

Influence of the surface area of the support on the activity of gold catalysts for CO oxidation

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Abstract

In the preparation of 1% Au/TiO₂ catalysts supported on either Degussa P-25 or anatase (90 m² g^{−1}) by deposition–precipitation, the gold content passes through a maximum at about the isoelectric point (pH ~6), but maximum specific rates occur at pH 8–9 because the Au particle size becomes smaller as the pH is further increased. The gold uptake increases with the surface area of the support (anatase, rutile, P-25) and is complete above 200 m² g^{−1}; adsorption of the gold precursor at pH 9 is shown to be equilibrium-limited. Highest activities are found with supports of ~50 m² g^{−1}. Catalysts made with high-area anatase (240 or 305 m² g^{−1}) are least active but show least deactivation. With Au/SnO₂ catalysts, gold uptake does not depend on the area of the support, and is highest at pH 7–8; very active catalysts (T_{50} = 230–238 K) are obtained using SnO₂ of 47 m² g^{−1}. Storing a catalyst at 258 K for 1 week dramatically improves its stability. Results for Au/CeO₂ and Au/ZrO₂ catalysts confirm that moderate support areas give the most active catalysts, and suggest that surface area is often more important than chemical composition.

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1. Introduction

No reaction has been more intensively studied than the gold-catalysed oxidation of CO [1]. Its attraction lies partly in its formal simplicity – three diatomic molecules react to form two diatomic molecules as products – and partly in the ease with which it may be performed, since many gold catalysts effect the reaction at room temperature, and several straightforward analytical methods are available to follow it. The facility with which the reaction occurs has prompted a number of enquiries into its likely mechanism [1], although statements of mechanism in the literature probably reveal more about the minds of the authors than they do about the reaction. Although the low-temperature oxidation of small concentrations of CO in air may be of limited practical importance, related processes such as its selective oxidation in H₂ and the water-gas shift have great potential, and lessons learned from the study of CO oxidation may find application there too.

The problems surrounding this reaction are of several kinds. First, the preparation of supported gold catalysts is subject to

many possible variations, all of which seem to affect its activity and stability [2], as well as other kinetic parameters (activation energy, orders of reaction) that are not always explored. These variable factors include, amongst others, the type of support used, the method of preparation (deposition–precipitation (DP), impregnation (IMP), coprecipitation (COPPT), etc.), the conditions of pH and temperature used, the gold content and its particle size, and conditions of calcination (if any) [2]. Second, the kinetic measurements are often superficial in character. Attention is not always given to the catalyst's bed temperature and to the possible occurrence of mass-transport limitation, and the catalyst's activity profile is often unwisely just reported as a single plot of conversion versus temperature [3]. What is then recorded as the measure of activity is T_{50} (the temperature for 50% conversion) or sometimes even T_{100} . The variety of conditions used for determining activity (temperature, catalyst weight, CO/O₂ ratio, flow-rate, etc.) make the comparison of our own work with that of others often problematic and sometimes impossible. The frequent restriction of reaction conditions to ambient temperature and above, and the use of gold contents higher than are really necessary (except when TEM or similar techniques are applied), hinder the construction of a comprehensive picture of the reaction.

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The supports that have been used may be classified as (1) those that are more or less easily reducible (TiO_2 , CeO_2 , Fe_2O_3 , SnO_2 , etc.) and (2) those that are irreducible (Al_2O_3 , SiO_2 , MgO , etc.). While with the first group the reaction may very probably involve some participation by the support in consequence of its partial reduction by CO, with the second group this is less likely, except through some role assigned to the support hydroxyl groups. Of the reducible supports, TiO_2 has been most often used, generally in the form of Degussa P-25, which contains both anatase (70%) and rutile (30%) [4]. However it also exists in other forms (brookite [5], mesoporous [6]), which have been less extensively studied. One parameter that has been largely neglected so far is the surface area or particle size of the support. Anatase, rutile, and other oxides are available in various states of dispersion, and in this work we examine the behaviour of these TiO_2 polymorphs and SnO_2 , CeO_2 and ZrO_2 in a variety of surface area forms.

2. Experimental

Procedures for catalyst preparation and testing were essentially as described before [7,8]. Catalysts were made by the method usually, but inaccurately, described as deposition–precipitation (DP), following method A [8]. The solution of HAuCl_4 was brought to the selected pH at 293 K, the support added, and the stirred suspension raised to 343 K where it remained for 1 h; the chosen pH was maintained throughout the preparation. After cooling, washing and drying, the precursors were stored in the dark and were not calcined before use. All preparations had a target gold content of 1%; actual contents were determined by atomic absorption analysis, and X-ray powder analysis was performed by a Siemens D500 diffractometer, using Cu $K\alpha$ radiation. XPS was carried out at the Johnson Matthey Technology Centre. The surface areas and suppliers of the supports used are listed in Table 1.

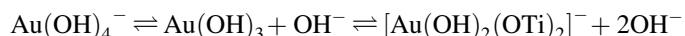
Oxidation tests were made using 0.5% CO in synthetic air between 183 and 373 K. In the normal procedure, the catalyst

was run in at 293 K until stable; the temperature was then lowered progressively by addition of Cardice or liquid N_2 to a methanol bath. Higher than ambient temperatures were obtained by use of an electric furnace [7,8]. Long-term activity tests were conducted at about 293 K, since it was impractical to maintain a subambient temperature over long periods.

3. Results and discussion

3.1. Effect of pH on the catalyst preparation

It is now well recognised that some quite complex chemistry takes place when the pH of the HAuCl_4 is varied in the method known as deposition–precipitation [2]. The composition of the gold species in solution is pH dependent and, broadly speaking, the hydrolysis of the Au–Cl bonds is progressive as the pH is raised, $\text{Au}(\text{OH})_4^-$ being the sole species above about pH 8. The charge on the surface of the support is also pH dependent, being negative above the isoelectric point (IEP) and positive below it. With P-25 as the support, the gold uptake is maximal around the IEP, but unfortunately the presence of chlorine retained in the electrostatically adsorbed precursor species causes agglomeration during drying and reduction, so that the specific rate (per g Au) at 243 K is low (Fig. 1) [7,8]. The gold uptake decreases rapidly above the IEP as the electrostatic mode of adsorption quickly disappears, but this is replaced by another type of reaction of the gold anions with the surface, the nature of which has been discussed [7]. In the region of pH 8–10 adsorption probably occurs via a neutral $\text{Au}(\text{OH})_3 \cdot \text{H}_2\text{O}$ which reacts as, e.g.



where $\text{T} = 2\text{TiO}^-$. The decreased retention at $>\text{pH } 9$ is due to the reversal of this equilibrium (see below). However as the pH is raised above 6, less agglomeration occurs during drying; smaller particles are obtained, and the specific activity rises. The reason for the loss of specific activity above pH 10 is not however clear, unless it is connected with the low gold loading (see below). These observations mean that this procedure applied to P-25 would be unacceptable as a method for large-scale manufacture: the desirable complete uptake of gold

Table 1
Sources and properties of the supports

Support	Area ($\text{m}^2 \text{g}^{-1}$)	Source	IEP ^a
P-25	55	Degussa	6+
Anatase	10	Rhone Poulenc	6
Anatase	37	Tioxide	6
Anatase	45	Alfa Aesar	6
Anatase	90	Millenium Chemical	6
Anatase	240	Aldrich	6
Anatase	305	Johnson Matthey	6
Rutile	4.4	Rhone Poulenc	5.5
Rutile	100	Johnson Matthey	5.5
SnO_2	10	Alfa Aesar	6.6
SnO_2	47	Aldrich	6.6
CeO_2	5	Sigma	6–7
CeO_2	35	Sigma	6–7
CeO_2	200	Johnson Matthey	6–7
ZrO_2	5	Alfa Aesar	6.4–8.2
ZrO_2	35	Aldrich	6.4–8.2
ZrO_2	100	Melcat	6.4–8.2

^a See Ref. [10].

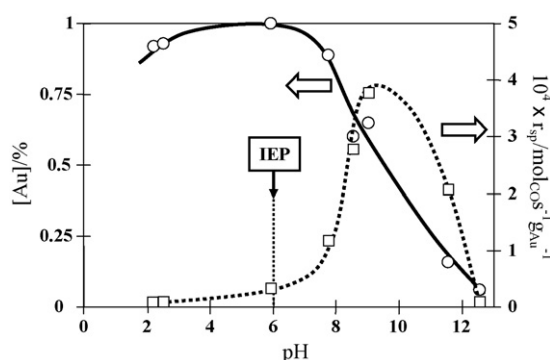


Fig. 1. Preparation of 1% Au/TiO_2 (P-25) catalysts by method A: dependence of gold uptake (\circ) and specific rate (\square) at 243 K on pH [7].

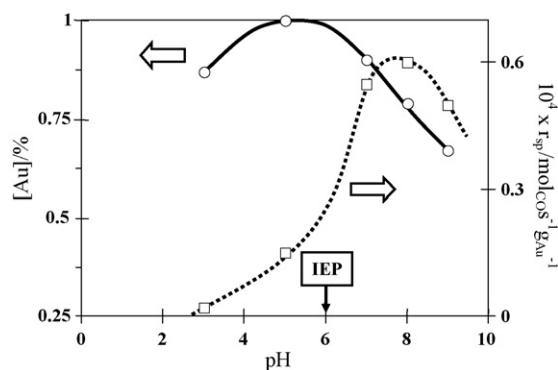


Fig. 2. Preparation of 1% Au/TiO₂ (anatase, 90 m² g⁻¹) catalysts by method A: dependence of gold uptake (○) and specific rate (mol_{CO} s⁻¹ g_{Au}⁻¹) at 243 K on pH (□) [8].

from solution leads only to a product of low activity, while high activity is only achieved when the gold retention is just 50–60%. Means of evading this dichotomy need to be sought.

In view of the critical nature of the pH choice and control, it is necessary to check its effect when other supports are employed. Anatase, being available in a wide range of surface area (Table 1) and particle size [9], is a suitable material for exploring their effects [8]. The effect of pH on gold uptake and specific activity for an anatase of 90 m² g⁻¹ is shown in Fig. 2; the results are very similar to those for P-25, although the maximum rate is much less and may occur at a slightly lower pH. We then must assume that the IEP of the other anatase samples does not vary, and therefore that highest rates will be found at the same pH; the value of 9 was used in all the other preparations. The IEP of rutile (Table 1) may be marginally lower than that of anatase [4,10], but not sufficiently different to affect the optimum pH.

3.2. Effects of varying the surface area of anatase

Fig. 3 shows that there is a marked and almost linear increase in the gold uptake as the surface area of the anatase is raised, and complete uptake is achieved at areas above about 200 m² g⁻¹; the points for rutile and for P-25 also lie close to the curve, as might be expected on the basis of the similarities of the IEPs [10]. The similarity of the results in Figs. 1 and 2 for P-25 and for anatase (90 m² g⁻¹) must therefore be something of a coincidence. It seems unlikely that a difference in IEP could account for so large a variation, but it is possible that the small uptakes found with the low-area supports (especially the 10 m² g⁻¹ anatase, Fig. 3) could be caused by the presence of modifiers (Nb, P, K) introduced to control the anatase to rutile phase change during calcination when making anatase for pigmentary use. Low levels of niobium (0.04%) were detected by XPS on the two anatase-supported catalysts investigated (90 and 305 m² g⁻¹ materials), as well as traces of chlorine and sulfur; there was no niobium on the rutile-supported catalyst (100 m² g⁻¹). Generally speaking, insufficient attention has been paid to analysing the surface composition of supports before their use.

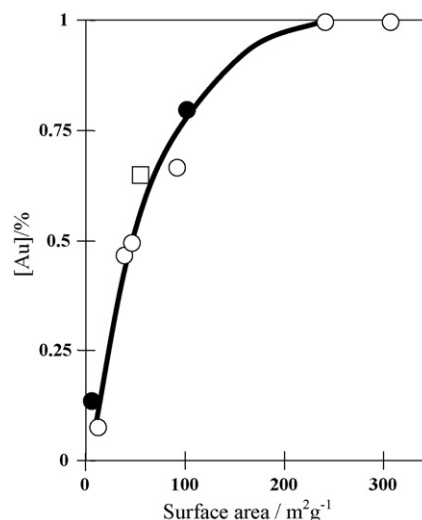


Fig. 3. Preparation of 1% Au/TiO₂ catalysts by method A: dependence of gold uptake on surface area of the support: ○ anatase, rutile, ● P-25 [8].

The obvious (and therefore probably incorrect) conclusion to be drawn from Fig. 3 is that the neutral gold species in solution at pH 9 are able to react only with some specific type of surface site that occurs in a roughly constant concentration for all types of TiO₂. Below about 125 m² g⁻¹ there are too few to react with all the gold species; the position of equilibrium then moves to the left as the amount of surface available decreases. Much higher gold loadings (up to 14%) are reported [5] to have been deposited on high-area forms of TiO₂, but perhaps less successfully on supports of less than ~80 m² g⁻¹ in area (see below). It immediately follows from the results in Fig. 3 and from the idea of an equilibrium-limited adsorption of a gold precursor that the fractional uptake of gold should decrease as the target level is raised, from 100% at very low loadings to some limiting value as high loadings are attempted. This is indeed the case with P-25 as support for preparations begun at either 298 or 343 K (Fig. 4); the limiting amount that can be adsorbed is about 2.5 wt%. A thumbnail calculation suggests that this implies the reactive sites are of the order of 15% of the total. A plot of the actual gold loading versus the intended value

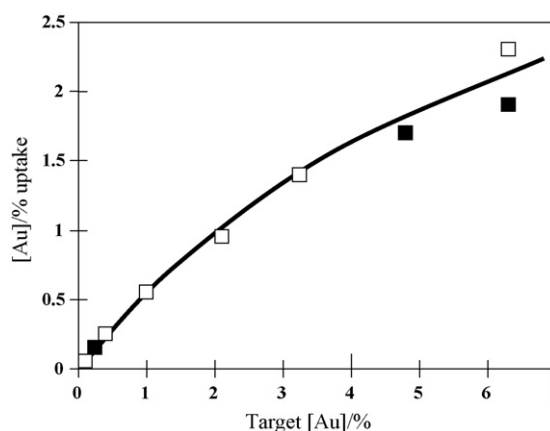


Fig. 4. Variation of gold uptake onto P-25 at pH 9 as a function of target loading; preparations started at 298 K (□) or 343 K (■).

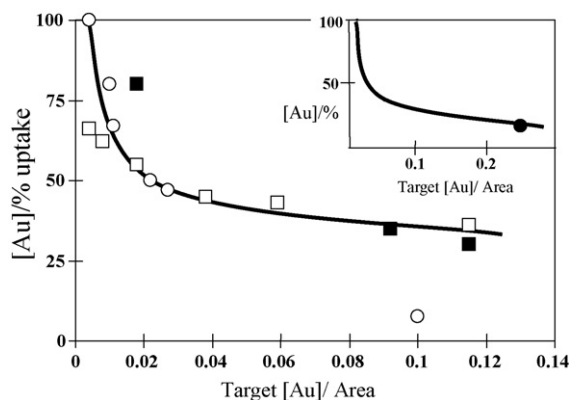


Fig. 5. Dependence of fractional gold uptake at pH 9 on the target loading divided by the support's surface area: \circ anatase, \bullet rutile, P-25. The curve corresponds to that in Fig. 4; the smaller scale insert shows that the low-area rutile ($4.4 \text{ m}^2 \text{ g}^{-1}$) lies on an extension of the same curve.

divided by the surface area (Fig. 5) brings the two sets of results together; the points for low loadings are somewhat scattered, probably due to analytical uncertainty, and the $10 \text{ m}^2 \text{ g}^{-1}$ anatase shows only a very low uptake, for reasons suggested above. The concept of an equilibrium-limited adsorption of the gold precursor at pH 9 is therefore firmly established. An equilibrium constant can be estimated, but the assumptions involved do not warrant it.

A surprisingly sharp dependence of specific rate at 243 K on surface area of the anatase supports has been found (Fig. 6). The highest rate occurs at $37 \text{ m}^2 \text{ g}^{-1}$, and it declines smoothly to much lower values as the area is increased, and there is clearly no merit in using supports of area greater than about $50 \text{ m}^2 \text{ g}^{-1}$, as others have done [5,9]. The two points for the rutile supports lie close to the line for anatase, but the highest rate is shown by Au/P-25; its particular merit could therefore be due to its having

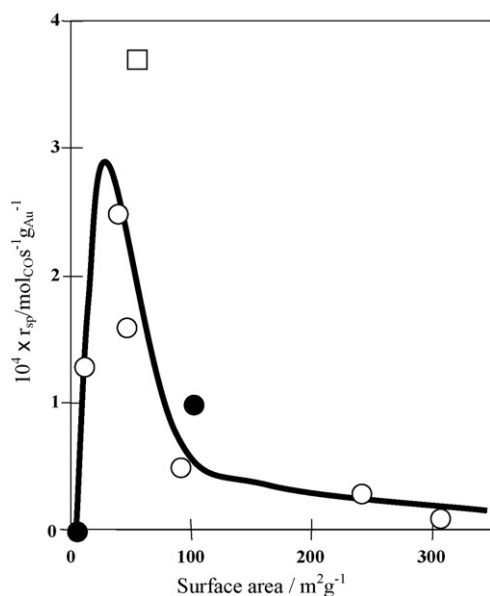


Fig. 6. Preparation of 1% Au/TiO₂ catalysts by method A: dependence of specific rate ($\text{molCO s}^{-1} \text{ gAu}^{-1}$) on support surface area: \circ anatase, \bullet rutile, P-25 [8].

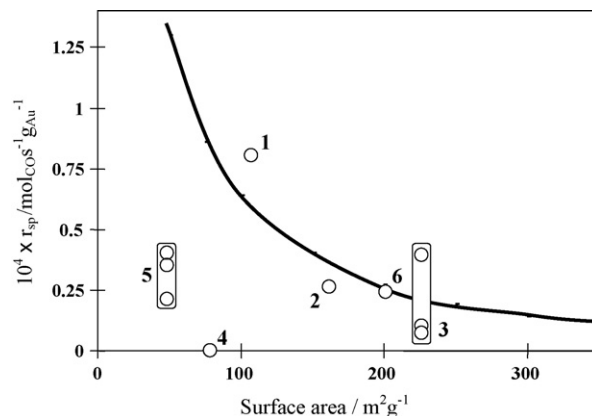


Fig. 7. Preparation of Au/TiO₂ catalysts: dependence of specific rate ($\text{molCO s}^{-1} \text{ gAu}^{-1}$) on surface area of various supports according to the literature—1: brookite, 235 K [5,6]; 2: mesoporous, 263 K [6]; 3: anatase, 235 K [5]; 4: rutile, 235 K [5,6]; 5: P-25, 235 K [5,6]; 6: rutile, 240 K [11]. See text for further details: the curve is the same as in Fig. 6.

an optimum surface area. The change produced by increasing the surface area from $50\text{--}80$ to $\sim 200 \text{ m}^2 \text{ g}^{-1}$ (Fig. 3) is almost the same as that which occurs when the pH is reduced from 9 to 6 (Figs. 1 and 2).

Three other studies have addressed the relevance of TiO₂ support structure/area/particle size [5,6,9]. Points for the specific rates at 235 K of Au/anatase ($225 \text{ m}^2 \text{ g}^{-1}$, $d_{\text{av}} \leq 10 \text{ nm}$) having 2.8%, 5.2% or 13% Au [5] lie close to the curve drawn through the points in Fig. 6 (see Fig. 7); those for 3.2% Au/brookite ($106 \text{ m}^2 \text{ g}^{-1}$, $d_{\text{av}} = 70 \text{ nm}$) [5] and for Au/mesoporous TiO₂, ($160 \text{ m}^2 \text{ g}^{-1}$) having 9–14% Au (!) [6] do as well, confirming the general validity of our results. There are however two major differences: 14% Au/rutile ($77.5 \text{ m}^2 \text{ g}^{-1}$) had a very low specific activity ($\sim 0.1 \times 10^{-4} \text{ molCO s}^{-1} \text{ gAu}^{-1}$) and 2.8% Au/rutile was quite inactive [5]; Au/P-25 with 4.5–7.2% Au was also less active by a factor of about 10 than our catalysts [5]. There are no obvious reasons for these low activities, but it must be remarked that all these catalysts having much higher gold loadings than we find desirable to use, predicated perhaps on the wish to study their structures by for example TEM. A value [11] for the specific rate shown by 7% Au/rutile ($200 \text{ m}^2 \text{ g}^{-1}$) at 240 K does however fit the curve in Fig. 7.

A further recent study has used a range of anatase samples having areas between 30 and $412 \text{ m}^2 \text{ g}^{-1}$ ($d_{\text{av}} = 23\text{--}9 \text{ nm}$) and Au contents of $\sim 0.3\text{--}0.7\%$ [9]. Rates were only measured at 298 K and, although the support of area $30 \text{ m}^2 \text{ g}^{-1}$ gave the highest initial rate, it deactivated quickly (5 h), after which all five catalysts had about the activity. From the initial rates one can derive some confirmation for our observed trend between 30 and $100 \text{ m}^2 \text{ g}^{-1}$ (Fig. 6), but it must be noted that those rates ought to be much faster since the temperature is 55 K higher than ours.

There are several possible explanations for the low activities shown when the support has a low area. The reaction may be poisoned by modifiers and, because of the proximity of the metal particles, they may be more prone to agglomeration caused by the heat of reaction. With very low area supports, the

gold may not be entirely on the support. The marked decrease in specific activity with increasing surface area is harder to explain. One obvious consequence is that, if the gold is uniformly deposited and the particle size remains the same, the mean separation of the particles will increase in proportion to the area. Remembering that the reaction is extremely exothermic, the transfer of heat from one particle to another by convection, or possibly radiation, may be considerable when particles are close together so that, provided this is not enough to cause sintering, its effect may be beneficial when the support has only a moderate area, but insignificant when the area is large. Techniques are available for determining the local temperature of metal particles in supported catalysts, but have not yet been applied to this system.

A different perspective on catalyst behaviour is obtained when long-term tests are performed. First of all we have noted that the activity of gold supported on the two highest area anatases (see Table 1) increases dramatically during the first few hours of use at 298 K. It rises from 5% to above 90% in the case of the $240 \text{ m}^2 \text{ g}^{-1}$ anatase, and from 20% to 55% with the $305 \text{ m}^2 \text{ g}^{-1}$ anatase (Fig. 8); this does not happen with the lower area supports. With Au/P-25 the conversion decreased linearly from 80% to 50% over the first 100 h; the Au/anatase ($10 \text{ m}^2 \text{ g}^{-1}$) also deactivated slowly, but with the two highest area supports the activity remained constant over extended periods (Fig. 8). The slow initial activation may result from the greater difficulty of reducing or decomposing the gold precursor when the support area is high; the greater stability in these cases may arise either from a much slower sintering (for the reasons given above) or from a readier migration of inhibiting carbonate ions from the neighbourhood of the gold particle to distant locations where they can do no harm.

3.3. The behaviour of Au/SnO₂ catalysts

SnO₂ is an active catalyst for CO oxidation in its own right above $\sim 473 \text{ K}$; it was shown long ago [12] that a Pd/SnO₂ catalyst was much more active for this reaction than either SnO₂ alone, or Pd/SiO₂, and it was speculated that the migration of CO from the Pd to the SnO₂ accelerated the reaction. The SnO₂ had an area of $200 \text{ m}^2 \text{ g}^{-1}$. It is of interest to

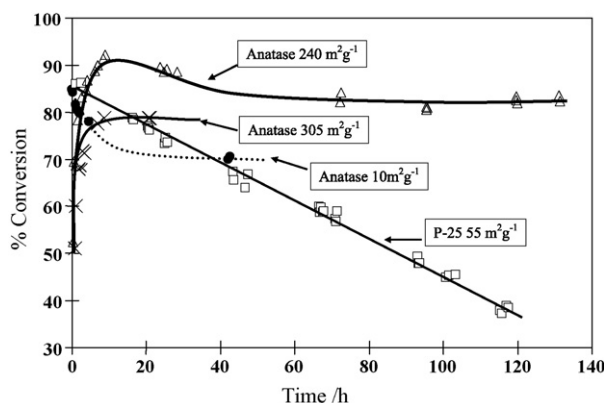


Fig. 8. Long-term activity tests at 298 K: \circ , anatase ($10 \text{ m}^2 \text{ g}^{-1}$); Δ , anatase ($240 \text{ m}^2 \text{ g}^{-1}$); \times , anatase ($305 \text{ m}^2 \text{ g}^{-1}$); P-25.

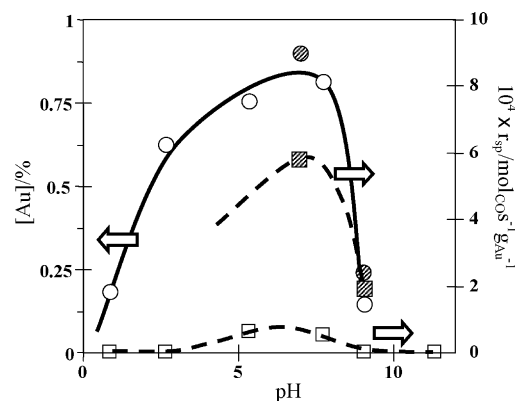


Fig. 9. Preparation of 1% Au/SnO₂ catalysts: dependence of gold content (\circ) and r_{sp} ($\text{mol CO s}^{-1} \text{ g}_{\text{Au}}^{-1}$) at 243 K (\square) on pH: open points, SnO₂ ($10 \text{ m}^2 \text{ g}^{-1}$); filled points, SnO₂ ($47 \text{ m}^2 \text{ g}^{-1}$).

see whether a similar effect occurs with gold. The effects of pH variation on gold uptake and on specific rate at 243 K are shown in Fig. 9 for supports of 10 and $47 \text{ m}^2 \text{ g}^{-1}$. Maximum uptake occurs at $\sim \text{pH } 7$, just above the IEP (6.6 [4]), as with TiO₂, but the difference is that the area has little effect, high uptake (82%) being obtained with the low-area support. This suggests that a much greater fraction of the surface is able to react with the gold complexes in solution than is the case with TiO₂. The rapid decrease between pH 8 and 9 may again be due to the reversal of the adsorption equilibrium. The area does however have an enormous effect on the activity; with the low-area support, rates are low, those being apparently zero in Fig. 9 having T_{50} values above (sometimes well above) 500 K , but the 0.9% Au/SnO₂ ($47 \text{ m}^2 \text{ g}^{-1}$) is more active than a corresponding Au/TiO₂ (P-25), and has a T_{50} of only 230 K . The difference in activities at pH 9 is even greater ($T_{50} = 238 \text{ K}$ compared to $>573 \text{ K}$). In view of these results it is not surprising to learn that a catalyst made with $7 \text{ m}^2 \text{ g}^{-1}$ SnO₂ at pH 9.5–10 and calcined at 673 K for 4 h had only minimal activity (specific rate = 1.25×10^{-5} at 573 K) [13]. It is risky to assume that the first condition of preparation tried will give a satisfactory result.

There are marked contrasts between SnO₂ and TiO₂ as supports. At pH 9 the uptake of gold on SnO₂ is much less than on anatase, suggesting that the position of equilibrium lies more towards the solution side. On the high-area SnO₂ we find very high activity and high uptake at pH 7, while with P-25 and anatase there is only low activity at this pH. If the activity of this Au/SnO₂ is due to its having small particle size, this may indicate a lesser mobility of adsorbed chlorine-containing species than over TiO₂.

The reason for the much greater activity shown when the higher area support is used may be due either to a particle size effect, or more probably is related to the effect found with Pd/SnO₂ [12]. If we suppose that each gold particle can activate a circular zone of support, where either CO spilling over from the metal can react with lattice oxide ion, or whence oxide ions can migrate to the metal to assist the reaction, the area of non-overlapping zones will be greater the greater the area of the support, if particle sizes are not too disparate.

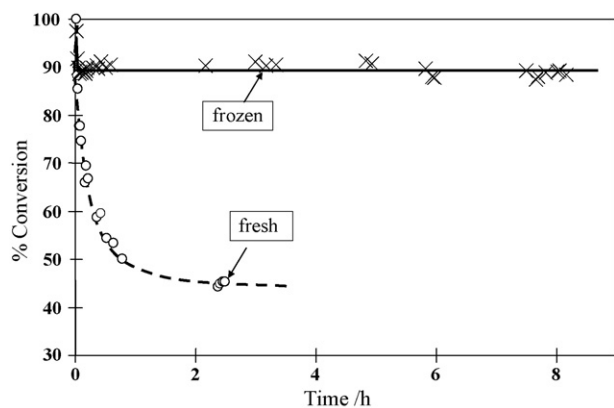


Fig. 10. Long-term activity tests, at 298 K for 0.9% Au/SnO₂ (10 m² g⁻¹); O, fresh; x, after 1 week storage at 258 K.

Our recent work with Au/SnO₂ catalysts has revealed another unexpected observation. We observed that catalysts made with the low-area SnO₂ in the optimum pH range (5–8) underwent massive initial deactivation (e.g. from 100% to 50% conversion in 8 h, Fig. 10); the rates recorded at 243 K in Fig. 9 were measured after this had taken place. Now as part of a study of the best conditions for storing supported gold catalysts, we kept part of this preparation in a refrigerator at 258 K for 1 week, after which it was life-tested (Fig. 8). Most surprisingly, after slight (10%) initial loss of activity it maintained constant conversion (90%) for at least 80 h. We believe that optimisation of support surface area and of storage conditions could lead to even more active Au/SnO₂ catalysts.

3.4. Au/CeO₂ and Au/ZrO₂

Only very brief studies have been made of these systems. With low-area CeO₂ (5 m² g⁻¹), reasonably active catalysts have been prepared using a pH in the range 7.5–9 (Fig. 11). The IEP of CeO₂ is approximately 6–7 [14], and the maximum uptake appears to be found between pH 5 and 8 (Fig. 11). However the uptake at pH 8 (20%) is much less than that found with either TiO₂ or SnO₂ at that pH, so it seems likely that only a small fraction of the CeO₂ surface can reaction with the solution complexes. Highest

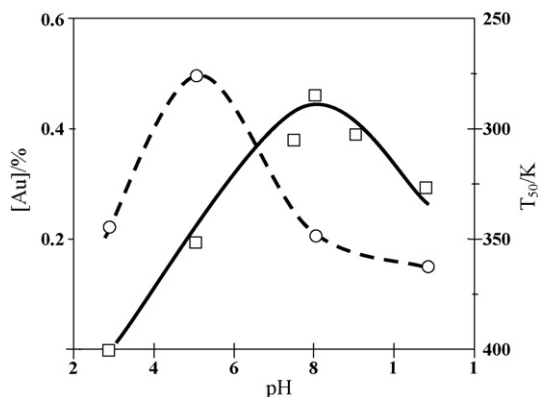


Fig. 11. Preparation of 1% Au/CeO₂ (5 m² g⁻¹): dependence of gold uptake (O) and T₅₀ (K) (□) on pH.

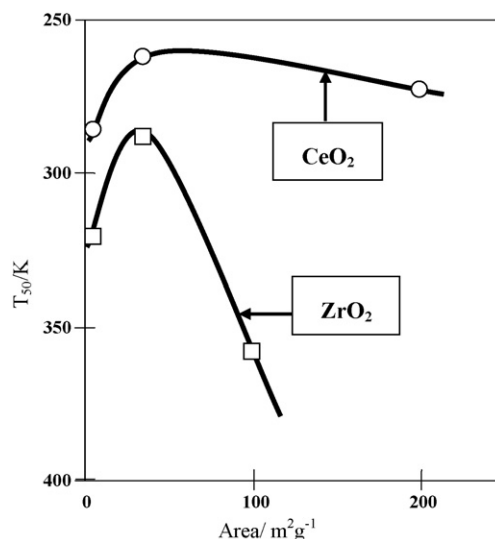


Fig. 12. Dependence of activity (T₅₀ (K)) of Au/CeO₂ (O) (pH 8) and Au/ZrO₂ (□) (pH 8.5) catalysts on surface area of the support.

activity is shown with the support of 35 m² g⁻¹ (T₅₀ = 261 K) (Fig. 12); this is in line with other recent work that shows a faster rate at 303 K with ceria of 85 m² g⁻¹ compared to 7 m² g⁻¹ [15]. Three samples of zirconia were examined as supports only at pH 8.5; once again, that having the medium surface area afforded the most active catalyst (Fig. 12).

4. Conclusions

It is instructive to combine our results for activity as a function of support surface area into one figure (Fig. 13), using the value of T₅₀ as the measure of activity. We find that with perhaps only two exceptions the points fall close to a common curve; maximum activities are found with supports having areas between 30 and 100 m² g⁻¹; supports of only low area (<10 m² g⁻¹) give catalysts of poor activity; and those whose areas are ≥200 m² g⁻¹ give products that are only modestly active. Of the various types of TiO₂ tried, the Degussa P-25 appears best, in disagreement with other published work [5]. The two exceptions to this general

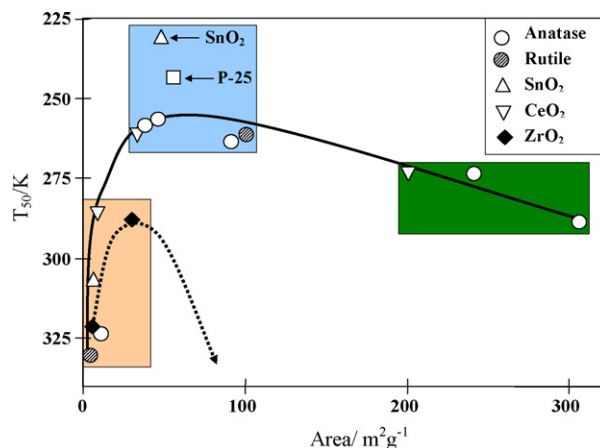


Fig. 13. Effect of surface area of various supports on activity (T₅₀ (K)) of gold catalysts (nominal 1% Au) prepared by DP at pH 9.

trend are (1) SnO_2 , which in the high-area form gives a catalyst of exceptional activity, and (2) ZrO_2 , where the optimum pH and conditions of preparation may not have been found.

Of the 'reducible' supports we have looked at, it appears that in most cases their surface area, rather than their chemical composition, provides the determining factor for obtaining good activity.

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