Dramatic promotion of gold/titania for CO oxidation by sulfate ions

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The activity of gold/titania catalysts for the room-temperature oxidation of CO can be dramatically enhanced by the addition of sulfate ions to the support; it appears that anion promotion of gold may be a general phenomenon and may be related to the direct modification of active gold sites in the case of sulfate ions, as evidenced by secondary ion mass spectrometry.

Gold has been known for a long time as an inert metal that does not possess much catalytic activity. However the pioneering work of Haruta *et al.* showed that nanoparticles of gold are catalytically highly active for CO oxidation.[1] Gold also exhibits high catalytic activity for many reactions when it is highly dispersed on the metal oxides.[2,3] In particular, CO oxidation on gold-supported oxides has been investigated in detail for its simplicity as well as on its technological importance.[4–6] The catalysts that were found to be most selective towards CO_2 contained transition-metal oxides that are also good oxidation catalysts. Gold nanoparticles have been deposited on various supports such as TiO_2, Al_2O_3, ZnO, Co_3O_4, MnO_2, MgO, Fe_2O_3, ZrO_2 *etc.* However, gold highly dispersed on TiO_2 was found to be more active for CO oxidation than on other supports.[2,7,8] The low-temperature oxidation of CO over supported gold catalyst is thought to proceed through the reaction of CO adsorbed on the gold surface with molecular oxygen activated at perimeter sites around the gold particles.[9,10]

Recent studies showed that sulfate ion could be anchored on surface of TiO_2 developing strong acidity. The sulfate ion forms S=O and O–S–O bonds in bulk and surface of TiO_2, creating unbalanced charge on Ti and vacancies and defects in the TiO_2 network.[11,12] For this, sulfated metal oxides can be used as solid acid catalysts in heterogeneous catalytic reactions for a wide variety of applications. The crystallinity is more or less dependent on the presence of sulfate ion, but not on the percentage of sulfate loading. The crystallite size decreases in the presence of sulfate ion as SO_4^{2-} species could possibly interact with the TiO_2 network and thus hinder the growth of the particle. The strength as well as the number of Lewis acid sites is higher in sulfated TiO_2. Our earlier studies[13–15] revealed that the method of preparation, source and concentration of sulfate ions affected the surface, textural as well as catalytic activities of TiO_2.

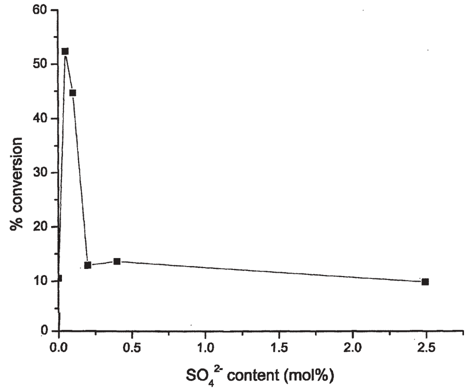

Fig. 1 Activity at 303 K for the various catalysts for CO oxidation as a function of the sulfate content.

The method of preparation plays an important role towards the physicochemical properties and catalytic activity of the catalyst. Several approaches have been considered for the synthesis of gold nanoparticles on metal oxide supports such as co-precipitation, deposition precipitation, gas phase grafting, liquid-phase grafting[16] co-sputtering[17] colloidal mixing[7] *etc.* Similarly the support TiO_2 can be prepared by methods such as hydrolysis of titanium salt, sol–gel, microemulsion *etc.* There is an advantage of synthesizing TiO_2 by gelling titanium alkoxides as in such preparations specific surface area, titania crystallite size and crystalline titanium phase can be controlled. Final properties of sol–gel catalysis can be controlled by varying the hydrolysis pH.[18]

The objective of the present research is to study the effect of method of preparation of the support and the effect of sulfate ion on the catalytic activity of gold-promoted TiO_2 towards CO oxidation. During the course of our study we noted that an unexpected promotional effect of nitrate ions on Au/TiO_2 for CO oxidation was reported by Hutchings and co-workers.[19]

The titania was a high purity form, prepared from Ti(IV) isopropoxide.† Sulfate was introduced by impregnation with dilute sulfuric acid and gold subsequently introduced using the single-step borohydride method.[20] The dramatic effect of sulfate treatment on CO oxidation activity, recorded at room temperature is shown in Fig. 1, where a >5-fold higher activity is found for relatively low sulfate loadings. We note that the absolute rate of CO oxidation on the unsulfated catalyst compares favourably with the highest rates found for other Au/TiO_2 catalysts, including those based on the use of Degussa P25 titania (specific rates of CO oxidation at 303 K are 0.05 (this work) and 0.10 mol CO (mol Au)$^{-1}$ s^{-1} for P25 based catalysts (see also ref. 25). The promotional effect of sulfate is clearly not due to the base catalyst being of unusually low activity. We further note that over several hours on stream none of the catalysts exhibited any marked tendency to increase or decrease their activity (less than 5% change relative in the absolute CO conversion over *ca.* 10 h). In an attempt to understand something of the origins of the sulfate promotional effect we have established that there are no dramatic

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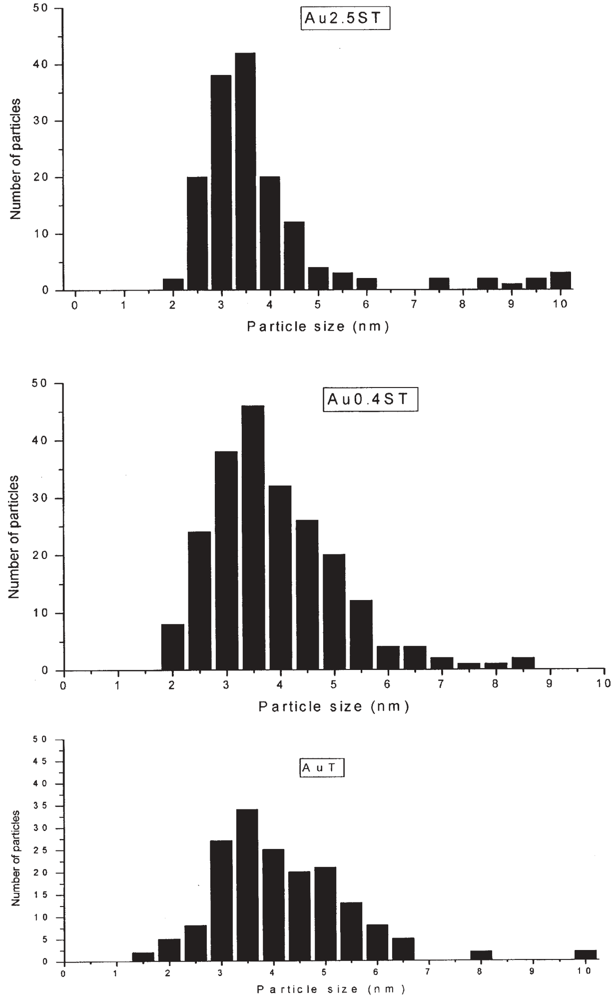

Fig. 2 Gold particle size distribution for (a) Au2.5ST, (b) Au0.4ST and (c) AuT.

differences between the gold particle size distributions obtained from transmission electron microscopy (Fig. 2). Sulfate treatment of oxides such as titania[21] and zirconia[22,23] is known to affect the specific surface area of the oxides, with increases seen after sulfate treatment. Table 1 shows that some increase in the BET surface area of the catalyst is also seen but we recorded these effects for relatively high sulfate contents only. Additionally, all the gold contents measured in these catalysts are very similar (Table 2) and close to the target 1 wt% loading.

We conclude that the promotional effect of sulfate on CO oxidation activity is unlikely to be due to any physical or textural changes in the catalyst system or to differences in total gold content. It appears more likely that chemical (electronic) effects are responsible. Examination of these catalysts by X-ray photoelectron spectroscopy suggest that there are no significant changes in the binding energy of gold, a result which is fully consistent with other work carried out in our laboratories on the sulfate treatment of Au/titania/P25 samples. Gross changes may well be difficult to detect at the very low sulfate content of our most active samples. The most active catalyst has a sulfate/gold mol ratio of only 0.12. It is tempting to speculate therefore that the effect might be due to direct interaction of sulfate ions with a small fraction of the total Au atoms present in the solids. Further, it may be that the sulfate anions are interacting with perimeter sites, which, on geometric considerations for our catalysts would involve about a fraction of about 0.1 of the total gold sites present. This is consistent with the idea that not all gold present in such catalysts may be contributing to CO oxidation activity,[24] and we have direct evidence from secondary ion mass spectrometry (SIMS) for such an interaction. The SIMS work reveals that species containing both Au and S are present on the surface. For $m/z = 277$ contributions are assigned to TiAuS, $TiAuO_2$, AuS_2O and/or $AuSO_3$ species. Using accurate mass comparisons the closest fit is provided by the AuS_2O species. However the differences in mass are very small and a more convincing argument is provided by consideration of the relative intensities of SIMS peaks obtained in studies carried out on related samples based on a commercial titania (Degussa P25) prepared by flame hydrolysis.[25] In that study the counts ratio for $m/z = 277$ and $m/z = 197$ (= Au) for a series of samples containing gold and added ions, excluding sulfate, are remarkably constant at 0.1. However the sulfate-modified sample exhibits a significantly higher ratio at 0.3, close to the value of 0.28 seen in the present study and the Au–S-containing entities are clearly implicated as being responsible for a significant fraction of the intensity of the peak at $m/z = 277$. The work clearly suggests that direct Au–sulfate ion interaction is present in the sample and this may explain the origin of the promotional effect.

Table 1 Surface area and pore volume of unsulfated and sulfated gold/titania

Sample	$S_{BET}/m^2\ g^{-1}$	Total pore volume/$cm^3\ g^{-1}$
TiO_2	57	0.09
2.5ST	73	0.13
AuT	83	0.17
Au2.5ST	89	0.18

Table 2 Au content of the catalysts

Sample	Gold content (wt%)
AuT	1.06
Au2.5ST	0.97
Au0.4ST	1.01
Au0.2ST	0.97
Au0.1ST	1.00
Au0.05ST	0.99

Work in progress in our Group does however suggest that anion mediated promotional effects are not confined to sulfate. Nitrate, phosphate, fluoride and chloride promotion of Au/TiO_2 catalyst for CO oxidation have all been observed,[25] particularly at relatively low anion contents. Note that there is a remarkable similarity in the profile in our Fig. 1 with a comparable figure reported for nitrate promotion of Au/TiO_2.[19] (We would stress here that two independently conducted series of experiments run in our laboratories yield near identical profiles as depicted in Fig. 1, although small differences in the absolute levels of percentage conversion were noted. The effect is essentially reproducible.)

Sulfate effects in CO oxidation catalyst have aroused some controversy in earlier work. Ruth *et al.*[11] and others[26] have shown that SO_2 treatment of Au or Pt catalyst led to deactivation. No promotional effects have been reported to date, but our work suggests that such effects are seen only for very modest anion incorporation levels and that at higher incorporations lower activities are indeed observed. Our work suggests that the anion promotional effect may be a very general one in gold catalysis, and we wonder whether the effect might not be entirely unrelated to the promotional action of electronegative elements for coinage metal catalysts as recently discussed by Zhang *et al*[27] in terms of the enhanced adsorption of CO.

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Notes and references

† *Experimental*: Titanium(IV) isopropoxide (Acros Organics, 98+%), propan-2-ol (ACE, 99.5%), nitric acid (UniLab, 55%) and deionised water were used to synthesise the support material. $HAuCl_4$ (Aldrich, 99.99%) was used as the gold precursor and $NaBH_4$ (Fluka) was used in the catalysts preparation. The intended gold loading on all catalyst samples was 1.0 wt%. A measured amount of titanium(IV) isopropoxide was placed in a beaker and 8 times its volume of propan-2-ol added to it. This was placed in an ice-bath with vigorous stirring and deionised water (preadjusted to pH 3 using dilute HNO_3) added to it dropwise. After complete precipitation the gel formed was refluxed at 353 K for 2 h, allowed to cool, filtered and then dried at 373 K for 4 h. This sample is symbolized as T373 hereafter. Aqueous impregnation using 0.01 M H_2SO_4 was used to incorporate SO_4^{2-} ions into the support at levels of 0.05, 0.1, 0.2, 0.4 and 2.5 mol% with respect to the support. The freshly prepared support together with the ion modified supports were calcined at 673 K for 3 h, a step which effectively fixes the sulfate ions to the surface. These samples are symbolized as T673, 0.05ST, 0.1ST, 0.2ST, 0.4ST and 2.5ST. The supports were suspended in deionised water and the required amount of dilute $HAuCl_4$ (0.01 M) added dropwise with continuous stirring. Two hours after complete addition of the gold precursor, the pH was raised to 8.5 using 15% NH_3 (aq) and aged for a further 2 h. A solution of $NaBH_4$ freshly prepared in deionised ice water was rapidly added to the mixture using a syringe in the required amount to ensure complete reduction of Au(III) to Au(0). The suspension was then filtered off, washed several times with warm deionised water, and oven-dried at 393 K for 2 h. The respective samples are symbolized as AuT, Au0.05ST, Au0.1ST, Au0.2ST, Au0.4ST and Au2.5ST. The activities of the catalyst samples toward the oxidation of carbon monoxide were measure using a fixed bed flow reactor. 100 mg of catalyst in each case was diluted with 400 mg of quartz and placed in the reactor. This was pretreated *in-situ* for 2 h at 673 K with 10% O_2 balance He at a flow rate of 40 ml min^{-1} and then allowed to cool to room temperature. The reactant gas mixture consisting of 10% CO, 5% O_2 and 85% He at a total flow rate of 40 ml min^{-1} was passed through the reactor and the effluent gases from the reactor analysed using gas chromatography. The activities of the catalysts were measured as a function of the reactor temperature from 303 K with 10 K stepwise increase in temperature. The properties of the samples were characterised by HRTEM, XRD, fire assay and gravimetric finish and nitrogen physisorption measurements. The mean particle size and particle size distribution of gold were determined by obtaining high-resolution transmission electron micrographs (HRTEM) for the Au-containing samples using a JEOL 2010 electron microscope with a LaB_6-cathode operated at a voltage of 200 kV. Powder X-ray diffraction (PXRD) data were collected using a Bruker AXS D8 equipped with a primary beam Göbel mirror, a radial Soller slit, a VÅntec-1 detector and using Cu-Kα radiation (40 kV, 40 mA). Data were collected in the 2θ range 20 to 90° in 0.021° steps, using a scan speed resulting in an equivalent counting time of 14.7 s per step. BET surface areas of all samples were measured using a Micromeritics Tristar 3000 by nitrogen adsorption–desorption isotherms at liquid-nitrogen temperature (−196 °C). Secondary ion mass spectrometry using an ION TOF 5 spectrometer was used to identify the elemental composition and the chemical status near the surface of the catalysts. In this process, a 25 kV Bi^+ ion beam with a pulsed current of 1 pA and a pulse rate of 10 kHz was used. The extractor was operated at 2 kV and charge neutralization was applied. The beam diameter was 1 micron and the analysis area was 100 × 100 microns and 128 × 128 pixels.

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