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CO oxidation activity of gold catalysts supported on various oxides and their improvement by inclusion of an iron component

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Abstract

A number of oxide-supported gold catalysts have been prepared by deposition–precipitation, with variation of the pH over a wide range, the optimum pH for high activity being 9 for TiO_2, 7.5 for Fe_2O_3, and 7 for SnO_2 and CeO_2. Whereas the activity shown by Au/TiO_2 and Au/Fe_2O_3 decreased linearly with time, Au/CeO_2 and Au/SnO_2 underwent an initial major deactivation. Addition of iron in the preparation lowered the rate of deactivation when TiO_2, SnO_2 and CeO_2 were used as supports, and imparted activity when as with Bi_2O_3 it was previously lacking. XPS revealed the existence of a broad multi-state iron-containing region, and TEM and STEM/EDX indicated that small gold particles (1.5–4 nm) were partly in contact with it. Improved stability is therefore due to gold particles being in contact with an iron phase such as FeO(OH); calcination removed the stabilisation.

Keywords: CO oxidation; Au catalysis; Deactivation

1. Introduction

The discovery that gold catalysts have high activity for the oxidation of CO has stimulated extensive research in the last decade [1]. The most widely used preparative method is the so-called deposition–precipitation suggested by Haruta et al. [2]; this leads to the formation of gold nanoparticles and very active catalysts. It is now evident this activity is directly linked to two main factors: (i) small particle size, (ii) the use of an oxide of a transition metal able to assist in the reaction [3,4].

We have previously listed some of the variables in the preparation of Au/TiO_2(P-25) catalysts, any of which could affect their performance in CO oxidation [5–7], and a preparation procedure has been formulated in which the optimum pH for high activity was proven to be 9. A further variable factor concerns the choice of the support. Its influence on the CO oxidation activity of supported gold catalysts has been discussed in many articles [1–4] but of the many transition and post-transition metal oxides that possess activity for catalytic oxidation, and which therefore might be of interest as supports for gold, the focus has been on the oxides of titanium and iron; oxides of nickel, cobalt, cerium and manganese have also been examined [1–4]. We now report on the use of the oxides of tin, zirconium and bismuth.

Activity is not however the only criterion that must be fulfilled for a suitable catalyst for CO oxidation; long-term stability is also a key feature. In many cases activity progressively decreases with time when reaction is carried out at about ambient temperature. This has been mainly ascribed to the formation on the support of carbonate or carboxylate groups that somehow interfere with the reaction [8]; the effect, which is greater when carbon dioxide is added [9], can be completely reversed by heating in oxygen to 573 K [8], although slight sintering of the gold particles or reduction of the support may also take place. Following a suggestion that increasing the basicity of the support may improve the stability [10], we have made and tested a series of iron-containing gold catalysts on several different supporting oxides to see whether the rate of deactivation during CO oxidation is thereby decreased. We find that the inclusion of iron has indeed a marked effect in increasing stability.

2. Experimental

In our initial DP method (Method A) [5,6], $HAuCl_4$ (Alfa-Aesar, 99.99%) solution with a concentration of 1×10^{-4} M was first prepared. Its pH was initially raised to 4–12.5 using

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NaOH solution (0.1–0.5 M), and TiO_2 (Degussa P-25, 55 $m^2\ g^{-1}$) was then added with stirring at room temperature (1 g/50 ml solution). For each preparation the initial pH (pH_i), the pH after the TiO_2 addition (pH_a) and the final pH (pH_f) were noted. Systematic pH decreases were observed just after TiO_2 addition and during the heating step. The resulting suspension was heated to 343 K and vigorously stirred for 1 h; after cooling it was filtered and the solid washed thoroughly with deionised water and then vacuum-dried at room temperature. Calcination was not usually performed but when used it was carried out under air (30 ml min^{-1}) at 673 K.

A slightly different method was used to study the effect of ph on the preparation of catalysts using SnO_2, CeO_2 and Fe_2O_3 as supports. After deciding an initial pH, addition of the support cause some fall in pH; subsequent addition of alkali brought it to a value about 1 unit below the target value, and it was kept at this value throughout the preparation by further addition of NaOH as necessary. Very low pH values (i.e. below that of the $HAuCl_4$ solution, pH 2.6) were obtained by adding nitric acid. The gold loading aimed for was 1%. The resulting suspension was then vigorously stirred for 1 h at 343 K; after cooling it was filtered and the solid washed thoroughly with deionised water and then vacuum-dried at room temperature.

A series of catalysts was prepared with TiO_2 (Degussa P-25), SnO_2, Fe_2O_3, ZrO_2, Bi_2O_3 (all supplied by Alfa Aesar) and CeO_2 (Sigma) by adding $Fe(NO_3)_3$ to the $HAuCl_4$ solution before adjustment of the pH with NaOH. It fell after adding the support, but was raised to 9 by NAOH and kept at this value throughout the preparation. Precipitation of $Fe(OH)_3$ occurred before the support was introduced, but was totally retained by it. The extent of the gold uptake varied, depending on the isoelectric point of the support (maximum 1%); the iron content was about 5% on all catalysts. Samples of different iron content were also prepared with SnO_2.

Oxidation of CO was carried out in a plug flow bed reactor, the catalyst being supported on a silica wool bed near the bottom of one side of a glass U-shaped reactor. The gas flow (0.50 vol.% CO) in synthetic air was introduced through a mass flow controller. Analysis was performed on-line by means of a Varian 3300 GC using a manual sampling valve, CTR1 column (Alltech), TCD, and helium carrier gas. Temperatures were measured using an in situ thermocouple well, the experiments being carried out between 183 and 373 K. Sub-ambient temperatures were achieved by mixing methanol with Cardice or liquid nitrogen; high temperatures were obtained by heating the reactor in a furnace.

The wt.% of gold and iron deposited was determined by Atomic Absorption analysis, calibration being first performed using $HAuCl_4$ and $Fe(NO_3)_3$ solutions of different concentration.

CO conversion was always measured as a function of the temperature. Activity was first tested at room temperature: after 3 h, any loss of activity had become very slow; so the reactor was then placed in a Dewar flask, and the temperature lowered, after which it was allowed to rise stepwise to a final value. The standard test used a 55 $cm^3\ min^{-1}$ reactant flow and 50 mg of catalyst (space velocity 17,000 h^{-1}). Temperature at 50% conversion (T_{50}) was always measured under the standard test conditions. To ensure that all the activity was firmly related to the presence of gold, the supports were also tested; under our standard test conditions none was active below 573 K.

We were concerned to determine activity under conditions of kinetic control since in the region of diffusion control its value would be underestimated. For several of the more active catalysts, the reaction was therefore also carried out at a higher space velocity (flow rate 150 $cm^3\ min^{-1}$, 20 mg of catalyst, space velocity 115,000 h^{-1}). Plotting of specific rates according to the Arrhenius equation revealed distinct regions corresponding to mass transport and kinetic control. Long-term experiments were carried out at room temperature for 50–100 h. Most of the catalysts tested were initially so active at room temperature as to give 100% conversion under standard conditions; clearly deactivation could be occurring unobserved if conversion continued at the 100% level, so the space velocity was increased to bring the conversion into the range 80–90%.

3. Results and discussion

3.1. Effect of pH variation using Degussa P-25 titania

The initial preparations were carried out by Haruta's DP method [2] as described in Section 2, Au/TiO_2(P-25) catalysts being prepared with the same initial concentration of the gold solution corresponding to a maximum gold uptake of 1 wt.%. In a previous study [6] we proved that the decisive pH was that used at the end of the preparation, just before filtration, so that only the final pH of the preparation will be taken into account in the discussion. The results are summarised in Table 1. The gold uptake was maximum at pH 6 and decreased at higher pH. This was ascribed to a change of the charge on the support, becoming increasingly more negative above the isoelectric point (∼pH 6) [11]. This results in an electrostatic repulsion of gold-containing anions. At the isoelectric point there are equal numbers of positive and negative charges, but even above pH 6 there may be some sites that are positively charged and that may interact with anionic gold species. Adsorption by electrostatic interaction is unlikely to be important in this region, so another adsorption mechanism has been suggested. This may involve a neutral $Au(OH)_3(H_2O)_n$ in solution in equilibrium with the anion [6].

Table 1
Effect of pH of the preparation (pH_f) on catalysts prepared by method A using Degussa P-25 TiO_2

Au (wt.%)	pH_f	T_{50} (K)	r_{sp} ($\times 10^4$ $mol_{CO}\ s^{-1}\ g_{Au}^{-1}$)	E_a (kJ mol^{-1})
0.92	2.2	>433	0.03	22
0.93	2.5	463	0.016	24
1	5.9	273	0.25	29
0.89	7.7	253	1.1	29
0.60	8.5	246	2.7	25
0.65	9	243	3.7	35
0.16	11.5	293	2.0	30
0.06	12.5	373	0.01	40

Column headings: Au weight percentage (Au wt.%), pH at the end of the preparation (pH_f), temperature at 50% conversion (T_{50}) using standard conditions, specific activity at 243 K (r_{sp}), activation energy E_a.

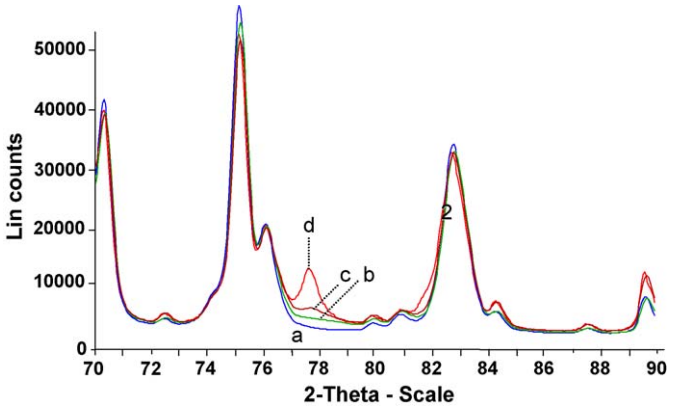

Fig. 1. XRD patterns in the region 70–90° 2θ; (a) TiO_2, (b) 0.6% Au/TiO_2, pH_f 8.5, (c) 0.92% Au/TiO_2, pH_f 6.4, and (d) 0.93% Au/TiO_2, pH_f 2.5.

Fig. 1 shows the XRD patterns of the catalysts prepared at pH 2.5, 6.4 and 8.5. The catalyst prepared at pH 8.5 gave a single weak peak at $2\theta = 77.4$ characteristic of a small particle size, but when the pH was decreased to 6.4 and 2.5 the peaks became sharper and characteristic of bigger particles. TEM (Fig. 2) confirmed the dependence of particle size on pH. In catalysts prepared at final pH 9 it was in the range 1.5–4 nm and the mean diameter measured with more than 100 particles was 2 nm. Preparation at final pH 6 led to a heterogeneous distribution of particle size in the range 4–20 nm and an average size of 10 nm. We also noticed at both pH values that the majority of the gold particles were multiply twinned (Fig. 2(c)).

Fig. 3 shows how CO conversion depended on temperature and on pH for uncalcined catalysts. Those prepared at pH 2–3 have a very poor activity; pH increase causes an activity enhancement up to pH 9, but the activity of the catalysts prepared at pH 11.5 and 12.5 is less, and at pH 12.5 it was again very low (Fig. 3). Both these catalysts quickly lost their activity.

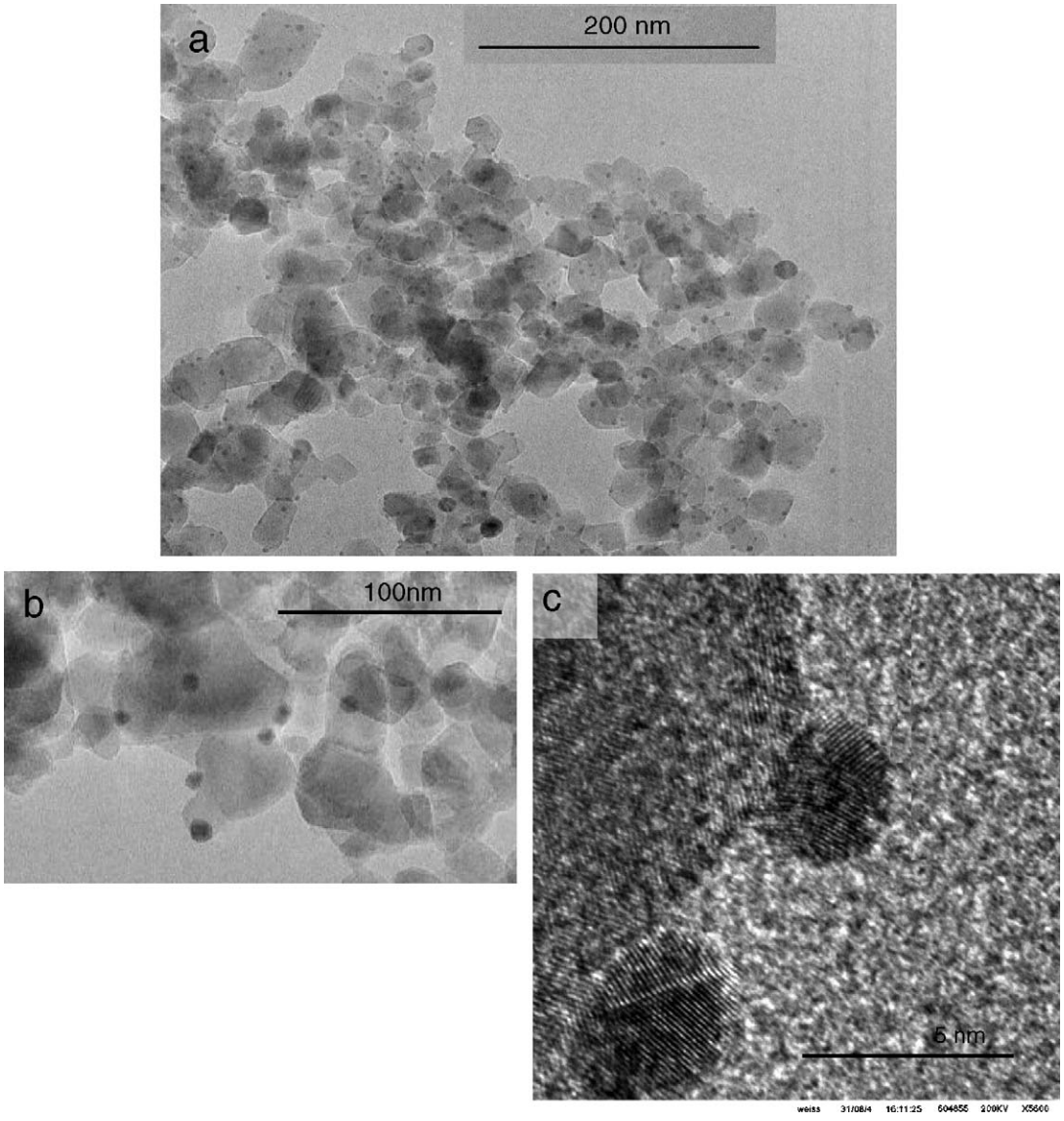

Fig. 2. Electron micrographs of (a) 2.3% Au/TiO_2(P-25) prepared at pH 9, (b) 1% Au/TiO_2(P-25) prepared at pH 6, and (c) 0.5% Au/TiO_2(P-25) prepared at pH 9.

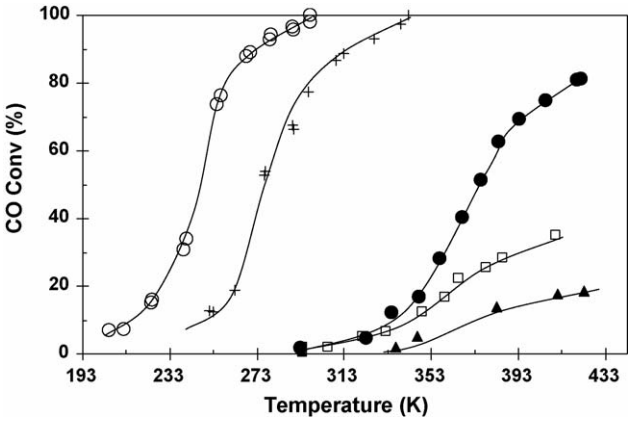

Fig. 3. CO conversion as a function of the temperature for catalysts made at various pH values using TiO_2(P-25). (▲) 0.92% Au/TiO_2, pH_f 2.2; (□) 0.93% Au/TiO_2, pH_f 2.5; (+) 1.07% Au/TiO_2, pH_f 5.9; (○) 0.60% Au/TiO_2, pH_f 8.5; (●) 0.06% Au/TiO_2, pH_f 12.5.

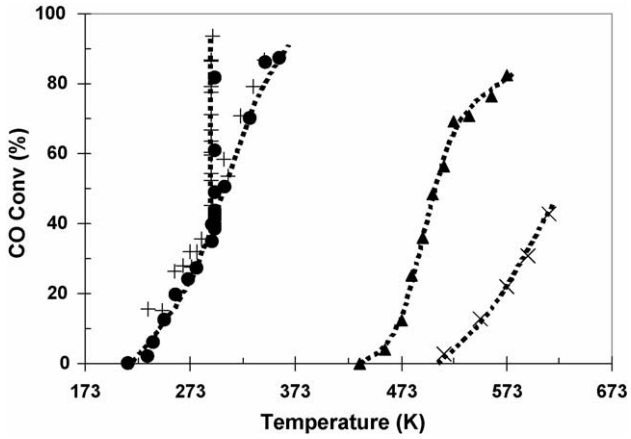

Fig. 4. CO conversion as a function of the temperature for catalysts made at various pH values, using SnO_2. (▲) 0.63% Au/SnO_2, pH 2.3; (+) 0.76% Au/SnO_2, pH 5.3; (●) 0.82% Au/SnO_2, pH 7.7; (×) 0.27% Au/TiO_2, pH 11.3.

Specific activities at 243 K are reported in Table 1, and an activity optimum at pH 9 of $3.7 \pm 0.4 \times 10^{-4}$ $mol_{CO}\ s^{-1}\ g_{Au}^{-1}$ is higher than those reported in the literature [12–15]. The most straightforward explanation of this activity variation is that an optimal gold particle size is obtained at pH 9. Its existence has been discussed in the literature, and a maximum efficiency for CO oxidation for particles in the range of 3–4 nm has been demonstrated for a model system [16]. At high pH there may be some $Au(OH)_5^{2-}$ anions in solution, leading to a strong repulsion between them and the support [17].

3.2. Effect of pH variation using other supports

It was shown long ago [18,19] that collaborative effects between metal and support were shown in the oxidation of CO. Pd/SnO_2 catalysts were more active than either SnO_2 alone or Pd/Al_2O_3, and a kinetic analysis [19] suggested that this was due to spillover of CO from the metal to the support, providing a flux of reactant to what without the metal would have been the slow step, namely, reaction with lattice oxygen in a Mars–van Krevelen mechanism. We have therefore examined gold catalysts supported on oxides that would be active in their own right, to see whether their activity in CO oxidation was in any unusual. A series of catalysts was prepared using SnO_2 (surface area 10 $m^2\ g^{-1}$), fixing the pH at 0.8, 2.3, 5.3, 7.7, 9 and 11.3 throughout the preparation; results are shown in Table 2 and Fig. 4. Catalysts prepared at pH 0.8–2.3 have a poor activity, higher activity being obtained with catalysts prepared at pH 5–8, but those catalysts undergo a large initial drop in activity that was not observed on Au/TiO_2 catalysts. The activation energy measured from the Arrhenius plots in the range of kinetic control was 13–15 kJ mol^{-1}, independent of pH. Specific rates measured at 243 K are nearly the same for the catalysts prepared between pH 5 and 8, the value

Table 2
Effect of pH of the preparation (pH_f) on catalysts prepared using various oxide supports

Catalysts	Area	Au (wt.%)	pH_f	T_{50} (K)	r_{sp} ($\times 10^4$ $mol_{CO}\ s^{-1}\ g_{Au}^{-1}$)	E_a (kJ mol^{-1})
Au/TiO_2	47	0.9	9	238	3.7	35
Au/SnO_2	10	0.19	0.8	>573	–	–
Au/SnO_2	10	0.63	2.6	313	–	–
Au/SnO_2	10	0.76	5.3	299	0.6	13
Au/SnO_2	10	0.82	7.7	306	0.5	15
Au/SnO_2	10	0.15	9.0	>573	–	–
Au/SnO_2	10	0.27	11.3	583	–	–
Au/CeO_2	5	0.23	3	>573	–	–
Au/CeO_2	5	0.49	5	353	0.02	30
Au/CeO_2	5	0.8	7.2	303	0.06	36
Au/CeO_2	5	0.2	8	283	0.65	31
Au/CeO_2	5	0.16	9	303	–	36
Au/CeO_2	5	0.14	10.8	333	–	27
Au/Fe_2O_3	45	0.95	7.5	233	3.95	40
Au/Fe_2O_3	45	–	9	263	–	45

Column headings: surface area of the support $m^2\ g^{-1}$ (Area), Au weight percentage (Au wt.%), pH at the end of the preparation (pH_f), temperature at 50% conversion (T_{50}), specific activity at 243 K (r_{sp}), deactivation rate during the first 10 h reaction (deactivation rate (% h^{-1}) 0–10 h), deactivation rate after 10 h reaction (deactivation rate (% h^{-1}) after 10 h).

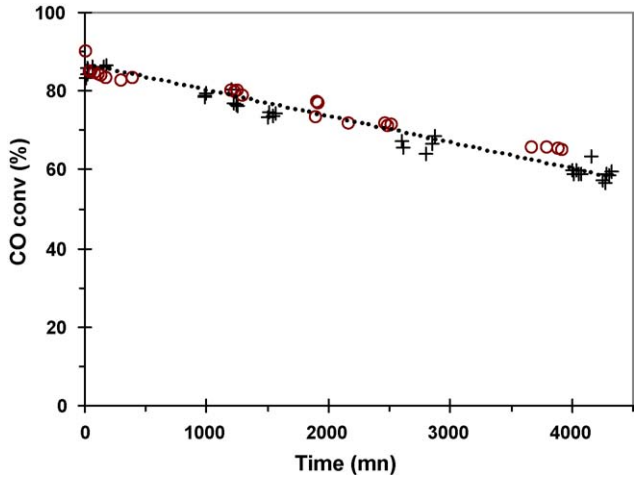

Fig. 5. Long-term test of room-temperature activity on (+) uncalcined 0.14% Au/TiO_2(P-25) (standard test conditions) and (○) 1% Au/TiO_2(P-25) (20 mg catalyst, 150 ml min^{-1} 0.5 vol.% CO (balance air)).

$(5 \times 10^{-5}\ mol_{CO}\ s^{-1}\ g_{Au}^{-1})$, being one order of magnitude lower than that obtained with the TiO_2-supported catalysts (Table 2). By analogy with them, the activity change is seemingly due to a particle size decrease with increasing pH. The specific activity is now optimum in a different range of values (pH 5–8).

The pH at which activity was maximal depended on the nature of the support (Au/Fe_2O_3, pH 7.5; Au/CeO_2, pH 7; see Table 2). By analogy with Au/TiO_2 catalysts, low pH favours the formation of large gold particles and low activity. With SnO_2 and CeO_2 the maximum rate is found at about two pH units above the isoelectric point (respectively, ∼4 and ∼6) as with TiO_2 (P-25, IEP ∼6), but with Fe_2O_3 it occurs below the IEP (∼8).

3.3. Catalyst deactivation

Two Au/TiO_2 catalysts in particular were studied; they contained either 0.15 or 1 wt.% metal. Both catalysts in the uncalcined state suffered of gradual decrease in conversion (0.2–0.3% h^{-1}), see Fig. 5. Calcination of the1 wt.% catalyst at 573 K for 2 h did not change the deactivation rate. An Au/TiO_2 catalyst containing 1 wt.% of gold previously calcined, and deactivated by use for 100 h at room temperature, was heated in air 573 K for 2 h. The initial conversion (80%) was totally recovered. If the interface between the support and the gold particles is the active phase for CO oxidation [3], deactivation could be caused by carbonate species that are formed on the TiO_2 surface surrounding the gold particles [8]; since deactivation is reversible, it appears that carbonate species are easily eliminated by heating the catalyst in air.

Whereas the activity shown by Au/TiO_2 (Fig. 5) and Au/Fe_2O_3 decreased linearly with time over about 4000 min, that of Au/SnO_2 at pH 5.3–7.7 (Fig. 4) and Au/CeO_2 at pH 5–10.8 underwent an initial catastrophic drop. Two experiments were carried out to clarify the reasons for the deactivation. (i) A catalyst previously calcined, and deactivated by use for 25 h at room temperature, was treated in air for 2 h at the same temperature; the initial conversion (80%) was only partly recovered. (ii) A catalyst previously calcined in air at 573 K, and consequently fully reduced, still suffered from an initial rapid deactivation. Carbonate formation is therefore not the only cause of the activity loss, and it is not connected with the reduction of the gold precursor. It may be a consequence of the reduction of the surface of the support in the neighbourhood of the gold particles, this being responsible for the CO_2 formed at the beginning (Fig. 4). Oxidation at 573 K may eliminate

Table 3
Effect of iron on the stability of oxide-supported gold catalysts for CO oxidation

Catalysts	Area	Au (wt.%)	Fe (wt.%)	pH_f	T_{50} (K)	E_a (kJ mol^{-1})	r_{sp} ($\times 10^4\ mol_{CO}\ s^{-1}\ g_{Au}^{-1}$)	Deactivation rate (% h^{-1})	
								0–10 h	After 10 h
Au/TiO_2	47	0.9	0	9	238	35	3.7	0.3	0.3
$FeAu/TiO_2$	47	0.8	4.9	6	268	50	0.2	–	–
$FeAu/TiO_2$	47	0.8	4.9	9	238	40	3.4	0.5	0.1
$FeAu/TiO_2$[a]	47	0.8	4.9	9	263	30	1	1.2	0.3
Au/SnO_2	10	0.82	0	7.7	306	15	0.5	8.25	–
Au/FeO_x–SnO_2	10	0.7	0.5	7	256	30	1.1	3.6	0.20
Au/FeO_x–SnO_2	10	0.5	4.3	7	245	38	1.8	2.8	0.35
Au/FeO_x–SnO_2	10	0.9	12	7	253	64	0.6	0.6	0.20
Au/FeO_x–SnO_2[a]	10	0.5	4.3	7	–	–	–	5	1.65
Au/CeO_2	5	0.8	0	7.2	303	36	0.06	7	–
Au/FeO_x–CeO_2	5	0.9	4.0	7.5	243	68	1.8	1.1	0.35
Au/ZrO_2	5	0.5	0	8.5	318	22	0.3	–	–
Au/FeO_x–ZrO_2	5	0.7	4.0	8.5	245	51	1.7	–	–
Au/Bi_2O_3	–	0.30	0	7.5	>623	–	–	–	–
Au/FeO_x–Bi_2O_3	–	1.0	4.8	7.2	269	41	0.4	0.75	0.30

Column headings: surface area of the support $m^2\ g^{-1}$ (area), Au weight percentage (Au wt.%), Fe weight percentage (Fe wt.%), pH at the end of the preparation (pH_f), temperature at 50% conversion (T_{50}), activation energy (E_a), specific activity at 243 K (r_{sp}), deactivation rate during the first 10 h reaction (deactivation rate (% h^{-1}) 0–10 h), deactivation rate after 10 h reaction (deactivation rate (% h^{-1}) after 10 h).

[a] Calcined at 573 K in air.

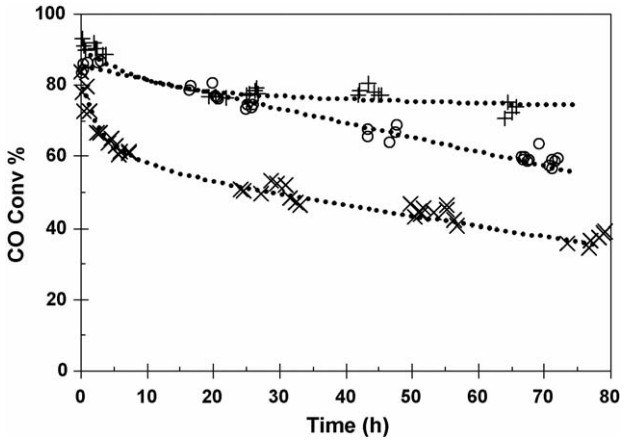

Fig. 6. CO conversion as a function of time, for uncalcined catalysts: (○) Au/TiO_2; (+) Au/FeO_x–TiO_2; (×) Au/FeO_x–TiO_2 calcined 573 K.

carbonate ions but not re-oxidise the surface, because a second oxidation after the second deactivation phase restored the activity to about the same value as after the first oxidation.

3.4. Influence of iron addition

Au/FeO_x–TiO_2 catalysts were prepared by fixing the final pH of the preparation at 6 and 9. As previously shown with Au/TiO_2 catalysts, highest activity was measured on catalyst prepared at pH 9 (Table 3). With all the other supports we consequently decided to fix the final pH of the preparations at a value corresponding to the optimum pH used during the preparation of the corresponding iron-free catalysts.

The inclusion of iron had a beneficial effect on the stability of the catalysts (Table 3 and Figs. 6 and 7). After slight deactivation during the first 15 h, the Au/FeO_x–TiO_2 remained perfectly stable for a further 50 h (Fig. 7), while the initial rapid deactivation shown by Au/SnO_2 was eliminated by the presence of the iron (Fig. 7); a similar advantage was also shown with ceria (Table 3). In all cases where activation energies have been measured, they are markedly higher when iron is present

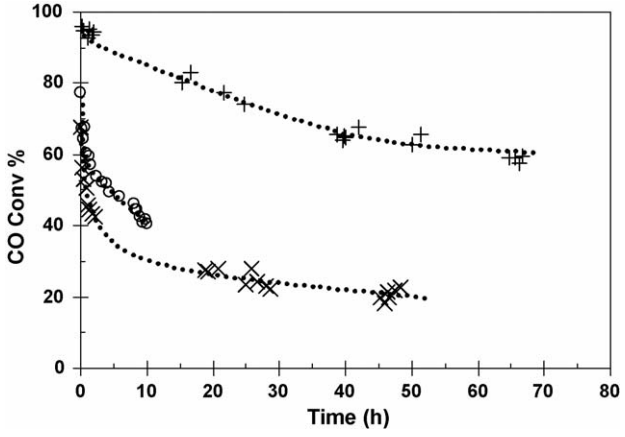

Fig. 7. CO conversion as a function of time, for uncalcined catalysts: (○) Au/SnO_2; (+) Au/FeO_x–SnO_2; (×) Au/FeO_x–SnO_2 calcined 573 K; standard test conditions.

(Table 3). Au/FeO_x–SnO_2 catalysts with ≈1% of gold and, respectively, 0.5, 4.3 and 12 wt.% of iron were also prepared; the increase of iron loading led to a very clear improvement in stability, and in particular to a slower initial deactivation; the activation energy increased progressively (Table 3). Inclusion of iron greatly increased the activity of Au/ZrO_2 and imparted activity when as with Bi_2O_3 it was previously lacking.

Inclusion of the nitrates of other elements in the same proportion as iron in the preparation of Au/TiO_2 catalysts was positively harmful, raising T_{50} to 339 K with cerium and to 356 K with nickel, manganese and cobalt. Most surprisingly the inclusion of molybdenum removed all activity up to 413 K and Au/FeO_x–SiO_2 (using a high-area SiO_2) was also totally without activity. The beneficial effects we have observed cannot therefore be due to the nitrate ion, which has recently been shown to have some positive effect [20]. Calcination of Au/FeO_x–TiO_2 and Au/FeO_x–SnO_2 at 573 K caused the appearance of an initial rapid deactivation of both catalysts.

The effect on deactivation rates of including iron is surprising as Au/Fe_2O_3 deactivates quite quickly (Table 2). However, our materials were dried only at room temperature, so that the iron component remains as the hydroxide or the hydrated oxide. XPS measurements on the Au/FeO_x–SnO_2 and Au/FeO_x–TiO_2 catalysts showed a broad Fe2$p_{3/2}$ signals probably due to there being multiple states including Fe^0 at 706.8, Fe^{II} at 709.0 eV and possibly Fe^{III} as in the hydrated oxide FeO(OH) at ∼711.5 (see Fig. 8 for an example). However, the presence of a ferrihydrite ($Fe_5HO_8{\cdot}4H_2O$) phase as has previously been proposed cannot be excluded [21]. The lower oxidation states in may arise by loss of oxygen from the sample under the radiation and high vacuum conditions obtaining during the measurement, and this may be helped by the presence of the gold. Two states of gold were detected, viz. Au^I and Au^0. In TEM on the Au/FeO_x–TiO_2, broad iron-containing regions >1 μm in size were detected, and EDX spectra suggested that gold is atleast partly in contact with iron oxide areas. The gold particle size distribution (1.5–4 nm, mean 2 nm) was the same in both the Au/TiO_2 and the Au/FeO_x–TiO_2 materials. It appears that many of the gold particles are in contact with an iron-containing phase (such as FeO(OH)); the negative effect of calcination (Table 3), which would convert it to Fe_2O_3, suggests that it is responsible for the better activity and stability. This is in line with deactivation experienced with the Au/Fe_2O_3 catalyst (Table 2). Freshly precipitated hydroxides have previously been recommended as supports [10], and recent work [22,23] (which we have also confirmed) shows that co-precipitated Au/FeO_x catalysts hold their activity at room temperature well.

Au/FeO_x–oxide catalysts have consequently two sorts of catalytic component, (i) gold deposited on the principal oxide, probably still suffering from deactivation due to carbonate formation, and (ii) gold deposited on possibly FeO(OH), which is clearly responsible for the high activity and stability. The relative contributions of these two functions will depend on the iron loading and on the surface area of the support. Thus with Au/FeO_x–SnO_2 the initial deactivation rate decreases as the iron content is raised, and the specific rate increases to a

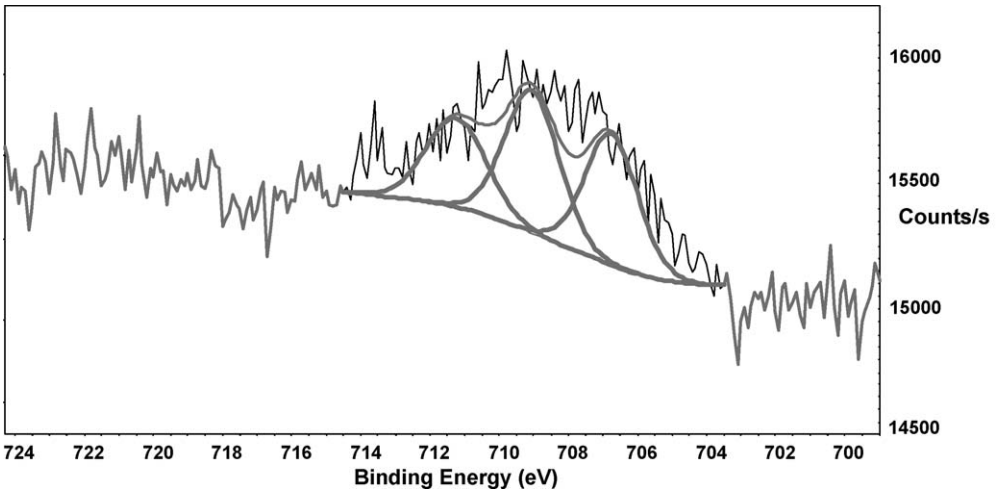

Fig. 8. Fe $2p_{3/2}$ XPS signals of Au/FeO_x–TiO_2 (4.9% Fe, 0.8% Au): multiple states include Fe^0 at 706.8 eV, Fe^{II} at 709.0 eV and Fe^{III} (e.g. as in the hydrated oxide FeO(OH)) at 711.5 eV.

maximum at an iron content of 4.3%; at the highest iron content, some of the gold may be encapsulated in the iron-containing phase. The failure to obtain activity with the Au/FeO_x–SiO_2 may be caused by most of the gold being on the high area SiO_2 and little if any on the small part of the SiO_2 surface on which there is some of the iron phase.

The apparent activation energy is always to some extent higher when iron is present than with the corresponding iron-free catalyst (Table 3). With Au/FeO_x–TiO_2 the increase is variable but is reversed by calcination; with Au/FeO_x–SnO_2 it rises progressively from 15 to 64 kJ mol^{-1} with the amount of iron. The fact that with many of the iron-containing catalysts the value of the activation energy is often close to that shown by Au/Fe_2O_3 (Table 2) supports the idea that the active sites do indeed involve iron species adjacent to gold particles. Except in the case of TiO_2, the increase in activation energy is accompanied by a rise in rate. This is unusual; it means that the temperature of the isokinetic point, (i.e. the point at which the Arrhenius plots for two catalysts cross and therefore their rates are equal [24]), lies below the experimental range.

The activation energies for the iron-free catalysts differ considerably (15–41 kJ mol^{-1}). If the previously proposed mechanism for CO oxidation [3] applies to all the oxide supports we have used, the slow step involves the reaction of a molecule of O_2 adsorbed on an anion vacancy on the support close to a gold particle with a CO molecule adsorbed on the gold. The activation energy therefore will include a term for the heat of adsorption of the O_2 molecule [24], and this may be expected to vary with the nature of the adjacent cation.

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