Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 137 (2008) 367–372

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Effect of the preparation method on Au/Ce-Ti-O catalysts activity for VOCs oxidation

M. Lamallem, H. El Ayadi, C. Gennequin, R. Cousin *, S. Siffert, F. Aïssi, A. Aboukaïs

Laboratoire de Catalyse et Environnement, E.A. 2598, Université du Littoral Côte d'Opale,
145 Avenue Maurice Schumann, 59140 Dunkerque, France

Abstract

Studies concerning the preparation of gold phases dispersed on binary Ce-Ti oxide ($Ce_{0.3}Ti_{0.7}O_2$) were performed in order to elaborate catalysts for total oxidation of VOCs. Solids containing gold, cerium and titanium were synthesized by impregnation and deposition precipitation (DP) method using NaOH, Na_2CO_3 or urea as precipitant agent. These catalysts have been characterized by means of total surface area (BET), X-ray diffraction (XRD), diffuse reflectance ultra-violet–visible spectroscopy (DR/UV–vis) and temperature programmed reduction (TPR) and their reactivity towards the oxidation of propene was studied. Thus, it was revealed that the gold-based material prepared by DP method using urea as precipitant agent was the most efficient catalyst towards the total oxidation of propene. Based on the characterisation data, it has been shown that the preparation method has an effect on the catalytic activity.

Keywords: Ceria; Titania; Gold; TPR; XRD; DR/UV–vis; Propene oxidation

1. Introduction

The increasing environmental awareness in the last two decades has prompted the emergence of stricter regulations covering automobile and industrial activities. Among these, the reduction of volatile organic compounds (VOCs) is particularly important because VOCs represent a serious environmental problem. The deep catalytic oxidation of these pollutants to carbon dioxide and water has been identified as one of the most efficient ways to destroy VOCs at low concentrations and to meet the increasingly stringent environmental regulations. In practice, the catalytic oxidation process requires heating large amounts of gas containing low concentrations of VOCs to the oxidation temperature. Therefore, highly active catalysts which work at lower temperatures are required.

In the last decade, it has been widely proved that it is possible to prepare gold nanoparticles deposited on metal oxide supports [1,2], which exhibit high catalytic activity towards oxidation reactions [3–15]. Supported gold catalyst on titania is often studied since its efficiency for the CO oxidation at room temperature are evidenced [1–10]. This activity depends on different parameters related to their preparation method [7] and the nature of the support [8]. Moreover, gold supported on cerium oxide has been shown to possess high activity for VOCs oxidation [11–15]. Ceria has been widely used in catalysis to purify vehicle exhausts and becomes the most rare earth oxide for controlling pollutant emission. It is known that ceria CeO_2 increases the dispersion of active components and its most important property is to serve as an oxygen reservoir which stores and releases oxygen via the redox shift between Ce^{4+} and Ce^{3+} under oxidizing and reducing conditions. The Ce^{3+}/Ce^{4+} redox cycle leads to high catalytic activity of CeO_2 [16–18]. However, since single CeO_2 would be sintered after calcination at 750 °C, some mixed oxides are prepared by adding anti sintered oxides like titanium [19,20].

Thus, a previous work [21] has shown that it seems to be interesting to combine the physico-chemical properties of gold, cerium and titanium in order to obtain a suitable catalytic material for the total oxidation of VOCs.

Therefore, the aim of this work is to deposit gold particles on $Ce_{0.3}Ti_{0.7}O_2$ and to investigate the effect of the preparation method on the catalytic total oxidation of propene. Propene was chosen as probe molecule for the catalytic oxidation, because it is often found in industrial exhausts and presents high

---

* Corresponding author. Tel.: +33 3 28 65 82 76; fax: +33 3 28 65 82 39.
E-mail address: Renaud.Cousin@univ-littoral.fr (R. Cousin).

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2007.12.141

photochemical ozone creation potentials (POCP) [22,23]. The gold-based catalysts have been characterised by various techniques, such as BET, XRD, DR-UV–vis and H_2-TPR, and attempts have been made to correlate the catalytic activity with the physico-chemical properties of the catalysts.

2. Experimental techniques

2.1. Catalyst preparation

Ce-Ti oxide was synthesized using sol–gel method [24]. An aqueous solution of cerium nitrate $Ce(NO_3)_3{\cdot}6H_2O$ and ethanol CH_3CH_2OH were added under stirring to another solution of ethanol CH_3CH_2OH and titanium(IV) isopropoxide $Ti(OC_3H_7)_4$ with molar ratio $Ti(OC_3H_7)_4/CH_3CH_2OH = 1/2$. The molar ratio between H_2O and titanium(IV) precursor is $H_2O/Ti(OC_3H_7)_4 = 5$. The solution was gelled after finishing the reaction between titanium(IV) isopropoxide $Ti(OC_3H_7)_4$ and water. The gel was dried at 80 °C during 24 h and finally calcined under air for 4 h at 600 °C to obtain $Ce_{0.3}Ti_{0.7}O_2$ (the number in subscript represent atomic proportion of each element in the oxide).

In this study, the gold-based catalysts ($Au/Ce_{0.3}Ti_{0.7}O_2$) were prepared by several methods: the deposition–precipitation method (DP) using different precipitating agents (urea, sodium hydroxide and sodium carbonate) and the classical method of impregnation.

Firstly, the gold-based catalysts (with a gold content of 4 wt%) were prepared by the deposition precipitation (DP) method [2]. Aqueous solution of tetrachloroauric acid ($HAuCl_4$) was added under stirring to an aqueous suspension of oxide support $Ce_{0.3}Ti_{O.7}O_2$ calcined at 600 °C and aqueous solution of urea in excess. The solution was heated at 80 °C to decompose urea and obtain pH equal to 6.7. The pH of solution was maintained at the value of 6.7 during 4 h to obtain high dispersion of fine gold particles on the oxide supports. The mixture was filtered and washed with deionised water at 60 °C several times in order to eliminate the chloride ions, dried during 24 h at 80 °C and finally calcined under air for 4 h at 400 °C.

Catalysts were also prepared with the DP method using sodium hydroxide or sodium carbonate as precipitating agent. One gram of the support ($Ce_{0.3}Ti_{0.7}O_2$) was added to an aqueous solution at 80 °C containing the suitable amount of gold. The pH of $HAuCl_4$ solution was adjusted to 8 by addition of NaOH or Na_2CO_3 (0.1 M) drop by drop under stirring during 4 h. The suspension was filtered, washed several times with hot water in order to eliminate Na^+ and Cl^- ions. The catalyst was then dried in the oven at 80 °C followed by a thermal treatment under air at 400 °C (2 °C min^{-1}) during 4 h. The code names of these catalysts are respectively: $Au/Ce_{0.3}Ti_{0.7}O_2$ [DP urea], $Au/Ce_{0.3}Ti_{0.7}O_2$ [DP NaOH] and $Au/Ce_{0.3}Ti_{0.7}O_2$ [DP Na_2CO_3].

Finally wetness impregnation was also used to prepare catalyst. The code name of this solid is $Au/Ce_{0.3}Ti_{0.7}O_2$ [Impregnation]. The support ($Ce_{0.3}Ti_{0.7}O_2$) was dispersed in an aqueous solution of $HAuCl_4$ with a volume of 100 mL for 1 g of the support. The support was impregnated during solution evaporation using a rotary evaporator at atmospheric pressure and a temperature of 80 °C. The solid was dried and calcined under air at 400 °C during 4 h.

2.2. Catalyst characterisation

To determine the elemental composition of samples, chemical analysis of Ce, Ti and Au was performed by inductively coupled plasma atomic emission spectroscopy at the CNRS Centre of Chemical Analysis (Vernaison, France).

BET surface area was measured by nitrogen adsorption at −196 °C in a Thermo-Electron QSurf M1 apparatus. Before analysis, the samples were treated under vacuum for 30 min at 120 °C.

XRD analysis was performed on a BRUKER Advance D8 powder X-ray diffractometer using Cu Kα radiation ($\lambda = 0.15406$ nm). Diffraction patterns were recorded over a 2θ range of 15–80° and using a step size of 0.02° and a step time of 4 s. The mean crystallite sizes were estimated using the Scherrer equation.

DR-UV–vis spectroscopy experiments were carried out on a VARIAN CARY 5000. The measurements were performed on air exposed samples at ambient temperature between 200 and 800 nm.

The temperature programmed reduction experiments were carried out in an Altamira AMI-200 apparatus. The TPR profiles were obtained by passing a 5% H_2/Ar flow (30 mL min^{-1}) through 50 mg of samples heated at 5 °C min^{-1} from ambient temperature to 900 °C. The hydrogen concentration in the effluent was continuously monitored by a thermoconductivity detector (TCD).

2.3. Catalytic activity measurements

Catalytic tests were carried out at atmospheric pressure in a conventional fixed bed microreactor using 100 mg of fine powder catalyst. The reactive flow (100 mL min^{-1}) is composed of air and 6000 ppm of propene. The reactants and the reaction products were analysed by a VARIAN chromatograph equipped with FID and TCD detectors. The catalysts were first activated at 400 °C for 4 h under air (2 L h^{-1}) and the conversion measurement was studied on slowly heating ramp between 20 and 400 °C at 1 °C min^{-1}. The temperature ramp of 1 °C min^{-1} was considered to be sufficiently slow to reach a pseudo-steady state at every point. Each catalytic activity measurements consisted of at least two heating–cooling cycles, to monitor possible catalyst deactivation processes. In general, the activity of the catalyst decreases slightly during the second or third heating–cooling cycle, but the difference between the cycles did not exceed 20 °C. Therefore, to compare the catalytic performance of different catalysts tested in this study, the conversion achieved during the second heating cycle will be used.

3. Results and discussions

Fig. 1 represents the conversion of propene as a function of the temperature in the presence of the catalytic support

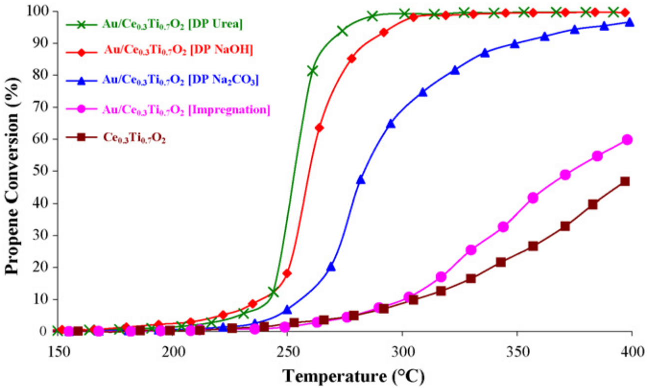

Fig. 1. Propene conversion on $Ce_{0.3}Ti_{0.7}O_2$ and gold-based catalysts prepared by several methods.

Table 1
Catalytic performances, gold loading, chlorine content and surface areas of catalysts

Catalyst	Temperature of propene conversion[a] (°C)		Au (wt%)	Cl (ppm)	S_{BET} ($m^2\ g^{-1}$)
	$T_{50\%}$	$T_{90\%}$			
$Au/Ce_{0.3}Ti_{0.7}O_2$ [DP urea]	253	270	3.30	<250	82
$Au/Ce_{0.3}Ti_{0.7}O_2$ [DP NaOH]	260	286	1.47	<250	70
$Au/Ce_{0.3}Ti_{0.7}O_2$ [DP Na_2CO_3]	284	357	1.96	<250	68
$Au/Ce_{0.3}Ti_{0.7}O_2$ [Impregnation]	374	–	1.52	7700	61
$Ce_{0.3}Ti_{0.7}O_2$	>400	–	–	–	86

[a] T_{50} and T_{90} correspond to the temperature of 50% and 90% of propene conversion.

($Ce_{0.3}Ti_{0.7}O_2$) and in presence of different gold-based catalysts. Thus, adding gold on the oxide support improves the catalytic activity for the propene oxidation. The propene conversion is performed at lower temperature and present 100% of selectivity towards formation of CO_2. When gold is deposited on the oxide using the DP method, a better activity is observed. This result indicates that the preparation method has an effect on the catalyst activity. Moreover, it seems that the choice of the precipitant agent during the catalyst preparation has an effect on the catalytic activity. Indeed, catalysts prepared by DP urea or NaOH (denoted $Au/Ce_{0.3}Ti_{0.7}O_2$ [DP urea] and $Au/Ce_{0.3}Ti_{0.7}O_2$ [DP NaOH]) are more active than catalysts prepared by DP Na_2CO_3 (denoted $Au/Ce_{0.3}Ti_{0.7}O_2$ [DP Na_2CO_3]). Thus, the preparation method seems to play an important role in the activity of propene total oxidation. In order to identify the origin and to explain these differences in activities, it is important to characterise the materials by physico-chemical techniques. This will allow identifying the favourable parameters to obtain suitable catalysts for oxidations of VOCs.

In order to define the quantity of gold and chlorine in the catalysts, elementary analyses were performed at the CNRS Center of Chemical Analysis (Vernaison, France). Results are shown in Table 1. Then, it could be noticed that gold content in the solid is not the same and depends on the synthesis method whereas at the moment of the preparation, 4 wt% of gold should be deposited on each oxide. Thus, the DP urea method appears to be the one to approach the desired content. For the other methods, an important loss of gold during synthesis is revealed. Regarding the catalytic results in Fig. 1 and Table 1, these solids can be classified by decreasing activities as follows:

$$\begin{aligned}&Au/Ce_{0.3}Ti_{0.7}O_2[DPurea] > Au/Ce_{0.3}Ti_{0.7}O_2[DPNaOH]\\&\quad > Au/Ce_{0.3}Ti_{0.7}O_2[DPNa_2CO_3]\\&\quad \gg Au/Ce_{0.3}Ti_{0.7}O_2[Impregnation] > Ce_{0.3}Ti_{0.7}O_2\end{aligned}$$

It can be seen that there are differences in the activity when gold has been precipitated. First of all, it could be related to the fact that the amount of gold deposited on oxide by precipitation with NaOH or Na_2CO_3 is much lower than urea. The significant difference comes from the conditions of precipitation. According to Zanella et al., the DP urea method in comparison with DP NaOH, permits the gradual and homogenous addition of HO^- ions in the solution. This method avoids local increase of pH and the precipitation of metal hydroxide in the solution [25].

Regarding the chlorine presence in the solids (Table 1), a low content in samples prepared with the DP method is observed whereas for the preparation by impregnation, a high content of chlorine in the form of chloride coming of $HAuCl_4$ precursor is evidenced. Knowing that chlorine is considered as a catalytic poison [3], this result allows us to explain the bad reactivity of the impregnated catalyst towards propene oxidation.

Concerning the evolution of the solid specific area, a low decrease is observed when the solid is prepared by the DP urea. For the impregnated solid, a decrease of 29% ($-25\ m^2\ g^{-1}$) is observed. This result indicates that the preparation of gold-based catalyst by impregnation is not favourable to obtain homogenous deposition of gold.

Fig. 2 shows the XRD patterns of catalysts. For the sample without gold ($Ce_{0.3}Ti_{0.7}O_2$), some diffraction peaks corresponding to the anatase phase (TiO_2) and the cerianite phase (CeO_2) are observed. These diffraction peaks are not well

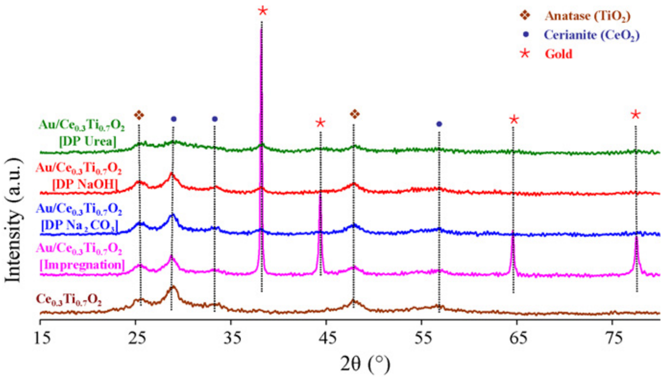

Fig. 2. XRD patterns of $Ce_{0.3}Ti_{0.7}O_2$ and gold-based catalysts prepared by several methods.

resolved and present low intensity. This result indicates that the Ce-Ti oxide is relatively amorphous. For the samples Au/$Ce_{0.3}Ti_{0.7}O_2$ prepared by DP method, deposition of gold induces the appearance of small diffraction peaks of polycrystalline gold. The high amorphous character of the samples can be deduced from the high level of noise detected in the patterns. Only peak at 38.28° characteristic of Au^0 is discernable and is very weak and broad. However, for Au/$Ce_{0.3}Ti_{0.7}O_2$ prepared by impregnation, well diffraction patterns characteristic to metallic gold (index-pattern 04-0784 data base JCPDS-ICDD) are revealed. A difference in the intensity of diffraction patterns corresponding to gold is observed between the solids prepared by DP and the one by impregnation. It is more significant for the Au/$Ce_{0.3}Ti_{0.7}O_2$ [Impregnation]. This observation suggests that this impregnated oxide contains big particles of gold. Indeed, using the Scherrer equation and considering this line at $2\theta = 38.28°$, an evaluation of the gold nanoparticle size was carried out. A crystal size of about 51.6 nm is obtained for the Au/$Ce_{0.3}Ti_{0.7}O_2$ [Impregnation] solid, whereas for those obtained by the DP method, the crystals size is between 6 and 7 nm. These results indicate that the DP method allows for a better dispersion of gold particles. Moreover, no change in the structure of the Ce-Ti-O support due to the introduction of gold is detected.

In order to identify the nature of the gold particles, the solids prepared by DP method were analysed by UV–vis spectrophotometry in diffuse reflectance. The obtained spectra are represented in Fig. 3. Beside support contribution, the UV–vis spectrum of the gold-based catalyst shows a new band at about 560 nm. This band is characteristic for the plasmon resonance of metallic gold particles. In gold metal nanoparticles, the plasmon absorption arises from the collective oscillations of the free conduction band electrons that are induced by the incident electromagnetic radiation. Such resonances are observed when the wavelength of the incident light far exceeds the particle diameter. This observation of this band attributed to surface plasmon resonance of fine gold metallic particles (some nanometers) is in accordance with the XRD study, which revealed particle sizes of approximately 6–7 nm. The small variations of wavelength of this type of bands are induced by the size, the form of crystallites, the surrounding environment and the interaction between gold and support. Furthermore, it is interesting to note that for Au/$Ce_{0.3}Ti_{0.7}O_2$ [DP urea] and Au/$Ce_{0.3}Ti_{0.7}O_2$ [DP NaOH] samples which are the most active catalysts, another absorption band at around 630 nm appeared which belongs to the longitudinal plasmon resonance band of aggregates or deviation from spherical geometry [7,26,27] of gold nanoparticles.

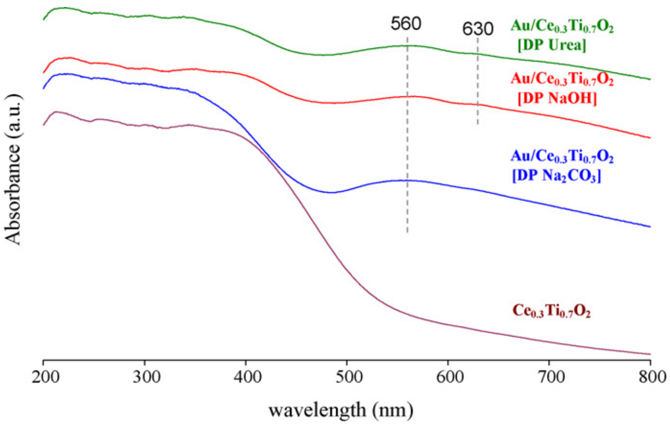

Fig. 3. DR-UV–vis spectra of $Ce_{0.3}Ti_{0.7}O_2$ and gold-based catalysts prepared by several methods.

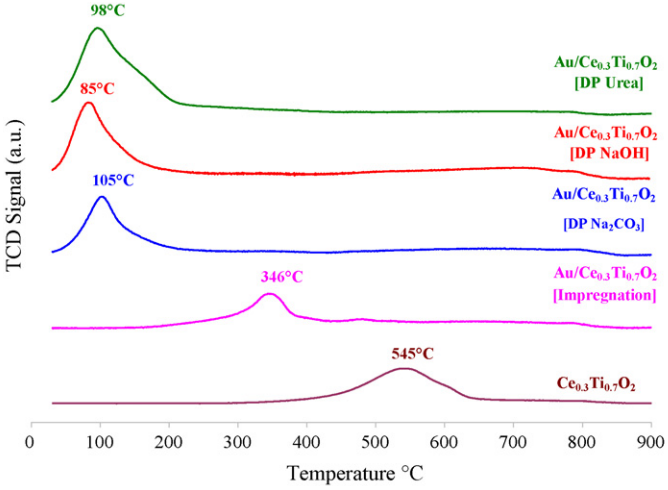

Fig. 4. H_2-TPR profiles of $Ce_{0.3}Ti_{0.7}O_2$ and gold-based catalysts prepared by several methods.

For a better understanding of the difference in catalytic reactivity between these solids, H_2-TPR experiment study was carried out. The results are shown in Fig. 4 and indexed in Table 2.

The TPR profile of the $Ce_{0.3}Ti_{0.7}O_2$ represented in Fig. 4 shows a massif peak of reduction at 545 °C, this is attributed to the reduction of surface oxygen species from ceria. When gold is added to the support, modification in the TPR profiles was observed. Indeed a reduction peak appears at lower temperature. This peak corresponds to the reduction of the oxygen species on the gold particles and on ceria. Andreeva et al. [28]

Table 2
Gold reduction peak position and H_2 consumption as function of preparation method

Catalyst	Temperature programmed reduction			
	Peak position (°C)	Calculated H_2 consumption $Au^{3+} \rightarrow Au^0$ (μmol g^{-1})	Experimental H_2 consumption (μmol g^{-1})	H_2 over consumption (μmol g^{-1})
Au/$Ce_{0.3}Ti_{0.7}O_2$ [DP urea]	98	251.3	1181.6	930.3
Au/$Ce_{0.3}Ti_{0.7}O_2$ [DP NaOH]	85	111.9	780.0	668.1
Au/$Ce_{0.3}Ti_{0.7}O_2$ [DP Na_2CO_3]	105	149.3	591.0	441.7
Au/$Ce_{0.3}Ti_{0.7}O_2$ [Impregnation]	346	115.8	316.9	201.1

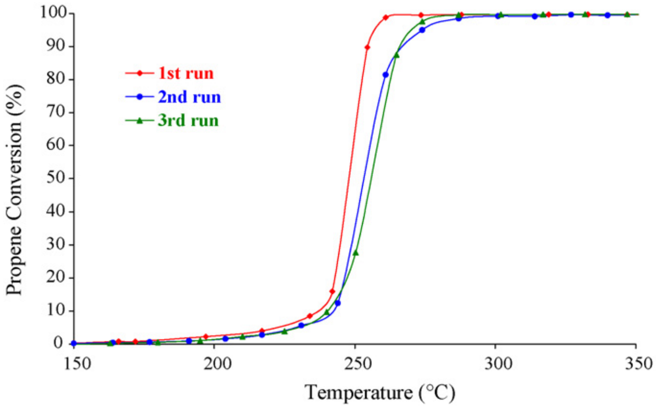

Fig. 5. Cycles of propene conversion on Au/$Ce_{0.3}Ti_{0.7}O_2$ [DP urea] catalyst.

have shown that adding noble metals (like gold) on CeO_2 permit to lower the reduction temperature of oxygen species on ceria surface.

Table 2 resumes the H_2-TPR experimental and calculated consumption of catalysts samples for peaks at low temperature (<400 °C). For the H_2 calculated consumption, we consider that gold species are in the ionic state Au^{3+}. Thus, knowing the gold content in solids and following the reduction reaction of Au^{3+} to Au^0, the amount of H_2 over consumption by the catalysts could be estimated. The H_2 over consumption exists for all gold-based catalysts but it is relatively high for the solids prepared by DP method. This result shows the influence of gold to facilitate the reduction of oxygen species from $Ce_{0.3}Ti_{0.7}O_2$ support surface on the border with gold. These results could be correlated to the results of the catalytic tests. Indeed, it can be noticed that the solid named Au/$Ce_{0.3}Ti_{0.7}O_2$ [DP urea] and $Ce_{0.3}Ti_{0.7}O_2$ [DP NaOH] show the best activity towards the total oxidation of propene, showing also higher hydrogen consumption at lower temperature. This observation could be explained by the interaction between gold nanoparticles and cerium oxide. Ceria is very well known for its oxygen storage capacity (OSC), defined as the capacity to release and accept oxygen. Centeno et al. [11] have studied the catalytic combustion of VOCs on Au/CeO_x/Al_2O_3, and they concluded that the presence of cerium ions has a positive influence on the fixation and the final dispersion of gold on alumina support. Moreover ceria stabilizes the gold particles with low crystallite size. In addition to these beneficial features, ceria, because of its redox properties, may improve the catalytic behaviour of the catalyst by increasing the supply of active oxygen. Similar conclusions were proposed by Scire et al. [12] in their study of VOC oxidation over Au/CeO_2. The mechanism of hydrocarbon oxidation over ceria and other reducible metal oxides is usually considered to be of the redox or Mars and van Krevelen type [11,12]. The key steps of this mechanism are believed to be the supply of active oxygen by the readily reducible oxide and its reoxidation by oxygen. Gluhoi et al. [14,15] have shown that gold-based catalysts that contain a transition metal oxide or ceria are highly active in propene oxidation. The role of the oxide is twofold: it stabilizes the gold particles against sintering (ceria) and provides active oxygen for the reaction (CeO_x, MnO_x, CoO_x, or FeO_x) via the Mars–van Krevelen mechanism.

Thus, based on the above presented results, Au/$Ce_{0.3}Ti_{0.7}O_2$ [DP urea] can be considered as the most promising catalyst of the series. However, in order to verify the stability of the gold catalyst, the propene conversion on Au/$Ce_{0.3}Ti_{0.7}O_2$ [DP urea] was performed on three heating–cooling cycles. Fig. 5 represents the catalytic performance as a function of temperature on each heating run. Same catalytic behaviour was obtained during these three runs cycles and no deactivation was observed. This result indicates a stability of the gold-based solid during the catalytic runs. The deposition of gold on $Ce_{0.3}Ti_{0.7}O_2$ using the DP urea method seems to be the most appropriate procedure to obtain favourable interaction between gold and oxide support in order to develop suitable catalyst for the total propene oxidation.

4. Conclusion

Au/$Ce_{0.3}Ti_{0.7}O_2$ catalysts were synthesised by several methods (deposition precipitation and impregnation) using $HAuCl_4$ as precursor compounds and their activity in the propene oxidation was evaluated. On the basis of the results reported, these solid can be classified by decreasing activities as follows: Au/$Ce_{0.3}Ti_{0.7}O_2$ [DP urea] > Au/$Ce_{0.3}Ti_{0.7}O_2$ [DP NaOH] > Au/$Ce_{0.3}Ti_{0.7}O_2$ [DP Na_2CO_3] ≫ Au/$Ce_{0.3}Ti_{0.7}O_2$ [Impregnation] > $Ce_{0.3}Ti_{0.7}O_2$. It can be concluded that the preparation method or the choice of the precipitating agent has an important effect on the activity of the gold-based catalyst. The physico-chemical study of the solids reveals that preparation method affects the gold dispersion on the support. Thus, the Au/$Ce_{0.3}Ti_{0.7}O_2$ prepared by DP using urea presents small gold crystallites size, low chlorine content and the higher H_2 over consumption and can be considered the most promising catalyst of this study.

Acknowledgements

The authors would like to thank the Urban Community of Dunkerque for the financial assistance allocated for the purchases of the UV–vis spectrophotometer and the specific area measurement apparatus. The ‘‘Conseil General du Nord’’, the ‘‘Region Nord-Pas de Calais’’ and the European Community (European Regional Development Fund) are gratefully acknowledged for financial supports.

References

[1] G.C. Bond, Catal. Today 72 (2002) 5.
[2] M. Haruta, Cattech 6 (2002) 102.
[3] I. Dobrosz, K. Jiratova, V. Pitchon, J.M. Rynkowski, J. Mol. Catal. A. 234 (2005) 187.
[4] S. Ivanova, C. Petit, V. Pitchon, Catal. Today 113 (2006) 182.
[5] R. Cousin, S. Ivanova, F. Ammari, C. Petit, V. Pitchon, in: Proceedings of the 2nd World Congress on Gold Applications, Vancouver, 2003.
[6] M. Daté, Y. Ichihashi, T. Yamashita, A. Chiorino, F. Boccuzzi, M. Haruta, Catal. Today 72 (2002) 94.
[7] R. Zanella, S. Giorgio, C.H. Shin, C.R. Henry, C. Louis, J. Catal. 222 (2004) 367.
[8] D. Andreeva, Gold Bull. 35 (2002) 82.
[9] A.C. Gluhoi, B.E. Nieuwenhuys, Catal. Today 122 (2007) 226.

[10] V. Idakiev, Z.Y. Yuan, T. Tabakova, B.L. Su, Appl. Catal. A 281 (2005) 149.

[11] M.A. Centeno, M. Paulis, M. Montes, J.A. Odriozola, Appl. Catal. A 234 (2002) 65.

[12] S. Scire, S. Minico, C. Crisafulli, C. Satriano, A. Pistone, Appl. Catal. B 40 (2003) 43.

[13] C. Della Pina, N. Dimitratos, E. Falletta, M. Rossi, A. Siani, Gold Bull. 40 (2007) 67.

[14] A.C. Gluhoi, N. Bogdanchikova, B.E. Nieuwenhuys, J. Catal. 229 (2005) 154.

[15] A.C. Gluhoi, N. Bogdanchikova, B.E. Nieuwenhuys, J. Catal. 232 (2005) 96.

[16] S. Pengpanich, V. Meeyoo, T. Rirksomboon, K. Bunyakiat, Appl. Catal. A 234 (2002) 221.

[17] K. Otsuka, Y. Wang, M. Nakamura, Appl. Catal. A 183 (1999) 317.

[18] H.C. Yao, Y.F. Yu Yao, J. Catal. 86 (1984) 254.

[19] D. Terribile, A. Trovarelli, J. Llorca, J. Catal. 178 (1998) 299.

[20] J. Rynkowski, J. Farbotko, R. Touroude, L. Hilaire, Appl. Catal. A 203 (2000) 335.

[21] C. Gennequin, M. Lamallem, R. Cousin, S. Siffert, F. Aïssi, A. Aboukaïs, Catal. Today 122 (2007) 301.

[22] R.G. Derwent, M.E. Jenkin, S.M. Saunders, Atmos. Environ. 30 (1996) 181.

[23] R.G. Derwent, M.E. Jenkin, S.M. Saunders, M.J. Pilling, Atmos. Environ. 32 (1998) 2429.

[24] L. Le Bihan, PhD theses, USTLille, 1997.

[25] R. Zanella, S. Giorgio, C.R. Henry, C. Louis, Phys. Chem. B 106 (2002) 7634.

[26] H. Huang, X. Yang, Colloids Surf. A: Eng. Aspects 255 (2005) 11.

[27] J. Zhu, Phys. Lett. A 339 (2005) 466.

[28] G. Munteanu, L. Ilieva, R. Nedyalkova, D. Andreeva, Appl. Catal. A 277 (2004) 31.