

Nanocast ordered Mesoporous Ceria as Support for Highly Active Gold Catalysts for Toluene total Oxidation

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ABSTRACT

AuCeO₂ catalysts were synthesized using ceria prepared by the nanocasting pathway using the mesoporous SBA-15 silica as structure template and cerium nitrate as the CeO₂ precursor via a solid–liquid route. These catalysts have been characterised by means: elemental analysis, H₂-TPR, X-ray powder diffraction (XRD), BET surface area, diffuse reflectance ultra-violet visible spectroscopy (DR/UV-vis). Catalytic oxidation of toluene was investigated on gold/cerium oxide catalysts prepared by deposition-precipitation with several loading of gold (1wt%, 2wt%, and 4wt %). The presence of gold has been found to enhance the activity of cerium oxide to the deep oxidation of toluene, the degree of this effect depending on the gold loading. The activity for toluene deep oxidation of the AuCeO₂ samples follows the order: 2wt% AuCeO₂ ~ 1wt% AuCeO₂ > 4wt% AuCeO₂. The AuCeO₂ catalysts are active at low temperature and selective for CO₂ and H₂O. The 1wt% AuCeO₂ catalyst exhibits a long-term stability. The results we obtained point out that the catalytic activity of the gold/mesoporous ceria system towards the deep oxidation of toluene

depends on the gold particle size and the amount of reducible surface oxygen species.

Keywords: mesoporous materials, ceria, gold, oxidation, toluene

1. INTRODUCTION

Volatile organic compounds are known as main contributors to air pollution, either directly, through their toxicity, or indirectly, as ozone precursors.

Many VOCs can cause cancers or serious other illnesses. Industrial processes are principally responsible for the VOC emissions. Removal of VOCs from gas streams can be applied by technologies classified into two groups: recovering ones with possible VOCs reuse and destroying ones [1]. VOCs catalytic oxidation is a chemical process in which hydrocarbons are mixed with air at specific temperatures to produce carbon dioxide (CO₂) and water (H₂O). Catalytic oxidation is a better way for VOCs removal than thermal combustion because required temperatures are lower and selectivities are higher [2]. Gold has been considered as a bad active phase because of its chemical inertness. Nevertheless, it has been

extensively proved nowadays that gold nanoparticles on metal oxides exhibit high catalytic activity in oxidation reactions and water-gas shift [3]. Moreover, the use of zeolites and macro-mesoporous oxide supports for noble metal based catalysts in the total oxidation of VOCs is known to be very interesting. [4,5]. CeO₂ has an oxygen storage capacity and is often used as support material for noble metal-based catalysts in oxidation reactions [6,7]. Gold supported on ceria has been reported as a promising catalyst for the total oxidation of volatile organic compounds [8-12].

The catalytic properties of AuCeO₂ have been found to be highly dependent on the size and morphology of ceria particles. The particle size reduction down to the nanoscale will create a large number of more reactive sides or edges that would improve the reaction activity [13, 14]. Some reports indicate that CeO₂ in the form of nanocrystalline particles is a key factor for achieving high activity for complete oxidation of CO and VOCs [15, 16]. Therefore, the synthesis of nanostructured ceria, especially with ordered mesoporous structure has been quite explored [17-21]. Ying et al. [21] reported that the gold catalysts supported on the mesoporous CeO₂ exhibited high catalytic activity and stability in benzene oxidation; complete conversion of 0.5% benzene in air to carbon dioxide could be achieved at 200°C and high benzene conversion was maintained at 200°C in a test of 50h duration whereas a gold catalyst supported on normal ceria powder suffered severe deactivation due to gold sintering when tested under the same conditions.

In the present paper, AuCeO₂ catalysts were synthesized using ceria prepared by the nanocasting pathway using the mesoporous SBA-15 silica as structure template and cerium nitrate as precursor via a solid-liquid route developed by Yue [20].

If a precursor has a low melting point, when it is simply mixed with a silica template, it may melt before decomposition into another solid phase which has a higher melting point and migrates into the mesopores of silica; decomposition and crystal growth of oxides inside the mesopores will result in mesoporous oxide. This method is solvent-free therefore environmentally friendly and never used to prepare catalysts for VOC oxidation. Moreover, the best method for gold deposition [3] was used with different loadings of gold (1wt%, 2wt%, and 4wt %). The presence of gold should enhance the activity of the catalyst towards the deep oxidation of toluene and led to totally selective ones for CO₂ and H₂O. Therefore, the aim of this study is focused on the activity and selectivity of new Au/mesoporous CeO₂ catalysts for VOC oxidation regarding the effect of gold content. Moreover, as a powerful catalyst must present a long-term stability, that parameter will be also studied in the paper.

2. METHOD

2.1 Mesoporous materials preparation

Mesoporous SBA15 were synthesized in a way similar to that of Zhao et al. [22]: 4g of amphiphilic triblock

copolymer poly (ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) (average molecular weight 5800, from Aldrich) was mixed in 120g of water and 8.64g of 2M HCl solution at 40°C while stirring followed by the addition of 8.54g of tetraethyl-orthosilicate (from Aldrich) to the homogenous solution under stirring. This gel mixture was continuously stirred at 40°C for 24h, and finally put in a Teflon-lined autoclave for 2 days at 100°C for crystallization. After cooling to room temperature, the solid product was filtered and dried at room temperature in air. Template removal was achieved by calcination in air at 500°C for 4h (heating rate: 1°C/mn).

Mesoporous ceria was synthesized according to the following procedure developed by Yue & Zhou [20]. One millimole of Ce(NO₃)₃.6H₂O was mixed with 0,15g of mesoporous silica and was ground for a few minutes in an agate mortar and pestle.

The mixture was then put into a crucible, which placed in a muffle furnace. The temperature was increased from room temperature to 500°C at a rate of 1°C/min and maintained at the final temperature for 4H. The specimen was then cooled down to room temperature. The silica template was removed by 2M NaOH solution at 80°C, the porous ceria was recovered by centrifugation and washed with distilled water three times.

2.2. Catalysts preparation

The 1wt%, 2wt% and 4wt% AuCeO₂ catalysts were prepared by deposition-precipitation method: Aqueous solution of tetrachloroauric acid (HAuCl₄) (3,65x10⁻⁴)M was added under stirring to an aqueous suspension of CeO₂ and an aqueous solution of urea (3,65x10⁻³)M in excess. The solution is heated at 80°C to decompose urea and obtain pH = 6-7.

The mixture was filtered and washed with deionised water at 60° C several times in order to eliminate the chloride ions, until there were no residual Cl⁻ ions as tested by AgNO₃, dried during 24 h at 80°C and finally calcined under air for 4 h at 400°C.

2.3. Characterization

Powder small- and wide-angle XRD patterns of the calcined samples were recorded on a Bruker AXS D5005 diffractometer equipped with monochromatized Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40kV, 30mA. Phase identification was performed by comparison with the information of the JCPDS database. The chemical analysis of Au was achieved by Atomic Emission Spectroscopy with Induced Coupled Plasma (ICP-AES) using a Varian Vista AX system. The surface area and pore size analysis of the samples were carried out by adsorption-desorption of nitrogen on a Micromeritics ASAP 2010 instrument (-196°C). Prior to N₂ adsorption, the samples were degassed under vacuum at 250°C for at least 6 h. The UV-Vis absorption spectra of the materials were recorded on a Cary 100 Scan UV/Vis spectrophotometer (Varian). The temperature programmed reduction experiments were carried out in an Altamira

AMI-200 apparatus. The TPR profiles are obtained by passing a 5 % H₂/Air flow (30 mL/min) through 70 mg of samples heated at 5°C/min from ambient temperature to 800°C. The hydrogen concentration in the effluent was continuously monitored by a thermoconductivity detector (TCD). The gold particles sizes were investigated by high resolution transmission electron microscopy (HRTEM) using Philips CM120 microscope coupled to an EDX analyser. Toluene oxidation was carried out in a conventional fixed bed microreactor and studied between 25 and 400°C (1°C min⁻¹).

The reactive flow was composed of air and 1000ppm of gaseous toluene. The flow rate through the reactor was set at 100 cm³.min⁻¹ that produced a space velocity of 10000 h⁻¹. The analysis of combustion products was performed evaluating the toluene conversion and the CO/CO+CO₂ molar ratio from a Varian micro-chromatograph.

3. RESULTS AND DISCUSSION

3.1. Characterization

3.1.1 X Ray Diffraction

The low-angle XRD patterns of CeO₂ and the AuCeO₂ catalysts with different gold contents are shown in Figure 1 (A). All the patterns exhibit one sharp diffraction corresponding to (100) reflexion which can be associated with the hexagonal symmetry characteristic of mesoporous SBA-15 showing that the ordered structure is maintained in the nanocasting process via a solid–liquid route. No differences on XRD patterns were observed before and after gold deposition suggesting that the introduction of gold does not induce any modification of the support phase.

Figure 1(B) shows the wide-angle XRD patterns; on each pattern, the diffraction peaks were perfectly indexed to a face-centred cubic (fcc) fluorite structure of CeO₂ (JCPDS Card No. 34-0394). The peaks were broadened to some extent, suggesting the small size of CeO₂ crystallites. Compared with the diffraction lines of pure mesoporous CeO₂, the catalysts 2wt% and 4% AuCeO₂ show a weak diffraction line of gold at 2θ = 38.5° besides the fluorite phase of CeO₂. Conversely, in the catalyst 1wt% AuCeO₂ the presence of gold is not visible suggesting that the metallic particle size may be smaller than the dimension required for detection (5nm) or in too low quantity.

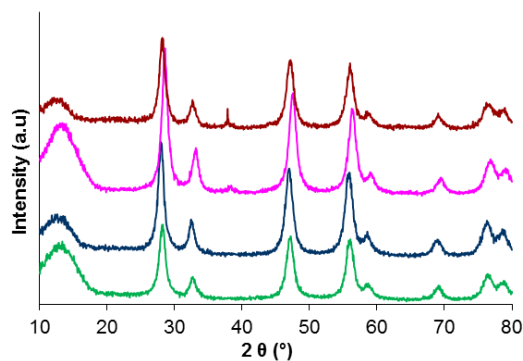


Figure 1: XRD patterns of CeO₂ and AuCeO₂ catalysts

3.1.2 N₂ Adsorption-Desorption isotherms

Figure 2 depicts the N₂ adsorption–desorption isotherms (A) and pore size distribution (B) of CeO₂ and the AuCeO₂ catalysts calcined at 400°C. The textural properties of the support and catalysts samples are listed in Table 1.

Table 1: Textural properties of catalysts

Sample	S _{BET} (m ² /g)	V _T (cm ³ /g)
CeO ₂	118	0.2809
1wt% AuCeO ₂	85	0.2415
2wt% AuCeO ₂	67	0.1373
4wt% AuCeO ₂	64	0.1736

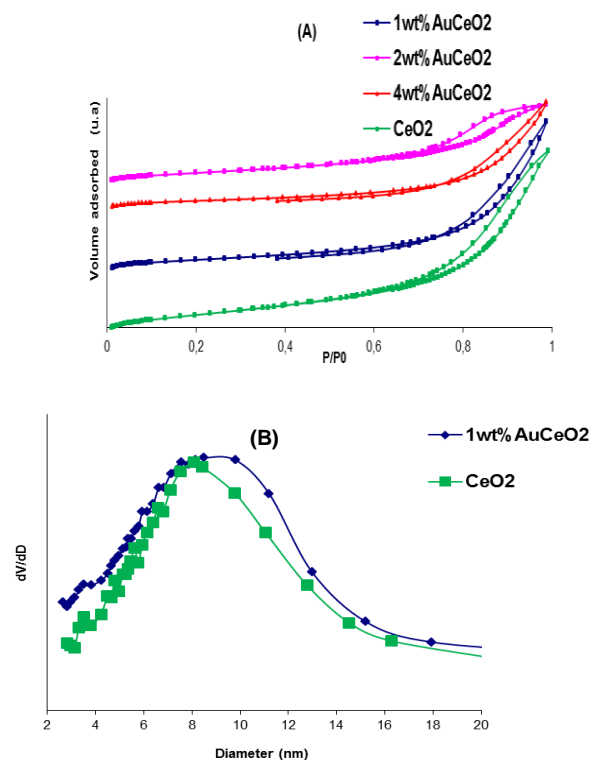


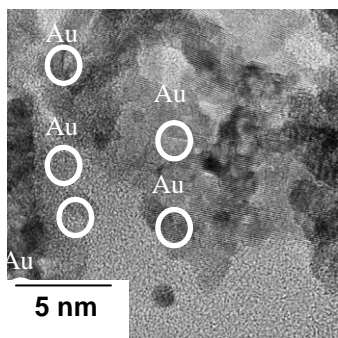
Figure 2: N₂ Adsorption-Desorption isotherms (A) and BJH pore size distribution of CeO₂ and AuCeO₂ (B)

Figure 2(A) shows that pure mesoporous CeO₂ has a jump at P/P₀ = 0.8 – 1.0 which is typical for mesoporous solids. This indicates that CeO₂ retains the mesoporous structure of the template. The shape of the isotherms of the AuCeO₂ catalysts is similar (type IV) to that of pure ceria. This indicates that the catalyst retains the mesoporous structure after loading gold particles. After loading gold particles, the pore volume and the BET surface area decrease with increasing gold content. Generally, when smaller gold particles are dispersed in the pore channels, the channels

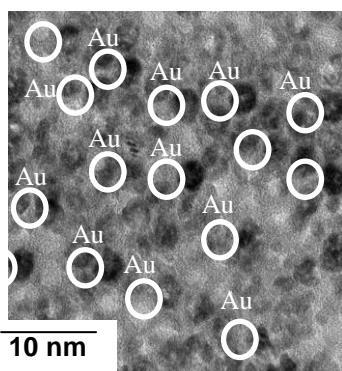
become narrow, the pore volume decreases and therefore the BET surface area decreases [23]. CeO₂ and 1wt% AuCeO₂ exhibit similar pore size distribution.

3.1.3. High Resolution Transmission Electron Microscopy

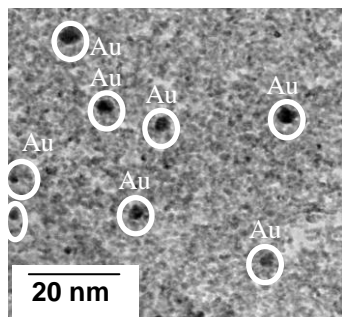
Figure 3 presents HRTEM images of the AuCeO₂ catalysts. In accordance with the XRD and N₂ adsorption-desorption results, the mesoscopic order of ceria could be clearly identified in the HRTEM views of AuCeO₂. Figures 3(A) and (B) are the HRTEM images of 1wt% AuCeO₂ and 2wt% AuCeO₂ respectively. It can be seen that the gold particles are mainly embedded in the mesoporous channels of CeO₂ and the particle size is mainly in the range of 2nm. With 2wt% AuCeO₂, occasional large gold particles with dimension of 20nm are found. Figure 3(C) is the HRTEM image of 4wt% AuCeO₂. Compared with Figures 3(A) and (B), it can be seen that the particle size of gold in the 4wt% AuCeO₂ catalyst is bigger than that in 1wt% AuCeO₂ and 2wt% AuCeO₂ and is between 5 and 30nm; therefore, the dispersion of gold particles is not uniform in the 4wt% AuCeO₂ catalyst.



(A) 1wt% AuCeO₂



(B) 2wt% AuCeO₂



(C) 4wt% AuCeO₂

Figure 3: HRTEM images of the AuCeO₂ catalysts calcined at 400°C. (A) 1wt% AuCeO₂, (B) 2wt% AuCeO₂, (C) 4wt% AuCeO₂

3.1.4 Diffuse Reflectance UV/Vis Spectrophotometry

In order to identify the nature of the gold particles, the catalysts were analysed by UV-Vis spectrophotometry in diffuse reflectance. The obtained spectra are represented in Fig.4. Beside support contribution, the UV-Vis spectra of the gold based catalysts show a new band at about 560nm. This band is due to the surface plasma absorption of the nanosized Au.

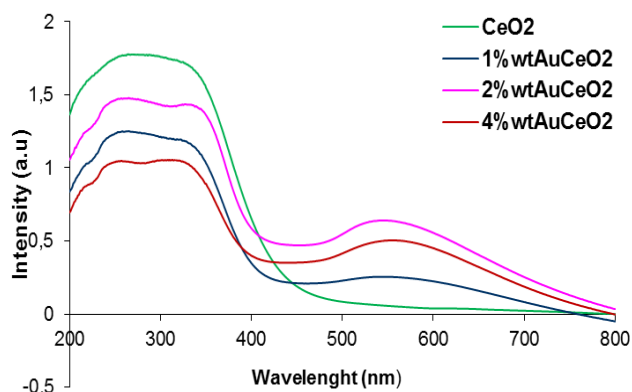


Figure 4: DR-UV-vis spectra of CeO₂ and gold based catalysts

Other additional absorption bands due to ionic gold or partly charged Au nanoclusters have not been detected in the spectra (absorption bands below 500nm).

3.1.4 Temperature Programmed Reduction

Figure.5 reports temperature programmed reduction (H₂-TPR) profiles carried out on CeO₂ and the AuCeO₂ catalysts.

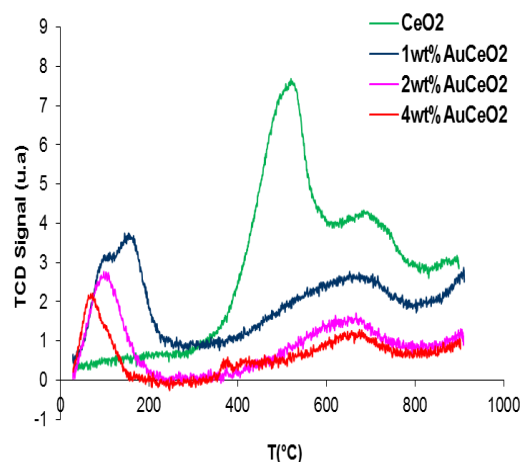


Figure 5: H₂-TPR profiles of CeO₂ and gold- based catalysts

The TPR profile of the CeO₂ sample is similar to those reported in the literature. The low temperature reduction

peak at 529°C and the high temperature peak at 700°C are commonly interpreted as the reduction of surface oxygen species and bulk phase lattice oxygen respectively [21]. When gold is added to the support, modification in the TPR profiles is observed. The peak related to the reduction of surface oxygen of ceria shifted to lower temperature as the gold loading increases. The gold catalyst may function by activating hydrogen that spills over to nearby ceria or by weakening the Ce-O bond adjacent to strongly bound gold species [24,10].

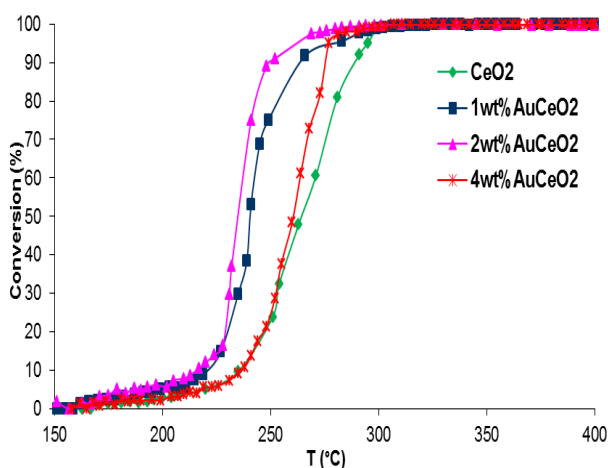


Figure 6: Toluene conversion on CeO₂ and gold-based catalysts

From figure.6, it can be inferred that the amount of reducible surface oxygen species in the 1wt% AuCeO₂ catalyst is higher than those of 2wt% AuCeO₂ and 4wt% AuCeO₂; a shoulder at 106°C was clearly discernable and tentatively assigned to the reduction of oxygen at defect sites as it has been reported that the formation of defect clusters lowered the energy barriers for oxygen desorption [25].

3.2. Catalytic activity for total toluene oxidation

Toluene oxidation curves versus temperature are presented

Catalyst	Temperature of Toluene conversion (°C)	Au (wt %)
	T _{50%}	
Conventional CeO ₂ [10]	600	-
CeO ₂	265	-
1wt% AuCeO ₂	240	0.8
2wt% AuCeO ₂	235	2.0
4wt% AuCeO ₂	262	3.2

in Fig. 6.

Table 2: T50 values (°C) for toluene oxidation for various AuCeO₂

The activity is given by the T₅₀ value (temperature for a conversion of 50%) (Table 2). The observed products are only carbon dioxide and water indicating complete combustion occurring during the reaction. From table 2, it can be inferred that the mesoporous ceria is more active than the conventional precipitated crystalline ceria [10]. In fact, over the mesoporous and the conventional CeO₂ the oxidation of toluene reached 50% of conversion at 265°C and 600°C respectively.

As also shown in Table.2, over 1wt% AuCeO₂, 2wt% AuCeO₂ and 4wt% AuCeO₂ catalysts, the oxidation of toluene reached 50% of conversion at 240°C, 235°C and 262°C respectively. It is worth noting that the T₅₀ shift, with respect to pure ceria, is significant for a gold loading 1wt% and 2wt%. It is highly probable that the presence of gold particles on the surface of ceria causes a decrease in the strength of the surface Ce-O bonds adjacent to gold atoms [26, 27] thus leading to a higher surface lattice oxygen mobility and therefore to higher reactivity of these oxygens. The 1wt% AuCeO₂ catalyst, for which a higher amount of reducible surface oxygen species has been found, exhibits a comparable activity to that of 2wt% AuCeO₂ catalyst.

It must be remind that 1wt% AuCeO₂ and 2wt% AuCeO₂ exhibit a same gold particle size which is smaller than that in 4wt% AuCeO₂ and this could explain the catalytic activity of these catalysts. Indeed, it has been reported that the activity of gold catalysts towards several reactions increases as the gold particle size decreases [28]. In our opinion the gold particle size is not the only factor to explain the catalytic activity of these catalysts, since the reactive oxygen for the combustion of VOCs can be provided by ceria. Our results point out that the catalytic activity of the gold/mesoporous ceria system towards the deep oxidation of toluene depends on the gold particle size and the amount of reducible surface oxygen species but also the porosity of the support.

It is worthy to investigate the catalytic stability of the AuCeO₂ catalyst in the catalytic combustion of toluene. For the test of catalyst stability, the best 1wt% AuCeO₂ catalyst was run in the toluene oxidation for 62h, for a low temperature of 230°C (figure 7). The toluene conversion at about 20% was chosen on purpose to increase the possible deactivation of the catalyst with time on stream.

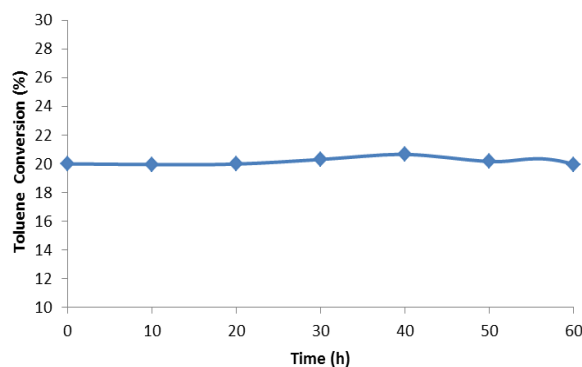


Figure 7: Evolution of conversion of toluene as a function of time on-stream at 230°C for the 1%wt AuCeO₂ catalyst

The catalytic activity and selectivity remain almost unchanged after 62h. Therefore, the 1wt% AuCeO₂ catalyst exhibits an expected long-term stability.

In conclusion, the lower gold content catalysts (1wt% AuCeO₂ and 2wt% AuCeO₂) are found to be highly active catalysts for deep oxidation of toluene. They are active at low temperature and selective for CO₂ and H₂O. The 1wt% AuCeO₂ catalyst exhibits a long-term stability showing that this new mesoporous ceria is of much interest as potential support for gold based catalysts for the deep oxidation of VOCs.

Moreover, our results point out that the catalytic activity of the gold/mesoporous ceria system towards the deep oxidation of toluene depends on the gold particle size and the amount of reducible surface oxygen species.

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REFERENCES

- [1]. F.Wyrwalsky, J-F. Lamonier, S. Siffert, A. Aboukaïs, Additional effects of cobalt precursor and zirconia support modifications for efficient catalyst in VOC oxidation. *Appl. Catal. B*, 70, 393-399 (2007).
- [2]. EC.Moretti, N.Mukhopadhyay, VOC ncontrol: Current practices and future trends. *Chem. Eng. Prog, July*, 20-26 (1993).
- [3]. T. Barakat, E. Genty, J.C. Rooke, R.Cousin, B.-L.Su, S.Siffert, Gold catalysts in Environmental remediation and water-gas shift technologies. (in press) *Energy Environ. Sci*, DOI: 10.1039/c2ee22859a. (2012)
- [4]. K. Bendahou, L. Cherif, S. Siffert, H.Tidahy, H. Benaïssa, A. Aboukaïs, The effect of the use of lanthanum-doped mesoporous SBA-15 on the performance of Pt/SBA-15 and Pd/SBA-15 catalysts for total oxidation of toluene. *Appl. Catal. A*, 351, 82-87. (2008).
- [5]. T.Barakat, J.C.Rooke, H.L.Tidahy, M. Hosseini, R. Cousin, J.F. Lamonier, J.M. Giraudon, G.De Weireld, B.-L. Su and S.Siffert Use of zeolites and macro mesoporous oxide supports for noble metal based catalysts in the total oxidation of VOCs; *ChemSusChem*, 4 (10), 1420-1430. (2011).
- [6]. Gennequin, M.Lamalle, R.Cousin, S.Siffert, F. Aïssi, A. Aboukaïs, Catalytic oxidation of VOCs on Au/Ce-Ti-O. *Catal. Today*, 122, 301-306. (2007).
- [7]. M. Lamalle, H. El Ayadi, C. Gennequin, R. Cousin, S. Siffert, F.Aïssi, A.Aboukaïs, Effect of the preparation method on Au/Ce-Ti-O catalysts activity for VOCs oxidation *Catal. Today.*, 137, 367-372. (2008).
- [8]. M.L. Jia, H.F. Bai Zhaorigetu, Y.N. Shen, Y.F. Li, Preparation of Au/CeO₂ catalyst and its catalytic performance for HCHO oxidation. *J. Rare Earths*, 26, 528-531. (2008).
- [9]. B.Solsona, T.Garcia, R. Murillo, A.M. Mastral, E.N. Ndifor, C.E. Hetrick, M.D. Amiridis, S.H. Taylor, Ceria and Gold/Ceria Catalysts for the Abatement of Polycyclic Aromatic Hydrocarbons: An In Situ DRIFTS Study. *Top.Catal.*, 52, 492-500. (2009).
- [10]. S.Scire, S.Minico, C.Crisafulli, C.Satriano, Pistone, C atalytic combustion volatile organic compounds on gold/cerium oxide catalysts. *Appl. Catal. B*, 40, 43-49. (2003).
- [11]. D.Andreeva, P. Petrova, J.W. Sobczak, L. Ilieva, M. Abrashev. Gold supported on ceria and ceria-alumina promoted by molybdena for complete benzene oxidation. *Appl. Catal. B*, 67, 237-245. (2006).
- [12]. L.Delannoy, K. Fajerweg, P. Lakshmanan, C. Potvin, C.Methivier, C. Louis, Supported gold catalysts for the decomposition of VOC: Total oxidation of propene in low concentration as model reaction. *Appl.Catal. B*, 117-124. (2010).
- [13]. LX.Yin, Y.Q. Wang, G S. Pang, Y.Koltypin, A. Gedanken, Sonochemical synthesis of cerium oxide nanoparticles-effect of additives and quantum size effect. *J. Colloid Interf. Sci*, 246, 78-84. (2002).
- [14]. X.W Xie, Y.Li, Z.Q.Liu, M. Haruta, W.J.Shen, Synthesis of Tin Dioxide Octahedral Nanoparticles with Exposed High-Energy {221} Facets and Enhanced Gas-Sensing Properties. *Nature*, 458, 746-749. (2009).
- [15]. S.-Y. Lai, Y. Qiu, S. Wang, Effects of the structure of ceria on the activity of gold/ceria catalysts for the oxidation of carbon monoxide and benzene. *J. Catal*, 237, 303-313. (2006)
- [16]. S. Carrettin, P. Concepción, A. Corma, J.M. López Nieto, V.F. Puntes Nanocrystalline CeO₂ increases the Activity of Au for CO Oxidation by

- Two Orders of Magnitude, *Angew. Chem. Int. Ed.*, 43, 2538-2540. (2004).
- [17]. T.Brezesinski, C. Erpen, K. Iimura, B. Smarsly, Mesoporous Crystalline Ceria with a Bimodal Pore System Using Block Copolymers and Ionic Liquids as Rational Templates. *Chem. Mater.*, 17, 1683-1690. (2005).
- [18]. D.M.Lyons, J.P.McGrath, M. A. Morris, Surface Studies of Ceria and Mesoporous Ceria Powders by Solid-State ^1H MAS NMR. *J. Phys. Chem. B*, 107, 4607-4617. (2003).
- [19]. D. Terribile, A. Trovarelli, C. de Leitenburg, G. Dolcetti, L.Lorca, Unusual Oxygen Storage/Redox Behavior of High-Surface-Area Ceria Prepared by a Surfactant-Assisted Route. *J.Chem. Mater.*, 9, 2676-2678. (1997).
- [20]. W. Yue, W. Zhou, Synthesis of Porous Single Crystals of Metal Oxides via a Solid-Liquid Route. *Chem. Mater.*, 19 (9), 2359-2363. (2007).
- [21]. F. Ying, S. Wang, C-T. Au, S-Y. Lai, Highly active and stable mesoporous Au/CeO₂ catalysts prepared from MCM-48 hard-template. *Micropor. Mesopor. Mater.*, 142, 308-315. (2011).
- [22]. D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Frederickson, B. F. Chmelka, G. D. Stucky, Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores. *Science*, 279, 548-52. (1998).
- [23]. L. Qian, M. Ming, Z. Yuqing, Preparation and Characterization of Nanostructured Au/TiO₂ Catalyst with High Thermal Stability. *Chin. J Catal.*, 27(12), 1111-1116. (2006).
- [24]. W. Deng, J.D. Jesus, H Saltsburg, M. Flytzani-Stephanopoulos, Low-content gold-ceria catalysts for the water-gas shift and preferential CO oxidation reactions. *Appl.Catal. A: Gen.*, 291,126-135. (2005).
- [25]. A.Trovarelli, (Ed.), *Catalysis by Ceria and Related Materials*, Catalytic Science Series, Imperial College Press, London, 2, 417-425. (2002).
- [26]. Q. Fu, A. Weber, M. Flytzani-Stephanopoulos, Nanostructured Au-CeO₂ Catalysts for Low-Temperature Water-Gas Shift. *Catal. Lett.*, 77, 87-95. (2001).
- [27]. C. Serre, F.Garin, G. Belot, G. Maire, Reactivity of Pt/Al₂O₃ and Pt-CeO₂/Al₂O₃ catalysts for the oxidation of carbon monoxide by oxygen. I: Catalyst characterization by TPR using CO as reducing agent. *J. Catal.*, 141, 1-8. (1993)
- [28]. G.C.Bond, D.T.Thompson, *Catalysis by Gold*. *Catal. Rev. Sci, Eng.*, 41,319-388. 1999