Selective oxidation of CO in the presence of H_2, H_2O and CO_2 *via* gold for use in fuel cells†

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An Au/Fe_2O_3 catalyst prepared using a two-stage calcination procedure achieves target conversion and selectivity for the competitive oxidation of dilute CO in the presence of moist excess H_2 and CO_2.

The recently established ability of gold to oxidise CO at relatively low temperatures[1] has a potential application in power-generation systems that combine a polymer electrolyte fuel cell (PEFC) with a catalytic reformer,[2] *e.g.* for electric vehicles. The reformer converts an organic fuel to a hydrogen-rich gas feed for the PEFC, which electrochemically oxidises the hydrogen to generate electricity and water. However, residual CO in the reformer output poisons the Pt anode at the relatively low PEFC operating temperature (*ca.* 80 °C).[3] Industry has adopted two approaches in an attempt to deal with this problem, thereby ensuring that effective performance of the PEFC can be achieved, namely, either to make the anode of the fuel cell more CO tolerant, or to develop catalytic systems capable of removing even trace amounts of CO from H_2 in the presence of excess CO_2 and water. We have now successfully addressed the latter of these two approaches. Although conceptually simple, the oxidation of CO in the presence of excess moist H_2 and CO_2, without oxidising the hydrogen or remaking CO *via* the reverse Water Gas Shift reaction, is a particularly difficult objective, which has so far only been achieved using a multistage reactor.[4] There have been no reported examples of this process being successfully carried out in a single catalyst bed under industrially relevant conditions. We now present a heterogeneous catalyst for the selective oxidation of CO in the presence of H_2 and CO_2 at 80 °C that gives stable catalyst performance under realistic fuel cell conditions.

Considerable effort has been applied to the design of suitable catalysts for the competitive oxidation of CO in the presence of H_2, and the most commonly used partial oxidation catalysts (alumina-supported Pt, Pt/Fe, Ru and Rh) are unsuitable since they require temperatures in the range 150–200 °C to be effective,[5–7] and even then significant conversion of H_2 is observed. Haruta and co-workers[8,9] first demonstrated that supported Au nanoparticles could be active at much lower temperatures, but again H_2 was oxidised together with CO at temperatures > 70 °C. Au/Fe_2O_3 catalysts have also been studied and Kahlich *et al.* used catalysts calcined at 400 °C but found that significant H_2 oxidation occurred at 80 °C.[10] Most recently, Qiao and Deng[11] showed that non-calcined Au/Fe_2O_3 catalysts, dried only at 120 °C, were very

selective for CO oxidation in the presence of H_2 at 25 °C, but the selectivity was lost at higher temperatures. To date, some of the best results for this demanding reaction have been reported by Grigorova *et al.*[12] for a Au/CeO_2 catalyst promoted with SnO_2, but even this catalyst gives significant (*ca.* 5%) H_2 conversion at temperatures > 70 °C with CO conversions of *ca.* 40–60%. Recently, Corma and co-workers[13] reported a nanocrystalline CeO_2-supported gold catalyst that gave appreciable selectivity at 60 °C for a dry CO/H_2 mixture. However, it is significant that these previous studies use dry reactants and consequently are not applicable to the humid conditions prevailing in the fuel cell application, which in addition also contains significant quantities of CO_2. The presence of excess CO_2 presents an additional problem since if the catalyst is active for the reverse water gas shift reaction then CO will be remade, and this is a key feature that has limited success in this field to date. An interesting development by Watanabe *et al.*[14] was the use of Pt–Fe supported on mordenite rather than alumina, but these catalysts are not robust under reaction conditions and generally suffer the same problems as the Pt–Fe/alumina catalysts; consequently they have not been commercially exploited.

We have studied Au/Fe_2O_3 catalysts prepared by coprecipitation.[15] Initially, the catalysts were investigated for CO oxidation in the absence of H_2 (Table 1). We subsequently investigated the addition of H_2 to the reactant gases (2 : 1 H_2 : CO molar ratio), but still using dry gases in the absence of excess CO_2, and this led to a decrease in CO conversion (Table 1), which is consistent with earlier studies.[9] Drying the 5 wt.% Au/Fe_2O_3 at 120 °C gave a catalyst that was active for H_2 oxidation at 27 °C (Table 1). Catalysts calcined at 550 °C, whether for 3 h or 8 h, retain considerable CO oxidation activity but show no oxidation of H_2 even at 73 °C. This activity was consistently observed for tens of hours of catalyst testing. Calcination of the material at lower temperature, *e.g.* 400 °C, gave a catalyst with activity for H_2 oxidation at 73 °C (Table 1). Interestingly, calcination at 400 °C followed by calcination at 550 °C did not reproduce the performance of a catalyst calcined only at 550 °C. This demonstrates the extreme sensitivity of this catalyst system to the calcination conditions, and this will be discussed subsequently. Calcining at 600 °C completely destroys the catalyst activity (Table 1). We investigated alternative supports and active metals, but no combination was as effective as the Au/Fe_2O_3 catalysts.[15] Au/TiO_2 and Au/Al_2O_3 catalysts were inactive for both CO and H_2 oxidation whereas the $Au/Pd/Al_2O_3$ and Pd/Al_2O_3 catalysts were only active for H_2 oxidation (Supplementary Table 2). 1 wt.% Au/CeO_2 was selective up to 52 °C but at higher temperature significant H_2 conversion was observed, which is consistent with the previous literature.[12]

Table 1 Oxidation of CO by 5% Au/Fe_2O_3 in the presence of $H_2{}^a$

Calcination conditions	CO conversion (%)				H_2 conv. (%)		
	No $H_2{}^b$ 27 °C	27 °C	50 °C	73 °C	27 °C	50 °C	73 °C
dried 120 °C, 8 h	*100*	100	92	90	7	40	85
400 °C, 3 h	*91*	68	84	91	0	0	17
400 °C, 3 h, then 550 °C, 2 h	*68*	37	71	80	0	0	5
550 °C, 3 h	*31*	17	25	33	0	0	0
550 °C, 8 h	—	12	19	37	0	0	0
600 °C, 3 h	*0*	0	0	0	0	0	0

^{a} 0.4 vol.% CO, 0.8 vol.% H_2, 16 vol.% O_2, 50 mg catalyst, GHSV = 30 000 h^{-1}. ^{b} 0.5% CO in air, 50 mg catalyst; GHSV = 24 000 h^{-1}.
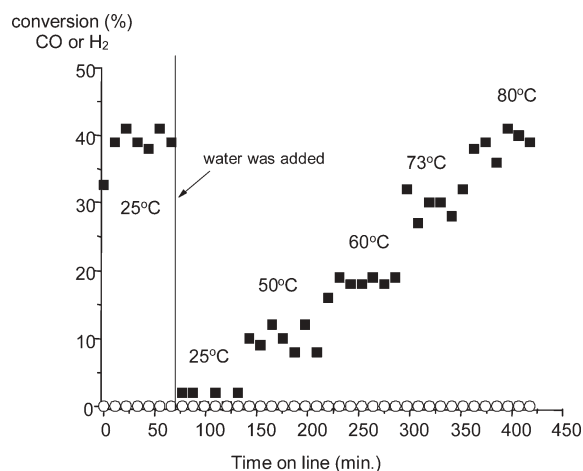
Fig. 1 Influence of the presence of water (4 wt.%) on the CO (■) and H_2 (○) conversion at different reaction temperatures for a 5% Au/Fe_2O_3 catalyst calcined in air at 550 °C. Reaction conditions: 0.4 vol.% CO, 0.8 vol.% H_2, 16 vol.% O_2, 50 mg catalyst, GHSV = 30000 h^{-1}.

On the basis of these initial results we were encouraged to investigate the effect of adding water vapour under these reaction conditions. Fig. 1 shows the influence of the presence of water (4 wt.%) in the feed at different reaction temperatures. The presence of water leads to a decrease in CO conversion that is recovered by increasing the reaction temperature. It should be noted that no H_2 conversion was observed even at a reaction temperature of 80 °C, showing the beneficial effect of water on the selectivity towards CO oxidation in the presence of H_2.

Operation in those fuel cell systems in which the hydrogen is generated by reforming hydrocarbons or oxygenates requires additional factors to be considered, since not only water vapour but CO_2 is present in excess.[2] For successful operation as a selective CO oxidation catalyst in a reformer–PEFC system, it must be operated at *ca.* 80 °C in a complex feed comprising CO, O_2, H_2, CO_2, H_2O and N_2, and be capable of reducing the CO concentration from about 1% to below 50 ppm – this is equivalent to a CO conversion of at least 99.5%. In addition, this conversion must be achieved without the addition of excess O_2 and the competitive oxidation of H_2 must be minimised. This is expressed as selectivity which is defined as the percentage of the oxygen fed that is consumed in the oxidation of CO, and for commercial operation a selectivity of 50% is acceptable, since at this selectivity minimal H_2 is oxidised to water. Taken together this represents a demanding target and this is summarised in Table 2 and Supplementary Table 1. Tests using our supported gold catalyst show that we can readily achieve this very demanding target when the Au/Fe_2O_3 catalyst is calcined in two stages (Fig. 2). The catalysts are exceptionally stable and have been operated successfully for extended periods. This is the first reported study for any catalyst that has fully met this required operational target in a single packed bed at realistically high space velocity. In Table 2 our results are contrasted with those of previous studies using Au/Fe_2O_3, and in Supplementary Table 1 with the most important results from the literature, confirming that we are the first to report this achievement. In addition, we have prepared two of the leading catalyst formulations, namely Au/Fe_2O_3 dried at 120 °C, and Au/CeO_2, and neither of these catalysts is capable of achieving the required target (Supplementary Table 1).

Analysis of the 5 wt.% Au/Fe_2O_3 catalysts using electron microscopy (Supplementary Fig. 1) shows that calcination of the catalyst increases the Au particle size: for the series (i) dried at 120 °C, (ii) calcined at 400 °C, (iii) calcined at 400 and 550 °C, (iv) calcined at 550 °C and (v) calcined at 600 °C; the Au particle sizes are 3.5, 3.7, 6.7, 8.0 and 16.1 nm respectively. For the same series of catalysts the surface areas are (i) 203, (ii) 45, (iii) 26, (iv) 16 and (v) 11 m^2 g^{-1} respectively. The dramatic loss of activity for catalysts calcined at temperatures greater than 550 °C is thus due to a combination of growth in the Au particle size and the loss of

Table 2 Comparison of Au/Fe_2O_3 catalysts for the selective oxidation of CO in the presence of H_2, H_2O and CO_2

T_{calc} °C	Reactant mixture composition					Conv%	Sel%	T °C
	CO	O_2	H_2	H_2O	CO_2			
Target	**0.8–1.0**	**0.4–1.0**	**50**	**2–10**	**20–24**	**> 99.5**	**> 50**	**80–110^c**
^{a}	0.9	0.9	50	4.7	22	99.8	51	80
400 °C[20]	*0.1*	*0.1*	66	10	22	^{b}	*29*	80
120 °C[11]	1	*4*	50	*0*	*0*	100	100	50
400 °C[19]	1	*1.25*	50	10	*15*	*65*	60	80
400 °C[19]	1	*1.25*	50	10	*15*	99.5	54.5	100

^{a} This work 400 °C + 550 °C. ^{b} Activity quoted as 0.003 mol CO (g Au·s). ^{c} Most PEFCs currently run at 80 °C. Figures in ***bold italics*** show where target requirements are not achieved.
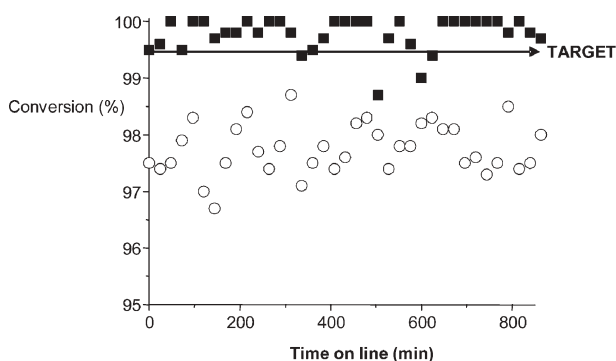
Fig. 2 Variation of CO (■) and O_2 (○) conversion with time on line for a 5% Au/Fe_2O_3 catalyst calcined in air at 400 + 550 °C. Reaction conditions: 80 °C, 0.9% CO, 0.9% O_2, 50% H_2, 22% CO_2, 4.7% H_2O with the balance N_2; 100 mg of catalyst were used with a total flow rate of 20 ml/min, GHSV = 12000 h^{-1}.

surface area. Au(4f) X-ray photoelectron spectra obtained for the Au/Fe_2O_3 samples calcined at different temperatures (Supplementary Fig. 2) show that for samples calcined at temperatures of 400 °C and lower, the signal comprises a marked doublet which we ascribe to the presence of cationic gold in addition to metallic gold. It is possible that this shift in binding energy is associated with a relatively sharp bimodal particle size distribution but the microscopy we have carried out does not reveal this to be the case (Supplementary Fig. 1). The spectrum for the sample calcined at 400 °C and subsequently 550 °C shows that all the cationic gold has now been reduced to metallic gold. The Au(4f) spectrum observed after calcination at 600 °C shows a significant increase in intensity, and a clear decrease in line-width, consistent with the diffusion of Au from the pores of the catalyst, and agglomeration to form metallic gold particles, which are inactive for both CO and H_2 oxidation.

It is important to determine the key factors controlling the enhanced activity and selectivity we have observed with the Au/Fe_2O_3 catalyst since previous studies have used similar catalysts and have come close to achieving the target, yet failed. The answer lies in the need to control the activity of the catalyst for the reverse water gas shift reaction whilst retaining CO oxidation activity. Two recent studies on model catalysts[16,17] are important in this respect since it has been shown that metallic gold, in particular morphologies, is very active for CO oxidation[16] whereas cationic gold is particularly effective for the water gas shift (WGS) reaction,[18] and consequently will also catalyse the reverse reaction:

$$CO_2 + H_2 \rightarrow CO + H_2O$$

This reaction leads to the formation of CO thereby ensuring the target CO conversion cannot be achieved. Hence the design criterion is to prepare a catalyst comprising small gold nanocrystals whilst ensuring that all cationic gold is removed. In our case we have achieved this by a two stage calcination procedure, but it is possible that other preparation strategies are equally feasible. A scrutiny of the results of previous studies presented in Supplementary Table 1 shows that Avgouropoulos *et al.*[19] came close to achieving the target at 100 °C, with a Au/Fe_2O_3 catalyst calcined at 400 °C, but required excess O_2 and low CO_2. Furthermore, in their studies the CO conversion decreased

markedly at higher temperatures due to the reverse WGS reaction catalysed by the residual cationic gold present in this sample.

We conclude that the most selective catalysts for CO oxidation in the presence of H_2 comprise relatively large Au nano-crystals (> 5 nm) supported on a reducible oxide. These initial results demonstrate that the calcination temperature used to prepare supported Au nano-crystals is of crucial importance. Most importantly it is essential that residual cationic gold is reduced during the pre-treatment since this, if present, will catalyse the reverse WGS reaction thereby decreasing CO conversion, and it is for this reason that previous Au formulations have failed to achieve this challenging target. Hence, by careful manipulation of the preparation conditions we have prepared a stable gold catalyst that can selectively oxidise CO in the presence of H_2, H_2O and CO_2 and successfully operate in the demanding environment of a fuel cell system, giving stable sustained performance. We have not fully optimised the formulation of this catalyst and so we anticipate further improvements in this exciting new development.

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