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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/TiO_2 catalysts supported on either Degussa P-25 or anatase (90 $m^2\ g^{-1}$) 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 $m^2\ g^{-1}$; adsorption of the gold precursor at pH 9 is shown to be equilibrium-limited. Highest activities are found with supports of ~50 $m^2\ g^{-1}$. Catalysts made with high-area anatase (240 or 305 $m^2\ g^{-1}$) are least active but show least deactivation.With Au/SnO_2 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 SnO_2 of 47 $m^2\ g^{-1}$. Storing a catalyst at 258 K for 1 week dramatically improves its stability. Results for Au/CeO_2 and Au/ZrO_2 catalysts confirm that moderate support areas give the most active catalysts, and suggest that surface area is often more important than chemical composition.

Keywords: CO oxidation; Gold on titania; Gold on ceria; Gold on tin oxide; Support surface area; Effect on activity

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 H_2 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/O_2 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 Kα 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.

Table 1
Sources and properties of the supports

Support	Area ($m^2\ g^{-1}$)	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].

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, $Au(OH)_4^-$ 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 $Au(OH)_3{\cdot}H_2O$ which reacts as, e.g.

$$Au(OH)_4^- \rightleftharpoons Au(OH)_3 + OH^- \rightleftharpoons [Au(OH)_2(OTi)_2]^- + 2OH^-$$

where T = $2TiO^-$. The decreased retention at >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

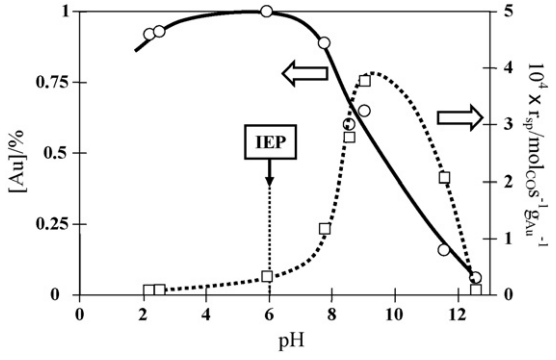

Fig. 1. Preparation of 1% Au/TiO_2 (P-25) catalysts by method A: dependence of gold uptake (○) and specific rate ($mol_{CO}\,s^{-1}\,g_{Au}^{-1}$) at 243 K on pH (□) [7].