Preferential oxidation of CO in H_2 over highly loaded Au/ZrO_2 catalysts obtained by direct oxidation of bulk alloy

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The intimate mixture of a skeletal gold structure with ZrO_2 nanoparticles obtained simply by oxidation of $Au_{0.5}Zr_{0.5}$ alloy at room temperature turns out to be an efficient catalyst for the selective oxidation of CO in the presence of hydrogen.

Interest in the catalytic potential of metal oxide-supported gold materials has been growing significantly in the last few years. Various hydrogenation and oxidation reactions, such as the oxidation of CO,[1] the water gas shift reaction,[2] the epoxidation of propylene,[3] the direct synthesis of H_2O_2 from H_2 and O_2[4] are now known to be catalysed by gold. Moreover, the ability of some supported gold-based catalysts to perform preferential CO oxidation in the presence of hydrogen (PROX)[5] makes gold very attractive from the perspective of hydrogen purification for fuel cell technology. However, although extensive work was initially devoted to the preparation and characterisation of such gold catalysts on various supports, most of the current preparation methods cannot easily be scaled-up.[6] Indeed, the ones derived from the usual chemical routes (deposition–precipitation, co-precipitation…) generally use the chlorinated $HAuCl_4$ precursor which implies either extensive washing or the application of post-synthetic heat treatments to remove the chlorides. The others, derived from physical routes, such as laser vaporisation[7] or oxidation of glassy Zr–Pd, Zr–Au and Zr–Au–Ag alloys,[8] are simply too costly to be considered from an industrial point of view.

Recently, some of us have re-investigated the Zr–Au system, which has led to a more complete version of the phase diagram, and it has been shown that the rapid oxidation of Zr–Au alloys at low temperature, which can be related to the presence of solid-state transformations occurring in the composition range 35–55 at.% Au, leads to an intimate mixture of gold and monoclinic zirconia particles (< 10 nm).[9]

Here, we report on the catalytic properties of this Au/ZrO_2 material, obtained simply by oxidation of the $Zr_{0.5}Au_{0.5}$ alloy at room temperature, in the oxidations of CO, H_2 and the preferential oxidation of CO in hydrogen-rich mixtures. The manner in which the oxidation of CO is affected by the presence of H_2 will be discussed. Finally, by comparing the activity of this new catalyst to those synthesised by the traditional chemical or physical methods, we will show that this preparation method could be an alternative route to prepare highly loaded and active PROX gold catalysts.

The metallic precursor $Zr_{0.5}Au_{0.5}$ is obtained by arc-melting of Zr and Au wires under an Ar atmosphere. The metallic sample is then roughly ground and oxidised in air at 298 K during one month, which leads to the formation of an intimate mixture of nanostructured gold and zirconia, as was previously shown.[9] The size of both the gold and zirconia crystallites, estimated from the broadening of X-ray diffraction peaks using the Scherrer formula, is found to be about 7 nm after one month, in agreement with TEM observations. New characterisation of the material indicates that this solid is essentially mesoporous with a specific surface area of 82 $m^2\ g^{-1}$. TEM studies using replicas (selective dissolving of the zirconia) give an insight into the morphology of the gold (Fig. 1), which appears as nanoparticles, mostly connected and arranged in 2D filament-like structures, with diameters higher than 5 nm and lengths of tens of nanometers. Since our Au/ZrO_2 material is ligand-free, no post-synthetic calcination or reduction steps are needed. Here, all the catalytic tests have been performed on the fresh materials without any pretreatment.

Considering the current state of knowledge in gold catalysis, it was interesting to find that this material (with gold entities larger than the usual active gold catalysts for CO oxidation) was actually active in CO oxidation (2% CO, 2% O_2 in He), as can be seen in Fig. 2. Some additional stability tests have shown that the catalyst is stable under CO oxidation conditions for 20 h at 383 K (temperature of half-conversion). The activity of our Au/ZrO_2 material is found to be 0.025 mmol $g_{Au}^{-1}\ s^{-1}$ at 350 K (25% CO conversion), which compares well with the activity of other Au/ZrO_2 catalysts described in the literature and prepared by very different methods (Table 1). We suggest that, although the gold "particle" size is higher than in the other catalysts, the peculiar structure of our oxide "support" (7 nm, nanocrystalline ZrO_2) could account for the activity observed. It has indeed recently been reported that a nanocrystalline ceria support enhances the activity of a Au/CeO_2 catalyst in CO oxidation by two orders of

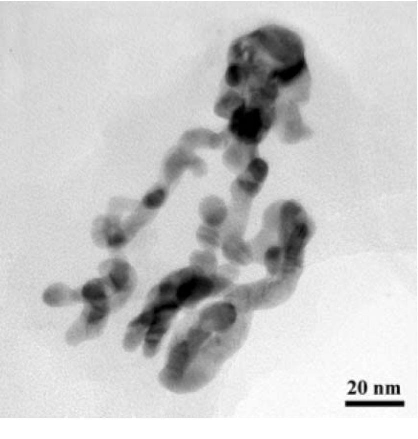

Fig. 1 TEM micrograph of a Au/ZrO_2 replica.

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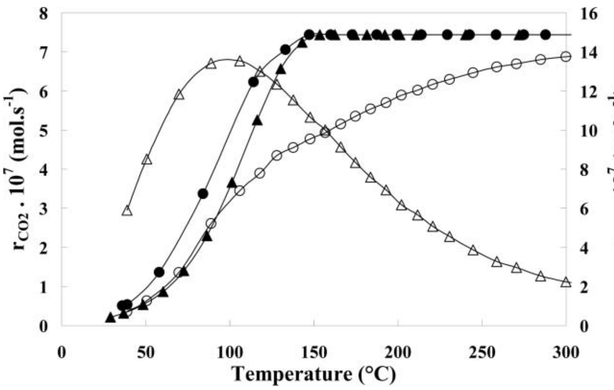

Fig. 2 CO oxidation rate (triangle) and H_2 oxidation rate (circle) over Au/ZrO_2 catalyst as a function of the reaction temperature. Testing conditions: 10 mg catalyst, total flow rate 50 sccm (standard cubic centimeter per minute), 2% CO (or 48% H_2), 2% O_2 in He for the H_2-free (or CO-free) mixture (dark symbols) or 2% CO, 48% H_2, 2% O_2 in He for the PROX mixture (open symbols). In the H_2-free and CO-free mixtures, maximum conversions are reached (100% for CO and 8.3% for H_2) when the oxidation rates become constant above 150 °C.

magnitude.[12] The catalytic properties of this material indicate that small gold particle size is, in some cases, not essential to achieve high activity in gold-catalysed CO oxidation and that structuration of the oxide support could play a so far underestimated role in this reaction.

In the oxidation of hydrogen (48% H_2, 2% O_2 in He), which was carried out in a large excess of H_2, the catalyst is more active than in the oxidation of CO (Fig. 2). Of course the large partial pressure of hydrogen could contribute to this phenomenon. Generally, the catalyst ability to oxidise CO more readily than H_2 is thought to be a prerequisite for selective CO oxidation in the presence of H_2.[13] Considering that the temperature corresponding to the conversion of 25% of O_2 is about 30 K lower in the H_2 oxidation reaction than in CO oxidation, our Au/ZrO_2 catalyst was not expected to be an ideal candidate for selective oxidation of CO in presence of a large excess of H_2.

However, the CO conversion is actually largely enhanced at low temperature ($T < 398$ K) when H_2 is present in the reactive mixture while the conversion of H_2 is at the same time decreased (Fig. 2). The actual selectivity is hence found to be much higher than that expected from the results obtained for the oxidations of CO and H_2 when O_2 is the only counterpart reactant gas. It reaches 87% at 35 °C (when 40% CO is converted) and decreases with increasing temperature to 55% at 100 °C (when 92% CO is converted) down to 10% at 300 °C. Furthermore, some stability tests have shown that the catalyst is stable under PROX conditions for 70 h at 366 K. The above results seem surprising since, for most Au supported catalysts,[5,13,14] the CO conversion is generally reported to decrease when H_2 is introduced in the reaction mixture, due to the competition of adsorption between H_2 and CO, as described by Schumacher *et al.* in the pressure range 0.03 kPa $< P_{CO} <$ 2 kPa.[14] The only observed beneficial effects of H_2 on gold catalysis relate mostly to the prevention of deactivation and/or regeneration of deactivated catalysts.[15]

On the other hand, it has been shown recently, first, that addition of water in CO + O_2 mixtures accelerated the CO oxidation rate over gold catalysts[16] and, second, that the effect of the H_2 co-reactant on the kinetics of the reaction over Au/TiO_2 was closely related to the partial pressure of CO and H_2.[14] This would explain why no general trend exists in the literature with respect to an amplification or a decrease of the CO oxidation rate in the presence of hydrogen. In the CO + O_2 + H_2 mixture under our conditions, the enhancement in CO oxidation could be due to the oxidation of H_2, which gives water (Fig. 2). This water product would then react as previously described, resulting in an increase in the CO oxidation rate without modification of the reaction pathway (activation energies unchanged).[16] However, we do not exclude the possibility of the formation, from the reaction of H_2 with O_2, of hydroperoxy-like intermediate species[17] which can oxidise CO.[18] This has already been invoked in the direct vapour-phase selective oxidation of propylene to propylene oxide over gold catalysts, using both molecular hydrogen and molecular oxygen,[19] and would account for the fact that the presence of H_2 in our CO + O_2 mixture does not only prevent deactivation but also enhances the CO oxidation rate.

In summary, we have shown that materials other than the state-of-the-art CO oxidation catalyst Au/TiO_2 can be used for the PROX reaction, by taking advantage of the beneficial effect of H_2 on the CO oxidation rate. We have demonstrated the potential of the spontaneous oxidation method to produce such highly loaded and active gold catalysts *via* the oxidation of a $Zr_{0.5}Au_{0.5}$ single-phase alloy in air at 293 K. This solvent-free method, which requires neither costly post-synthetic heat treatments nor the costly set-ups involved in the physical routes of preparation, is thought to be an alternative route in terms of cost and environment. This could be indeed a suitable method for the preparation of active gold catalysts on a large scale.

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Table 1 Activity of various Au/ZrO_2 catalysts in the oxidation of CO (2% CO, 2% O_2 in He)

Preparation	Au (wt%)	d (nm)	P_{CO} (mbar)	P_{O_2} (mbar)	CO oxidation rate (mmol$_{CO}$ g$_{Au}^{-1}$ s^{-1})	Ref.
Laser vaporisation	0.05	2.9	20	20	0.078	7
Colloid deposition	1.7	2	2.5	2.5	0.008	10
Coprecipitation	1.0	4	2.5	2.5	0.027[a]	11
Oxidation of ZrAu alloy	61.5	> 7	20	20	0.025	This work

[a] Extrapolated from the temperature of 30% conversion to a reaction temperature of 350 K assuming an energy of activation of 30 kJ mol^{-1}.

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