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Supported gold catalysts for CO oxidation

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Abstract

Catalysts containing gold clusters dispersed on different oxide supports (CeO_2, ZrO_2, La_2O_3) were developed as alternative materials to platinum group metals (PGM), widely used in catalytic exhaust gas treatment. The catalysts were prepared by the innovative combustion synthesis method (SCS) and then characterized by XRD, BET, TEM and SEM-EDS analyses, whereas their catalytic activity towards CO oxidation was tested in a temperature programmed combustion (TPC) apparatus. Combustion synthesis allowed to achieve in a single step 5–25 nm Au clusters supported on nanostructured metal oxides powders. Significant catalytic activities were measured in the range 150–250 °C which has to be regarded as a good basis for further development. A more lengthy classical precipitation method at pH 8 was indeed also applied to the preparation best performing catalyst (2 wt.% Au-La_2O_3) thereby getting better results in a fresh state but practically equal after prolonged ageing (800 °C for 5 h). TPR analyses were carried out to elucidate the nature of the support-gold synergism of the 2 wt.% Au-La_2O_3 catalyst, which appears to be dominated by the size of the gold clusters.

Keywords: Combustion synthesis; CO oxidation; Catalytic combustion; Au; La_2O_3; CeO_2; ZrO_2

1. Introduction

Diesel oxidation catalysts (DOCs) are widely adopted to convert CO, HCs and the soluble organic fraction (SOF) of particulate present in diesel exhaust gases. Catalysts capable of removing these pollutants are worldwide based on platinum, palladium and rhodium dispersed on a variety of supports. One of the main target of the present investigation is to employ gold as active catalyst for CO oxidation, thereby reducing the dependence from ‘‘traditional’’ platinum group metals (PGMs) market fluctuations (regarding both price and availability), often linked to their strategic harvesting locations (South Africa, Russia, etc.). The addition of new actors to the present three key-players (i.e. Pt, Pd, Rh) may reshape the dynamics of the market itself, leading to new equilibria, with potential considerable advantages from the final price standpoint.

Over the past few years supported gold catalysts gained in interest due to their surprisingly high catalytic activity towards various reactions [1]. Among them, the one that most catches the eye, is the low temperature CO oxidation [2–6]. The catalytic performance of gold strongly depends on the particle size, in such a way that smaller particles entail higher activities [7]. Gold-based catalysts containing nanoparticles can catalyse many reactions under conditions where bulk metallic gold is inactive. It is generally known that the addition of a metal to oxides (e.g. PGMs on CeO_2 and/or La_2O_3 [8,9]) can modify the intrinsic catalytic properties of the oxides, possibly increasing the activity, selectivity or stability of the obtained products. As far as the reaction mechanism is concerned, up to now it has not been well recognized if the reaction proceeds exclusively on metallic gold particles [1,10] or it may possibly occur preferentially at the edges of gold particle involving either sites on the adjacent support or gold atoms influenced by the support [11]. Furthermore, it has been pointed out that the reaction may occur only on the support, involving adsorbed CO molecules migrated from the gold particles by spillover and oxygen species of the support [2]. Clearly, these mechanisms could coexist. In the three cases, the interface between the gold particles and the supports plays a determinant role in the catalytic activity of the sample.

The work presented in this paper deals with a comparative and mechanistic study of the oxidation of CO over gold, supported on zirconia, ceria and lantana. The key feature of this investigation lies in the innovative method used to prepare the above catalysts (solution combustion synthesis—SCS [12]) in single step, i.e. in a more rapid and straightforward manner than

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conventional impregnation–precipitation at controlled pH. The main goal of this paper is to replace noble metals characterized by a highly fluctuating market cost, with gold for the application of exhaust gas after treatment. In this case, after a brief start-up, the temperatures are always above 150 °C. Issues like catalytic activity and durability at these temperatures are also addressed in the paper.

2. Experimental

2.1. Catalyst preparation and characterization

A series of catalyst supports (CeO_2, ZrO_2, La_2O_3) were prepared via a highly exothermic and self-sustaining reaction, the so-called SCS method. This technique is particularly suitable for producing nanosized particles.

A crucible containing a concentrated aqueous solution of various precursors (metal nitrates and urea) was located in a oven at 600 °C for few minutes, so as to ignite the following very fast reactions referred to ceria, zirconia or lanthana supports, respectively:

$$6Ce(NO_3)_3 + 14CO(NH_2)_2 \rightarrow 6CeO_2 + 14CO_2 + 23N_2 + 28H_2O \quad (1)$$

$$3ZrO(NO_3)_2 + 5CO(NH_2)_2 \rightarrow 3ZrO_2 + 5CO_2 + 8N_2 + 10H_2O \quad (2)$$

$$2La(NO_3)_3 + 5CO(NH_2)_2 \rightarrow La_2O_3 + 5CO_2 + 8N_2 + 10H_2O \quad (3)$$

The overall set of reactions is markedly exothermic, which leads within the reacting solid mixture to a thermal peak well exceeding 1000 °C for a few seconds. Under these conditions nucleation of oxide crystals is induced, their growth is limited and nanosized grains can be obtained, as earlier anticipated.

The Au-based catalysts (2 wt.% Au-CeO_2, 2 wt.% Au-ZrO_2 and 2 wt.% Au-La_2O_3) were prepared according to the same reaction written above, by adding $HAuCl_4$ to the aqueous solutions in order to directly obtain carriers supporting 2 wt.% of gold. The catalysts were then calcined in air at 500 °C for 4 h as a common stabilisation treatment.

The catalyst that showed the best performance (2 wt.% Au-La_2O_3) was also prepared according to a two steps SCS-precipitation route. The metal oxide, previously prepared by SCS, was suspended in an aqueous solution buffered at pH 8 by NaOH addition [13]. Then, $HAuCl_4$ was added drop by drop to obtain a final catalyst with the same, 2 wt.% gold loading. The suspension was stirred for 12 h and then filtered, washed and dried in air at 90 °C. The catalyst was then calcined in air at 500 °C for 4 h, so as to set a common basis for a comparison with its SCS-prepared counter part.

A catalyst containing 2 wt.% of Pt-γ-alumina, simulating a commercial catalyst was also prepared by SCS as a reference and reduced in a 4.95 vol.% H_2/Ar mixture at 400 °C for 5 h prior to use.

Scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS) (Hitachi, model S4700 FESEM) were used to investigate the morphology as well as the elemental composition and distribution of all the catalysts. Direct observation of the obtained nanosized Au clusters was performed by transmission electron microscopy (TEM; Philips CM 30 T). All the catalysts were then ground in a ball mill at room temperature and characterized. X-ray diffraction (PW1710 Philips diffractometer equipped with a monochromator for the Cu Kα radiation) was used on all fresh catalysts to examine whether the desired oxide structure was actually achieved.

The BET specific surface areas of the prepared catalysts were evaluated from the linear parts of the BET plot of the N_2 isotherms, using a Micromeritics ASAP 2010 analyser.

2.2. Catalytic activity tests

The activity of the prepared catalysts was evaluated by temperature programmed combustion (TPC), according to standard operating procedures: a gas mixture (2300 ppm CO; 7 vol.% O_2, He = balance) was fed, via a set of mass flow controllers, to the catalytic fixed-bed microreactor enclosed in a quartz tube placed in an electric oven ($W/F = 0.12$ g s/cm^3). The tubular quartz microreactor (4 mm i.d.) was loaded with 800 mg of pelletised catalyst (0.2–0.5 mm granules obtained by sequential pressing, crushing and sieving). The reaction temperature was controlled through a PID-regulated oven and varied from room temperature to 550 °C at a 5 °C min^{-1} rate. The CO conversion was monitored with a CO/CO_2 NDIR analyser (ABB). A computer recorded both the fixed bed temperature and the CO/CO_2 outlet concentration as a function of time. Moreover, catalyst durability was established by maintaining the 2 wt.% Au-La_2O_3 catalyst fixed bed at 500 °C for periods up to 150 h under the same feed conditions adopted for the TPC runs.

2.3. Ageing tests

The 2 wt.% Au-La_2O_3 catalysts prepared via the two different methods described were submitted to a thermal treatment at 800 °C for 5 h in static air. These samples underwent the same characterization and catalytic activity test procedures of the fresh ones.

2.4. TPR analysis

Some further analyses were performed on the best catalysts before and after the thermal ageing treatment in a Termoquest TPD/R/O 1100 analyser, equipped with a thermal conductibility (TCD) detector. A fixed bed of catalyst was enclosed in a quartz tube and sandwiched between two quartz wool layers; prior to each temperature-programmed reduction (TPR) run, the catalyst was heated under an O_2 flow (40 ml/min) up to 500 °C. After a 30 min stay in O_2 flow at this temperature as a common pretreatment, the reactor temperature was then lowered down to room temperature by keeping the same flow rate of oxygen, thereby allowing complete oxygen adsorption over the catalyst. Afterward, He was fed to the reactor at 10 cm^3/min flow rate and kept for 1 h at room temperature in order to purge out any excess oxygen molecule. The catalyst was then heated to 600 °C at a constant heating rate of 10 °C/min using a 4.95 vol.% H_2/Ar mixture. The amount of the H_2 reacted away could be monitored via the TCD detector.

X-ray diffraction was employed on the catalysts which underwent each TPR analysis, to check whether the crystalline structure had been retained or not, and to detect the possible appearance of new phases.

3. Results and discussion

As earlier mentioned the nature of the active sites, and the cause of catalytic activity in Au, is still disputed, and is under intense study. However, one aspect of Au catalysis is generally accepted: the effectiveness of the Au/M_xO_y catalysts depend greatly on the Au clusters size. Our work is focused on developing a novel approach for the preparation of highly dispersed Au catalysts. The innovative, cheap and fast combustion synthesis method has been tuned to produce homogeneous, very fine, crystalline powders without the intermediate decomposition and/or calcining steps which other conventional synthesis routes would require. In addition, the co-synthesis of both the oxide carrier crystals and of gold clusters was also attempted.

All data regarding the catalysts are listed in Table 1: T_{50} refers in particular to the temperature of half conversion of CO into CO_2. The specific surface areas of the prepared catalysts have values in the range 10–40 m^2/g, except for the 2 wt.% Pt-γ-Al_2O_3 catalyst having a surface area of about 300 m^2/g. It is rather surprising that Au-added catalysts are characterized by a specific surface area higher than the oxides synthesised in the absence of the Au precursor. It is likely that the formation of Au clusters, which do not react with the supporting oxides, limits the degree of sintering of the co-synthesised oxide crystals, which in turns brings about higher specific surface areas.

The investigations by XRD (not shown) revealed the presence of a pure and crystalline phase, reflections of metallic gold were always detected by this technique.

Table 1
Collection of results of catalyst characterization tests concerning catalytic activity towards CO oxidation and BET specific surface area

Catalyst	T_{50} (°C)	BET (m^2/g)
CeO_2	306	13.9
2 wt.% Au-CeO_2	272	36.9
ZrO_2	321	19.1
2 wt.% Au-ZrO_2	242	33.9
La_2O_3	282	10.7
2 wt.% Au-La_2O_3	185	17.9
2 wt.% Au-La_2O_3 SCS-precipitation	145	13.1
2 wt.% Au-La_2O_3 aged 800 °C 5 h	244	17.8
2 wt.% Au-La_2O_3 SCS-precipitation aged 800 °C 5 h	237	12.9
2 wt.% Pt-γ-Al_2O_3	224	301.2

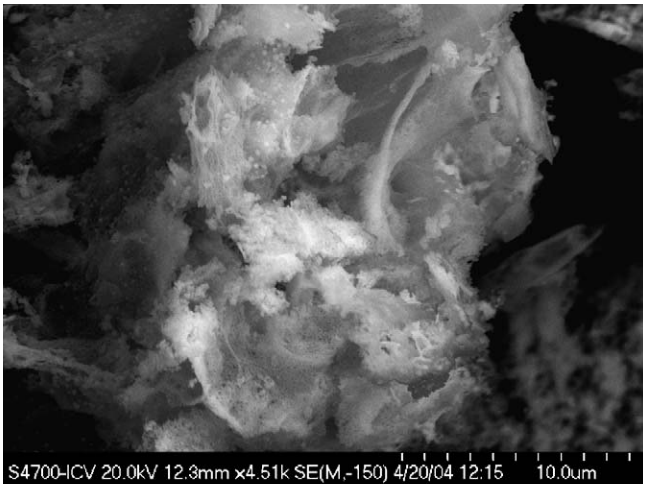

Fig. 1. FESEM micrograph of the 2 wt.% Au-CeO_2 catalyst microstructure.

As far as the microstructure of the catalyst crystals agglomerates is concerned, Fig. 1 (referring to the 2 wt.% Au-CeO_2 catalyst) shows how it is rather spongy. This is a consequence of the sudden release of a large amount of gases during the combustion synthesis, owing to the decomposition/combustion of the reacting precursors. This microstructure should help reducing internal mass transfer resistances.

Conversely, Fig. 2 illustrates a TEM picture of the 2 wt.% Au-La_2O_3 catalyst produced via SCS. It regards the catalyst

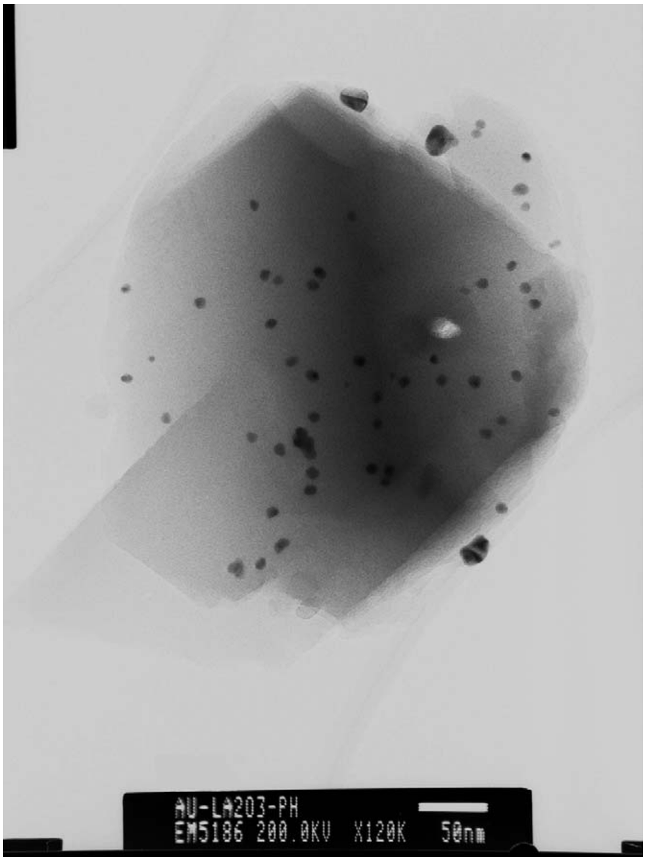

Fig. 2. TEM micrograph of the catalyst 2 wt.% Au-La_2O_3.

which showed the highest activity among those prepared by the SCS method. However, it is well representative of all the crystal sizes of the prepared catalysts. By employing this direct observation technique values of the Au cluster size of 5–25 nm could be estimated, which are slightly higher than those obtained by more complex methods reported in literature [14,15].

Fig. 3 compares the CO conversion plots as a function of temperature of all the considered catalysts. In all cases, the presence of gold strongly enhances the rate of carbon monoxide oxidation. The 2 wt.% Au-CeO_2 catalyst presents a higher activity than that of pure ceria. Considering the T_{50} values a decrease of 34 °C, from 306 to 272 °C, was obtained. A better performance was observed for the zirconia support: the presence of gold plays here a very positive role on the activity, as deduced from the more significant reduction of the T_{50} value. However, lantana-supported gold showed the best performance with a T_{50} lower than 200 °C and an appreciable activity already at 100–150 °C. The durability and stability of the 2 wt.% Au-La_2O_3 catalyst was tested by maintaining it at 500 °C for periods up to 150 h with the same feed conditions adopted for the TPC runs. The durability data (figure not reported for the sake of briefness) showed that the CO oxidation activity remained practically unaffected.

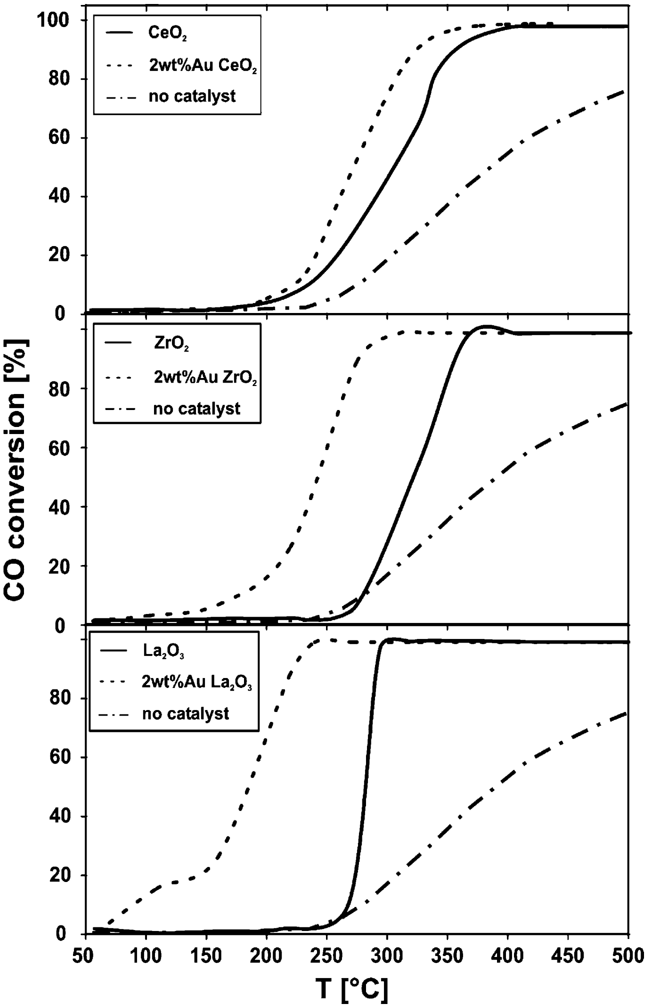

Fig. 3. CO to CO_2 conversion vs. temperature over the fresh catalysts prepared by SCS.

It is rather interesting to notice how, despite the lowest specific surface area, the lantana-based catalysts are delivering the best performance towards CO oxidation.

It has been reported that the nature of the support material as well as the physical state of the support can influence the catalytic activity of the resulting gold catalysts [16–18]. By comparing the results obtained with the various catalysts (characterized by comparable Au cluster sizes) one can indeed deduce that the activity of our Au/M_xO_y catalysts may not result exclusively from Au, as the support itself may be involved in the reaction mechanism.

Fig. 4 compares the catalytic activities of fresh and aged lantana-based catalysts prepared by SCS and SCS-precipitation methods. The fresh 2 wt.% Au-La_2O_3 obtained by SCS-precipitation showed a better performance than that of its SCS counter part. The half conversion temperature of CO was lowered from 185 to 145 °C. However, after the thermal treatment at 800 °C for 5 h, the two samples gave a similar performance with a T_{50} of about 240 °C. In the same figure the catalytic activity of the 2 wt.% Pt-γ-Al_2O_3 sample was also reported. The catalytic activities of the gold-based catalyst after a dramatic thermal ageing are surprisingly analogous to the fresh Pt-based catalyst having a surface area much higher than the others. This results is rather important in an application perspective. However, one must consider that only CO oxidation is here considered, i.e. just one of the numerous reactions promoted in a Diesel oxidation catalyst.

Fig. 5 compares TEM pictures of the 2 wt.% Au-La_2O_3 catalyst obtained by SCS-precipitation before (a) and after (b) the ageing treatment. Au cluster size of 1–4 nm could be estimated for the as prepared catalyst. A sintering phenomenon occurred at 800 °C and the Au particles size increased, ranging between 20 and 40 nm. The same Au cluster was also observed for the SCS 2 wt.% Au-La_2O_3 catalyst, which once again confirms that the support being equal, the activity is strictly related to the Au cluster size. However, as BET data remained almost unchanged, one can deduce that the sintering process did not affect the surface area of the metal oxide supports.

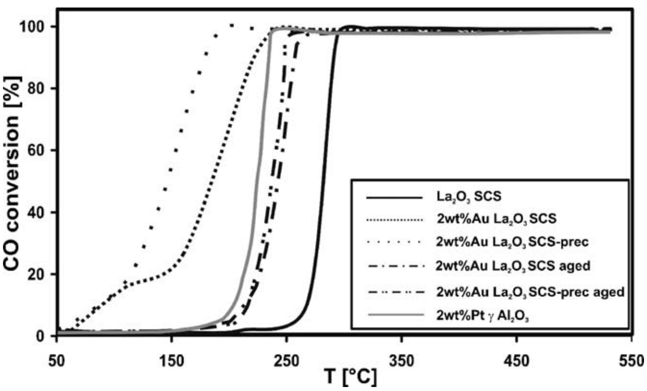

Fig. 4. CO to CO_2 conversion vs. temperature over fresh and aged lantana-based catalysts prepared by SCS and SCS-precipitation methods as well as over the 2 wt.% Pt-γ-Al_2O_3.

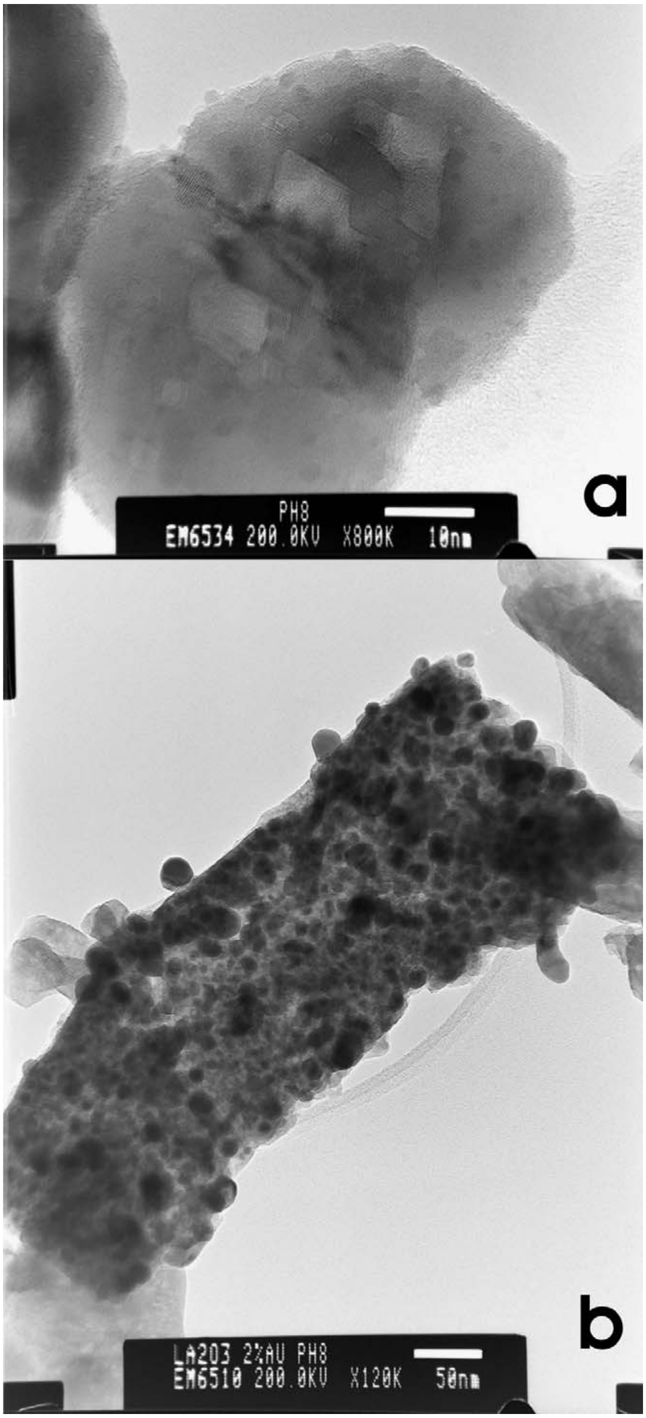

Fig. 5. TEM micrograph of the lantana-based catalysts prepared by SCS-precipitation method: (a) as prepared; (b) after the ageing treatment at 800 °C for 5 h.

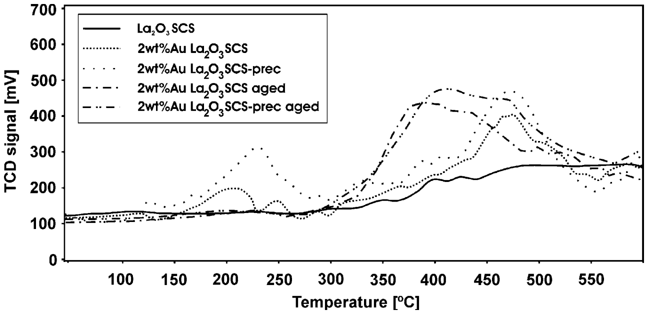

Fig. 6. Results of temperature programmed reduction tests on lantana-based catalysts prepared by SCS and SCS-precipitation methods before and after the ageing treatment at 800 °C for 5 h.

As stated earlier, some further TPR runs were performed on lantana-based catalysts to possibly get further information about the nature of gold-support interaction before and after thermal deactivation. The results of such investigations are reported in Fig. 6. The activity order of samples is in good agreement with the temperature at which hydrogen exerts its reducing effect. The easiness to provide oxygen by metal oxide supports seems to be directly correlated with the gold cluster dimension. As far as the Au cluster size increases (e.g. after ageing) the catalysts tend indeed to be reduced at higher temperatures. As the overall amount of oxygen reacted away in all TPR runs is not dramatically different, the obtained results suggest that when the gold clusters are particularly small, independently of the preparation method, they can help at least part of the oxygen present over the catalyst surface to react with hydrogen.

4. Conclusions

Supported gold catalysts capable of a CO oxidation activity similar to those of PGMs have been developed. The innovative combustion synthesis technique was adopted successfully because it was possible to produce in an easy and low-cost ‘‘one step’’ way catalysts as active towards CO oxidation as those synthesized by more expensive and binding modus operandi after ageing at temperatures that they should well face in real exhaust gas condition. The success of these catalysts might lead to substitution of the highly expensive platinum group catalysts generally adopted in Diesel oxidation catalysts if they will prove to be effective for the entire set of reactions to be promoted there. Particularly, the 2 wt.% Au-La_2O_3 catalyst was synthesized, capable of igniting CO combustion even below 150 °C and to obtain a total CO conversion below 260 °C also after a severe thermal treatment. Studies are now in progress to better elucidate the role of gold-support interaction on the catalytic activity achieved, as well as on optimisation the catalyst preparation routes for the sake of minimising the size of the gold clusters deposited and rendering them more stable at high temperatures, thereby further improving their application potential.

References

[1] M. Haruta, Catal. Today 36 (1997) 153.
[2] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, M.J. Genet, B. Delmon, J. Catal. 144 (1993) 175.
[3] J. Grunwaldt, C. Kiener, C. Wögerbauer, A. Baiker, J. Catal. 181 (1999) 223.
[4] M.A. Bollinger, N.A. Vannice, Appl. Catal. B 8 (1996) 417.
[5] M. Daté, M. Haruta, J. Catal. 201 (2001) 221.
[6] J. Grunwaldt, M. Maciejewski, O.S. Becker, P. Fabrizioli, A. Baiker, J. Catal. 186 (1999) 458.

[7] A. Wolf, F. Schüth, Appl. Catal. A 226 (2002) 1.
[8] M. Skoglundh, H. Johansson, L. Lowendahl, K. Jansson, L. Dahl, B. Hirschaauer, Appl. Catal. B 7 (1996) 299.
[9] Y.F. Yu-Yao, J.T. Kummer, J. Catal. 106 (1987) 307.
[10] F. Boccuzzi, A. Chiorino, S. Tsubota, M. Haruta, J. Phys. Chem. 100 (1996) 3625.
[11] S.D. Lin, M. Bollinger, M.A. Vannice, Catal. Lett. 17 (1993) 245.
[12] A. Civera, M. Pavese, G. Saracco, V. Specchia, Catal. Today 83 (1–4) (2003) 199.
[13] M.A. Centeno, M. Paulis, M. Montes, J.A. Odriozola, Appl. Catal. A 234 (2002) 65.
[14] J.R. Mellor, A.N. Palazov, B.S. Grigorova, J.F. Greyling, K. Reddy, M.P. Letsoalo, J.H. Marsh, Catal. Today 72 (2002) 145.
[15] Q. Xu, K.C.C. Kharas, A.K. Datye, Catal. Lett. 85 (2003) 229.
[16] A.I. Kozlow, A.P. Kozlova, H. Liu, Y. Iwasawa, Appl. Catal. A 182 (1999) 9.
[17] M.M. Schubert, S. Hackenberg, A.C. Van Veen, M. Muhler, V. Plzak, R.J. Behm, J. Catal. 197 (2001) 113.
[18] G.C. Bond, D.T. Thompson, Catal. Rev. Sci. Eng. 41 (34) (1999) 319.