



Deep oxidation of pollutants using gold deposited on a high surface area cobalt oxide prepared by a nanocasting route

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ABSTRACT

Gold deposited on a cobalt oxide with high surface area (138 m² g⁻¹), obtained through a nanocasting route using a siliceous KIT-6 mesoporous material as a hard template, has demonstrated high activity for the total oxidation of propane and toluene, and ambient temperature CO oxidation. The addition of gold promotes the activity when compared to a gold-free Co₃O₄ catalyst prepared using the same nanocasting technique. The enhanced catalytic activity when gold is present has been explained for the deep oxidation of propane and toluene in terms of the improved reducibility of cobalt oxide when gold is added, rather than to the intrinsic activity of metallic gold particles. The improved behaviour for CO oxidation has been linked to the simultaneous presence of Au^{δ+} and Au⁰.

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1. Introduction

Amongst the number of methods employed to remove volatile organic compounds (VOCs), catalytic oxidation is considered as one of the most efficient and effective, since it eliminates pollutants yielding only carbon dioxide and water [1]. One additional advantage for catalytic oxidation is the particular ability to eliminate VOCs, both gases and condensables, especially if the concentration of the VOC in the effluent stream is low [2–4]. Amongst VOCs, linear short chain alkanes are some of the most difficult to destroy, and especially methane [5,6] which is not strictly a VOC, presents a global warming potential of about 20 times greater than CO₂. Another light paraffin, propane, is also released to the atmosphere in increasing amounts, since LPG, composed of primarily propane and butane, is increasingly used as a substitute for gasoline and diesel in transport vehicles. Currently around 12 million drivers worldwide are using LPG vehicles, since they produce less harmful

emissions in terms of particulates, CO and CO₂ than conventional fuels. However, during LPG combustion some unburnt hydrocarbons are emitted to the atmosphere. Therefore, a catalyst that completely removes propane, which is more difficult to eliminate than butane at low concentrations, is essential to reduce the impact on the environment [7]. Stationary power sources can also release propane to the atmosphere in relatively high concentrations, and hence the control of propane emissions is important for a range of applications.

Although noble metals are usually employed for the elimination of VOCs there are some oxides of non noble metals which can present comparative activity. Amongst metal oxides cobalt oxide, in the form of Co₃O₄, has been demonstrated to be one of the most active non noble metal oxides for VOC elimination [8–10], and in the case of propane it seems to be the most active [8–10]. It has been reported that cobalt oxides with high surface areas not only increase the catalytic activity but also the activity normalized per surface area [11–13] if compared to a conventional Co₃O₄. This enhanced catalytic activity has been related to an improved reducibility [11], a higher concentration of O-electrophilic species [12] and a higher amount of oxygen vacancies [13]. One way to synthesize cobalt oxides with high surface area is through a nanocasting route which in the case of cobalt oxide can exceed

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170 m² g⁻¹ [14]. This method allows the synthesis of ordered cobalt oxide with a structure determined by the shape of the pores of the mesoporous silica used as a hard template. In recent work fully replicated Co₃O₄ and Au/Co₃O₄ catalysts have been found to be very active towards total oxidation of traces of ethylene [15]. This method makes it possible to prepare metal oxides with high areas using high heat treatment temperatures. These ordered materials have demonstrated high catalytic activity in the total oxidation of several volatile organic compounds, which is remarkably higher than that obtained by conventional Co₃O₄. However, both the catalytic activity and the specific activity are higher if the degree of replication is lower than for fully ordered replicas [13]. This fact has been related to the higher concentration of highly reactive oxygen defects in the non-fully replicated cobalt oxides. Additionally, this mainly disordered sample still presents a very high surface area. The degree of replication of the cobalt oxide can be controlled by adjusting the synthesis parameter, such as the temperatures of both the aging and the calcination temperature of the mesoporous silica used as a hard template [13,16,17].

In the present paper the total oxidation of propane, toluene and CO has been studied over optimized catalysts, which were prepared following the combination of two methodologies. The first is by the addition of gold to several metal oxides by coprecipitation or deposition–precipitation, as this has been shown previously to increase the catalytic activity during the oxidation of alkanes [8–10]. The second is to prepare non-fully ordered nanocast Co₃O₄, which presents a high surface area, and shows outstanding catalytic performance for the deep oxidation of VOCs [11–13]. Consequently, we have prepared a partly ordered cobalt oxide that presents a high surface area (138 m² g⁻¹) and to this gold has been added through a deposition–precipitation method.

2. Experimental

2.1. Preparation of catalysts

High surface area cobalt oxide has been prepared using a mesoporous silica as a hard template. Below the details of the preparation of the silica template, the final cobalt oxide and the gold on cobalt oxide catalysts are described.

2.1.1. Synthesis of the mesoporous silica (KIT-6 silica)

In this work, a mesoporous silica template was used as a hard template, this was a three-dimensional Ia3d cubic arrangement of pores, KIT-6. The detailed preparation is described in Refs. [18,19]. During the preparation procedure the sample was aged at 80 °C and finally the products were calcined in flowing air at 550 °C for 6 h at a heating rate of 10 °C min⁻¹.

2.1.2. Preparation of high surface area cobalt oxide

For the synthesis of the cobalt oxide, siliceous KIT-6 was used as a template. Thus, 0.15 g of KIT-6 was dispersed in 5 ml of ethanol

with 0.4 g of cobalt nitrate. After 30 min of stirring, the ethanol was removed by evaporation through heating the mixture overnight at 120 °C in an oven. Afterwards, the resulting powder was heated in a ceramic crucible in an oven at 350 °C for 6 h to completely decompose the nitrate species. The impregnation step was repeated with 5.0 ml of the metal salt solution in order to achieve higher loadings. After evaporation of the solvent, the resulting material was calcined at 550 °C for 6 h. Finally, the silica template was removed at room temperature using a 2 M NaOH aqueous solution. The NaOH etching of silica was repeated four times, each time using a fresh portion of NaOH solution (5 ml). The Co-oxide catalyst was recovered by centrifugation, washed with water and finally dried at 120 °C. The catalyst has been denoted as C.

2.1.3. Preparation of gold deposited on the mesoporous cobalt oxide

The Au/CoOx catalysts were prepared by a deposition–precipitation method. Cobalt oxide prepared using silica as a hard template was mixed with distilled water and stirred at room temperature. To this paste, a solution with the appropriate amount (Au-loadings of 1, 4 and 6 wt.% of gold) of HAuCl₄·3H₂O was added. The mixture was adjusted to pH = 9 with an aqueous solution of NaOH, and was then aged for 1 h with vigorous stirring, filtered and washed with cold and hot water. The catalyst was either dried overnight at 80 °C (4AuC-w sample) or dried at 80 °C and calcined at 250 °C for 3 h in static air (1AuC, 4AuC, 6AuC catalysts). In Table 1 some characteristics of the samples are shown.

2.2. Characterization techniques

Catalyst surface areas were determined by multi-point N₂ adsorption at 77 K. The data were treated in accordance with the BET method.

Powder X-ray diffraction was used to identify the crystalline phases present in the catalysts. A Bruker D8 Advance Series 2 diffractometer with a CuK_α source operated at 40 kV and 40 mA was used.

Temperature programmed reduction was performed using a Micromeritics Autochem 2910 apparatus with a TCD detector. The reducing gas used was 10% H₂ in argon with a total flow rate of 50 ml min⁻¹ (GHSV ~ 8000 h⁻¹). The temperature range explored was from room temperature to 900 °C with a heating rate of 10 °C min⁻¹.

TEM (HRTEM), Selected Area Electron Diffraction (SAED) and EDX experiments were conducted using a Field Emission Gun (FEG) TECNAI G2 F20 microscope operated at 200 kV. To prepare TEM samples the catalysts were finely powdered in an Agate mortar, and then treated by sonicating in absolute ethanol for several minutes, and a few drops of the resulting suspension were deposited onto a holey-carbon film supported on a copper grid, which was subsequently dried.

Table 1
Physico-chemical characteristics of cobalt containing catalysts.

Catalyst	Au-loading (wt.%) (EDX) ^a	S _{BET} (m ² /g)		Crystal size (nm)		XPS Co ²⁺ /Co ³⁺	XPS binding energy (eV)			
		Fresh	Used ^b	Co ₃ O ₄ ^c	Au ^d		Co2p _{3/2}	Co2p _{1/2}	Au4f _{7/2}	Au4f _{5/2}
C	0	138	138	17.0	–	0.59	780.1/781.4	795.5/797.2	–	–
1AuC	1.1	129	n.d.	17.0	2–6	n.d.	n.d.	n.d.	n.d.	n.d.
4AuC-w	n.d.	133	n.d.	16.6	n.d.	1.93	780/781.7	794.9/796.7	83.7/85.8	87.4/89.5
4AuC	4.3	132	133	15.6	2–6, 10–20	0.12	780/782	794.9/797	83.7	87.4
6AuC	6.3	106	n.d.	19.9	2–5, 10–20	n.d.	n.d.	n.d.	n.d.	n.d.

^a By EDX real gold loading (assuming gold as metallic gold and cobalt as Co₃O₄).

^b Used in propane oxidation for 8 h.

^c Mean crystallite size determined by XRD through the Scherrer equation.

^d By TEM.

XPS measurements were made on an Omicron ESCA+ photoelectron spectrometer using a non-monochromatized MgK α X-ray source ($h\nu = 1253.6$ eV). Analyser pass energy of 50 eV was used for survey scans and 20 eV for detailed scans. Binding energies are referenced to the C1s peak from adventitious carbonaceous contamination, assumed to have a binding energy of 284.5 eV.

2.3. Catalyst activity determination

Catalytic VOC oxidation activity was measured using a fixed bed laboratory micro-reactor. For each experiment, 250 mg of powdered catalyst was placed in a 1/2 in. o.d. quartz reactor tube. The reactor feed contained 8000 vppm propane or toluene in air with a total flow rate of 50 ml min⁻¹. The differences between the inlet and outlet concentrations were used to calculate conversion data. In order to corroborate these data the chromatographic area of CO₂ was used as the comparative reference.

Catalytic activity for CO oxidation was also measured using a fixed bed reactor. For each experiment, 50 mg of powdered catalyst was placed in a 1/4 in. o.d. quartz reactor tube. The reactor feed contained 5000 vppm CO in air with a total flow rate of 21.5 ml min⁻¹ and the reaction temperature was fixed at 25 °C using a thermostatically controlled water bath.

For all reactions, the reactants and products were analysed by an online gas chromatograph with a thermal conductivity and a flame ionization detector. Two chromatographic columns were employed: (i) Porapak Q (for CO₂ and hydrocarbons) and (ii) Molecular Sieve 5A (to separate CO, O₂ and N₂).

Blank experiments were conducted in an empty reactor which showed negligible activity over the temperature range used in this study.

3. Results and discussion

3.1. Catalyst characterization

Reproducibility of the preparation of the gold-free cobalt oxide was checked by repeating the synthesis procedure for 4 different batches, and surface areas between 132 and 146 m² g⁻¹ were obtained. All of these batches were mixed and the resulting catalyst presents a surface area of 138 m² g⁻¹. Some properties of the catalysts synthesized are shown in Table 1. By adding gold to the partly ordered cobalt oxide, the surface areas do not significantly vary except for the catalysts with the highest loading, where a surface area drop of about 25% takes place.

The N₂-adsorption isotherm and the pore distribution of the gold-free sample show that the replication of the mesoporous silica has not been achieved, although the preparation method has yielded a large surface area material. Similar pore size distributions have been observed for the gold containing samples (Fig. 1A).

The phase composition and structural characterization of samples were examined by several techniques. Powder X-ray diffraction (XRD) and Selected Area Electron Diffraction (SAED) were used to identify the crystalline phases present in the specimens. Fig. 1 shows the XRD patterns at low (Fig. 1B) and high angle (Fig. 1C) for C, 4AuC-w and 4AuC catalysts. It can be observed that, regardless of the presence of gold, the XRD patterns of all samples are very similar. At low angles the presence of a small peak at approximately 1°, indicative of a partial ordered mesoporous structure, is clearly observed for all the samples, meanwhile at higher angles all the diffraction peaks can be readily indexed to a pure cubic phase [space group: Fd3m(227)] of Co₃O₄ ($a = 8.072$ Å) (Fig. 2b), which are in good agreement with the literature results (JCPDS 76.1802). On the other hand, in gold containing samples one new peak at 38.2° related to metallic gold could emerge. However, this diffraction feature was not distinguishable in the uncalcined sample, 4AuC-w, whereas after calcination at 250 °C, (4AuC) it can be roughly identified.

Transmission electron microscopy investigation has also been carried out on these samples since it provides the direct observation of the morphology and the distribution of gold and cobalt oxide particles. In Fig. 2a it can be appreciated that the gold free cobalt oxide hardly presents an ordered structure, with one part consisting of a rather ordered zone roughly maintaining the shape of the pores of the mesoporous KIT-6, and a second more extensive zone which is formed by single tubes and dispersed nanoparticles. This trend is maintained for the gold containing samples. In the calcined gold catalysts a high number of gold particles can be identified with both small and larger diameters. In the case of the catalyst with the lowest gold loading (1AuC) a gold particles size, ranging from 2 to 6 nm, was mainly observed. For 4AuC the mean gold particle size increased and together with large gold clusters of 10–20 nm, some particles of 3–6 nm were also apparent (Fig. 2c). For the catalysts with the highest gold loading (6AuC) two distinctly different morphologies were also observed (Fig. 3). One zone roughly maintained the ordered mesoporous structure with small gold particles in the 2–5 nm range, on the other hand, there was a second area that seemed to have completely lost the ordered structure and also presents very large particles with Au sizes ranging from 10 to 20 nm.

It is interesting to note that gold and Co₃O₄ particles were localized and analysed by means of high resolution TEM images and EDX mapping techniques. In fact Fig. 4 shows the TEM and EDX mapping of Au and cobalt oxide particles in the 6AuC sample.

Fig. 5 shows TPR profiles of the fresh catalysts. The reduction of Co₃O₄ has been reported to proceed in two steps: (i) Co₃O₄ to CoO and (ii) CoO to Co [20]. According to the TPR experiments, it is clear that there are two main reduction bands, although some other shoulders can be observed and therefore other intermediates different from CoO are likely to exist. In Fig. 5 it can be observed that

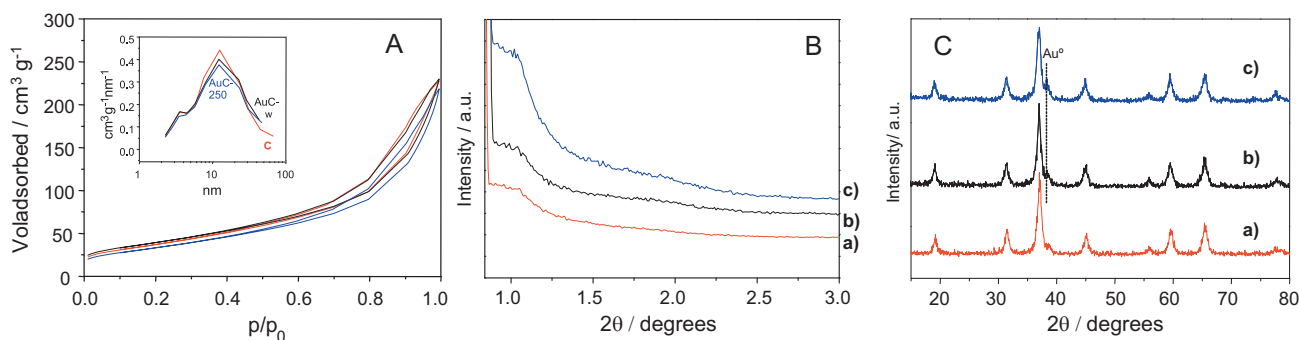


Fig. 1. Pore distribution and N₂-adsorption isotherm (A) and XRD patterns of gold-free and gold containing cobalt oxide catalysts at low (B) and (C) wide angle. Catalysts: (a) C, (b) 4AuC-w, and (c) 4AuC.

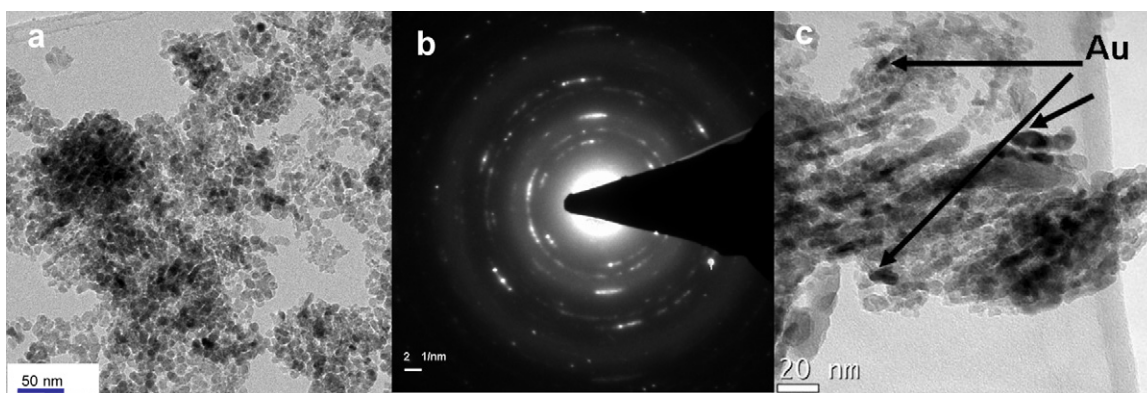


Fig. 2. High resolution TEM images of gold free and containing mesoporous Co_3O_4 : (a) C, (b) SAED pattern for C, and (c) 4AuC.

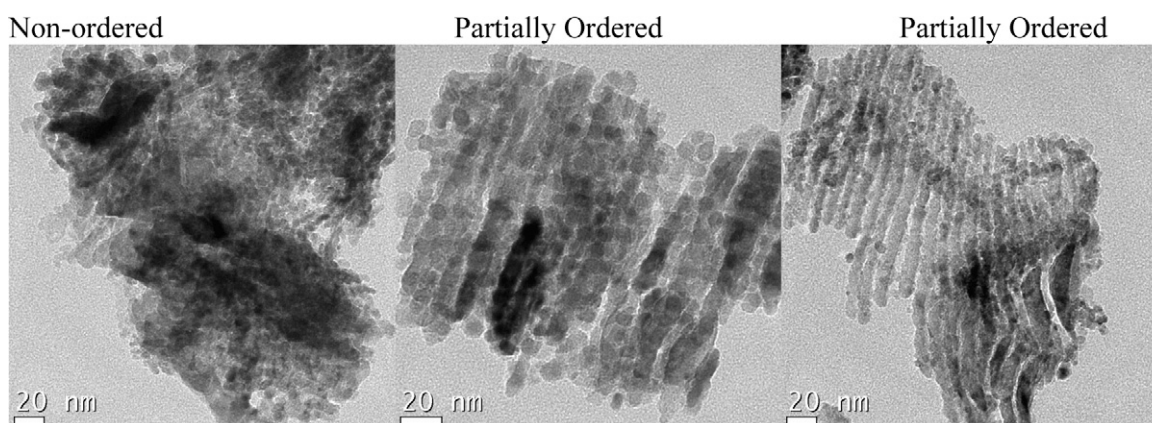


Fig. 3. High resolution TEM images of the 6AuC catalyst.

the addition of gold shifts the reduction peaks towards lower temperatures by approximately 40°C for 4AuC and 6AuC, which are the catalysts with the highest gold loadings. Hence, we can suggest that the presence of gold improves the reducibility of the cobalt oxide according to the TPR experiments, which could be a positive factor in the improvement of the toluene and propane oxidation rates, since these reactions have been reported to proceed by a Mars–van Krevelen (redox) mechanism. In the case of the catalyst with the

lowest gold loading, 1AuC, a similar reduction profile to the gold free sample was observed. It is noteworthy to comment that the ability of gold to dissociate molecular hydrogen is still a matter of debate. A significant group defend the stance that gold particles are inert towards H_2 dissociation, whilst other authors have proposed that small gold particles are reactive to produce active hydrogen [21,22]. If gold is not capable of dissociating molecular hydrogen then the shift of the reduction bands towards lower temperatures

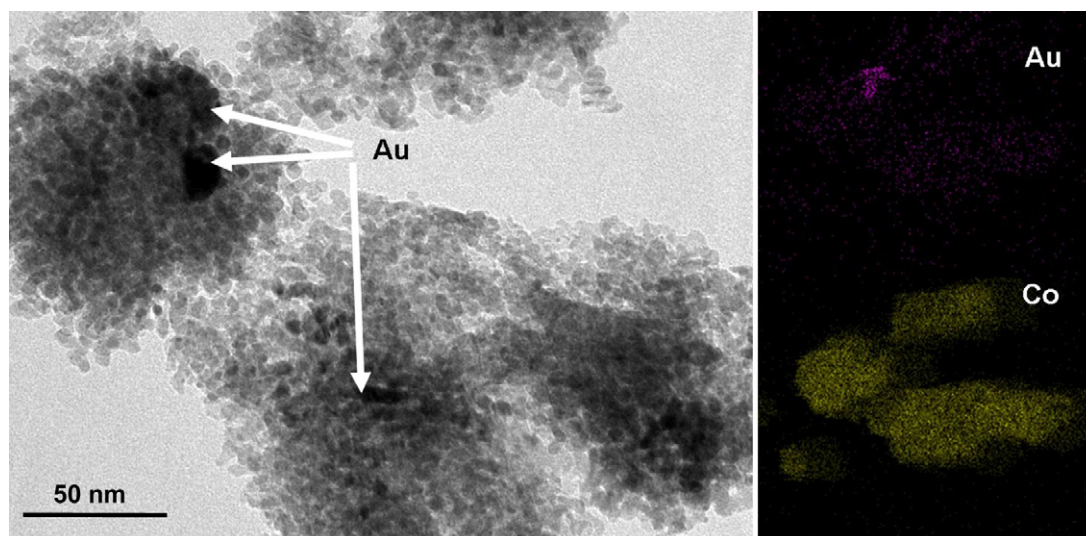


Fig. 4. HRTEM images and XEDS analysis for Co and Au in the 6AuC catalyst.

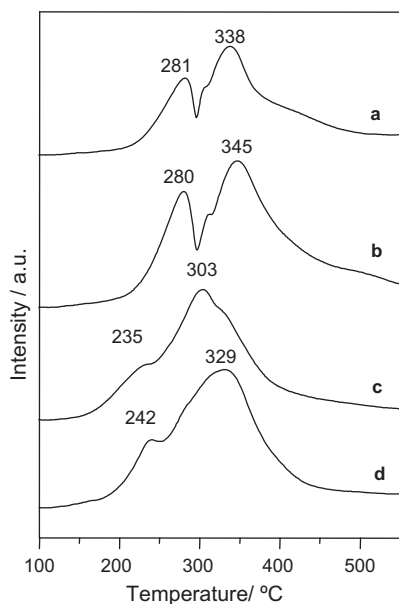


Fig. 5. Temperature programmed reduction for gold free and gold containing mesoporous Co_3O_4 templated by Kit-6. Experimental conditions in text. Catalysts: (a) C, (b) 1AuC, (c) 4AuC, and (d) 6AuC.

must be due to the improved reducibility of Co_3O_4 when gold is present. In this sense we can observe that the catalysts with the lowest gold content, 1AuC, did not present an appreciable shift in spite of the small size of the gold particles on this catalyst according to the TEM results.

XPS experiments have also been conducted on the gold containing catalysts (Table 1). The surface oxidation state of gold in these materials depends on the temperature of treatment. Samples heated at 250°C display XPS curves typical of Au^0 species, meanwhile a mixture of both cationic $\text{Au}^{\delta+}$ and metallic gold was detected for the sample heated at a lower temperature of 80°C , as can be observed in Fig. 6. In fact, XPS Au 4f spectra for calcined samples display binding energies typical of metallic gold nanoparticles (around 83.7 and 87.4 eV). In the case of the uncalcined catalyst (4AuC-w) the presence of peaks at around 85.8 and 89.5 eV indicates the presence of cationic Au^{3+} , although peaks corresponding to metallic gold (around 83.7 and 87.4 eV) have also been observed. This is in accordance with the XRD pattern, which only shows an Au^0 diffraction peak ($2\theta = 38.2^\circ$) of low intensity for the calcined catalysts.

The addition of gold also influences the local chemical environment of Co atoms. Fig. 7 shows the $\text{Co}2p$ core-level spectra measured by XPS for samples C, 4AuC and 4AuC-w. In all these spectra, the main spin-orbit doublet is located around 781 and 796 eV and presents two contributions arising from Co^{2+} and Co^{3+} . The deconvolution of the $\text{Co}2p$ spectra has been performed by a Gaussian-fitting procedure after subtraction of a Shirley-type background, for example Fig. 8 shows the deconvoluted XPS spectra for sample C. The corresponding binding energies, which are shown in Table 1, are in good agreement with those in the literature [13,23] as is the energy difference between the peak of Co^{2+} and its satellite (about 6 eV). It can be noticed that the satellite doublet, which is mostly originated from photoexcitation of Co^{2+} states, only appears in the calcined 4AuC sample to a small degree, this fact as well as the fitting procedure indicates that the proportion of surface $\text{Co}^{2+}/\text{Co}^{3+}$ is lower in this sample. Table 1 shows the $\text{Co}^{2+}/\text{Co}^{3+}$ ratio on the surface for these selected catalysts. It can be observed that after the deposition of gold on the C support the proportion of Co^{2+} significantly increases, as the $\text{Co}^{2+}/\text{Co}^{3+}$ ratio changed from 0.59 to 1.93. However when the 4AuC-w sample was calcined the amount

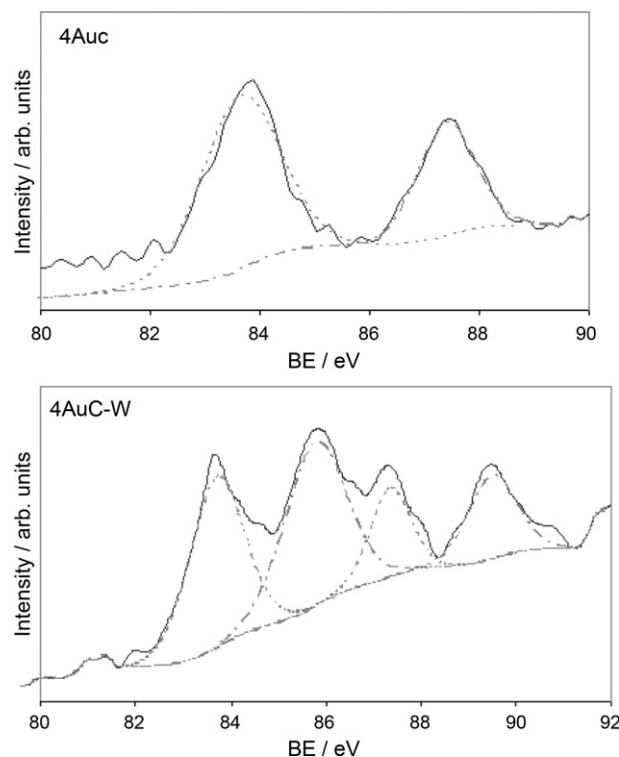


Fig. 6. Au4f core levels measured by XPS in samples 4AuC and 4AuC-w.

of Co^{2+} drastically decrease ($\text{Co}^{2+}/\text{Co}^{3+}$ ratio = 0.12 for 4AuC). Furthermore, during the calcination of the gold-containing sample the mean oxidation state of both gold and cobalt on the surface varied. Thus most of the Co^{2+} was oxidized ($\text{Co}^{2+} \rightarrow \text{Co}^{3+}$), and all of the cationic gold was reduced ($\text{Au}^{3+} \rightarrow \text{Au}^0$).

3.2. Catalytic results

Both the catalysts with high surface area cobalt oxide and with gold-loading (calcined) have been tested for propane, toluene and CO oxidation to CO_2 . The dried 4AuC-w catalyst has only been tested for CO oxidation, since it has only been treated at 80°C and the propane and toluene reactions take place at temperatures over 100°C .

CO_2 was virtually the only reaction product observed during propane and toluene oxidation over the gold-free cobalt oxide. Only during propane oxidation small amounts of propylene were observed at low conversions. In any case selectivity to CO_2 of 100% was obtained in all cases when propane conversion exceeded 5%. For the gold containing catalysts CO_2 was the only reaction product observed throughout.

An improvement of the catalytic activity has been observed in the deep oxidation of propane when gold was present in loadings of 4 wt.% and above (Fig. 9). For the catalyst with a low loading, 1AuC, no perceivable difference compared to the gold free sample has been observed. Thus, one of the best catalytic results reported to date has been obtained with the 4AuC and 6AuC catalysts in the present work, since complete conversion was obtained at only 225°C . For comparative purposes the catalytic results of a reference Co_3O_4 (cobalt oxide prepared by the evaporation of an aqueous solution of cobalt nitrate and calcined at 500°C [11]) has also been included, and it shows a catalytic activity lower than any of the catalysts synthesized in this work. Finally, we have to indicate that these catalysts, both gold free and the gold containing samples, present stable catalytic performance with time-on-line for the duration of the experiments. Thus the conversion remained stable at 180°C

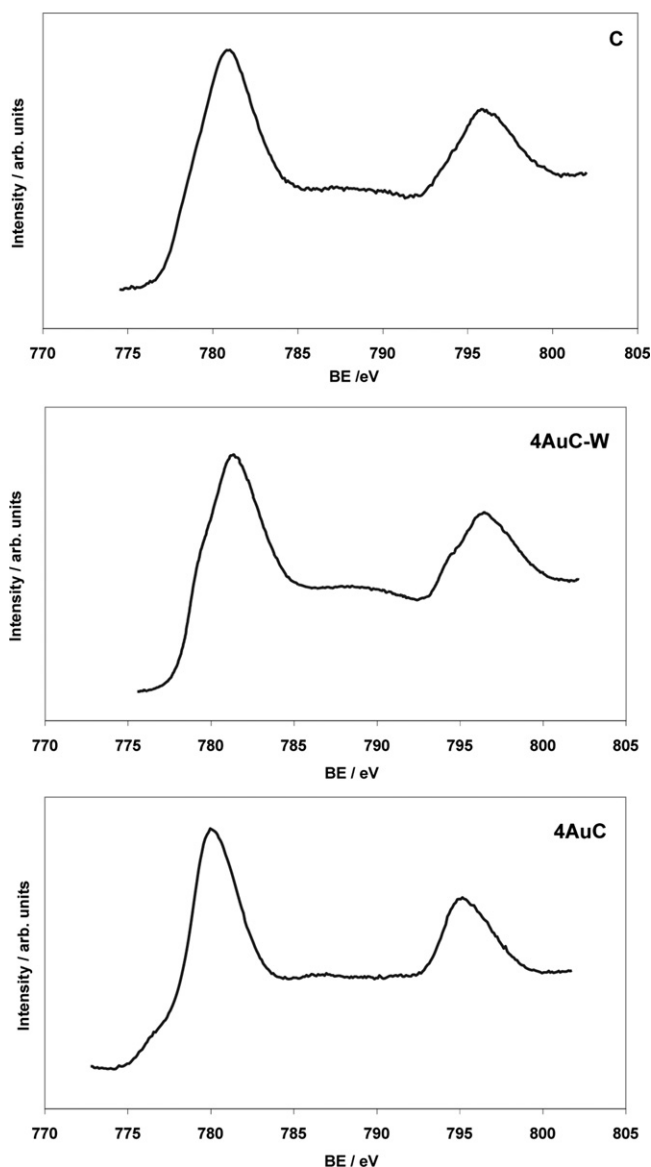


Fig. 7. Co2p core levels measured by XPS in samples C, 4AuC and 4AuC-W.

for propane oxidation for at least 8 h. As example, Fig. 10 shows the results obtained for the 4AuC sample, showing an excellent stability as it has been previously reported for cobalt nanocasted catalysts [13].

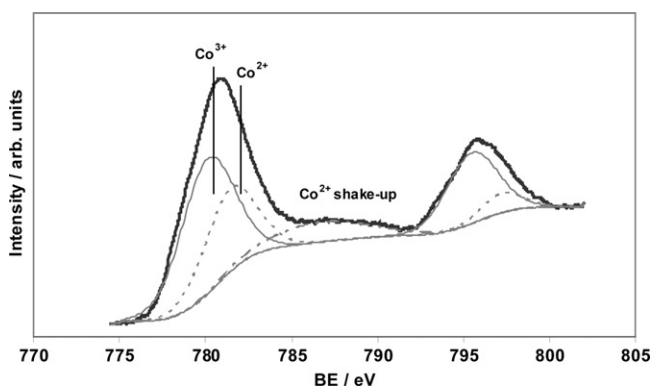


Fig. 8. Decomposed Co2p XPS spectra for sample C.

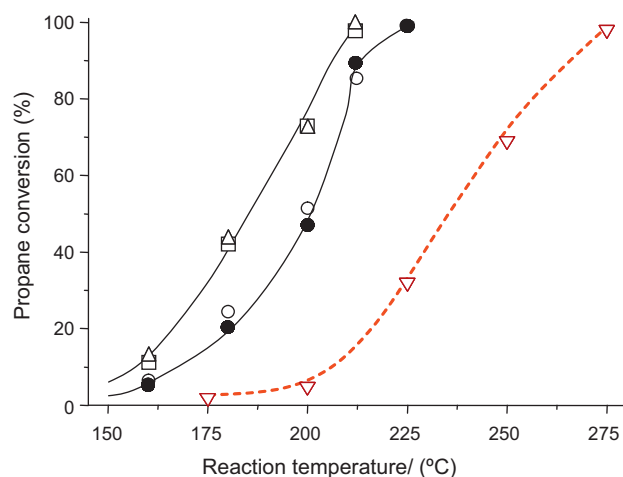


Fig. 9. Variation of the propane conversion with the reaction temperature for gold free and gold containing Co_3O_4 samples. Catalysts: (●) C, (○) 1AuC, (□) 4AuC, (△) 6AuC, and (▽) cobalt nitrate calcined. Reaction conditions in text. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

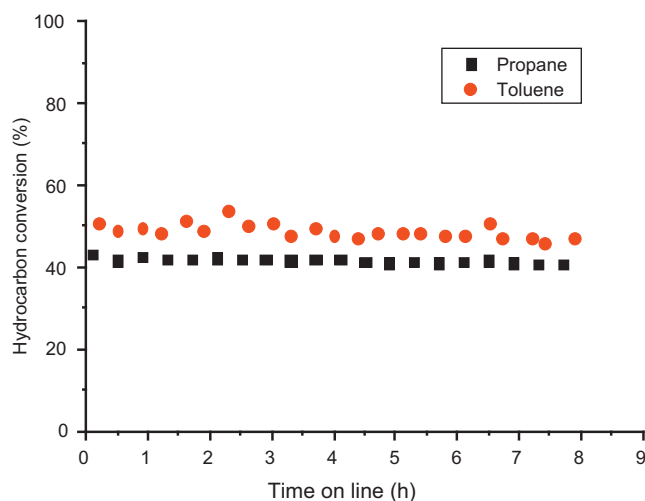


Fig. 10. VOC conversion with time on line at 180 °C for 4AuC sample. (■) Propane and (●) toluene. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Some toluene oxidation experiments were also conducted on C and 4AuC samples. The catalyst with gold was remarkably more active than the sample without gold (Table 2). Again, both catalysts were stable with time-on-line for 8 h at 180 °C. Conversion data for the 4AuC sample are plotted in Fig. 10.

During the CO oxidation the addition of gold as expected did lead to an increase in the CO conversion. The gold-free cobalt oxide, C, was completely inactive for ambient temperature CO oxidation. However, the calcined gold catalyst, 4AuC, presented low activity, with a CO conversion of around 2% (Fig. 11). Conversely, the uncalcined gold catalyst, 4AuC-w, showed a high and stable activity reaching 96% conversion under ambient conditions. These data clearly demonstrate that the Co_3O_4 prepared by a nanocasting route is an excellent support for gold nanoparticles for CO oxidation. The excellent catalytic behaviour of this catalyst has been demonstrated by comparing its performance against a reference catalyst, the Au/Fe-oxide of the World Gold Council [24], showing similar performance. The catalyst of the WGC shows an initial conversion of 99–100% but deactivates with the time on line decreasing the conversion until 93% after 110 min on line. In contrast, using

Table 2
Catalytic results for gold free and gold containing cobalt oxide catalysts for the deep oxidation of propane and toluene.

Catalyst	Propane oxidation ^a				Toluene oxidation ^a			
	Catalytic activity (10^{-2} g _{C3} /g _{cat} /h)	Specific activity (10^{-4} g _{C3} /m ² /h)	T10 ^b (°C)	T50 ^b (°C)	Catalytic activity (10^{-2} g _{tol} /g _{cat} /h)	Specific activity (10^{-4} g _{tol} /m ² /h)	T10 ^b (°C)	T50 ^b (°C)
C	8.2	6.0	170	205	18.0	13.1	170	200
1AuC	8.8	6.9	170	200	n.d.	n.d.	n.d.	n.d.
4AuC	12.6	9.2	160	195	34.4	25.7	150	180
6AuC	12.4	11.5	160	195	n.d.	n.d.	n.d.	n.d.

^a Reaction conditions in text at a reaction temperature of 200 °C.

^b T10 and T50 are the reaction temperature for propane/toluene conversions of 10 and 50% respectively.

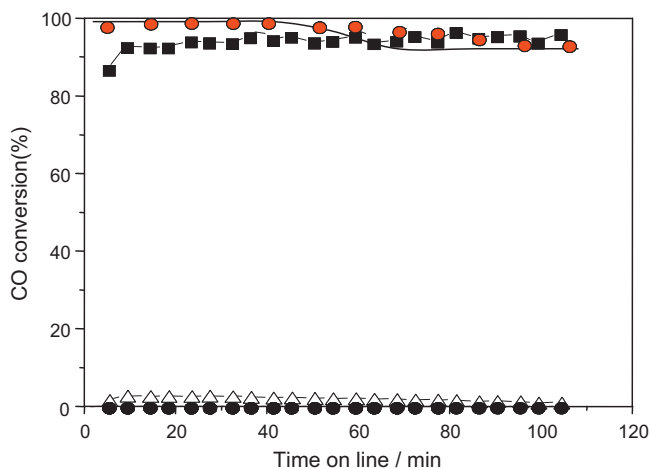


Fig. 11. Variation of the CO conversion with the time on line over gold free and gold containing cobalt oxide catalysts. Reaction conditions detailed in text. Reaction temperature = 20 °C. Symbols: (●) C, (■) 4AuC-w, (△) 4AuC, and (●) Au/Fe₂O₃-WGC. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

the 4AuC-w catalyst the CO conversion remains stable during the whole experiment.

3.3. Comments on the catalytic activity of the catalysts

Gold on a high surface area cobalt oxide has been shown to be very active in the deep oxidation of propane and toluene. This high catalytic activity in the elimination of VOCs can be related to: (i) the high intrinsic activity of Co₃O₄, (ii) the elevated number of active sites due to the high surface area of the cobalt oxide support, and (iii) the presence of gold which leads to an enhanced reducibility and possibly to a faster reoxidation of the cobalt oxide active sites.

The high surface area of the cobalt oxide employed as a support means, apart from a higher amount of active sites, an additional enhancement of the catalyst reducibility [11]. However, the reducibility is not the only factor to be considered. Thus, the presence of electrophilic oxygen species [12] or the presence of oxygen vacancies could also have an influence [13] on enhancing activity. Also interestingly, in a previous paper [25] the increased activity of the gold–cobalt oxide catalyst for propane oxidation was associated with the faster reoxidation of the cobalt oxide during the redox cycle.

Accordingly, improved activity has been observed in the total oxidation of VOCs with the Au/Co₃O₄ catalysts synthesized in the present work, although this improvement compared to the Co₃O₄ support can be qualified as moderate, as a shift towards lower temperatures of around 15 °C was evident. Furthermore, enhancements in the catalytic activity seem to be complicated since almost total conversion is achieved at very low temperatures, just slightly over 200 °C. The increase of the catalytic activity due to gold does not

seem to be related to the activating capacity of gold alone since at these reaction temperatures (at approximately 200 °C) gold cannot activate hydrocarbons such as propane [8,26]. Neither the gold particle size seems to be determining since the catalyst with the lowest gold content, 1AuC, presents the smallest sized particles and in this case no promoting effect has been observed. However a link between the catalytic activity and the catalyst reducibility can be appreciated in Fig. 12 where the temperature of the first maximum in the TPR profiles has been plotted against the catalytic activity for propane oxidation. This relationship between activity and reducibility is not surprising taking into account that hydrocarbon oxidation on metal oxides occurs through a Mars–van Krevelen mechanism, implying surface lattice oxide ions as the active oxygen species [27]. Additionally the calcined gold catalysts present a higher concentration of Co³⁺ on the surface than the cobalt oxide support, and much higher than the uncalcined gold catalysts. According to a previous paper [23] gold–cobalt oxide catalysts prepared by coprecipitation present more oxygen vacancies than the corresponding gold free cobalt oxide, but according to the present work the concentration of Co³⁺ on the surface is higher in the gold containing than in the gold free cobalt oxide catalyst. This different Co²⁺/Co³⁺ ratio in the bulk and on the surface suggests that the presence of gold facilitates the reoxidation of the cobalt and the oxygen transfer from the lattice to the surface, thus increasing the catalytic activity for the redox reactions. Therefore, the improved catalytic performance of gold containing catalysts must be related to the improved redox behaviour of cobalt oxide when gold is present in the catalyst.

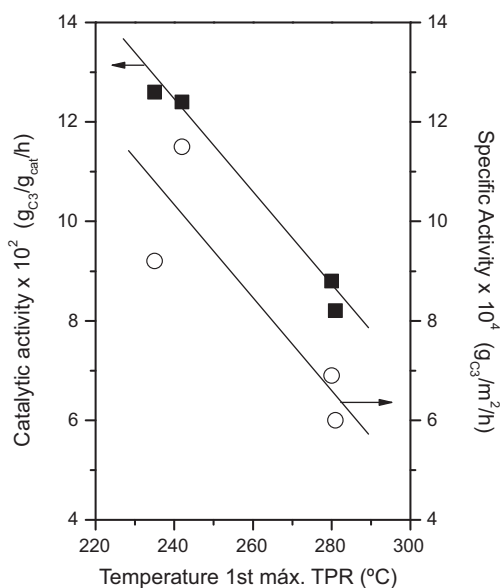


Fig. 12. Relationship between the temperature of the maximum of the first band in the TPR profile with the catalytic activity in the propane oxidation. Reaction conditions in text. Reaction temperature = 200 °C.

On the other hand, the oxidation of CO to CO₂ presents important differences in terms of mechanism and active sites with respect to the oxidation of hydrocarbons. We would like to just remark on the excellent catalytic performance obtained for the uncalcined gold catalyst. The purpose of this article is not to propose the catalytic active sites of gold species for CO oxidation, as there are plenty of proposals and exhaustive studies, but some observations can be made. According to the XPS results the gold calcined samples showed gold present only as metallic gold with particle sizes between 2 and 20 nm (Figs. 2 and 3), with sizes mainly greater than 8 nm, which is considered too large to present high catalytic activity. However, in the highly active uncalcined sample gold is present as both metallic (Au⁰) and cationic (Au³⁺) which has been reported to be desirable for this reaction [28,29]. There is not a general agreement over the mechanism for the catalytic oxidation of CO into CO₂ and the nature of the active sites. Meanwhile some authors propose that just tiny metallic gold particles are the active sites for this reaction [30–32], other authors propose the need of the coexistence of both cationic gold and metallic gold [33,28,34], as it can be observed in this work. Accordingly, Bond and Thompson [33] proposed a model in which the active catalysts contain both gold atoms and cationic gold. The role of the Au^{δ+} would be to bind the metallic gold particle to the support and prevent the sintering of tiny gold particles. On the other hand, Au⁰ would provide a site for the chemisorption of the carbon monoxide, meanwhile a partially reduced support surface with anion vacancies would be the adsorption sites for oxygen.

4. Conclusions

It has been demonstrated that the addition of gold to a high surface area cobalt oxide produces optimal materials (very active and stable) as catalysts for the deep oxidation of propane and toluene to CO₂. For these catalysts we have simultaneously used two approaches in order to improve the activity for total oxidation. These are (i) a cobalt oxide prepared through a preparation procedure that results in the desired crystalline phase (Co₃O₄) with a suitably high surface area, and (ii) the addition of gold to this material through an appropriate preparation procedure of deposition–precipitation that enhances the reduction/oxidation rates. Moreover, due to the relatively low temperatures necessary to oxidize propane and toluene these catalysts are stable with time-on-line for at least 8 h.

In the case of ambient temperature CO oxidation the addition of gold to the cobalt oxide has resulted in a large increase of the catalytic activity. The cobalt oxide alone cannot activate CO at room temperature. However, the uncalcined gold catalyst, which contains both Au³⁺ and Au⁰, has shown a high activity, remarkably higher than that of the calcined gold catalyst, in which gold is only present as Au⁰.

Finally, it can be pointed out that although gold is significantly more expensive than the other catalyst components and its addition will increase the cost of the catalyst, the amount of gold added is relatively low and there remains scope to reduce it further. More importantly, the clear performance enhancement when gold is added means that the increased cost of the catalyst could be less significant than the improved activity.

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