

Application of Heterogeneous Gold Catalysis with Increased Durability: Oxidation of CO and Hydrocarbons at Low Temperature

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Abstract

2% Au/Al₂O₃ catalysts were prepared by a novel method involving Direct Anionic Exchange (DAE). The method produces strong bonding of the gold complex (HAuCl₄) to the alumina support with no loss of gold during the subsequent steps of preparation. The complete removal of chloride from the catalyst was achieved by washing with concentrated ammonia. This procedure ensures a better activity and prevents sintering during calcination as shown by TEM.

The catalysts were tested for the oxidation of CO and of saturated and unsaturated hydrocarbons (C₁ to C₃). The catalysts showed high activities over a range of concentrations and temperatures relevant to applications in automotive exhaust cleaning. Furthermore, a remarkable resistance to thermal ageing at 600°C in the absence or presence of water was observed, due to the presence of the strongly anchored nanosized gold particles obtained during the preparation step.

Introduction

Pollution originating from cars has become one of the major issues for public authorities for both health and environmental protection. As a result, automotive regulations have been adopted in Europe, USA and Japan. As a consequence, the solution to meet them is the catalytic oxidation and reduction of several harmful pollutants found in automotive exhaust gas streams. However, new emissions control regulation technologies are still being developed to meet ever more stringent mobile source emissions (1).

Gasoline is a mixture of hydrocarbons which is oxidized in air, to produce energy. However, a number of incomplete combustion products are formed, mainly unburned hydrocarbons and CO. Nitrogen oxides (NO_x) result from the thermal fixation of the nitrogen by reaction with oxygen from the air at high temperature. The transformation of these pollutants into harmless CO₂, H₂O and N₂ is achieved by means of a three-way catalyst (TWC) located in the exhaust pipe. A TWC is able to reduce the deleterious emissions by up to 95% when it is fully warmed up by the exhaust gas, i.e. at a temperature higher than 450°C. But state-of-the-art technology gasoline fuelled vehicles emit 90% of such exhaust emissions within the first minutes of operation following a cold start. These initial high emissions are mainly due to the inefficient oxidation of hydrocarbons when the operating temperature of the catalytic converter is below 300°C. Therefore, catalysts which are active at low temperature for oxidation of cold-start emissions and which can also withstand high temperature during the normal operating conditions are required.

The activity of gold in the form of nanoparticles for catalytic oxidation of CO below room temperature no longer needs to be proven. Some studies have revealed the good behaviour of gold catalysts towards the oxidation of hydrocarbons which compare fairly well with Pt and Pd, the precious metals usually used for TWC (2,3). But the major drawback to gold lies in its thermal stability. It is usually accepted that above 400°C, gold catalysts undergo severe sintering and the remaining activity is no longer sufficient for an application.

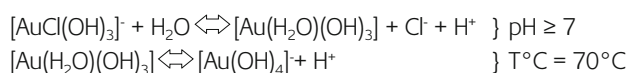
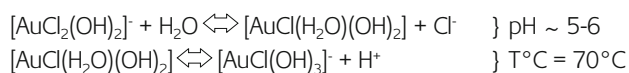
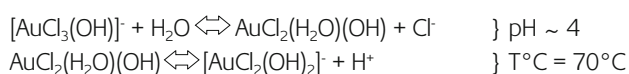
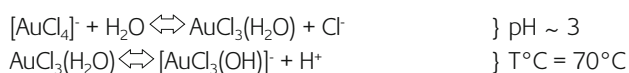
Therefore, the main objectives of the work reported in this paper were to prepare a gold catalyst on alumina and ceria, which are common supports used in catalytic exhaust devices, and to characterise the gold catalyst in terms of activity and resistance to ageing for the oxidation of carbon monoxide and hydrocarbons for low temperature applications.

Experimental

Preparation of gold catalysts and ageing procedures

A novel method of preparation has been developed, based upon the direct anionic exchange (DAE) of the gold species with the hydroxyl groups of the support (4). Aqueous solutions of HAuCl_4 of concentration $1.44 \times 10^{-4} \text{ mol l}^{-1}$ (pH 3.5) were used in order to obtain a final Au loading of 2 wt. %.

Belevantsev et al. (5) reported that the gold precursor, tetrachlorauric acid, hydrolyses in aqueous solution to yield a variety of gold complexes formed as a function of temperature and pH. The principal reaction at room temperature is the formation of the aquo complex $[\text{AuCl}_3(\text{H}_2\text{O})]^0$ by replacement of one ligand Cl^- by a water molecule. This reaction is followed by a complex deprotonation and leads to the formation of the charged complex: $[\text{AuCl}_3(\text{OH})]^-$. This stage is reported as being the limiting step of hydrolysis and is promoted by heating. The concentration of $[\text{AuCl}_4]^-$ decreases as pH increases and a variety of hydrolysed species result (6). The relative quantity of each species: $[\text{AuCl}_3(\text{OH})]^-$, $[\text{AuCl}_2(\text{OH})_2]^-$, $[\text{AuCl}(\text{OH})_3]^-$ and $[\text{Au}(\text{OH})_4]^-$ depends upon the pH value and on the concentration of the gold precursor as described by the following chemical equations:



The support, $\gamma\text{-Al}_2\text{O}_3$ powder with a BET surface of $90 \text{ m}^2 \text{ g}^{-1}$, was sieved with the fraction 125-250 μm retained. The gold solution was heated to 70°C and the support added. After 20 min, 50 ml concentrated (25 mol l^{-1}) ammonia solution was added in order to completely remove the chloride ions. The slurry was aged 20 min, filtered and washed with warm water. The slurry was then dried in an oven at 120°C overnight and calcined in air at 300°C for 4 h. The same catalyst was also made as described without washing with ammonia. The ammonia treatment successfully removes the chloride ligands from the gold chlorohydroxy complexes and chloride simply attached on the support. Chemical analysis of Au and Cl in the samples was performed by inductively coupled plasma atom emission spectroscopy at the CNRS Center of Chemical Analysis (Vernaison, France). The detection limit is 150 ppm for Cl. Chemical analysis was performed after sample calcination. The Au weight loading of the samples is expressed in gram of Au per grams of calcined sample: $\text{wt \% Au} = \frac{m_{\text{Au}}}{(m_{\text{Au}} + m_{\text{Al}_2\text{O}_3})} \times 100$. The

gold loading was found to be 2wt% for a water-washed sample and 1.37 wt% for an ammonia-washed sample. The level of chlorine was found to be 0.33wt% for water-washed sample and below 150 ppm for ammonia-washed sample.

Caution/safety note: *The contact of ammonia with gold solution can result in the formation of gold ammonia complexes ("fulminating gold") which are explosive (7). Using this washing procedure may not be dangerous as the gold complexes are strongly attached to the support by DAE. However, it is necessary to be certain that there is no gold in the solution before the addition of ammonia, as Cosumo (20) reported that "supported metal catalysts which contain gold should never be prepared by impregnation of a support with solutions which contain both gold salts and NH_4OH . The dried catalysts contain extremely shock sensitive gold-nitrogen compounds which might explode with the lightest touch".*

Catalytic testing and ageing procedures

Various unburned hydrocarbon species may be emitted from hydrocarbon flames. In general, there are two classes of unburned hydrocarbons: 1) small molecules that are the intermediate products of combustion resulting from the breaking of the C-C chain and 2) larger molecules that are formed by pyro-synthesis in hot, fuel-rich zones within flames, (e.g. benzene, toluene, xylene, and various polycyclic aromatic hydrocarbons). Small unsaturated molecules are usually difficult to oxidise. Therefore, the study was focused on this type of molecule and the catalysts were evaluated for the oxidation of several hydrocarbons (CH_4 , C_2H_6 , C_2H_4 , C_2H_2 , C_3H_6 and C_3H_8). A study of the activity for CO oxidation was also undertaken, as this reaction is a probe reaction for the particle size, as there is general agreement that the activity increases as particle size decreases (8,9). The reaction is structure-sensitive and therefore a difference in the activity reflects a change of the particle size. The CO oxidation was performed at atmospheric pressure using a fixed bed quartz micro-reactor packed with 50 mg catalyst and a gas mixture of 1.5% CO and 4% O_2 in helium with a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$ (GHSV in CO oxidation $23,000 \text{ h}^{-1}$). The oxidation of hydrocarbons was performed using 200 mg of catalyst and a mixture containing 1500 ppm hydrocarbon and 4% O_2 in helium with a flow rate of $75 \text{ cm}^3 \text{ min}^{-1}$ (GHSV $\sim 15000 \text{ h}^{-1}$). The flow was adjusted by means of Tylan flow controllers. The temperature was monitored and controlled by a Eurotherm system. The analysis was performed by Rosemount Infrared analysers for both CO and CO_2 , and by gas chromatography for hydrocarbon (DB-Wax column, 2m. long, 2.5mm of interior diameter). The experiment was repeated several times in order to measure the reproducibility. The catalyst performance was assessed in terms of the T_{50} temperature, defined as the temperature at which 50% conversion was obtained. Before each test, the catalyst was treated at 300°C in air for 2 hours to removed physi-sorbed water and CO_2 .

Two ageing procedures were used, i.e. heating in situ in air at 600°C for 12 hours or heating ex situ at 600°C in air containing 5% H₂O at a flow rate 200 cm³ min⁻¹ for 12 hours. All the catalysts were systematically characterised by Transmission Electron Microscopy and X-Ray Diffraction. The procedure of ageing in air was used at laboratory scale as it usually mimics quite well real ageing on an engine bench (10). Although this temperature is lower than the one generally used, i.e. 900 to 1100°C, it is considerably higher than the temperature at which gold sintering occurs, as reported in the literature (11,12).

Results and Discussion

1. CO oxidation Effect of chloride

Chloride is known to have a sintering effect during thermal treatments. This is due to the ease with which gold and chloride ions combine to form bridges, favouring the growth of the particles upon heating (13). Furthermore, chlorine also has a poisoning effect on the CO oxidation reaction by blocking the active sites (14). Therefore, removing chloride is an essential step to produce an active catalyst. To achieve this, the catalyst was washed with concentrated (25 mol.l⁻¹) NH₄OH. After filtration, the sample was calcined and the activity measured in CO oxidation. This type of washing prevents the particle size growing during the thermal treatment and hence gold nanoparticles strongly anchored to the support are obtained. The very positive effect of such a washing procedure can be seen in Figure 1, with a gain of 95°C in T₅₀, i.e. a decrease from 163°C for the H₂O-washed catalyst to 68°C for the ammonia-washed sample.

However, for ammonia-washed samples, a change in the shape of the conversion curve is observed. There is a plateau in activity between 50 and 150°C and full activity is restored above 150°C. This plateau could be attributed to temporary deactivation of active sites caused by formation of bicarbonate species on the surface, observed by IR (results not shown). When the temperature is increased, the concentration of these species decreases and the access to the active sites is restored.

The improvement of catalytic activity is related to the

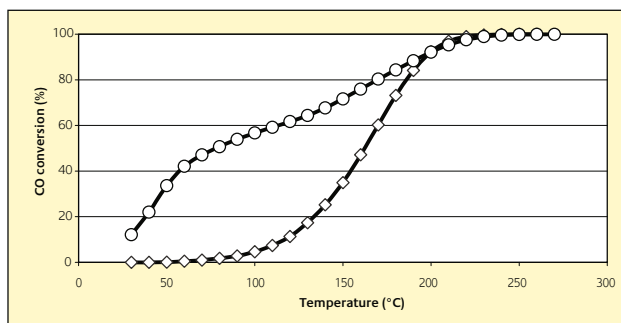


Figure 1
Effect of the washing procedure: washed with NH₃ solution 4M at 25°C (O), washed with water at 70°C (□)

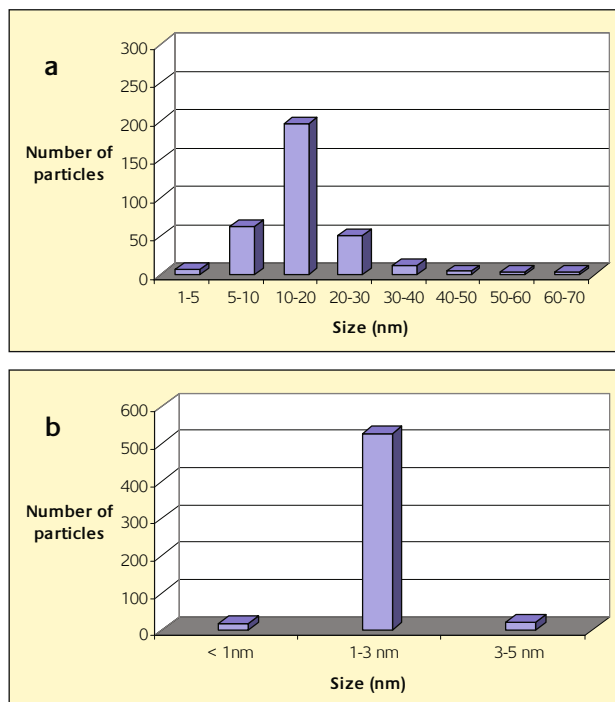


Figure 2
Particles size distribution obtained by TEM a) DAE washed with water, b) DAE washed with ammonia solution

particle size, as shown in Figure 2. The average particle size from the distribution obtained by TEM is ca. 16 nm (measured over 338 particles) for the water-washed sample and decreases to 1.9 nm (measured over 569 particles) for ammonia-washed sample. This latter sample presents a very narrow particle size distribution and high degree of metal dispersion. The achievement of such a low size for gold particles on an alumina support is remarkable as dispersing gold on such a support is not possible by the current “deposition-precipitation” method, although Datye et al (21) observed a similar Au particle size, 2.1–2.4 nm, on an Au/Al₂O₃ catalyst after ammonia washing.

2. Oxidation of Hydrocarbons Effect of carbon number

The oxidation of alkanes from C₁ to C₃ was studied with the ammonia-washed catalyst and the results are presented in Figure 3. The activity sequence is act(C₂H₆) > act(C₃H₈) > act(CH₄). The activity of the gold catalyst is lower than that

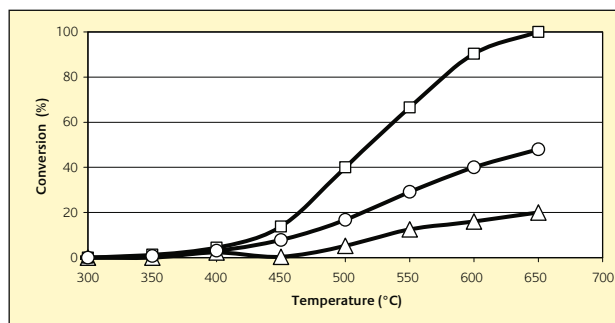


Figure 3
Conversion of alkanes on 2% Au/Al₂O₃ : (□) C₂H₆, (O) C₃H₈, (Δ) CH₄

Table 1*C-C and C-H bonding energies in hydrocarbons*

Hydrocarbon	C-C bond energy (kJ mol ⁻¹)	C-H bond energy (kJ mol ⁻¹)
CH ₄	–	438
C ₂ H ₆	330	410
C ₃ H ₈	334	401
C ₂ H ₂	836	522
C ₂ H ₄	611	430
C ₃ H ₆	351	410

obtained from other noble metals such as Pt or Pd (15) where the activity increases as the number of carbons increases in the chain. This is explained by the fact that the governing factor for the rate of reaction is the rupture of the C-H bond during the sorption process and that the energy of this bond decreases from methane to propane, the values being given in Table 1 (16).

On gold catalysts, the sequence of activity is unusual, therefore a factor other than the dissociation energy of the C-H bond should be taken into consideration. The small size of gold clusters confers special electronic properties which could lead to marked variations in the bonding energies of the adsorbate to the metal atoms of the lattice. Therefore, there is probably a fraction of oxygen poor surface which is readily poisoned by the hydrocarbon residue which occurs more rapidly for propane than for ethane.

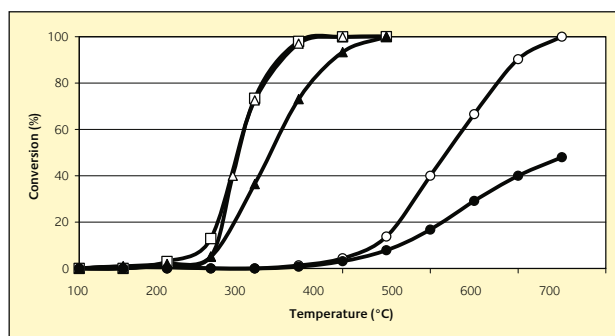
Effect of carbon unsaturation

Exhaust gas contains a large proportion of unsaturated small molecules, such as C₂H₄, C₂H₂ and C₃H₆. In this study, the activities for C₂ and C₃ oxidation were evaluated. In Table 2, the C₂H₂, C₂H₄ and C₂H₆ temperatures at 10% / 50% / 100% conversion (T₁₀, T₅₀ and T₁₀₀) are reported, whereas an evaluation of conversions with reaction temperature is shown in Figure 4. The conversion of C₃ (C₃H₆ and C₃H₈) is also displayed for comparison. For C₂ oxidation, the sequence of activity is: act(C₂H₂) ≈ act(C₂H₄) > act(C₂H₆). For C₃ oxidation, the sequence activity follows the same trend, i.e. the oxidation of the unsaturated hydrocarbon is easier than for the saturated one. Conversely, there is no influence of the degree of unsaturation between C₂H₂ and C₂H₄. The fact that the C-C energy is quite different for these two molecules (see Table 1), suggests that it is the π-bonding adsorption which controls the reaction rate rather than the rupture of the C-C bond.

Table 2

Activity of 2% Au/Al₂O₃ for C₂ hydrocarbons expressed by T₁₀, T₅₀ and T₁₀₀.

	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆
T ₁₀ (°C)	242	243	255
T ₅₀ (°C)	280	283	318
T ₁₀₀ (°C)	360	360	450

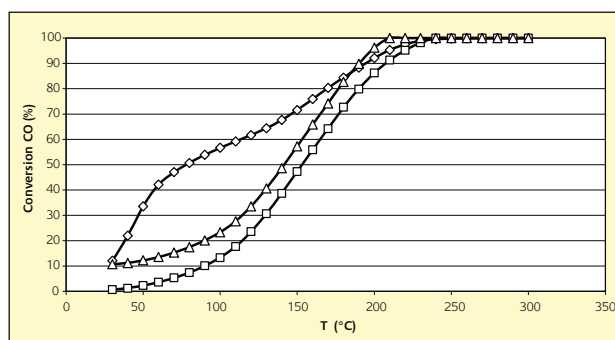
**Figure 4**

Activity of 2% Au/Al₂O₃ on HC oxidation, (□) C₂H₂, (Δ) C₂H₄, (○) C₂H₆, (▲) C₃H₆, (●) C₃H₈

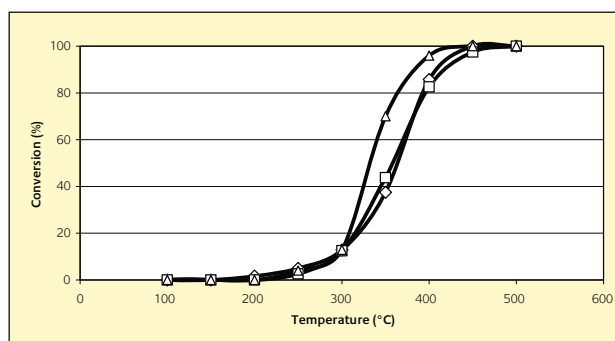
Ageing effect

Two ageing procedures were used, i.e. heating in situ in air at 600°C for 12 hours or heating ex situ at 600°C in air with 5% H₂O (200 cm³ min⁻¹) for 12 hours. The effects for CO, C₂H₂, C₂H₄ and C₂H₆ are shown in figures 5, 6, 7 and 8 respectively.

For the 3 hydrocarbon molecules, there is a limited deactivation. These results are very unusual for a gold catalyst since it usually sinters very easily, even at temperatures as low as 400°C (17,18). This is generally considered as the major drawback for an application in automotive emission control. This observed behaviour is due to the fact that sintering does not occur, as confirmed by XRD in Figure 9. After the thermal ageing at 600°C in the absence or presence of water, the diffraction peak for gold remains unobservable, confirming the presence of small

**Figure 5**

Ageing effect on CO oxidation, (◇) Fresh, (Δ) aged in air at 600°C for 12 hours, (□) aged in air + 5% H₂O at 600°C for 12 hours

**Figure 6**

C₂H₂ oxidation on 2% Au/Al₂O₃ catalyst, (Δ) Fresh, (□) aged in air at 600°C for 12 hours, (◇) aged in air + 5% H₂O at 600°C for 12 hours

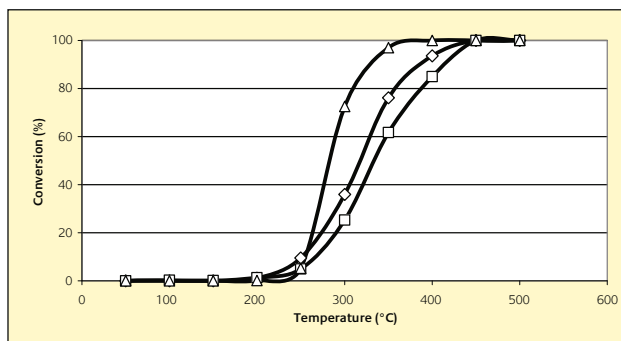


Figure 7

C₂H₄ oxidation on 2% Au/Al₂O₃ catalyst, (Δ) Fresh, (□) aged in air at 600°C for 12 hours, (◇) aged in air + 5% H₂O at 600°C for 12 hours

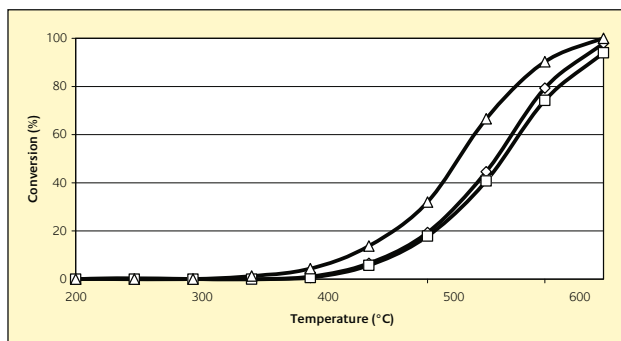


Figure 8

C₂H₆ oxidation on 2% Au/Al₂O₃ catalyst, (Δ) Fresh, (□) aged in air at 600°C for 12 hours, (◇) aged in air + 5% H₂O at 600°C for 12 hours

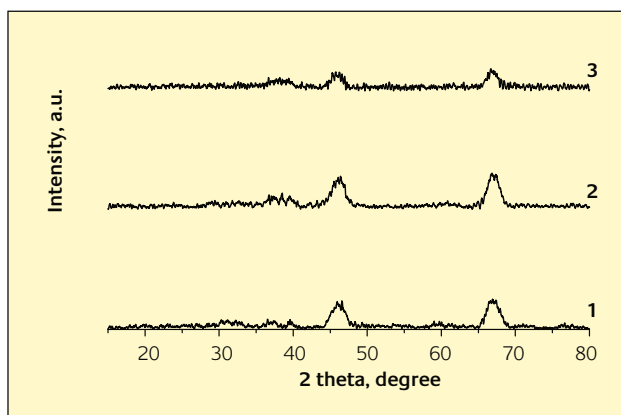


Figure 9

XRD pattern of: 1) Al₂O₃, 2) 2% Au/Al₂O₃ as prepared washed with ammonia, 3) 2% Au/Al₂O₃ washed with ammonia after test in HC oxidation with calcination at 600°C + 5% H₂O

particles. The most surprising result is probably the total absence of particle growth after the exposure to 600°C, as proven by the TEM distribution in Figure 10. The particle size, which was 1.9 nm after preparation with ammonia washing (Fig. 2), increases slightly to 2.6 nm (measured over 534 particles) after ageing at 600°C. The presence of 5% H₂O at the same temperature does not affect the average particle size, which remains small with an even slightly lower value of 2.3 nm (measured over 425 particles).

The reason lies in the fact that the method of preparation by direct anionic exchange (DAE) leads to the formation of small particles strongly anchored to the support. The

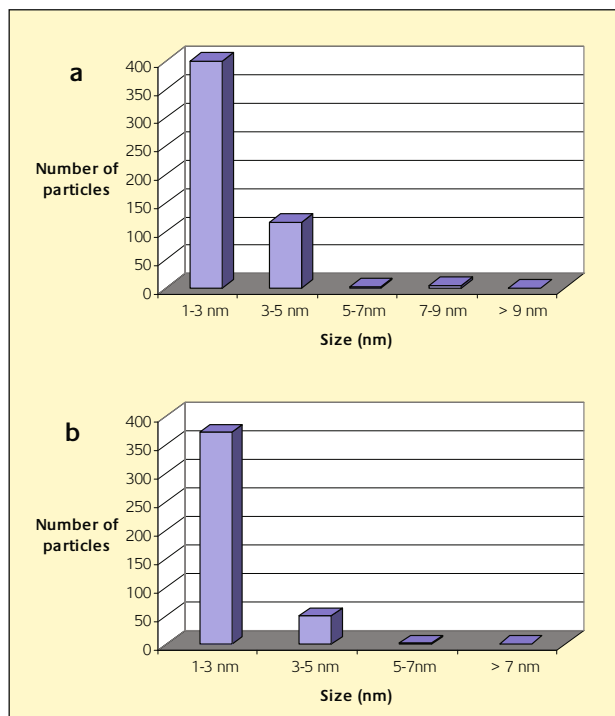


Figure 10

Particles size distribution of 2% Au/Al₂O₃ washed with ammonia obtained by TEM a) aged in air 600°C, 12 hours b) aged in air + 5% H₂O 600°C, 12 hours

complete removal of chloride by ammonia washing restricts the mobility of the gold species during the thermal treatment. Such results are very promising, as thermal resistance has always been the principal handicap to an application in automotive catalysis. In the case of the Al₂O₃ support, the activities obtained for molecules previously proving difficult to oxidise, such as C₂H₂, are already within a range of temperature suitable for an application. The same preparation method could easily be applied to supports with which even lower temperatures were obtained rendering gold catalysis even more attractive for the low light-off application (19).

Conclusions

It is possible to prepare highly dispersed gold on alumina using the Direct Anionic Exchange preparation technique. The catalyst obtained by this method contained nanosized particles which are active in the oxidation of CO. The activity can be strongly improved by the complete removal of chloride using an ammonia washing procedure. The catalyst, tested in various reactions of saturated and unsaturated hydrocarbons from C₁ to C₃, reveals an activity which is in an appropriate range of temperature for automotive exhaust emission control applications. Furthermore, the catalyst is almost perfectly resistant to oxidative ageing treatments to temperatures as high as 600°C and the loss of activity remains minor. The average gold particle size increase is very limited. The presence of water during the ageing treatment does not provoke a further deactivation. This is due to the

strong bonding of the gold precursor during the preparation step which, along with the removal of chloride, inhibits sintering.

The choice of ageing procedure has been made according to our experience in the field on TWC. Indeed, the use of air is justified in the sense that it usually mimics fairly well the ageing on bench test which is both costly and time consuming. However, the temperature is far below the one usually used, i.e. 600°C instead of 900 to 1100°C, but gold is reported to sinter at temperatures as low as 300°C and confirms an earlier report (21) of thermal resistance to sintering at 600°C when ammonia washing is employed. This result shows that it is possible to overcome the problem of gold catalyst deactivation usually observed after exposure to high temperatures and opens up the perspectives for applications for gold catalysis in automotive emission control technology, but the use of ammonia does have safety risks (see above).

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