

Unexpected promotion of Au/TiO₂ by nitrate for CO oxidation

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The catalytic activity for Au/TiO₂ for CO oxidation can be significantly enhanced by the addition of nitrates and this may relate to the variable catalyst performance observed in many studies.

One of the most surprising recent observations is that gold, when dispersed as nano-crystals on an oxide support, can be highly effective for the oxidation of CO at very low temperatures.^{1,2} This has led to a dramatic increase in the interest in gold as a catalyst, not only for CO oxidation but for selective oxidation reactions such as the epoxidation of propene,³ the selective oxidation of alcohols^{4,5} and the selective oxidation of hydrogen to hydrogen peroxide.⁶ Interest in the factors controlling the high reactivity is showing no abatement: recently Corma and co-workers⁷ showed that by using nano-crystalline CeO₂ as a support the activity of CO oxidation could be enhanced by a factor of two, and Haruta *et al.* have shown⁸ that water plays a crucial part in the origin of the high activity for this reaction. Most of the high activity catalysts reported to date are prepared using precipitation methods, either co-precipitation or deposition precipitation, often using nitrates as reagents; furthermore, it is well known that the preparation method employed can be of crucial significance.⁹

In this communication, we present the first observation that nano-crystalline gold catalysts for CO oxidation at ambient temperatures can be promoted by the addition of nitrate by a simple impregnation method. To date the subject of the promotion of the catalytic activity of gold by the addition of additional cations and anions has received no attention. This is surprising since there are numerous examples of the promotion of heterogeneous catalysts, particularly the activity or selectivity of supported metal catalysts, using this methodology.^{10,11} Perhaps the most notable examples are the enhancement in activity of iron catalysts by the addition of alkali metal cations for either ammonia synthesis¹² or the Fischer Tropsch reaction.¹³ Often, catalyst formulations can only be used on a commercial basis with the addition of these important components. It was this background that prompted us to study the role of potential promoters in nano-crystalline gold heterogeneous catalysts for the oxidation of carbon monoxide at ambient temperature.

We have selected Au/TiO₂ for investigation as this is known to be a very active catalyst for this reaction.^{14,15} We prepared the catalyst by deposition precipitation using a nitrate-free method.[†] Subsequently, aqueous solutions with different concentrations of dopants (sodium nitrate, potassium nitrate, sodium acetate or sodium citrate) were added by impregnation. The catalysts were dried at 120 °C and were not heat treated or washed after impregnation to ensure that the anions were retained intact. Using

this methodology two types of additives can be examined, *viz* cations (Na⁺ or K⁺) or anions (NO₃⁻, CH₃COO⁻, or C₆H₅O₇³⁻), and these were contrasted with a Au/TiO₂ catalyst that was treated with water alone in an analogous manner, to ensure all catalysts had been treated the same way prior to use as catalysts for the oxidation of CO.

The catalysts were evaluated for the ambient temperature oxidation of carbon monoxide using air.[†] The Au/TiO₂ catalyst prepared by treatment with water alone gave a high catalytic activity for CO oxidation, and we adjusted the flow conditions in the reactor so that the CO conversion was typically *ca.* 70%. The effect of time on line on CO conversion for Au/TiO₂ catalysts modified with sodium nitrate is shown in Fig. 1, and it is apparent that the activity is stable for several hours after an initial stabilisation period. Surprisingly, the addition of low concentrations of sodium nitrate (0.00625 and 0.0125 wt.% of NaNO₃) leads to CO conversions of *ca.* 90%, a significant improvement in catalytic activity when compared with the catalyst treated with water (*ca.* 70%). However, higher concentrations of sodium nitrate lead to much lower CO conversion, and for the catalyst containing 0.0375 wt.% Na the CO conversion was very close to zero under our test conditions.

To determine if the observed promotion is due to the addition of Na⁺ or NO₃⁻ (or both) a series of experiments were carried out in which different anions and cations were added to the Au/TiO₂ catalyst (Fig. 2). The addition of aqueous solutions of sodium citrate or sodium acetate led to a dramatic decrease in the catalytic performance for CO oxidation. In particular, negligible CO₂

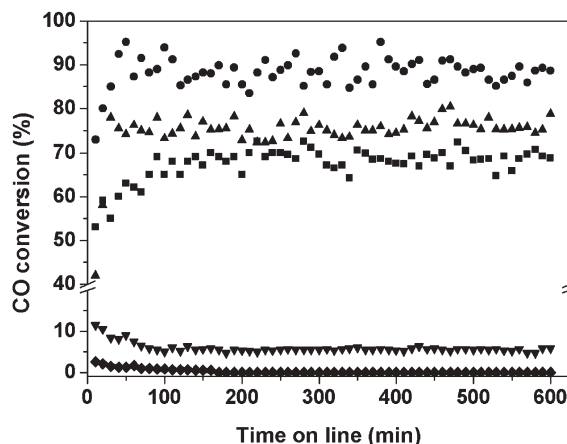


Fig. 1 Plot showing the evolution of the catalytic activity for CO oxidation with the time on line, for sodium nitrate modified Au/TiO₂ catalysts: 0 wt.% Na (■), 0.00625 wt.% Na (●), 0.0125 wt.% Na (▲), 0.025 wt.% Na (▼), 0.0375 wt.% Na (◆). Reaction conditions are given in the experimental section.

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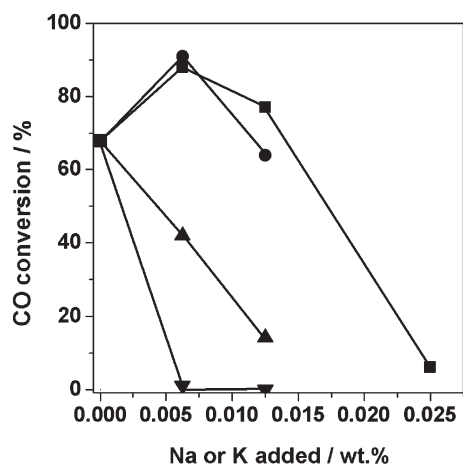


Fig. 2 Graph showing the influence of the alkali metal dopant (Na or K) on the activity for CO oxidation. Alkali source: Na-nitrate (■), K-nitrate (●), Na-citrate (▲), Na-acetate (▼). Reaction conditions are given in the experimental section; time on line = 500 min.

formation was observed when sodium acetate was used. However, the impregnation of the catalyst with potassium nitrate gave an increase in the CO conversion similar to that observed when sodium nitrate was used. Most importantly, the observed promotion effect is not short lived and we have observed sustained enhancement for the duration of our catalyst tests, *i.e.* 10 h (Fig. 1).

To determine if the effect can still be observed if air is replaced by another oxidant we investigated the oxidation of CO using N_2O (Fig. 3). The only reported study¹⁶ using this oxidant found that it was significantly less effective than dioxygen. In agreement with that result, we found that for a given catalyst, the CO conversions decreased (by a factor of *ca.* 15) when N_2O was employed as oxidant. However, it is significant that the promotional effect was still observed when low concentrations of sodium nitrate and potassium nitrate were added, and higher CO conversions were obtained (Fig. 3). The degree of promotion achieved was similar for both O_2 and N_2O as oxidants.

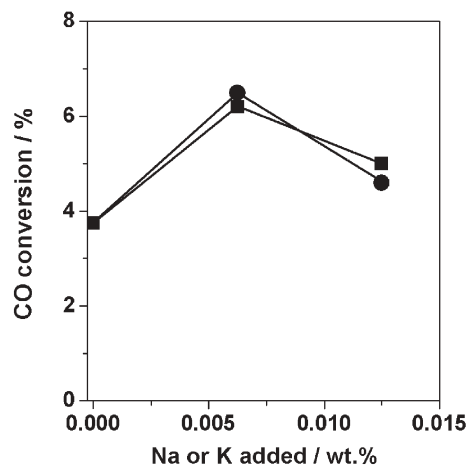


Fig. 3 Graph showing the influence of the alkali (Na or K) content added to the catalyst on the activity for CO oxidation using N_2O as oxidising agent. Alkali source: Na-nitrate (■), K-nitrate (●). Reaction conditions are given in the experimental section; time on line = 500 min.

XPS results indicate that there is no change in the oxidation state of the gold due to the nitrate treatment. The surface concentrations of nitrate are below the detection limits of our spectrometer. Furthermore, there is no significant change in the surface area of the catalysts following modification (Table 1). Taking into account the preparation method, the different catalytic behaviour observed can be due to the presence in the catalysts of (i) water, (ii) alkali metal cations (sodium or potassium) and/or (iii) anions. Since the presence of water must be equivalent for all the samples, as we have specifically treated all catalysts in an identical manner, we do not consider residual water resulting from low temperature drying to be important in this case, or at least it will affect all samples equally. Since the addition of sodium citrate and sodium acetate both give a significant decrease in CO conversion we conclude that Na^+ and/or citrate/acetate acts as a poison for the Au/TiO₂ catalyst for CO oxidation, in agreement with previous studies.^{9,17} As the promotional effect is observed with the addition of low levels of sodium and potassium nitrate we propose that the presence of nitrates, added *via* a simple impregnation step, exerts a promotional effect on a Au/TiO₂ catalyst, increasing the CO oxidation rate. The origin of the effect is, as yet, unclear but a possible explanation could involve site blocking, or the formation of new sites at the periphery of the gold crystallites.

The observation of a significant enhancement in activity by the addition of trace amounts of nitrate is significant for two reasons. Firstly, this is the first unambiguous observation that the activity of supported gold nano-crystals can be enhanced by the addition of promoters, and it is likely that other cations and anions will induce similar effects. In these initial studies we observe an increase in activity by at least a factor of two for a nitrated treated catalyst when compared with the catalyst treated with citrate, but containing an equivalent concentration of Na^+ (Fig. 2). This is similar to the pronounced increase in activity observed recently by Corma and co-workers *via* manipulation of the morphology of the support.⁷ Secondly, many groups have commented on the distinct problems associated with the reproducibility of the preparation of very active gold catalysts.¹⁸ Our experiments help provide one explanation of these observations, since many supported Au catalysts involve precipitation methods using a nitrate as one of the components. If the residual nitrate is not removed thoroughly, or nitrate removal is variable, then it is a distinct possibility that variable activity will result. Furthermore, we consider the observation of this promotion effect may aid the design of improved supported nano-crystalline gold catalysts.

Table 1 Surface areas of different catalysts after anion-doping

Anion	Amount of cation (Na or K) added (wt.%)	Surface area ($m^2 g^{-1}$)
—	—	45
NO_3^-	0.00625	45
NO_3^-	0.0125	47
NO_3^-	0.025	43
NO_3^-	0.0375	39
NO_3^-	0.00625	46
NO_3^-	0.0125	44
CH_3COO^-	0.00625	45
CH_3COO^-	0.0125	47
$C_6H_5O_7^{3-}$	0.00625	46
$C_6H_5O_7^{3-}$	0.0125	48

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Notes and references

† The Au/TiO₂ catalyst containing 1.4 wt.% Au was prepared by a deposition precipitation method. The preparation procedure was as follows: an aqueous solution of chloroauric acid (5 ml of a solution prepared by dissolving of HAuCl₄·3H₂O (5.0 g) in distilled water (250 ml)) was added with stirring to a slurry of TiO₂ (1.0 g, P25-Degussa, S_{BET} = 50 m² g⁻¹) in water (50 ml). The slurry was adjusted to pH 9.0 by the addition of aqueous sodium hydroxide (0.25 mol l⁻¹). The resulting mixture was vigorously stirred at room temperature for 1 h, filtered, and washed with distilled water several times to ensure that chloride was totally removed. The solid was dried at 80 °C overnight. Modified Au/TiO₂ catalysts were prepared by impregnating the dried Au/TiO₂ catalyst with aqueous solutions of sodium nitrate, potassium nitrate, sodium acetate or sodium citrate (5 ml g⁻¹ catalyst) with a range of concentrations (0.0125, 0.025, 0.0375 and 0.050 mg of alkali per ml) to ensure that a series of modified catalysts were obtained. The materials were dried in air (120 °C, 3 h) prior to use as a catalyst. A blank catalyst was prepared in an analogous manner by treating the dried Au/TiO₂ material with water (5 ml g⁻¹ catalyst) without the addition of the sodium or the potassium salt. This material was also dried in air (120 °C, 3 h) prior to use as a catalyst. BET surface area measurements using nitrogen adsorption were carried out using a Micromeritics ASAP 2000 instrument. The gold content of the unmodified Au/TiO₂ was determined by atomic absorption spectroscopy. The surface areas of the impregnated catalysts were not affected markedly by the impregnation process and were found to all be in the range 40–50 m² g⁻¹ using the BET method. The X-ray diffraction patterns of the catalysts showed no characteristic reflections for metallic gold and as expected showed the two crystalline phases of titania, *i.e.* anatase and rutile. The catalytic activity was determined in a fixed bed quartz micro reactor (3 mm id), operated at atmospheric pressure using

either air or nitrous oxide as oxidants. The feed comprised either CO/air (mol ratio = 0.5/99.5) or CO/Ar/N₂O (mol ratio = 0.5/4.5/95). The combined flow rate was maintained at 50 ml min⁻¹ and a constant catalyst loading (15 mg) was employed. The catalyst temperature was maintained at 25 °C by immersing the reactor in a thermostatically controlled water bath. The reaction products were analysed using on-line gas chromatography (Porapak Q and Molecular Sieve 5A). X-ray photoelectron spectra were recorded on a VG EscaLab 220i spectrometer, using a standard AlK α X-ray source (300 W) and an analyser pass energy of 20 eV. Samples were mounted using double-sided adhesive tape and binding energies are referenced to the C(1s) binding energy of adventitious carbon contamination taken to be 284.7 eV.

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