au/TiO_2 and Au/Al_2O_3. Considering that surface hydroxyl groups promote low temperature CO oxidation,[16,23] the hydrophilic Au/TiO_2 and Au/Al_2O_3 surfaces are consistently more active than the OH-free Au/$SiO_{2\text{-}R972}$ surface. In this hydrophobic catalyst, activity for CO oxidation is not mediated by the support,[31] which is clearly "inert" according to the Schubert classification;[32] oxidation activity is triggered by the presence of hydrogen,[33] which has been shown to open up sacrificial reductant-mediated pathways for oxygen activation.[34,35] It is noted that Au/$SiO_{2\text{-}R972}$ is intrinsically more active (TOF_{max} = 0.83 s^{-1}, Fig. 2) than Au_p/$SiO_{2\text{-}500}$ (TOF_{max} = 0.4 s^{-1}),[36] in which passivation of the material is obtained *after* formation of gold particles on the oxide surface.

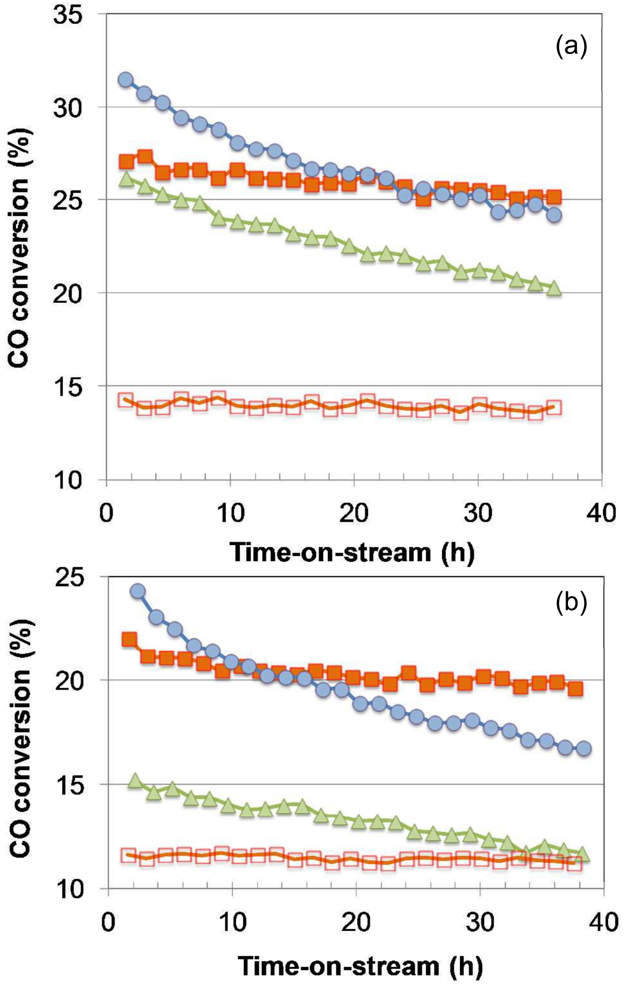

Fig. 3: Stability vs. time-on-PROX stream at 50°C of Au/$SiO_{2\text{-}R972}$ (0.8 μmol Au □ and 1.6 μmol Au ■) Au/TiO_2 (●) and Au/Al_2O_3 (▲), directly following the PROX cycle presented in Fig. 2 (a), after subsequently performing CO oxidation for 114 h (b)

Furthermore, Au/$SiO_{2\text{-}R972}$ appears much more stable with time-on-stream than the hydrophilic catalysts (Fig. 3). While the CO conversion level steadily drops from ca. 32 to 24% and from ca. 26 to 20% in about 36 h at 50°C in the PROX stream over Au/TiO_2 and Au/Al_2O_3, respectively, the CO conversion level achieved over a single load of Au/$SiO_{2\text{-}R972}$ remains constant at about 14% (Fig. 3a). By increasing the load of the hydrophobic catalyst, higher conversion levels can be obtained, which are similarly stable over time. Besides, after undergoing subsequent CO oxidation, Au/Al_2O_3 loses a subsequent part of its activity and continues to deactivate with time-on-PROX stream, so that, in the long run, Au/$SiO_{2\text{-}R972}$ becomes as active as Au/Al_2O_3 (Fig. 3b).

This enhanced stability is attributed to the peculiar catalyst

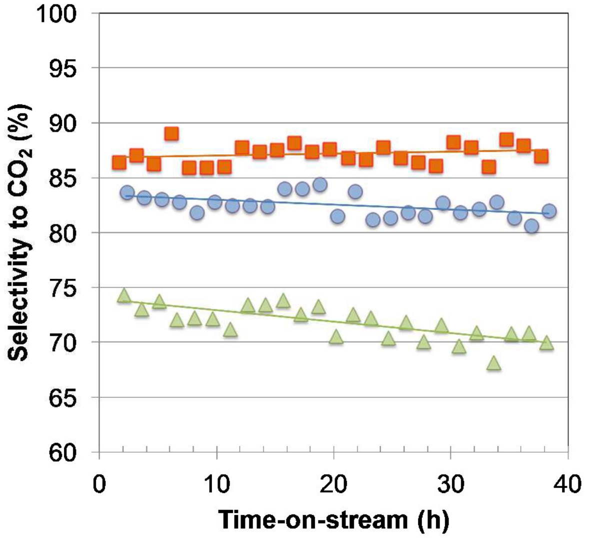

Fig. 4: Selectivity in the PROX reaction (50°C) obtained over Au/$SiO_{2\text{-}R972}$ (■) Au/TiO_2 (●) and Au/Al_2O_3 (▲)

surface. The support hydrophobicity may indeed concentrate and facilitate reactant adsorption and product desorption over Au NP. More specifically, methyl-terminated $SiO_{2\text{-}R972}$ likely inhibits carbonatation[37] of the Au/support interface while improving and boosting CO_2 desorption and freeing CO adsorption sites. Hence, at a temperature at which OH-mediated H_2/H_2O "cleaning" of the carbonate-contaminated Au/Al_2O_3[38] and Au/TiO_2[39] surface is inefficient (< 100°C),[12] passivated Au/$SiO_{2\text{-}R972}$ displays much more stable PROX activity.

Finally, the virtual absence of surface OH groups, which provide sites for water formation in H_2/O_2 atmospheres,[23] can also account for the improved PROX selectivity (>85%) observed over Au/$SiO_{2\text{-}R972}$ (Fig. 4).

In conclusion, OH-free Au/$SiO_{2\text{-}R972}$ exhibits a catalytic activity in the PROX reaction which is comparable to that observed over hydrophilic surfaces. Although the absence of surface hydroxyl groups prevents the catalyst to reach the state-of-the-art activities initially displayed by Au/TiO_2 and Au/Al_2O_3, it brings long-term stability with time-on-stream and superior selectivity. This new example, of CO oxidation activity of gold nanoparticles dispersed over a hydrophobic, "inert"[32] support, clearly emphasizes the role of hydrogen as a promoter for the gold-catalyzed oxidation of CO at low temperature. Unlike support-mediated oxygen activation, hydrogen-only mediated oxygen activation takes full advantage of a hydrophobic surface, which is much more resistant against CO/CO_2 and thus remains free of poisonous carbonate species.

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Notes and references

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