Catalytic Performance of Gold Catalysts in the Total Oxidation of VOCs

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Abstract

Catalysts for the oxidation of volatile organic compounds (VOCs) were prepared by supporting 1% gold on cerium and zirconium oxides (CeO_2, $Ce_{0.5}Zr_{0.5}O_2$, ZrO_2) using a simple impregnation method followed by reduction of gold in the presence or absence of ammonia (N). The catalysts were tested in model reactions, namely the total oxidation of benzene, hexane and chlorobenzene, using a micro flow reactor at atmospheric pressure in the temperature range 100-500°C and their activity was compared to that of Au/TiO_2 and Au/Fe_2O_3 reference catalysts supplied by the World Gold Council (WGC). Benefits on the light-off temperatures were observed by adding gold to cerium-containing oxides: 100% conversion of hexane was obtained with $Au/Ce_{0.5}Zr_{0.5}O_2$ at the lowest temperature (300°C). Full conversion of benzene was reached at only 250°C with Au/CeO_2 (N), at 290°C with Au/Fe_2O_3 (WGC) and at 300°C with $Au/Ce_{0.5}Zr_{0.5}O_2$. In the case of chlorobenzene oxidation, the addition of gold was of even greater relevance because of a drop in the light-off temperature of over 100°C for $Au/Ce_{0.5}Zr_{0.5}O_2$ and Au/CeO_2, with respect to the gold-free oxide supports; but in this case rapid deactivation took place.

Introduction

The recent discovery of the catalytic activity of gold in CO oxidation (1,2) has enhanced the interest in applying this metal to the selective oxidation of organic compounds either in the liquid phase (1-6) or the gas phase (7-12) and using olefins, alcohols and aldehydes as common substrates. Application of gold catalysis to the total combustion of volatile organic compounds (VOCs) has already been reported (8-12). As a general comment, it has been found that the catalytic activity of gold is greatly improved when used in the form of nanoparticles in the range 3-5 nm and deposited on certain oxidic supports (13). In the case of CO oxidation, it is known that not only the size of the supported gold particles but also the interaction between these particles and the support, as well as the preparation techniques, are important factors affecting stability and hence activity of the resulting catalysts (14,15). In fact, more active catalysts are obtained by deposition-precipitation or co-precipitation methods as compared to incipient wetness methods (16). Furthermore, due to the high mobility of the gold nanoparticles, high surface area supports are needed to stabilize the nanoparticles in a dispersed state; and the catalytic activity in oxidation reactions is enhanced when the gold is deposited onto oxide supports having the ability to undergo redox cycles such as CeO_2, V_2O_5 or TiO_2 (17,18).

Our attention is here focused on VOCs, particularly organic compounds of an anthropogenic nature emitted from many industrial processes and transportation activities, that can produce photochemical oxidants by reaction with nitrogen oxides in the presence of sunlight (19). Using this definition, many volatile organic compounds are included in this class, such as aliphatic, aromatic and halogenated hydrocarbons, alcohols, ketones, aldehydes, esters and acids. Due to their hazardous and toxic nature, as well as their contribution to smog formation, they are considered to be major contributors to air pollution (20). Increasing concerns about the detoxification of hydrocarbon pollutants, as well as the growing emission of VOCs, is leading to the development of abatement technologies. Among the technologies already available, catalytic combustion allows much lower temperatures (~500°C) with respect to thermal incinerators (1000-1200°C) (21,22) and, as a consequence, it induces only a minor environmental impact, avoiding the production of NO_x and saving energy. In this paper we report results using Au/CeO_2, $Au/Ce_{0.5}Zr_{0.5}O_2$ and Au/ZrO_2 catalysts, prepared by the simple incipient wetness method, in the total oxidation of a representative group of VOCs (hexane, benzene and chlorobenzene). In order to compare the different experimental procedures for preparing the catalyst, gold reduction has been performed under basic and acidic conditions. In particular we used ammonia for allowing an easy removal of chloride ion after impregnation (16). Our investigations also included two reference catalysts (Au/Fe_2O_3 and Au/TiO_2) supplied by World Gold Council (WGC) (23).

2 Experimental

2.1 Chemicals

Gold sponge (purity 99.99%), $NaBH_4$ (purity >96%), benzene (purity>99.7%, to be handled with care under hood), hexane (purity >95%), chlorobenzene (purity >98%), NH_4OH (28% in water) and HNO_3 (65% in water) were purchased from Fluka; HCl (37% volumetric solution) from Riedel-de Haen. H_2O MilliQ obtained using an Academic A-10 Millipore apparatus. CeO_2 (V_P = 0.2 ml g^{-1}) and $Ce_{0.5}Zr_{0.5}O_2$ (V_P = 0.4 ml g^{-1}) from Grace-Davison and ZrO_2 (V_P = 0.3 ml g^{-1}) from Mel-Chemical were used as received. Microstructural characterization of the oxide supporting material is reported in Table 1. Reference gold catalysts, Au/Fe_2O_3 powder and Au/TiO_2 powder, were supplied by World Gold Council.

2.2 Catalyst preparation

Two different series of catalysts, having a 1% wt/wt nominal loading of Au, were prepared using an impregnation technique. In the first series, the calculated amount of $HAuCl_4$, prepared dissolving metallic Au sponge in *aqua regia* and diluted to the appropriate volume with water, was firstly impregnated onto the oxide support. The resulting powder (1g) was then contacted with 0.8 ml of a concentrated aqueous solution of ammonia and reduced with 2.7 ml of a freshly prepared $NaBH_4$ solution ($NaBH_4$:Au = 5:1). The choice of this reducing agent enabled fast reduction of the Au^{3+} to Au^0 at room temperature, in preference to thermal treatment at high temperature with H_2. The wet powder was filtered, washed several times with water in order to ensure the thorough removal of either chloride, which gives rise to poisoning/sintering effects, or ammonia which can lead to explosions (24). The washed catalyst was then dried at 100°C for 2 h. The catalysts produced using ammonia are denoted by (N).

In the second series, the gold-based catalysts were prepared as described above but gold was reduced without adding ammonia, therefore in acidic conditions due to the $HAuCl_4$ solution.

2.3 Catalyst characterization

The specific surface area for each sample was determined according to the BET method, from nitrogen adsorption and desorption single point isotherms at liquid nitrogen temperature (77 K) with a Thermo Quest Surface Area Analyzer. Particle dimensions were measured by XRD technique using a Rigaku D III-MAX horizontal-scan powder diffractometer with Cu $K\alpha$ radiation, equipped with a graphite monochromator. The size of gold crystallites was estimated from peak half-widths by using Scherrer's equation with correction for instrumental line broadening (25). In many cases, catalyst characterization has been performed on both fresh and used samples.

2.4 Catalytic tests

Reactions were carried out in a quartz fixed bed reactor (h = 400 mm, d = 10 mm) in an air flow at atmospheric pressure at the following gas hourly space velocity (GHSV): n-hexane 28300 h^{-1}; benzene 20300 h^{-1}; chlorobenzene 9200 h^{-1}. Oxygen in the feed was ca. 25% in excess with respect to the stoichiometric value, using 2% reactant in air and the catalysts were tested in the temperature range 100-500°C. Each hydrocarbon was fed to the reactor by bubbling air in a Vapor-Liquid-Saturator (VLE) and the resulting stream properly diluted with a second airflow. Air streams were regulated through Brooks mass-flow controllers. Steady state conversion data at each temperature were obtained by measuring the disappearance of the reactant in the outlet stream, with an on-line GC (HP 5890 II) equipped with a WAX 30 column and thermal conductivity detector (TCD) after 1 h of time on stream. The sensitivity towards hydrocarbons in the stream was better than 0.01%.

3 Results and discussion

3.1 Characterization

1% wt/wt gold catalysts were prepared by impregnation of CeO_2, ZrO_2 and $Ce_{0.5}Zr_{0.5}O_2$ with $HAuCl_4$, followed by reduction with $NaBH_4$. This latter step was performed either in the presence or in the absence of ammonia and BET and XRD measurements have been performed on the resulting dark pink/blue powders (Tables 1 and 2). Owing to peak overlapping, the diameter of gold on the ZrO_2 support could not be determined.

All the materials exhibited relevant surface area decrements after the catalytic cycle with different reagents at 500°C. $Ce_{0.5}Zr_{0.5}O_2$, however, showed a remarkable thermal stability and even a surface area increment was observed after converting hexane and benzene, as reported in Table 1.

Gold nanoparticles on different supports showed a size in the range of 6-17 nm, as determined by XRD analysis in the fresh samples, and no noticeable effect of ammonia addition before reduction was observed, except with Au/CeO_2 (N) which almost doubled the gold nanoparticle's size with respect to its ammonia-free counterpart (Au/CeO_2 prepared without ammonia) (Table 2). It is worth noting the simple impregnation method produced, in our case, gold particles in the range 6-17 nm far from the 'ideal' range (3-5 nm) mentioned in the introduction. However, their catalytic activity is important as documented by the different behaviour on various oxides, due to a synergistic interaction between gold and the supporting material, both actively participating in the oxidation process. Moderate increments of the average Au crystallite dimension were noted after their use in hexane and benzene oxidation, with the exception of the decrement in $Au/Ce_{0.5}Zr_{0.5}O_2$ (N), whereas strong growth was always detected after reaction with chlorobenzene. In the last case, the particle growth is probably due to the presence of HCl in the gaseous products, which facilitates the mobility of the metal.

Table 1

BET surface area of fresh and used materials after a catalytic cycle at the final temperature of 500°C for 1 h.

Catalyst	SA (m^2/g)			
		Used		
	Fresh	Hexane	Benzene	Chlorobenzene
CeO_2	90	52	47	33
Au/CeO_2 (N)	71	34	54	39
Au/CeO_2	72	33	51	43
$Ce_{0.5}Zr_{0.5}O_2$	91	134	109	79
Au/$Ce_{0.5}Zr_{0.5}O_2$ (N)	95	62	89	80
Au/$Ce_{0.5}Zr_{0.5}O_2$	97	91	93	85
ZrO_2	55	28	38	38
Au/ZrO_2 (N)	48	39	38	47
Au/ZrO_2	47	43	33	53

Table 2

Catalyst	Au particles diameter (nm)			
		Used		
	Fresh	Hexane	Benzene	Chlorobenzene
Au/CeO_2	6.2	10.8	12.2	39.8
Au/$Ce_{0.5}Zr_{0.5}O_2$	13.7	16.2	16.1	64.5
Au/CeO_2 (N)	11.1	18.0	11.8	40.1
Au/$Ce_{0.5}Zr_{0.5}O_2$ (N)	17.4	13.3	17.0	37.2

3.2 Catalytic oxidation

The light-off temperature and conversion data collected during the complete oxidation of hexane, benzene and chlorobenzene at different temperatures are reported in Figures 1a,b - 3a,b, for home-made catalysts and two WGC reference catalysts. The blank test with the empty glass reactor ('non catalytic' test) was performed in order to determine the light-off temperature due to the thermal effect. Under the conditions used, an initial oxidation temperature of 330°C was observed for hexane, accompanied by a consistent conversion increasing from 53 to 69% at 500°C (Figures 1a, 1b), which was partially due to cracking phenomena, as indicated by the presence of lower molecular weight products in the GC analysis. No appreciable oxidation took place below 500°C with benzene (Figures 2a, 2b) and chlorobenzene (Figures 3a, 3b) reagents in the absence of catalysts.

The catalytic data for the oxidation of hexane (Figures 1a) indicate a low light-off temperature (150°C) for untreated CeO_2 but only a low conversion (13%). As the temperature was increased, it was possible to obtain 97% conversion at 300°C. Deposition of gold on this material caused a drop of 20°C in the light-off temperature and a fairly good conversion (70%) at 150°C, without any additional benefit at higher temperature (Figure 1b). The combined effects due to surface area (SA) (Table 1) and gold promotion should be taken into account for understanding the better behaviour of the lower SA Au/CeO_2 up to 150°C and of the higher SA CeO_2 over this temperature. The benefit of a high SA is confirmed also in the case of Au/$Ce_{0.5}Zr_{0.5}O_2$, which had almost the same SA after the use, and was more active than the catalyst prepared with ammonia showing a SA drop of 35%. Untreated ZrO_2 and $Ce_{0.5}Zr_{0.5}O_2$ were not effective in lowering the thermal light-off temperature. However, gold supported on $Ce_{0.5}Zr_{0.5}O_2$ produced the best performance of 100% conversion at 300°C, whereas cerium free-catalysts (Au/ZrO_2) produced lower conversions.

For hexane oxidation, the WGC reference catalyst, Au/TiO_2 was almost ineffective for lowering the light-off temperature and showed a conversion profile similar to that observed in the case of the empty reactor while the Au/Fe_2O_3 reference catalyst started its activity at 250°C and led to a modest conversion of 64% at 300°C.

With benzene oxidation, the preliminary test in the absence of catalyst showed no conversion up to 500°C. As in the case with hexane oxidation, low light-off temperatures (190-200°C) were observed with ceria and ceria-zirconia supports (Figure 2b). In particular, Au/CeO_2 prepared with NH_3 also showed the highest efficiency expressed by the total

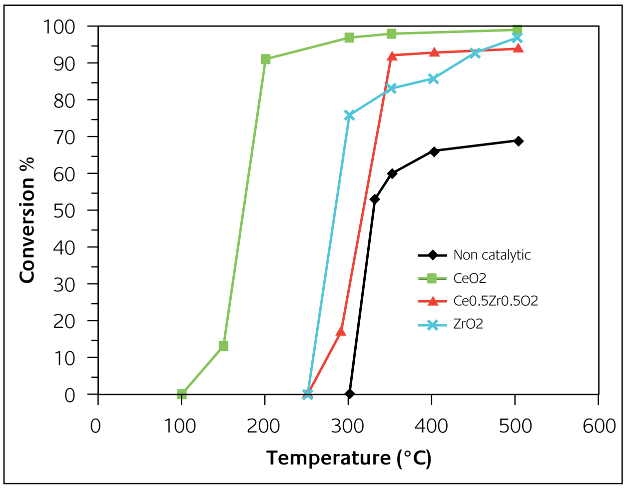

Figure 1a

Thermal profile of the metal oxide supports for hexane oxidation.

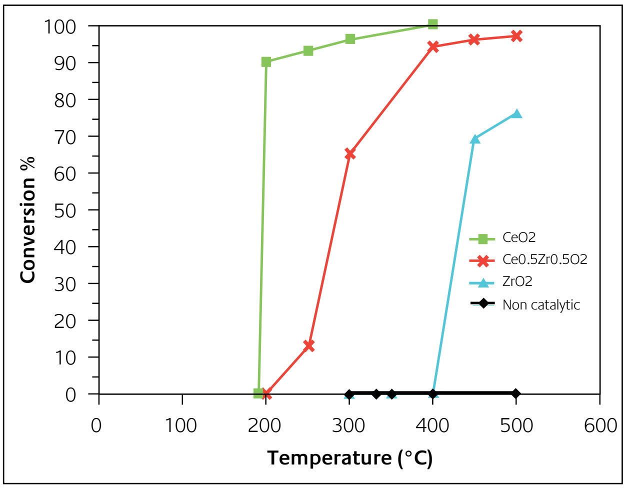

Figure 2a

Thermal profile of the metal oxide supports for benzene oxidation.

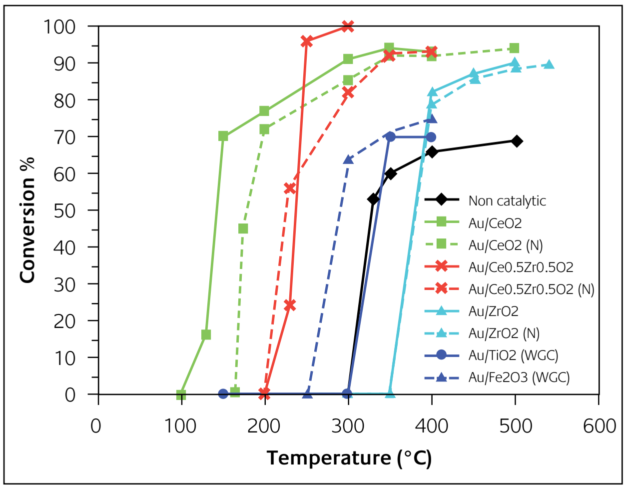

Figure 1b

Thermal profile of the gold catalysts for hexane oxidation.

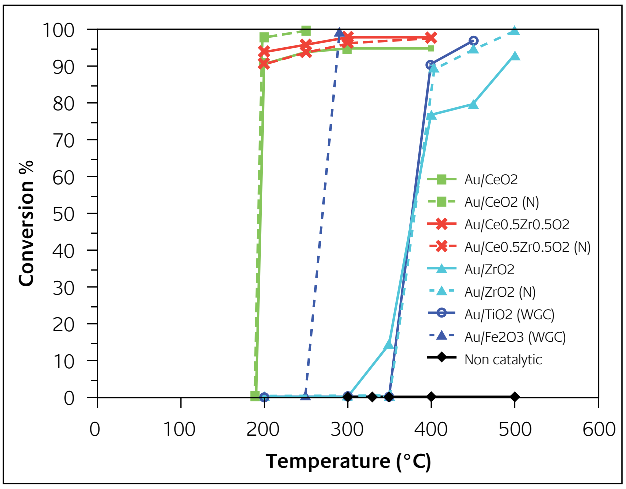

Figure 2b

Thermal profile of the gold catalysts for benzene oxidation.

conversion at 250°C. Of great relevance is the behaviour of the WGC reference catalyst Au/Fe_2O_3 showing 100% conversion just at the light-off temperature of 290°C.

The complete oxidation of benzene has recently been investigated by Andreeva's group using gold-promoted vanadia dispersed on TiO_2, ZrO_2 (9,10) and, more recently, gold modified CeO_2 $-V_2O_5$ (11,12). These investigators have indicated an important synergistic effect induced by gold which can be evaluated by the relevant increment in benzene conversion at 200°C, passing from 63% to 100% in the case of 4wt%V_2O_5 on Au/CeO_2 prepared by deposition-precipitation, compared with 4wt%V_2O_5 on CeO_2. Although the use of different catalytic systems and different experimental conditions does not allow a direct comparison, we have detected a quite high catalytic effect of the untreated CeO_2 just around 200°C, with a consequent less pronounced effect of gold on its performance.

In any case, the addition of gold to CeO_2 and $Ce_{0.5}Zr_{0.5}O_2$ enhanced the catalytic performances also in our experiments: with Au/CeO_2 (N), 98% conversion was achieved at 190°C and use of Au/$Ce_{0.5}Zr_{0.5}O_2$ led to 94% conversion at 200°C. In order to evaluate the stability of the Au/CeO_2 (N) catalyst, benzene conversion at 250°C has been monitored for 36 hours on stream (Figure 4). The data indicate a constant conversion of 96% throughout the test, during which the gold particle size remained unchanged (Table 2).

It is known that the disposal of chlorinated hydrocarbons requires special care in thermal incinerators, in particular a treatment using up to 1200°C. Comparing the results of catalytic conversion of benzene (Figures 2a, 2b) and chlorobenzene (Figures 3a, 3b) with ceria and zirconia derivatives, we have observed a greater stability induced by the presence of the chlorine substituent, which caused a shift of the conversion profiles to higher temperatures. For chlorobenzene, we noted the lowest light-off temperature at 300°C with Au/$Ce_{0.5}Zr_{0.5}O_2$ (N) and Au/CeO_2, which should be compared to the relative inertness of the unsupported oxides. At the intermediate temperatures (350-400°C), Au/CeO_2 and Au/CeO_2 (N) led to important performances whereas the highest conversion was 90% at 500°C for Au/$Ce_{0.5}Zr_{0.5}O_2$ (N).

In any case, gold addition increased the catalytic activity of all the supporting materials but did not promote their total combustion even at 500°C (Figure 3b). A high

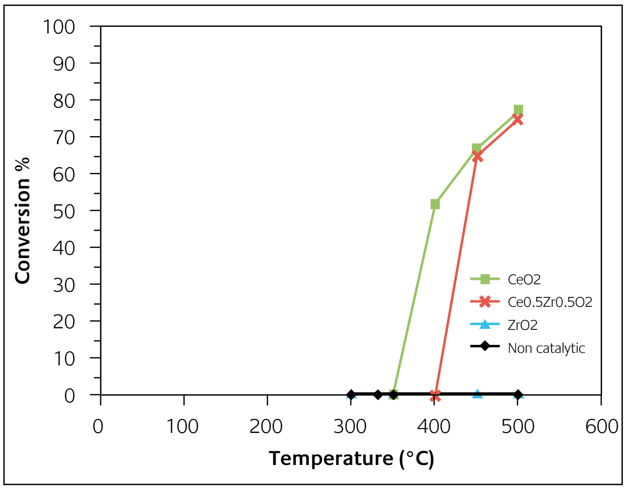

Figure 3a

Thermal profile of metal oxide supports in chlorobenzene oxidation.

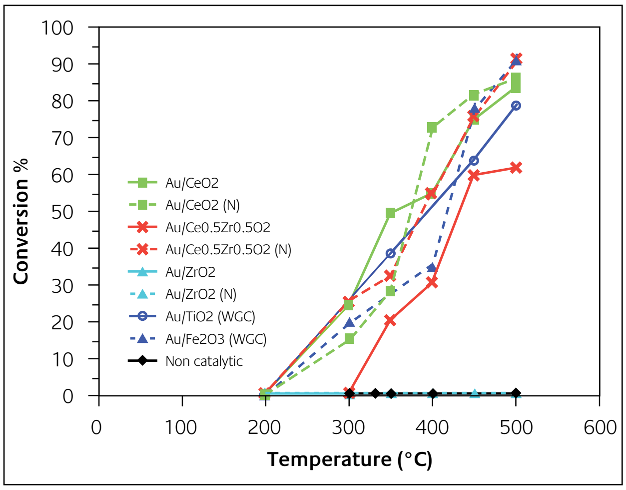

Figure 3b

Thermal profile of gold catalysts in chlorobenzene oxidation.

selectivity towards total combustion was always obtained in the first hour on stream, consistent with the absence of fragmentation products in the GC analyses. However, the most efficient catalysts, Au/$Ce_{0.5}Zr_{0.5}O_2$ (N) and Au/CeO_2, turned from dark pink to a yellow-brown colour after a few hours. The change of the catalyst aspect towards a 'gold like' colour and the simultaneous decrease of the catalytic performance suggest that metal leaching or deactivation are occurring. XRD analysis indicated the growth of Au particles from 6.2-17.4 nm to 37.2-64.5 nm (Table 2). Evaluation of the catalyst decay was further investigated by a test performed with Au/$Ce_{0.5}Zr_{0.5}O_2$ (N) at 500°C: chlorobenzene conversion sharply decreased after 2 h from 90% to 56% and after 9 h on stream the catalyst became completely inactive (Figure 4). Meanwhile unidentified by-products appeared in the GC analysis.

In the case of Au/ZrO_2, catalyst deactivation resulted too fast for evaluation of its catalytic performance. It is worth noting that the WGC reference catalyst Au/Fe_2O_3 was found to have a comparable activity to the gold on CeO_2 and on $Ce_{0.5}Zr_{0.5}O_2$ (N) catalysts. Moreover, it deactivated similarly after a few hours.

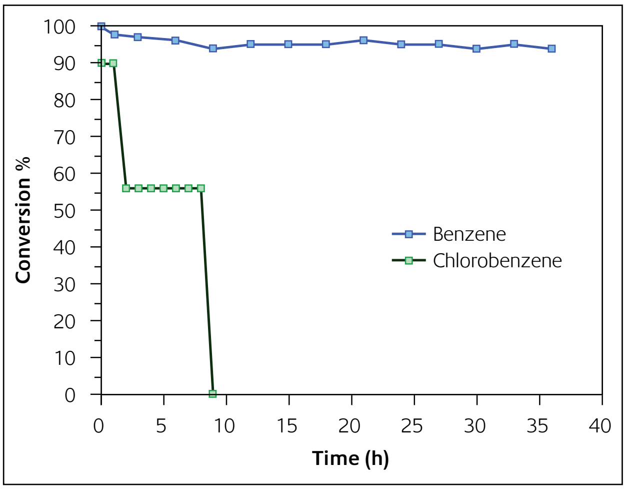

Figure 4

Catalyst-life test for Au/CeO_2(N) in benzene and Au/$Ce_{0.5}Zr_{0.5}O_2$(N) for chlorobenzene oxidation,

4 Conclusions

A series of gold catalysts where gold is deposited on cerium and zirconium oxides has been evaluated in the total oxidation of hexane, benzene and chlorobenzene. The catalytic behaviour at different temperatures indicated that the addition of gold to the supporting material enhances the catalytic activity, as indicated by lowering the light-off temperature and the temperature of maximum conversion. For comparison, the WGC Au/TiO_2 catalyst was not very active, whereas Au/Fe_2O_3 showed a behaviour comparable to the Au/CeO_2 and Au/$Ce_{0.5}Zr_{0.5}O_2$ prepared for this study. It is interesting to note that light-off and total combustion temperatures are influenced by the type of VOC and the metal oxide being used. As shown in the case of hexane oxidation, a compromise between gold promotion and surface area decrease should be considered when trying to understand the catalytic behaviour. Therefore, a general trend of the dependence of the catalytic activity on the nature of the support is hard to derive, except in the case of ZrO_2 where its low area led to limited catalytic performance.

The catalysts were stable during hexane and benzene oxidation, but underwent rapid deactivation in the presence of chlorobenzene, arising from metal particle growth. This latter point represents a limit to the use of gold-based catalyst for the disposal of chlorinated organic compounds.

It is notable that for benzene oxidation the Au/CeO_2(N) catalyst is stable over 36h at 250°C, with conversion being a steady 96%, and the gold particle size remained unchanged.

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Michele Rossi obtained his master's degree in Industrial Chemistry at the University of Milan and was full professor of Chemistry at the University of Bari, after which he joined the Faculty of Science - Inorganic Chemistry - at the University of Milan. After discovering the nitrogen fixation, a new field in organometallic chemistry, he has been a pioneer in the application of gold catalysis to the liquid phase oxidation of alcohols and sugars, as described in a number of papers and patents. At the Vancouver GOLD 2003 Conference he was presented with the prize for the most innovative research.

Cristina Della Pina received a master's degree in Industrial Chemistry at Milan University and has just been awarded the Ph.D. degree in Industrial Chemistry, under Prof. Rossi's supervision. Her work focuses on the development of novel gold catalysts for the selective oxidation of organic compounds which has resulted in a number of achievements reported in recent papers. She was hosted at Duisburg-Essen University by Prof. G. Schmid applying Atomic Force Microscopy to gold nanoparticles.

Nikolaos Dimitratos worked as a postdoc researcher in the Inorganic Chemistry department at the University of Milan for the Auricat project (Catalysis by Gold) funded by the EU. He graduated in Chemistry (1998) and received his PhD from Liverpool University in the field of heterogeneous catalysis. His research deals with liquid and gas phase oxidation. He is now collaborating with Prof. G. Hutchings at Cardiff University, UK.

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Attilio Siani earned his master's degree in Industrial Chemistry at University of Milan in 2004. His research experience with heterogeneous catalysis started by Prof. Rossi's research group in 2003, being engaged in an experimental thesis entitled 'Gold Based Catalysts for Hydrocarbon Deep Oxidation'. Attilio joined Dr. Amiridis' group in July 2004 as a PhD student. His present research focuses on the development, synthesis, and characterization of nano-structured noble metal catalysts.

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