Effects of preparation methods on gold/titania catalysts for CO oxidation

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ABSTRACT

The enhancing effect of sulphate ions added to titania supports for the oxidation of carbon monoxide, catalyzed by gold, supported on the titania has been shown to be generally applicable to more than one type of titania. It seems from examining the characterization and catalytic data that the sulphate promotional effect is mainly due to a direct chemical effect on catalytically active sites.

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1. Introduction

Since the pioneering work of Haruta et al. showed that nanoparticles of gold are catalytically highly active for CO oxidation [1], much interest has been generated in the factors affecting catalytic behaviour. The support is known to exert a considerable influence and particular attention has been given to titania since gold supported on this oxide has been found to be more active for CO oxidation than gold on other supports [2–4]. 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 [5,6].

Recent studies have shown that the acidity of titania can be strongly increased by treatment with sulphate ions, with the formation of be S=O and O—S—O bonds in bulk and surface, creating unbalanced charge on Ti and vacancies and defects in the TiO_2 network [7,8]. Only recently however has it been demonstrated that the use of sulphated titania leads to enhanced activity for supported gold, at least in the CO oxidation reaction [9,10] and there is evidence from SIMS (secondary ion mass spectrometry) studies that at least some sulphate ions directly interact on the surface with gold sites.

Most work to date is based on the use of titania in the form of type P25 material, manufactured by Degussa. There have been almost no reports of a systematic investigation of the role that the nature of the titania has on the catalytic properties of supported gold. Since earlier studies [11–13] revealed that the method of preparation, source and concentration of sulphate anions affected the surface, textural as well as catalytic activities of TiO_2, it was decided to explore further the effect of the type of titania preparation on catalysis by Au/titania and, in the same study to examine the effect of sulphation of the titania.

2. Experimental

2.1. Preparation of titania

One series of hydrated titania was prepared at pH 3 by adding dilute ammonia dropwise to the stirred aqueous solution of titanium tetrachloride (Spectrochem, Bombay). The gel obtained was filtered and washed repeatedly to remove Cl⁻ (filtrate testing negative to AgNO₃ test), dried at 393 K for 10 h, powdered to 45–75 μm mesh size and kept for anion impregnation.

The second series was prepared by a sol–gel method taking titanium isopropoxide as the titania precursor at pH 3. 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 HNO₃) added to it dropwise. After complete precipitation, the gel formed was refluxed
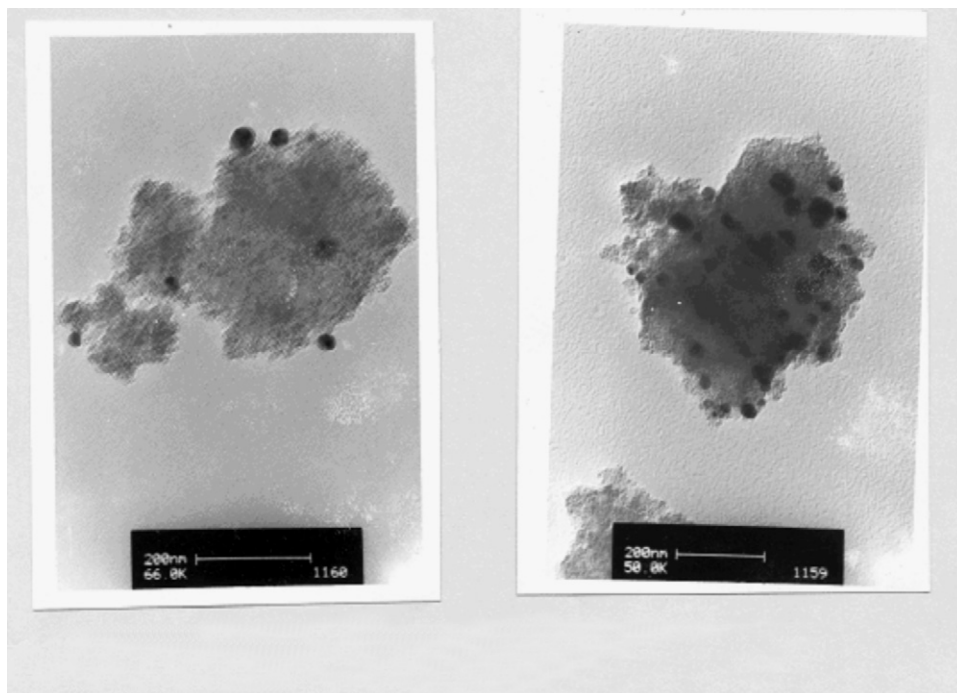
Fig. 1. 1Au/TiO$_2$, prepared from TiCl$_4$ dried at 110 °C.

at 353 K for 2 h, allowed to cool, filtered and then dried at 393 K for 4 h.

The third series of titania samples was prepared from titanium tetrachloride in the presence of a surfactant (sodium dodecyl sulphonate) at pH 3. The calculated amount of SDS (SDS/TiCl$_4$ = 0.8) dissolved in distilled water, was added to TiCl$_4$ solution with vigorous stirring. After 1 h of stirring, the pH of the solution was adjusted to 3 using dilute NH$_3$. The resultant slurry was heated at 75 °C for a day under autogeneous pressure. Then it was filtered thoroughly to remove the surfactant and Cl$^-$.

2.2. Preparation of sulphated titania

At the beginning of the study, titania precursors prepared by the three methods were treated with SO$_4{}^{2-}$ ions to a level of 2.5 mass% by aqueous wetness impregnation with dilute H$_2$SO$_4$ (concentration = 1.0 M). The suspended mass was evaporated to dryness on a hotplate while stirring and was then dried in an oven at 393 K. The freshly prepared supports together with the ion-modified supports were calcined at 673 K for 3 h, a step which effectively fixes the sulphate ions to the surface. These samples are symbolized as 2.5SHT, 2.5SGT and 2.5SST hereafter. By preliminary investigation it was confirmed that higher amounts of sulphate loaded into titania are not desirable for low temperature CO oxidation and among all the sample titanias prepared, that derived from the by sol–gel method shows the highest activity. So, an aqueous impregnation using 0.01 M H$_2$SO$_4$ was used to incorporate SO$_4{}^{2-}$ ions into the titania prepared by sol–gel method as support at different levels of 0.05, 0.1, 0.2 and 0.4 mass% with respect to the support. These samples are symbolized as GT673, 0.05SGT, 0.1SGT, 0.2SGT and 0.4SGT.

2.3. Preparation of gold supported on titania

The supports were suspended in deionised water and the required amount of dilute HAuCl$_4$ (0.01 mol dm^{-3}) added dropwise with continuous stirring. Two hours after complete addition of the gold precursor, the pH was raised to 8.5 using 15% NH$_4$OH

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 for complete reduction of Au(III) to Au(0). The suspension was then filtered, washed several times with warm deionised water and dried overnight at 393 K for 2 h. The respective samples were symbolized as Au2.5SHT, Au2.5SGT, Au2.5SST, AuGT, Au0.05SGT, Au0.1SGT, Au0.2SGT and Au0.4SGT.
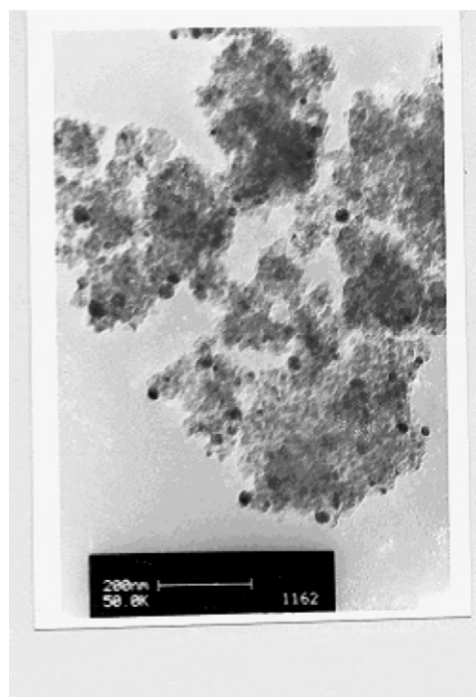

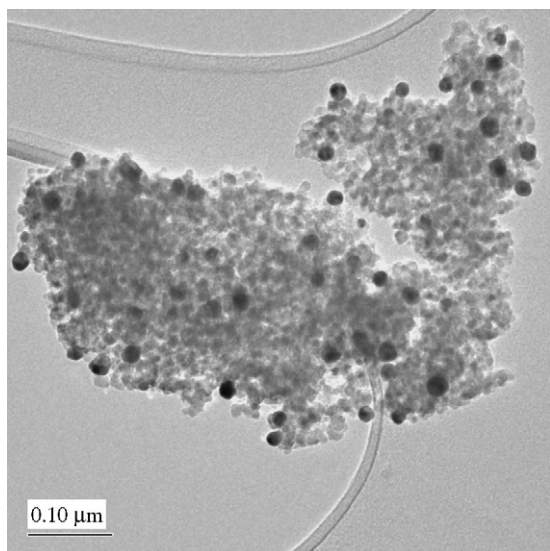**Fig. 2.** 1Au/TiO$_2$ prepared from TiCl$_4$ dried at 200 °C.
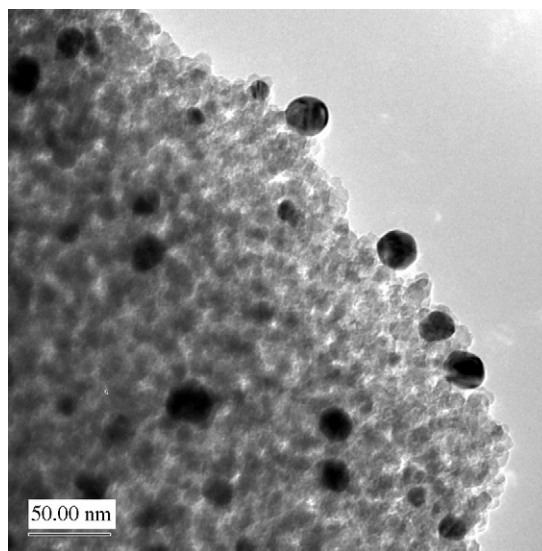
Fig. 3. TEM photograph of AuGT.

Fig. 5. TEM photograph of Au2.5SGT.

2.4. Characterization

The X-ray powder diffraction patterns were recorded in a Philips PW 1710 diffractometer with automatic control. The patterns were run with monochromatic Cu Kα radiation, using a scan rate of $2°$/min.

FTIR Spectra were taken using JASCO FTIR-5300 in KBr matrix in the range 400–4000 cm^{-1}.

The UV–vis DRS spectra of samples were recorded using a UV–vis spectrophotometer (Varian, Cary-1E, Australia). Pellets of 2 mm thickness were prepared taking 0.05 g of sample along with boric acid. The spectra were recorded in the range of 800–200 nm using boric acid as the reference standard.

Electron Probe Micro Analysis was carried out in a JEOL Super-probe (JEOL JXA-8100, Japan). Powdered samples were pasted in the sample holder and coated with carbon using a vacuum coater. The working voltage was kept at 20 kV with a beam current in the range 40–100 nA. Area scanning mode was used for qualitative analysis and X-ray scanning used to measure the elemental distribution.
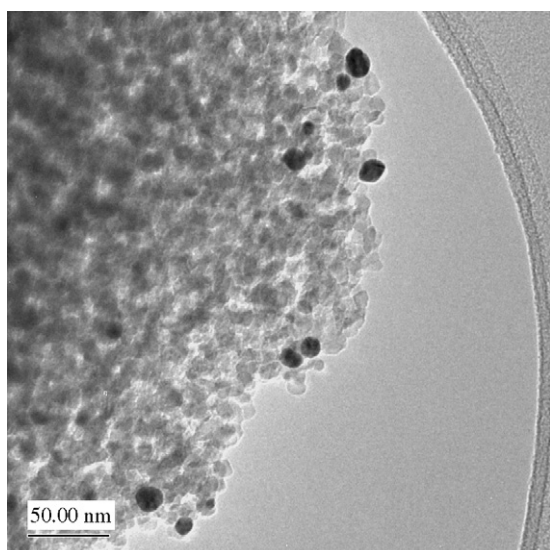
The mean particle size and particle size distribution of gold were determined by obtaining high-resolution transmission electron micrographs (HRTEM) for the Au-containing samples using a JEOL 2010 electron microscope with a LaB_6-cathode operated at a voltage of 200 kV.

BET surface areas of all samples were measured using a Micromeritics Tristar 3000 by nitrogen adsorption–desorption isotherms at liquid nitrogen temperature (77 K).

Secondary ion mass spectrometry using 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 neutral-
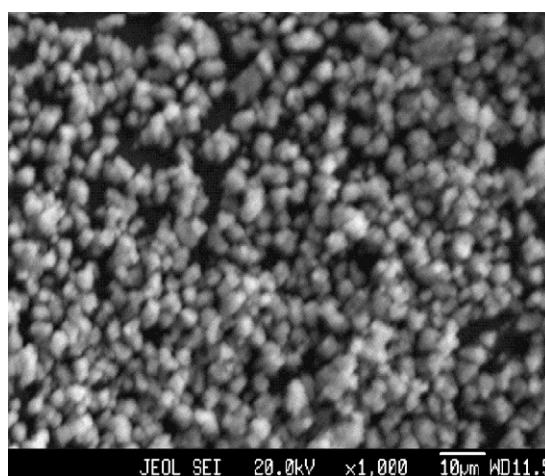

Fig. 6. SEM of $1Au/TiO_2$, titanium isopropoxide, 400 °C.

Table 1
surface area and pore volume of unsulphated and sulphated gold/titania

Sample	S_{BET} (m^2/g)	Total pore volume (cm^3/g)
TiO_2	57	0.09
$2.5SO_4{}^{2-}/TiO_2$	73	0.13
$1Au/TiO_2$	83	0.17
$2.5SO_4{}^{2-}/1Au/TiO_2$	89	0.18

Fig. 4. TEM photograph of Au0.4SGT.

Table 2
Activity of various catalysts for CO oxidation as a function of temperature

Reaction temperature (°C)	1 mass% Au/TiO$_2$ (TiO$_2$ from TiCl$_4$)	1 mass% Au/2.5 mass% SO$_4^{2-}$–TiO$_2$ (TiO$_2$ from TiCl$_4$)	1 mass% Au/TiO$_2$ (TiO$_2$ from isopropoxide)	1 mass% Au/2.5 mass% SO$_4^{2-}$–TiO$_2$ (TiO$_2$ from isopropoxide)	1 mass% Au/TiO$_2$ (TiO$_2$ from TiCl$_4$ in presence of SDS)	1 mass% Au/TiO$_2$ (TiO$_2$ from SDS in presence of SDS)	1 mass% Au/2.5 mass% SO$_4^{2-}$–TiO$_2$ (TiO$_2$ from TiCl$_4$ in presence of SDS)
30	0.0	2.0	4.6	3.8	5.9		0.0
40	0.0	2.6	6.3	6.5	8.6		1.7
50	0.0	3.4	7.1	13.9	9.5		2.9
60	0.0	4.6	8.7	21.2	14.0		3.9
70	0.0	6.1	9.5	31.0	21.4		6.4
80	0.0	8.1	14.2	39.0	27.3		12.4
90	0.0	10.3	16.0	48.3	34.8		15.2
100	0.0	15.2	18.8	55.0	39.2		19.2
120	0.0	25.4	22.2	77.2	62.2		25.1
150	0.0	52.6	40.6	98.2			43.9

ization was applied. The beam diameter was 1 μm and the analysis area was 100 μm × 100 μm and 128 × 128 pixels.

2.5. Catalytic activity evaluation

The activities of the catalyst samples towards the oxidation of carbon monoxide were measured using a fixed bed flow reactor. Hundred milligram of catalyst 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$_2$ and balances 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$_2$, 5% O$_2$ and 85% He at a flow rate of 40 ml min^{-1} was passed through the reactor and the effluent gases from the reactor analysed using gas chromatography.

3. Results and discussion

3.1. Characterization

The reflections for polycrystalline gold are expected at $2\theta = 38.2(100\%)$, $44.4(52\%)$, $64.6(32\%)$ and $77.4(36\%)$. From XRD pattern of 1 mass% Au/TiO$_2$, there is weak peak at 2θ value of 38.2°, 44.6°, 64.6° which may due to the presence of gold in these samples. The intense peak at 25.3° is due to the anatase phase of TiO$_2$. Surface area and pore volume (Table 1) of 2.5SGT samples are higher, compared with the values found for other samples. Sulphate modification resulted in a higher surface area and higher pore volume.

TEM images of samples prepared from TiCl$_4$ and impregnated with 1 mass% gold dried at 110 °C (AuHT series) show gold particles of size 20 nm dispersed on TiO$_2$ surface (Fig. 1). After heat treatment it was found that there is *decrease* in particle size of to about 11 nm (Fig. 2). With samples prepared from Ti-isopropoxide (AuST series), there is uniform distribution of gold nanoparticles (4–5 nm) over TiO$_2$ surface compared to that prepared from TiCl$_4$. There is not much change in particle size with sulphate loading (Figs. 3–5). From SEM images (Figs. 6 and 7) it is observed that for samples in which sulphate is present, the particle size becomes smaller is compared with those in the e unsulphated samples. The EPMA analysis (Figs. 8 and 9) results reveal that the gold nanoparticles are uniformly distributed over titania. It is also found that though sulphur is present in very low amount it is distributed over the whole network. This may contribute to the enhanced activity of this sample for low temperature CO oxidation. From the UV–vis DRS spectra of samples, it is found that the sulphated gold titania sample prepared from titanium isopropoxide shows a sharp peak at 550 nm compared with other samples which show a broad peak. The peak at
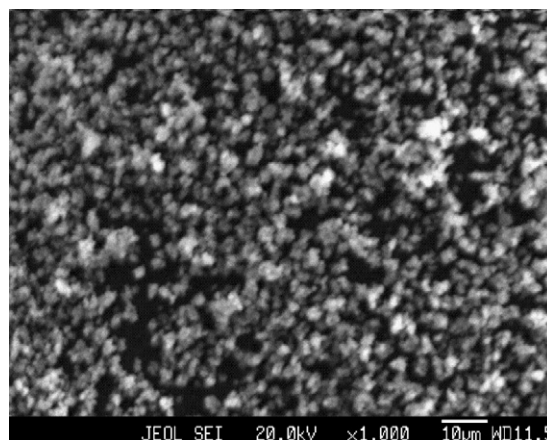

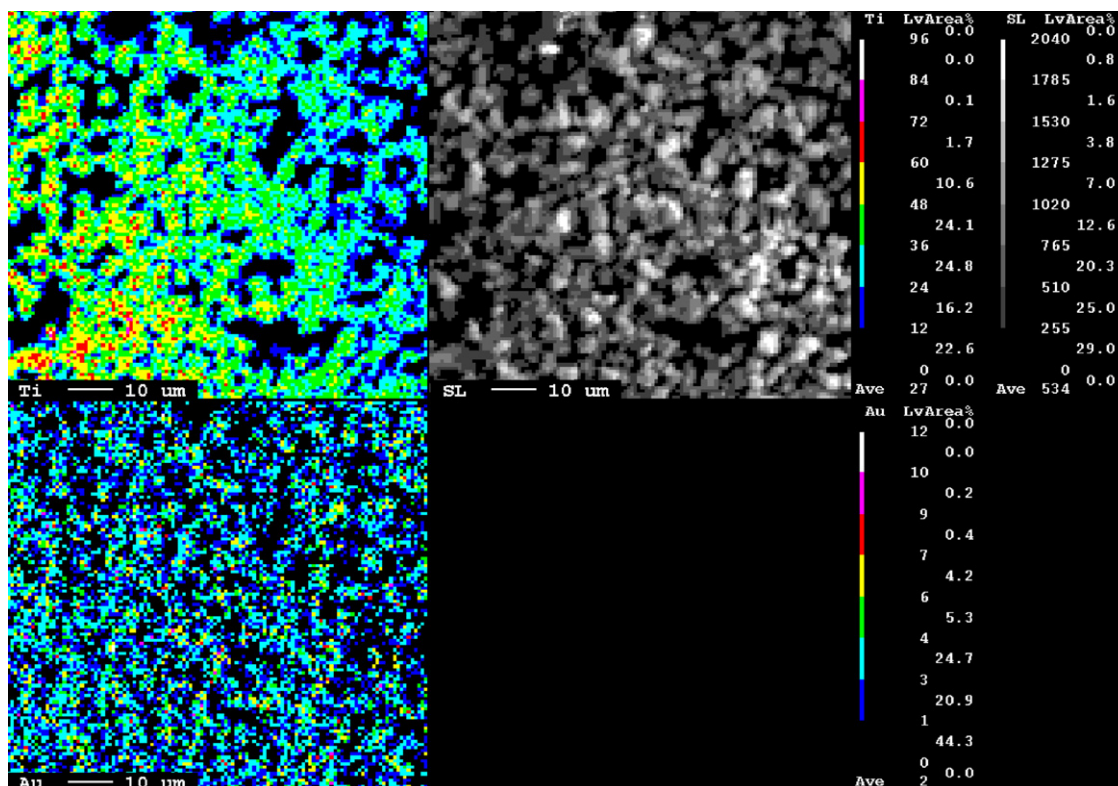**Fig. 7.** SEM of 2.5SO$_4$/1Au/TiO$_2$, titanium isopropoxide, 400 °C.

Fig. 8. Elemental mapping of 1Au/TiO$_2$, titanium isopropoxide, 400 °C.
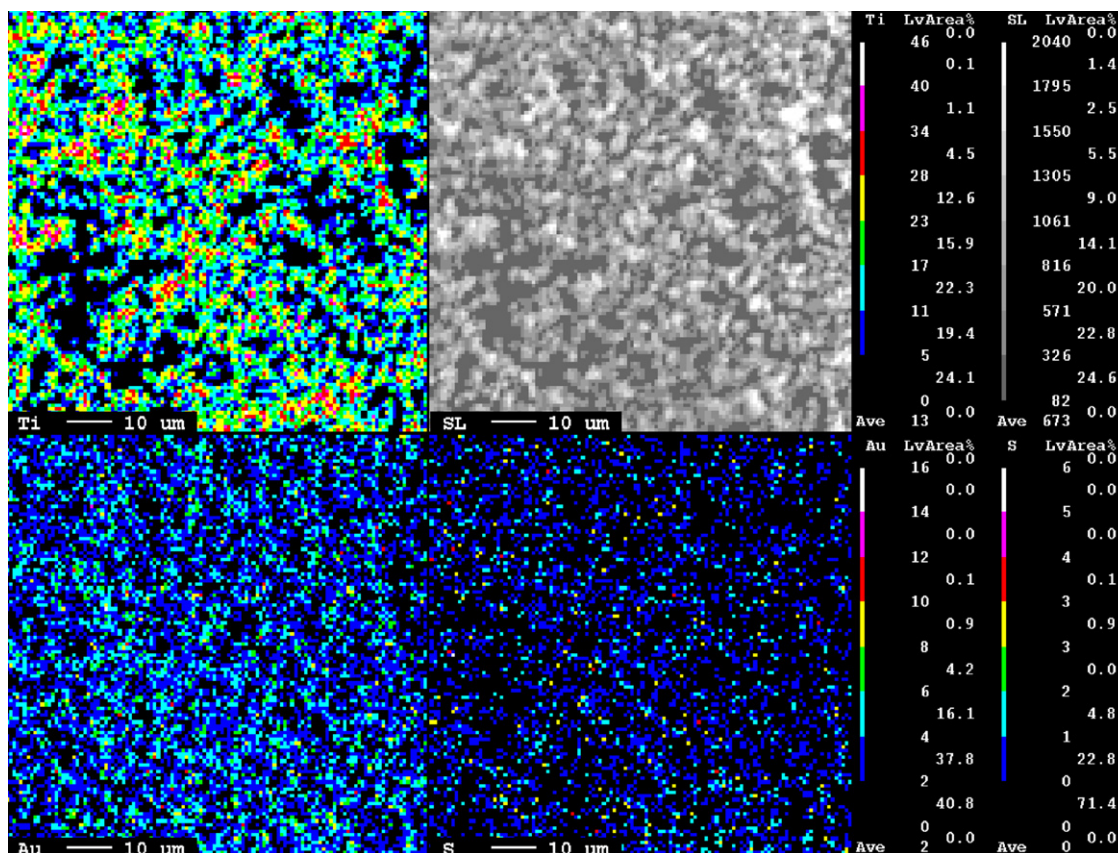

Fig. 9. Elemental mapping of 2.5SO$_4$/1Au/TiO$_2$, titanium isopropoxide, 400 °C.

Table 3
Au content of the catalyst

Sample	Gold content (mass%)
AuGT	1.06
Au2.5SGT	0.97
Au0.4SGT	1.01
Au0.2SGT	0.97
Au0.1SGT	1.00
Au0.05SGT	0.99

550 nm is almost certainly due to the presence of gold nanoparticles in the titania matrix.

3.2. CO-oxidation

The Au/TiO$_2$ samples prepared from TiCl$_4$ (AuHT) were inactive up to 100 °C, but when sulphated with 2.5 mass% SO$_4^{2-}$ (Au2.5SHT), the CO oxidation process initiates at 30 °C and CO conversion gradually increases to 53% at 150 °C (Table 2). In the case of the Au/TiO$_2$ sample, when the titania support is prepared from titanium isopropoxide, (AuGT), the CO oxidation starts from 30 °C and gradually increases to 41 at 150 °C. But it is interesting to observe that when the same sample was impregnated with 2.5 mass% SO$_4^{2-}$ (Au2.5SGT) the CO conversion increases to 98% at the same temperature. The sample prepared in the presence of SDS containing sulphate (1.5 mass%) shows 84% conversion without further addition of sulphate. The CO conversion decreases to 42% when the sample loaded with 2.5 mass% SO$_4^{2-}$. So it can be concluded here that low amount of sulphate is responsible for enhancing the activity of gold loaded titania and high amount of sulphate is detrimental for CO oxidation. We examined catalysis on the series of low sulphate-loaded samples (0.05GT, 0.1GT, 0.2GT and 0.4GT) with 1 mass% gold. The dramatic effect of sulphate treatment on CO oxidation activity, recorded at room temperature, where an over 5-fold higher activity is found for relatively low sulphate loadings. We note that the absolute rate of CO oxidation on the unsulphated 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. [14]). The promotional effect of sulphate 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 in 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 sulphate promotional effect we have established that there are no dramatic differences between the gold particle sizes distributions obtained from transmission electron microscopy. Sulphate treatment of oxides such as titania [15] and zirconia [16,17] is known to affect the specific surface area of the oxides, with increases seen after sulphate 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 sulphate contents only. Additionally, all the gold contents measured

in these catalysts are very similar (Table 3) and close to the target 1 mass% loading.

We conclude that the promotional effect of sulphate 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 sulphate treatment of Au/titania/P25 samples. Gross changes may well be difficult to detect at the very low sulphate content of our most active samples. The most active catalyst has a sulphate/gold mol ratio of only 0.12 and elsewhere [9,10] we have proposed a direct Au-sulphate ion interaction is present in these types of catalysts. The present study also reveals that the source of the titania has a considerable influence on the CO oxidation of gold supported on these supports. Overall, the comparatively poor activity of the AuHT sample obtained from titanium tetrachloride may be due to the inhibiting effects of Cl ions and/or the larger Au particle size, but it is noteworthy that sulphate treatment considerably enhances the activity of this catalyst. The isopropoxide-derived titanium support is associated with much higher levels of CO oxidation activity, and these solids can be further promoted by sulphate treatment.

Acknowledgments

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