Applied Catalysis B: Environmental 125 (2012) 222–246

Contents lists available at SciVerse ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Review

Supported gold catalysts for the total oxidation of volatile organic compounds

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ARTICLE INFO

Article history:
Received 3 April 2012
Received in revised form 26 May 2012
Accepted 30 May 2012
Available online 6 June 2012

Keywords:
Au
VOC
Support
Preparation
Mechanism
Combustion
Environmental protection

ABSTRACT

This review intends to describe and critically analyze the growing literature dealing with the use of supported gold catalysts in the catalytic deep oxidation of volatile organic compounds (VOC). Among the wide family of VOC, attention has been given to the oxidation of saturated (methane, ethane, propane, isobutane, n-hexane) and unsaturated (acetylene, ethylene, propene) aliphatic compounds, aromatic hydrocarbons (benzene, toluene, xylenes, naphthalene), alcohols (methanol, ethanol, n- and iso-propanol), aldehydes (formaldehyde), ketones (acetone), esters (ethylacetate). Moreover, the oxidation of chlorinated VOC (dichloromethane, o-dichlorobenzene, o-chlorobenzene), as well as of nitrogen-(trimethylamine) and sulphur-containing (dimethyldisulfide) compounds has been addressed.

The reaction mechanism and the influence of different factors, such as the nature and the properties of the support, the Au particle size and shape, the electronic state of gold, the preparation method and the pretreatment conditions of catalysts, the nature and the concentration of the organic molecule, are discussed in detail.

Contents

1. Introduction

1.1. Brief introduction on volatile organic compounds

Volatile organic compounds (VOC) are recognized as major responsible for the increase in global air pollution due to their

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http://dx.doi.org/10.1016/j.apcatb.2012.05.047

contribution to ozone and photochemical smog [1–3]. Anthropogenic sources of VOC include mainly outdoor sources, such as chemical, pharmaceutical and power plants, petroleum refineries, gas stations and dry cleaners, food processors, textile manufacturers, etc. A large variety of VOC are also emitted from household products (indoor sources), such as office supplies, printers, insulating materials, solvents and cleaning products, pressed woods, restaurant and domestic cooking, wood stoves, etc.

The nature of VOC depends on the emission source and comprises a large variety of compounds, such as alkanes, olefins, alcohols, ketones, aldehydes, aromatics, halogenated hydrocarbons [2]. Among the most common and toxic not halogenated compounds, there are formaldehyde, benzene, toluene, propylene, phenol, acetone, styrene. Formaldehyde, causing cancer in animals and humans, is an important chemical widely used by industry to manufacture building materials and household products. Moreover, an increasing amount of formaldehyde is produced due to growing utilization of ethanol-based biofuels in cars [4]. Aromatics and alkenes are the major families of pollutants in industrial and automotive emissions. In particular propylene and toluene are recognized as highly polluting molecules because of their high POCP (Photochemical Ozone Creativity Potential) [5,6]. Polycyclic aromatic hydrocarbons (PAHs) represent another important family of volatile environmental pollutants mainly generated during combustion processes [7]. Halogenated and more especially chlorinated VOC (such as dichloromethane, chloroform, carbon tetrachloride, 1,2-dichloroethane, trichloroethylene, tetrachloroethylene) have widespread applications in industry and require special attention on account of their toxicity and high stability [8].

The VOC emissions are regulated by the legislation of European Union since 1999, when the Solvent Directive (1999/13/EC) was launched. In 2005, the Commission of the European Communities published the Thematic Strategy on Air Pollution [9] and, then, in 2006 the Goteborg protocol fixed that the maximum VOC emission level by 2020 in the EU countries should be reduced by nearly half as compared to the base year 2000 [10]. As stated in this directive the "*full implementation of current legislation would not be sufficient to meet the 2020 targets of the Thematic Strategy. Further measures are needed in particular in the field of industrial emissions*" [10].

Best available techniques for reducing emissions of VOC from major stationary sources include primary and secondary measures [11]. The primary measures focus on modification of process design (e.g. process flow parameters, operating temperature, feed gas composition). However, the process conditions are often limited and other strategies to reduce emissions must be used, referred to as secondary measures and focused on post-process elimination of VOC, i.e. thermal and catalytic oxidation, adsorption and filtration [11]. Among these methods, catalytic combustion is the most effective for low concentrations of organic emissions [12,13]. Selection of the catalytic materials for various organic pollutants has been the subject of many studies and the optimization of catalyst formulation does not appear an easy task, because of the large variety of organic molecules and the complicated nature of VOC mixtures encountered in practice.

Two classes of catalysts, noble metals and transition metal oxides, are the most promising in the area of VOC combustion [14,15]. Regarding unsupported metal oxide catalysts, ceria alone or combined with other elements in mixed oxides or doped oxides (CoO_x, MnO_x, CuO, ZnO, Fe_2O_3, TiO_2, Al_2O_3, ZrO_2) is recognized as an efficient catalyst in the total oxidation of several types of VOC molecules [14,16–19]. Among supported metal catalysts, platinum and palladium have been the most studied, but other metals, such as rhodium and gold, were also reported as active catalysts [14,15].

1.2. Brief introduction on gold catalysts

For many years gold was generally regarded as a poor catalyst due to its chemical inertness towards reactive molecules such as oxygen and hydrogen, therefore being not considered worth of investigation in catalysis. Between 1987 and 1989 Haruta et al. [20,21] demonstrated that surface adsorption and reactivity of gold could be enhanced by creating defective surface structures through downsizing of gold nanoparticles. They showed that metallic gold, if present as small particles (<5 nm), specially when dispersed on metal oxides, exhibited a remarkable activity towards oxidation reactions. In particular, a very high catalytic activity was found in the low temperature CO oxidation, with some systems (e.g. Au/Fe_2O_3) reported to be active already at $-80\,^{\circ}C$. Haruta stated that gold catalysts can be advantageous over other noble metals in low temperature reactions because the bonding strength of adsorbates on Au defective sites is moderate and still weaker than that on Pd and Pt [22].

Since pioneering works of Haruta, research and industrial interest in catalysis by gold extraordinarily increased with an exponential growth in the number of published articles dealing with the use of gold both as homogeneous and heterogeneous catalyst, some of these papers confirming that, for some applications, gold properties are much superior to those of the platinum group metals. Some important reviews [23–27] and one comprehensive book [28] have appeared, covering general aspects related to physical properties and characterization of gold nanoparticles as well as the preparation of supported gold catalysts and their use in a large number of applications, such as CO and CO_2 hydrogenation, hydrogenation and selective oxidation of hydrocarbons, alkenes epoxidation, NO_x reduction, water-gas shift reaction, CO oxidation and preferential CO oxidation in the excess of hydrogen, total oxidation of VOC.

Our review is devoted to the application of gold catalysts for the total oxidation of VOC, in so as we noticed that none of the above cited reviews/book contains an in-depth discussion on this important environmental topic, with only half/one page dedicated.

In one of the first key review on VOC combustion [13] none of the references included dealt with the use of gold. The author stated that among noble metals (Pt, Pd, Ag and Au) only Pt and Pd and a few alloys are used as catalysts in the catalytic combustion of VOC because the high temperatures generally employed can cause sintering, volatility loss and irreversible oxidation of the other metals. The first significant papers dealing with gold catalysts appeared later in 1995–1996 [29–31], reporting high activity of Au/Co_3O_4 for the combustion of methane [29] and the oxidative destruction of chloromethane [31] and of $Au/\alpha Fe_2O_3$ for the combustion of methanol, formaldehyde and formic acid [30]. Since then the number of articles, dealing with VOC combustion on Au catalysts underwent to a dramatic growth. In one of the recent review on catalytic combustion of VOC on non-noble metal catalysts [14], an entire small chapter is dedicated to the application of Au-containing catalysts. The growing interest is well demonstrated by Fig. 1, which depicts the number of papers on VOC combustion on gold, taken into consideration in this review, as a function of the publication year.

2. Role of the support

The performance of gold catalysts for VOC deep oxidation has been reported to be dependent on many factors, namely the nature and the properties of the support, the loading of gold, the size, the shape and the electronic state of gold nanoparticles, the preparation method and the pretreatment conditions of catalysts, the nature and the concentration of the organic molecule to be combusted. Despite a lot of studies were carried out in order to distinguish the

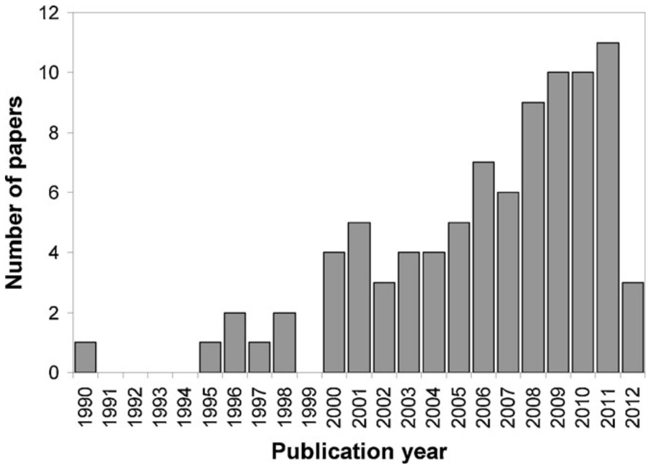

Fig. 1. Number of research papers reported in the references of this review, dealing with gold catalysts for VOC combustion, vs. year of publication (data of 2012 refer only to first two months).

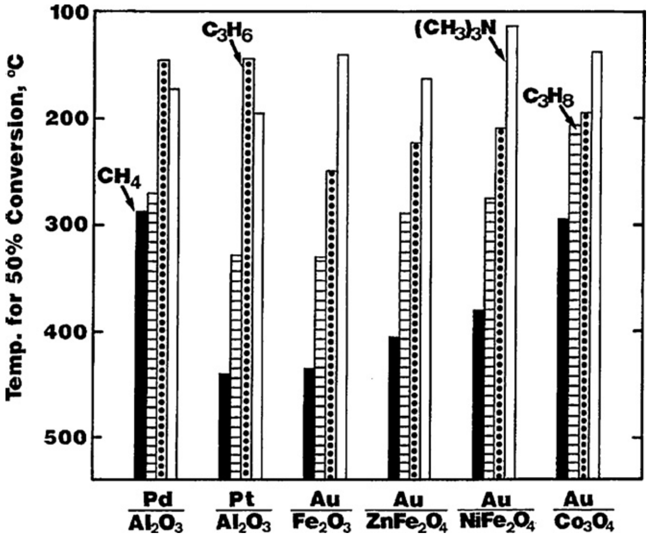

Fig. 2. Temperature for 50% conversion in the catalytic combustion of hydrocarbons. Pd/Al_2O_3 and Pt/Al_2O_3, metal loadings 1 wt%, prepared by impregnation. Au catalysts: Au/metal oxide = 1/19, prepared by coprecipitation, calcined in air at 400 °C. Concentration of reactant gases in air: CH_4 0.25 vol.%, C_3H_8 and C_3H_6 0.1 vol.%, $(CH_3)_3N$ 0.05 vol.%. Space velocity: $2 \times 10^4\ h^{-1}\ ml\ g_{cat}^{-1}$.

Taken from Ref. [32].

role of each single factor, the relationships existing among some of them and the possibility of a co-operative synergistic effect make really hard to derive a general trend.

Certainly, among all above cited factors, several authors ascribe to the support a fundamental role in addressing the catalytic performance of supported gold catalysts towards VOC oxidation. In general, the support has been reported to participate in the control of the amount of gold anchored on the surface as well as the size and the shape of gold particles. Moreover the support has been claimed to directly take part to the reaction pathway when reducible oxides are considered. In this case, in fact, the resulting anion vacancies (surface lattice oxygens) close to gold particles have been suggested as the sites of oxygen adsorption and activation.

As it can be seen in Table 1, which summarizes the main data of research papers on VOC combustion over Au catalysts discussed in this review, a large number of metal oxides (single or mixed) were reported in the literature as support for gold. The first studies on the support effect towards catalytic combustion of VOC were carried out by research groups of Waters et al. [29] and Haruta [32]. Both of them reported Au/Co_3O_4 as the most active system in the combustion of light alkanes compared to other Au/metal oxides. Waters et al. [29] found the following order of activity in the low temperature combustion of methane: $Au/Co_3O_4 > Au/NiO > Au/MnO_x > Au/Fe_2O_3 \gg Au/CeO_x$. On the basis of XPS data, the above activity order, apart from Au/NiO catalyst, was related to the oxidation degree of gold in the oxidized state (position of the $4f_{7/2}$ Au band), providing active sites for oxygen activation at low temperature. Therefore the role of the support was supposed to be essentially that of influencing the gold oxidation state, contributing directly to the measured activity only at higher temperatures. It must be underlined that the validity of these assumptions, as stated by the same authors, had to be proved with other key data, not available at that time, such as Au content and size as well as surface area of catalysts. Haruta [32] found that Au/Co_3O_4 is more active than Au/Fe_2O_3, $Au/NiFe_2O_4$ and $Au/ZnFe_2O_4$ for the complete oxidation of saturated (CH_4 and C_3H_8) and unsaturated (C_3H_6) hydrocarbons (Fig. 2). Notwithstanding the author stated that catalytic activity is markedly dependent on both metal oxide and particle size of Au, no explanation on the role of the support was provided. However, in the same paper it was reported that $Au/\alpha Fe_2O_3$ and $Au/NiFe_2O_4$ were, instead, the most active for the oxidative decomposition of trimethylamine, probably due to a stronger affinity of iron oxides towards nitrogen compounds. Therefore Haruta implicitly suggested that the support is somehow involved in the adsorption/activation of the VOC molecule.

An interesting point of view on the role of the support was provided by the work of Andreeva et al. [33,34], who investigated the total oxidation of benzene over Au/V_2O_5 on titania and zirconia. The occurrence of a synergistic effect between gold and vanadia, more pronounced on titania than on zirconia, was claimed to explain the higher activity of $Au/V_2O_5/TiO_2$ compared to $Au/V_2O_5/ZrO_2$ (Fig. 3). The authors suggested [34] that activation of oxygen occurred on finely divided gold nanoparticles while benzene was activated on vanadium oxide surface. In the presence of gold, predominantly polyvanadate structures were formed on the surface, being more active in the benzene oxidation than monovanadate species and bulk V_2O_5. The deposition of gold lead to a lengthening of the V=O bond (higher vanadium oxide reducibility, with easier $V^{5+} \rightarrow V^{3+}$ reduction step) and to a higher electron delocalization.

The participation of the support lattice oxygens in the reaction pathway of the VOC combustion over oxide supported gold catalysts was pointed out for the first time by the research group of Scirè and co-workers [35–37], who investigated the total oxida-

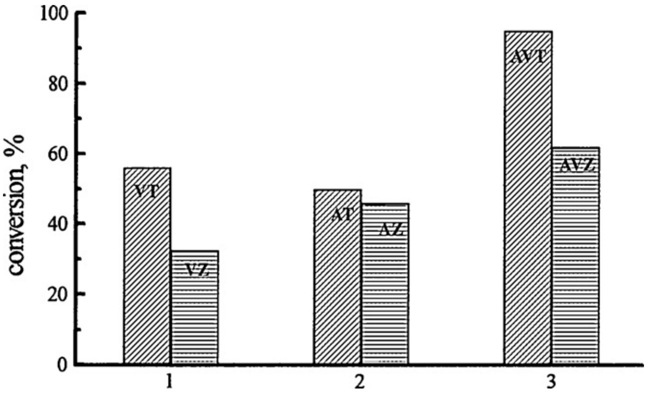

Fig. 3. Catalytic activity in complete benzene conversion at 250 °C with molecular oxygen: 1, vanadia supported samples; 2, gold supported samples; 3, gold–vanadia supported samples.

Taken from Ref. [34].

Table 1
Main data of research papers on VOC combustion over Au catalysts reported in this review.

First Author (publ. year)	Ref. no.	Catalyst	Preparation method	Au (wt%)	VOC type	VOC conc.	Pre-treatment
Aida (1990)	[122]	Au on Co_3O_4, Al_2O_3, Fe_2O_3, Cr_2O_3, SnO_2	CP	5, 6.4, ~11	CH_3Cl, CCl_2F_2	1 vol.%	400 °C air
		Au/SiO_2	IM	14.7			
Albonetti (2008)	[116]	Au/FeO_x/TiO_2	CDP	0.6–6	Toluene, o-DCB	1400 ppm	400 °C N_2, H_2, air
Albonetti (2010)	[114]	Au/FeO_x/TiO_2	CDP	2–6	Toluene	1400 ppm	400 °C N_2
Andreeva (1998)	[33]	Au/TiO_2, Au/V_2O_5/TiO_2, Au/ZrO_2, Au/V_2O_5/ZrO_2	DP	–	Benzene	0.019 mol m^{-3}	400 °C air
Andreeva (2001)	[34]	Au/TiO_2, Au/V_2O_5/TiO_2, Au/ZrO_2, Au/V_2O_5/ZrO_2	DP	3	Benzene	0.019 mol m^{-3}	400 °C air
Andreeva (2003)	[44]	Au/V_2O_5/CeO_2	DP	3	Benzene	4.2 g m^{-3}	400 °C air
Andreeva (2004)	[46]	Au/V_2O_5/CeO_2–Al_2O_3	DP	2.3–3	Benzene	3.8 g m^{-3}	400 °C air
Andreeva (2006)	[45]	Au/CeO_2, Au/MoO_x/CeO_2, Au/MoO_x/CeO_2–Al_2O_3	DP	2.8–3	Benzene	4.2 g m^{-3}	400 °C air
Bastos (2012)	[84]	Exotemplated Au/MnO_2 and Au/CeO_2	IM	0.75–1.08	Ethylacetate, ethanol, toluene	1 g C m^{-3}	None
Blick (1998)	[86]	Au/MgO	IM	0.04–15	Methane	46%	Calcined 800 °C
Bonelli (2011)	[94]	Au/FeO_x/CeO_2	CDP	1–2.7	CH_3OH, toluene	0.7% CH_3OH, 0.14% toluene	400 °C N_2
Bonelli (2011)	[93]	Au/FeO_x/SBA-15	CDP	1.9–2	Methanol	2600 ppm	400 °C N_2
Cellier (2007)	[89]	Au/TiO_2, Au/MnO_2	DP, AA	1.3–2.6	n-Hexane	125 ppm	300 °C H_2, O_2, air
Centeno (2002)	[41]	Au/CeO_2/Al_2O_3 Au/Al_2O_3	DP	1.46–2.5	n-Hexane, benzene 2-propanol	120, 250, 500 ppm	Calcined 500 °C
Centeno (2005)	[42]	Au/TiO_xN_y, Au/TiO_2	DP	0.75–2.94	n-Hexane, benzene, 2-propanol	120, 250, 500 ppm	Calcined 300 or 500 °C
Chen (1996)	[31]	Au/Co_3O_4	CP	0.2–10	CH_2Cl_2	500 ppm	Calcined 350 °C
Chen (2008)	[108]	Au on ZrO_2, SiO_2, CeO_2, Fe_2O_3	IM	2.24–3.10	HCHO	100 ppm	Dried 80 °C
Choudhary (2008)	[57]	Au on Fe_2O_3, Al_2O_3, Co_3O_4, MnO_2, CeO_2, MgO, Ga_2O_3 and TiO_2	HDP	2.48–7.46	CH_4	1 vol.%	400 °C air
Delannoy (2010)	[81]	Au/TiO_2, Au/CeO_2, Au/Al_2O_3	HDP	0.02–4	C_3H_6	1200 ppm	300 °C H_2, 500 °C O_2(9%)/He
Della Pina (2006)	[113]	Au/CeO_2, Au/ZrO_2, Au/$Ce_{0.5}Zr_{0.5}O_2$	IM	1	Hexane, benzene, chlorobenzene	–	100 °C air
Deng (2010)	[95]	Au/Al_2O_3	DP	1.6–5	Methanol, ethanol, 2-propanol, n-propanol	2–79.8 g m^{-3}	300 °C N_2, H_2, O_2
Dominguez (2007)	[96]	Au/Al_2O_3 and Au/CeO_2 on ceramic foams	IE	0.0015–0.06	2-Propanol	12,000 ppm	500 °C O_2(21%)/He
Gasior 2004	[78]	Au/MO_x (M = Mg, Si, Sn, Fe, Ti, Ce)	DP	1	C_3H_8, C_3H_6	7.1% (C_3H_8), 10% (C_3H_6)	400 °C air
Gennequin (2007)	[79]	Au/CeO_2–TiO_2	HDP	2.67–3.48	C_3H_6	6000 ppm	400 °C air
Gennequin (2009)	[80]	Au/CeO_2–TiO_2, Au/CeO_2–TiO_2–ZrO_2	HDP	2.64–3.30	C_3H_6, toluene	6000 ppm (C_3H_6), 1000 ppm (toluene)	400 °C air
Gluhoi (2004)	[47]	Au/MO_x/Al_2O_3 (M: Li, Rb, Ce, Mn, Zr)	HDP	3.2–4.7	C_3H_6	4 vol.%	–
Gluhoi (2005)	[48]	Au/MO_x/Al_2O_3 (M: Li, Rb, Mg, Ba)	HDP	3.5–4.2	C_3H_6	–	300 °C H_2(4%)/He
Gluhoi (2005)	[49]	Au/MO_x/Al_2O_3 (M: Ce, Mn, Co, Fe)	HDP	4.1–5.5	C_3H_6	4 vol.%	300 °C H_2(4%)/He
Gluhoi (2006)	[71]	Au/CuO/Al_2O_3	HDP	4–7.4	C_3H_6, C_3H_8	4 vol.%	300 °C H_2(4%)/He
Gluhoi (2007)	[50]	Au/MO_x/Al_2O_3 (MO_x = alkali, TM, ceria)	HDP	3.2–4.5	CH_4, C_3H_8	4 vol.%	–
Grisel (2000)	[38]	Au/Al_2O_3	DP; HDP, IM	2.6–5.1	CH_4	0.8 vol.%	300 °C H_2
Grisel (2001)	[39]	Au/MO_x/Al_2O_3 (M: Cr, Mn, Fe, Co, Ni, Cu and Zn)	HDP	5	CH_4	0.8 vol.%	300 °C H_2, 400 °C O_2
Grisel (2002)	[40]	Au/Al_2O_3, Au/CeO_x/Al_2O_3	HDP	5	C_3H_6	–	–

Table 1 (*Continued*)

First Author (publ. year)	Ref. no.	Catalyst	Preparation method	Au (wt%)	VOC type	VOC conc.	Pre-treatment
Haruta (1996)	[30]	Au/αFe_2O_3	DP, CP, IM	1	Methanol, HCHO, HCOOH	0.5 vol.%	400 or 300 °C air
Haruta (1997)	[32]	Au/Co_3O_4, Au/Fe_2O_3, Au/$NiFe_2O_4$, Au/$ZnFe_2O_4$	CP	5	CH_4, C_3H_6, C_3H_8, $(CH_3)_3N$	0.25 vol.% (CH_4), 0.1 vol.% (C_3H_6, C_3H_8), 0.05 vol.% ($(CH_3)_3N$)	400 °C air
Hong (2010)	[107]	Au/ZrO_2	HDP	0.25–4.0	HCHO	3000 ppm	200–450 °C air
Hosseini (2007)	[73]	Au–Pd/TiO_2 mesoporous	DP	1	C_3H_6, toluene	1000 ppm	400 °C air + 200 °C H_2
Hosseini (2009)	[145]	Au–Pd/TiO_2/ZrO_2	DP	1	C_3H_6, toluene	1000 ppm	400 °C air + 200 °C H_2
Idakiev (2003)	[61]	Au/V_2O_5 on mesoporous TiO_2 and ZrO_2	DP	5	Benzene	4.2 g m^{-3}	250 or 400 °C air
Ivanova (2006)	[72]	Au/Al_2O_3	DAE	2	CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_3H_8	1500 ppm	300 °C air
Jia (2005)	[99]	Au/CeO_2, Au/TiO_2	DP	2	HCHO	–	200 °C air
Jia (2008)	[54]	Au/CeO_2	DP	1	HCHO	3 vol.%	300 °C air
Kim (2004)	[70]	Au/TiO_2 e Pt/Al_2O_3 mixtures	DP	1.93	C_3H_6	400 ppm	Calcined 350 °C
Kim (2009)	[117]	Pt–Au on ZnO/Al_2O_3	IM	2.1	Toluene	1.8 vol.%	400–700 °C air, 400-600 °C H_2
Kucherov (2009)	[126]	Au, Au–Pd, Au/Rh on TiO_2, H-ZSM5, MCM-41, H-beta	DP (TiO_2), IE (zeolites)	1–4	DMDS	1000 ppm	280–300 °C H_2(10%)/Ar
Lai (2006)	[56]	Au/CeO_2	DP	0.7–1.5	Benzene	0.5 vol.%	Calcined 300–700 °C
Lakshmanan (2010)	[82]	Au/CeO_2–Al_2O_3	HDP	0.88–0.97	C_3H_6	1200 ppm	500 °C O_2(9%)/He, 300 °C H_2
Lamallem (2008)	[136]	Au/$Ce_{0.3}Ti_{0.7}O_2$	IM, DP, HDP	1.47–3.30	C_3H_6	6000 ppm	400 °C air
Lamallem (2009)	[53]	Au/$Ce_{0.3}Ti_{0.7}O_2$	HDP	3	C_3H_6	6000 ppm	400–600 °C air
Li (2008)	[101]	Au/iron oxide	CP	0.73–7.1	HCHO	6.25 mg m^{-3}	Dried 65 °C
Li (2010)	[115]	Au/CeO_2	DP, CP, MCD	0.9–3	Toluene	1000 ppm	400 °C air
Liu (2012)	[103]	Macroporous Au/CeO_2	ADP	0.56	HCHO	0.06 vol.%	Dried 60 °C
Liu (2008)	[97]	Au/CeO_2, Au/Fe_2O_3, Au/TiO_2, Au/Al_2O_3	DP	1.4–1.7	2-Propanol	0.05%	200–500 °C air
Ma (2011)	[106]	Mesoporous Au/CeO_2, Au/Co_3O_4 Au/Co_3O_4–CeO_2	Nanocasting	1	HCHO	200 ppm	Calcined 300 °C
Mellor (2002)	[77]	Au/CoOx/Rh/ZnO/BaO on zirconia–ceria or titania	DP	1	Gasoline and diesel exhausted gas	350 ppm C_3H_8 + 350 ppm C_3H_6 (gasoline), 75 ppm C_3H_8 + 25 ppm C_3H_6 (diesel)	450 °C O_2(5%)
Miao (2001)	[144]	Au–Pt/Co_3O_4, Au–Pd/Co_3O_4	CP	0.2–5	Methane	1%	400 °C air
Minico (2000)	[35]	Au/iron oxide	CP	0.9–8.2	Methanol, ethanol, 2-propanol, acetone, toluene	0.7 vol.%	300 °C O_2(10%)/He
Minico (2001)	[37]	Au/iron oxide	CP	8.2	Methanol, ethanol, 2-propanol, acetone, toluene	0.7 vol.%	200–450 °C O_2(10%)/He
Nedyalkova (2009)	[111]	Au/CeO_2, Au/TiO_2, Au/MoO_x/CeO_2 Au/MoO_x/TiO_2, Au/VO_x/CeO_2, Au/VO_x/TiO_2	DP	3	Benzene	4.2 g m^{-3}	400 °C air
Okumura (2003)	[123]	Multicomponent Au/Fe_2O_3–Pt/SnO_2–Ir/La_2O_3	DP	2	Trymethylamine, o-chlorophenol, dioxine derivatives	1 vol.% (Trymethylamine, o-chlorophenol)	400 °C air
Ousmane (2011)	[58]	Au/CeO_2, Au/TiO_2, Au/Al_2O_3, Au/CeO_2–Al_2O_3	DP	1.1–1.3	C_3H_6, toluene	1000 ppm	Dried 120 °C
Ousmane (2011)	[59]	Au/TiO_2, Au/ZnO, Au/Al_2O_3	DP	1	C_3H_6	1000 ppm	120 °C H_2(5%)/N_2
Petrov (2000)	[76]	Au/mixed oxides (ceria and titania)	CP	0.2–2.5	Exhausted gases, CH_4, methanol	700 ppm HC, 0.25–2.5 vol.% CH_4, 10.5 vol.% methanol	Calcined 450 °C
Ruth (2000)	[69]	Au/TiO_2	DP	1	C_3H_8	0.4%	400 °C air

Table 1 (*Continued*)

First Author (publ. year)	Ref. no.	Catalyst	Preparation method	Au (wt%)	VOC type	VOC conc.	Pre-treatment
Santos (2010)	[74]	Au/TiO_2	IM, LPRD	0.5–0.9	Ethanol, toluene	4 g C m^{-3}	Dried 100 °C (LPRD), calcined 500 °C(IMP)
Scirè (2001)	[36]	Au/Fe_2O_3	CP	3.5	Methanol, 2-propanol toluene	0.7 vol.%	300 °C O_2(10%)/He
Scirè (2003)	[43]	Au/CeO_2	DP, CP	4.7–5	Methanol, 2-propanol, toluene	0.7 vol.%	C 450 °C O_2(10%)/He
Scirè (2010)	[98]	Au/CeO_2	DP, CP	4.3–4.6	Methanol, acetone, toluene	0.7 vol.%	C 300 °C O_2(10%)/He
Shen (2008)	[102]	Au/CeO_2	CP	<0.85	HCHO	0.06 vol.%	Calcined 300–700 °C
Sobczak (2008)	[92]	AuMCM-41, AuVMCM-41, AuNbMCM-41, AuVNbMCM-41	CP	1	Methanol	4 vol.%	400 °C He
Solsona (2006)	[51]	Au on CoO_x, MnO_x, CuO, Fe_2O_3, CeO_2, TiO_2	CP, DP, IM	3–5	CH_4, C_2H_6, C_3H_8	0.5 vol.%	400 °C air
Solsona (2009)	[143]	Au/CoO_x	CP	2.7	C_3H_8	0.5 vol.%	C 425 °C air
Solsona (2009)	[55]	Au/CeO_2	DP	3	Naphtalene	100 ppm	C 400 °C air
Solsona (2011)	[142]	Au/hopcalite	CP	1–6	C_3H_8	5000 ppm	300–500 °C air
Solsona (2011)	[52]	Au/Co_3O_4 with high surface area	DP	1–6	C_3H_8, toluene	8000 ppm	250 °C air
Solsona (2012)	[146]	Au/Co-UVM-7	DP	0.4–1.21	C_3H_8, toluene	1000 ppm	500 °C air
Walther (2009)	[87]	Au/TiO_2, Au/ZnO, Au/Al_2O_3	DP	0.84–1.02	CH_4	33.3–80 vol.%	React. mixture 100 °C
Wang (2006)	[90]	Au/iron oxide aerogels	Sol–gel	1.2–5	Methanol	2 vol.%	265–500 °C O_2(50%)/N_2
Waters (1995)	[29]	Au/Co_3O_4, Au/NiO, Au/MnO_x, Au/Fe_2O_3, Au/CeO_x	CP	5	CH_4	1.48 vol.%	200 °C O_2
Wu (2011)	[60]	Au/ZnO, Au/MgO, Au/Al_2O_3	CDP	1.25–1.69	Benzene, toluene, p-xylene	2.1–0.4 g m^{-3}	Calcined air
Wu (2011)	[119]	Au/Co_3O_4, Au/MgO, Au/Al_2O_3	CDP	1.40–1.69	Toluene, p-xylene	0.6 g m^{-3} toluene, 0.4 g m^{-3} p-xylene	Calcined air
Yang (2008)	[112]	Au/CeO_2, Au/V_2O_5/CeO_2	DP	0.74–4.23	Benzene	4.1 g m^{-3}	Calcined 400 °C
Ying (2010)	[88]	Au/CeO_2	DP	0.4–0.5	Isobutane	1 vol.%	100–500 °C air
Ying (2011)	[64]	Mesoporous Au/CeO_2	ADP	1.1–1.7	Benzene	0.5 vol.%	Calcined 300 °C
Zhang (2007)	[100]	Pt, Rh, Pd e Au su TiO_2	IM	1	HCHO	100 ppm	Calcined 400 °C
Zhang (2009)	[63]	Macroporous Au/CeO_2	ADP	1–4	HCHO	0.06 vol.%	Calcined 60–400 °C
Zhang (2010)	[62]	Mesoporous Au/ZrO_2	DP	0.06–0.85	HCHO	90 mg m^{-3}	Dried 60 °C air

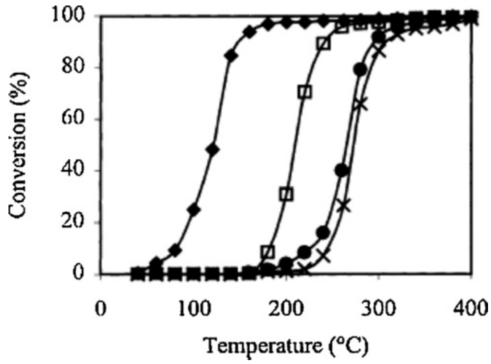

Fig. 4. Methanol conversion as a function of reaction temperature on Au/Fe_2O_3 (♦), Ag/Fe_2O_3(□), Cu/Fe_2O_3 (●) and Fe_2O_3 (×) samples.
Taken from Ref. [36].

tion of methanol, 2-propanol, acetone and toluene over Au/iron oxide. In a first paper [35] gold was found to strongly enhance the rate of VOC oxidation with an effect, stronger for alcohols than for acetone and toluene, related to the interaction degree between the organic substrate and the oxide surface. The high activity of Au/iron oxide catalysts was attributed to the capacity of highly dispersed gold to weaken the Fe–O bond thus increasing the mobility of the lattice oxygen, supposed to be involved in the reaction through a Mars–van Krevelen (MKV) mechanism. Interestingly in a comparative study among IB metals (Au, Ag, Cu) supported on iron oxide [36] the authors reported that gold was the most active IB metal in promoting the VOC combustion (Fig. 4), putting in relation the activity with the extent of iron oxide lattice distortion. The elucidation between the role played by gold and that of the support was specified in another paper where the influence of catalyst pretreatment toward the VOC combustion over Au/iron oxide was investigated [37]. It was inferred that $Au^{\delta+}$ and ferrihydrite are more active species in the VOC combustion compared to Au^0 and hematite respectively.

The role of the support, strictly associated to that of the Au size, was also claimed by Grisel et al. in the methane oxidation over Au/Al_2O_3 [38] and Au/MO_x/Al_2O_3 (M = Cr, Mn, Fe, Co, Ni, Cu, Zn) [39] catalysts. They suggested that on alumina, non reducible support, CH_4 is dissociatively adsorbed on Au or the Au/Al_2O_3 perimeter and reacts with active O originating from dissociative adsorption of O_2 near the Au/Al_2O_3 perimeter or dehydroxylation of the Al_2O_3 surface at high temperatures. On Au/MO_x/Al_2O_3 catalysts, the activity was found to depend on both the Au size (favoured by small Au particles) and the identity of the MO_x, being in the order: $CuO_x > MnO_x > CrO_x > FeO_x > CoO_x > NiO_x > ZnO_x$ (Fig. 5). With these multicomponent systems the reaction was supposed to take place at the Au/MO_x perimeter, with CH_4 being adsorbed on Au, and MO_x being the supplier of oxygen. The existence of a synergistic effect between gold and the partially reducible support (ceria) was also reported by the same authors on Au/CeO_2/Al_2O_3 [40] in the low temperature combustion of propene. Centeno et al. [41] also studied the oxidation of some representative VOC (*n*-hexane, benzene and 2-propanol) over Au/Al_2O_3 and Au/CeO_2/Al_2O_3 catalysts. They confirmed that the presence of gold enhances the rate of VOC oxidation, gold supported on CeO_2/Al_2O_3 showing considerably higher activity than Au on pure alumina. The authors concluded that there is a mutual action between ceria and gold, ceria enhancing the fixation of gold, its dispersion and oxidation state, gold increasing the mobility of the ceria lattice oxygen. The key role of the support was pointed out by the same authors [42] comparing results of Au/TiO_xN_y (titanium oxynitride) and Au/TiO_2 catalysts. It was concluded that the combustion of VOC on these catalysts depends on the nature of the support.

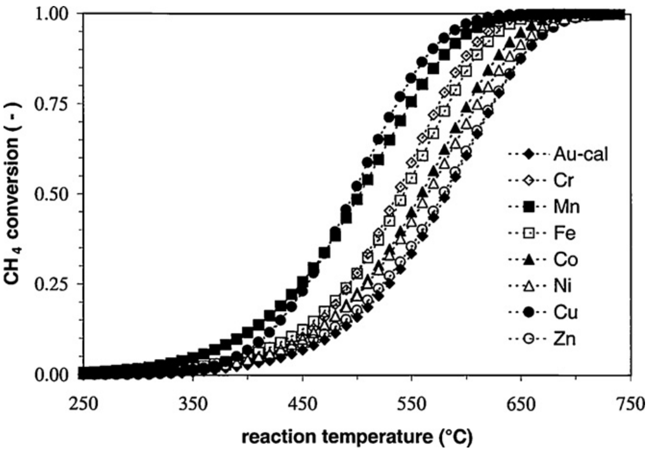

Fig. 5. CH_4 conversion versus temperature (°C) over Au/Al_2O_3 calcined at 400 °C (Au-cal) and Au/MO_x/Al_2O_3 (M = Cr, Mn, Fe, Co, Ni, Cu, and Zn); sigmoidal fits (—).
Taken from Ref. [39].

The use of Au/ceria catalysts in the catalytic combustion of some representative VOC (2-propanol, methanol and toluene) was addressed by Scirè et al. [43]. They investigated Au/ceria catalysts prepared by coprecipitation (CP) and deposition–precipitation (DP) and found that gold enhances the activity of ceria, being more effective when gold is added by DP. It was demonstrated that DP catalysts contain a higher amount of surface gold particles, which are also smaller than those found in CP samples. On the basis of TPR experiments they suggested that there is a direct relationship between surface oxygen mobility of the gold/ceria system and its catalytic activity towards the oxidation of VOC. It was proposed that small gold nanoparticles weaken the surface Ce–O bonds adjacent to Au atoms, thus enhancing the reactivity of ceria lattice oxygens. Analogously to Au/iron oxide system, a MKV mechanism was proposed also for Au/ceria catalysts.

The use of a high reducible support as ceria for Au/V_2O_5 and Au/MoO_x systems was also reported by Andreeva et al. [44,45]. A strong interaction between gold/vanadia (or gold/molybdena) and ceria was proved, with a synergic effect leading to smaller gold and ceria nanoparticles and therefore higher active oxygen species compared to the corresponding Au/ceria catalysts. It was suggested that gold enhances the reducibility/reactivity of both VO_x (or MoO_x) and ceria surface species. In any case the catalytic performance were attributed to a great extent to the nature of ceria, as a consequence of the formation of more coordinatively unsaturated sites on the surface and the occurrence of an electron density transfer from the support to the small gold particles. The importance of surface oxygens of ceria in the oxidation activity was also pointed out over Au/V_2O_5 supported on mixed ceria–alumina systems [46]. It was found that the benzene oxidation activity on mixed ceria–alumina was lower than that observed on the corresponding catalysts on pure ceria (Fig. 6). The presence of a non-reducible oxide was therefore detrimental to the activity enhancing only the stability of the catalytic system by preventing both gold and ceria agglomeration.

Gluhoi et al. [47–49] investigated the role of different oxide additives on the propene total oxidation activity of Au/Al_2O_3 reporting two distinct behaviours as a function of the type of oxide. The beneficial effect of alkali (earth) metal oxides (MO_x, with M = Li, Rb, Mg, or Ba) [47,48] was attributed to a structural promotion of these additives, which induce a decrease in the size of Au^0 particles, assumed to be the active species, and stabilize them against sintering. No direct participation of the MO_x was, in fact, observed with no change in the activation energy of the process. A different explanation was instead proposed when MO_x was a reducible

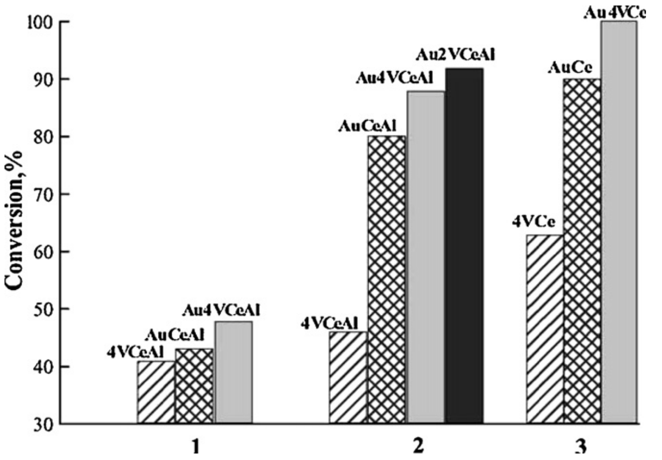

Fig. 6. Catalytic activity in CBO at 200 °C of the catalysts on (1) ceria:alumina (1:4); (2) ceria:alumina (1:1); (3) pure ceria.

Taken from Ref. [46].

transition metal oxide (M = Ce, Mn, Co or Fe) [49]. In this latter case, in fact, the interfacial effect created by the metal-support interaction was considered more important than the Au size. Transition metal oxides (ceria was the most active) were supposed to act as both structural and chemical promoters, stabilizing gold particles against sintering and providing active oxygen for the reaction. To analogous results came the same research group [50] investigating the performance of MO_x promoted Au/Al_2O_3 catalysts (M = alkali (earth), transition metal and cerium) in the combustion of saturated hydrocarbons (methane and propane). The addition of various MO_x to Au/Al_2O_3 improved both methane and propane oxidation activity. In the case of methane, the most efficient promoters were FeO_x and MnO_x, whilst for C_3H_8 a direct relationship was found between catalytic performance and average size of gold particles only with alkali (earth) metal oxide containing catalysts. The effect of Au size became less important when additives were transition metal oxides and ceria. It was proposed that the C–H bond activation, considered the crucial step in the oxidation of these hydrocarbons, is related to the presence of Au (decrease in the activation energy), whereas the availability of appropriate oxygen species is connected to the identity of the MO_x. The role of the alkali (earth) metal oxides was then related to the stabilization of gold nanoparticles, whereas transition metal oxide and ceria may be involved in oxygen activation.

A direct comparison among the performance of Au catalysts supported on a series of metal oxides such as CoO_x, MnO_x, CuO_x, Fe_2O_3, CeO_2 and TiO_2, towards the catalytic combustion of light hydrocarbons (methane, ethane and propane) was carried out by Solsona et al. [51] (Fig. 7). A correlation between oxide reducibility and catalytic activity was found and attributed to the enhancement of the redox properties of the oxide induced by gold due to the introduction of surface defects at the gold/oxide interface, involved in alkane activation. This was also confirmed by the same group [52] in a more recent study on the deep oxidation of propane and toluene on gold on high surface area cobalt oxide (Fig. 8).

Lamallem et al. [53] pointed out the importance of the support toward the VOC combustion, reporting that calcination of the support (Ce–Ti oxide) at 400 °C gave more active catalysts compared to 500 and 600 °C treatment, due to a higher surface area and then higher amount of active oxygens of the support treated at lower temperature. The role of the support preparation conditions was also pointed out by Jia et al. [54] on Au/CeO_2. The authors concluded that the addition of a dispersant (PEG6000) and the use of microwave in the preparation process improve the catalytic activity (HCHO combustion) of Au/CeO_2 catalysts, being beneficial in enhancing the interaction between the support and gold species.

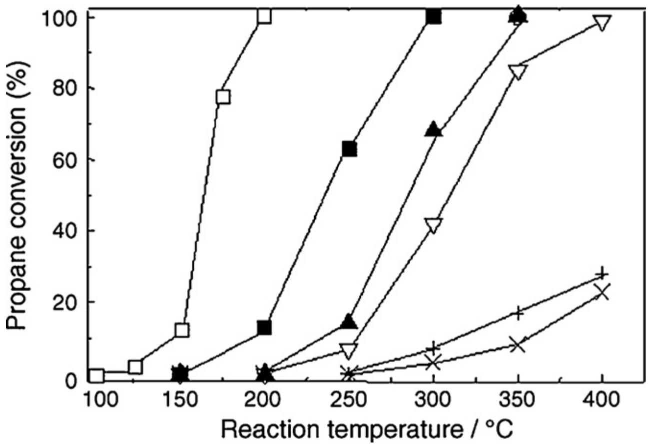

Fig. 7. Evolution of propane conversion with reaction temperature for propane combustion over gold-containing catalysts. Symbols: (□) Au/CoO_x, (■) Au/MnO_x, (▲) Au/CuO, (▽) Au/Fe_2O_3, (×) Au/CeO_2 and (+) Au/TiO_2.

Taken from Ref. [51].

The predominance of the support characteristics over gold ones in determining the combustion activity of gold/ceria catalysts was described by Solsona et al. [55] in the naphthalene total oxidation. On the basis of XRD and DRIFT data they stated that gold did not participate directly in the oxidation of naphthalene to CO_2, changes in the activity of the Au-promoted ceria samples being due to variations in the properties of the ceria, providing active sites for the reaction. They proposed that active sites include surface hydroxyl groups, where naphthalene can adsorb and react, and lattice oxygen sites, involved through a MVK mechanism. This should explain the reason why Au/CeO_2 was less active that the bare ceria. The fundamental role of the ceria structure on the activity of gold/ceria was also pointed out by Lai et al. [56] in the benzene deep oxidation. They stated that the presence of high surface area ceria, on which activation of benzene occurs, is determining for the

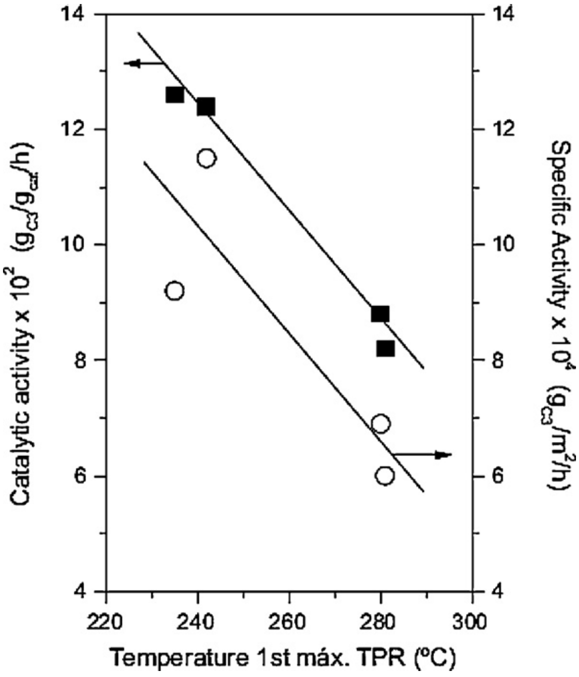

Fig. 8. Relationship between the temperature of the maximum of the first band in the TPR profile with the catalytic activity in the propane oxidation (reaction temperature = 200 °C).

Taken from Ref. [52].

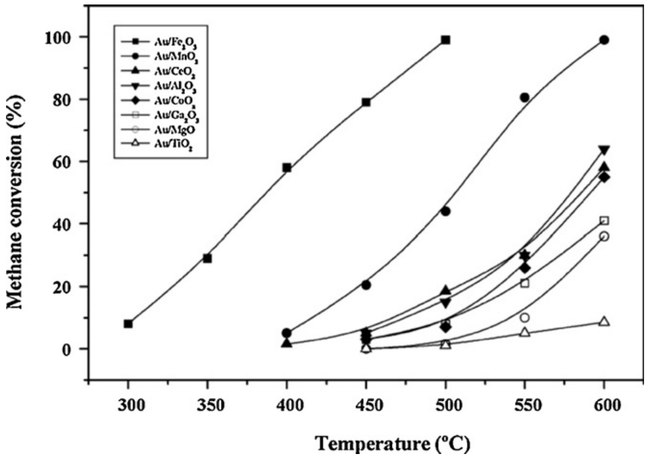

Fig. 9. Influence of the catalyst support in the supported gold catalysts (prepared by the HDP method) on the methane combustion at different temperatures (GHSV = 51,000 h^{-1}).

Taken from Ref. [57].

oxidation activity, the function of gold being instead secondary, aiding the dissociation of the surface oxygen. Interestingly a different behaviour was found in the CO oxidation for which the activation of CO on nanogold particles was instead essential for the activity of gold/ceria catalysts.

Choudhary et al. [57] confirmed the importance of the support in the catalytic combustion of methane over Au/oxides catalysts. They found that gold supported on reducible oxides (Fe_2O_3 and MnO_2) exhibit higher catalytic activity than catalysts on non-reducible or difficult to reduce metal oxides (Al_2O_3, MgO, Ga_2O_3, TiO_2) (Fig. 9). Among all systems Au/Fe_2O_3 showed the best performance, notwithstanding it exhibited bigger Au particles (8.5 nm). They concluded that the methane combustion is essentially controlled by the Au-support interactions, which affect the electronic properties of supported gold.

Ousmane et al. [58] compared the results of Au/CeO_2, Au/TiO_2, Au/Al_2O_3 and Au/CeO_2–Al_2O_3 in the total oxidation of propene and toluene. They found that Au/CeO_2 was the most active system (Fig. 10) and reported that the nature of the support and its point of zero charge (PZC) influence the amount of deposited gold, resulted to be the highest on ceria and titania having the lowest PZC values. Au particle size and catalytic performance were assumed to be strongly dependent on the gold-support interaction, which is higher when reducible oxides (ceria, titania) are used, being the main requisite for improving gold dispersion and achieving high oxidation activity. This was also confirmed by the same group [59] in another work where Au catalysts supported on three mesoporous oxides (TiO_2, ZnO and Al_2O_3) were tested in the propene deep oxidation and Au/TiO_2 was found to be the best performing one. Wu et al. also compared the catalytic performance of Au catalysts supported on three oxides (ZnO, Al_2O_3 and MgO) towards the deep oxidation of benzene, toluene and xylenes (BTX) [60]. The much higher activity of Au/ZnO compared to Au/Al_2O_3 and Au/MgO was attributed to strong metal-oxide interaction effects between Au and ZnO, originated from the very small difference of lattice parameter between Au {1 1 1} and ZnO {1 0 1} atomic planes.

An interesting perspective, stressing the importance of the support properties, was provided by some works in which nanostructured mesoporous oxides, with high surface area and uniform pore size, were used as support of gold. The first investigation was carried out by Idakiev et al. [61] over Au/V_2O_5 supported on mesoporous titania and zirconia in the benzene combustion. They found that gold/mesoporous zirconia had high activity, comparable to that of gold–vanadia/mesoporous zirconia. The interesting reactivity of the gold/mesoporous zirconia sample, in the absence of vanadia promotion, was attributed to the specific properties of the mesoporous material and related to the enhanced electron density transfer from mesoporous zirconia to small gold particles. Superior catalytic performance of Au/mesoporous ZrO_2 (surface area of 447 $m^2\,g^{-1}$) compared to the conventional Au/ZrO_2, was also reported by Zhang et al. [62] in the HCHO combustion. This was related to the better dispersion of gold on the mesoporous oxide surface and explained on the basis of a reaction mechanism involving adsorbed formate species on gold and oxygen molecules on the lattice vacancies of the support. A positive influence of an ordered structure of the ceria (3DOM, i.e. three dimensional ordered macroporous ceria with adjustable pore sizes, from 80 to 280 nm, and interconnected networks of spherical voids) on the performance of Au/CeO_2 catalysts towards the HCHO combustion was also reported by Zhang et al. [63]. In particular, catalysts with 80 nm pores displayed the highest catalytic activity due to the highest surface area (active sites) and the optimal pore size leading to an uniform distribution of small Au nanoparticles. A higher activity and stability of gold catalysts supported on a mesoporous ceria, prepared using MCM-48 as hard template, compared to the corresponding DP catalyst, was reported in benzene oxidation by Ying et al. [64]. They explained the better performance with the presence on the mesoporous sample of smaller ceria particles, with a higher proportion of reducible surface oxygens, also providing more sites for gold anchoring on the surface, leading to a higher gold dispersion (smaller Au particles). Moreover, the strong interaction between gold and ceria on the mesoporous Au/CeO_2 prevented

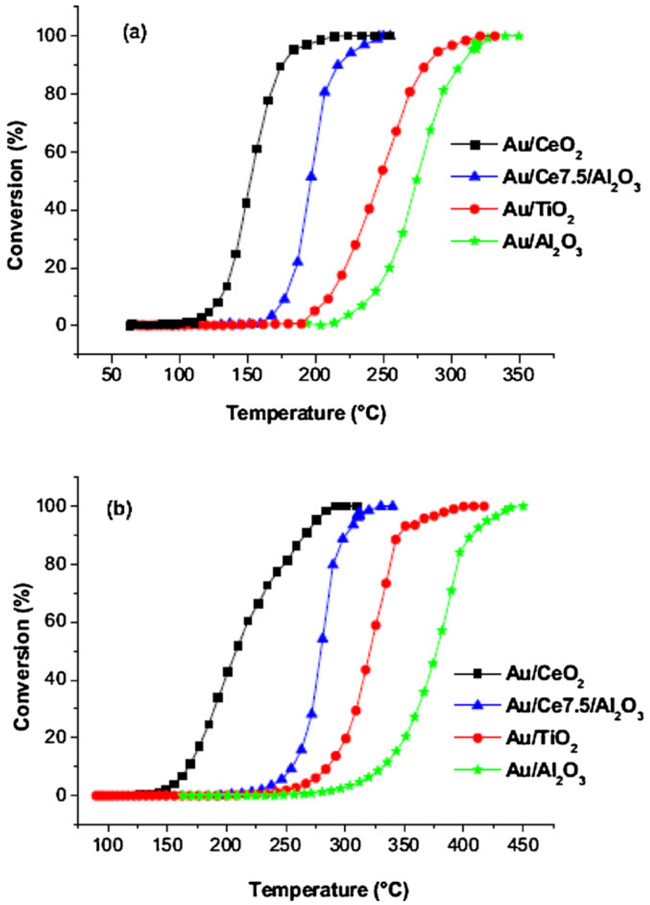

Fig. 10. Conversion (%) of (a) propene and (b) toluene versus temperature over gold supported catalyst (third catalytic run).

Taken from Ref. [58].

gold sintering, thus explaining the high stability of the mesoporous samples.

3. Effect of the VOC nature

A recent bibliometric analysis of world research trends on VOC from 1992 to 2007 has demonstrated that both detection and removal of three VOC, benzene, toluene and formaldehyde, has represented the main aim of the research in the past years [65]. The literature survey of the VOC catalytic oxidation, presented in the present review, shows that propene and toluene are among the most investigated probe molecules, because alkenes and aromatics, which are emitted by industrial and automotive exhausts, have high photochemical ozone creativity potential (POCP) [66]. Moreover, other unburned hydrocarbons species, belonging to the VOC family, were concerned mostly over the last years. In general two classes of unburned hydrocarbons can be distinguished: short chain molecules resulting from the breaking of the C–C chain (such as CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_8, C_3H_6) and aromatic hydrocarbons (e.g. benzene, toluene, xylenes, etc.) formed by pyrosynthesis in hot, fuel-rich zones within flames. As surveyed in the present review, many studies dealing with gold catalysts have focused the attention on the oxidation of such hydrocarbons at low-temperature under excess oxygen, to mimic conditions of VOC combustion.

3.1. Saturated and unsaturated aliphatic hydrocarbons

A large number of hydrocarbons has been efficiently destroyed over supported gold catalysts [67,68]. Combustion of unsaturated and saturated aliphatic hydrocarbons, such as propene, propane and methane is generally achieved over gold catalysts at higher temperatures than over palladium and platinum catalysts [69–74]. Total oxidation of saturated hydrocarbons (CH_4 and C_3H_8) has been reported to take place in the most efficient way over Au/Co_3O_4, claimed as the most active catalyst among supported gold ones [32,75]. Such Au/Co_3O_4 catalyst has been declared to be more active than Pt/Al_2O_3 and as active as Pd/Al_2O_3 for the complete oxidation of methane [23,29,32]. However, these results were obtained using highly different loadings of the active metal, 5 wt% of Au and 1 wt% of Pt or Pd. Conversely, Gluhoi et al. reported that Pt/Al_2O_3 is superior to any gold-based catalyst for a similar loading of the noble metal [71]. It was also found that propene oxidation takes place on Pt and Pd/Al_2O_3 at lower temperature than over Au/Co_3O_4 [32]. Ivanova et al. [72], investigating the oxidation of saturated and unsaturated hydrocarbons (C_1–C_3) over Au (2 wt%)/Al_2O_3 catalysts, also reported that hydrocarbon oxidation activity of Au catalysts is lower than that obtained with other noble metals such as Pt or Pd. In the same paper they pointed out the effect of the number of carbon atoms in the hydrocarbon chain, reporting that over Au catalysts, differently from other noble metals, the conversion of alkanes changed in the order: $C_2H_6 > C_3H_8 > CH_4$. Moreover an effect of the carbon unsaturation was observed, unsaturated hydrocarbons being oxidized easier than the saturated ones, except for C_2H_2 and C_2H_4.

A significant conversion (60%) of C_3H_8/C_3H_6 mixtures was achieved at 25 °C over a mixed catalyst consisting of gold (0.2–2.5 wt%) coupled with cobalt oxide supported over CeO_2/TiO_2, which was found more effective than platinum metals group (PMG) catalysts even in the presence of moisture and sulphur dioxide [76]. The abatement of C_3H_8/C_3H_6 mixtures, simulating gasoline and diesel exhausts, was also investigated by Mellor et al. over a gold based three-way catalyst (TWC) deposited over a zirconia-stabilized ceria/zirconia/titania and containing CoO_x, Rh, ZnO and BaO as promoters [77]. Under gasoline engine conditions at sub-stoichiometric (0.6 vol.% O_2) and super-stoichiometric concentrations (0.9 vol.% O_2), 50% conversion of hydrocarbons was achieved at 310 and 240 °C, respectively. Under highly oxidising conditions (7.5 vol.% O_2), typical of diesel engine, the hydrocarbon oxidation was favoured and 50% conversion was achieved at 170 °C. As compared to the performances of PMG-based catalysts, which operate efficiently at temperatures not lower than 300 °C, the abatement of the C_3H_8/C_3H_6 mixture over Au–cobalt promoted three-way catalyst is effective during the low-temperature start-up and idling phases of the driving conditions.

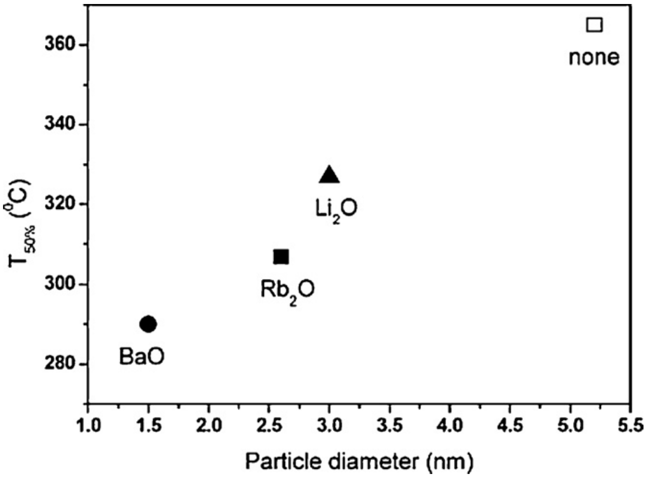

Fig. 11. Temperature needed for 50% C_3H_6 conversion versus the average gold particle size (HRTEM) of unpromoted (□) and Li_2O (▲), Rb_2O (■) and BaO (●) promoted Au/Al_2O_3 catalysts.
Taken from Ref. [48].

Propene combustion was investigated by the Nieuwenhuys group in a series of papers [40,47–49,71] using Au/Al_2O_3 catalysts promoted with reducible or alkali (earth) metal oxides. The activity of Au/Al_2O_3 was strongly improved by the addition of transition metal (Ce, Fe, Mn, Co) oxides being in the order: $Au/CeO_x/Al_2O_3$ (full propene conversion at 200 °C) > $Au/FeO_x/Al_2O_3$ > $Au/MnO_x/Al_2O_3$ > $Au/CoO_x/Al_2O_3$ > Au/Al_2O_3 (full propene conversion at 400 °C) [49]. A less pronounced beneficial effect was achieved by doping Au/Al_2O_3 with alkali (earth) metal oxides (M = Li, Rb, Mg, Ba) [48]. In this case the best results were obtained with $Au/BaO/Al_2O_3$ which achieved 50% C_3H_6 conversion at 290 °C, much lower temperature than 360 °C registered for unpromoted Au/Al_2O_3 (Fig. 11). A good activity enhancement, depending on gold loading, was also observed by doping Au/Al_2O_3 with CuO [71]. It must be noted that the best catalyst, Au (7.4 wt%)/CuO (12 wt%)/Al_2O_3, was in any case less active than an alumina supported Pt (4.8 wt%) sample. Interestingly on all catalysts the oxidation of propane required higher temperatures.

Gasior et al. investigated the C_3H_6 oxidation in the presence of H_2, using a gas mixture composition (C_3H_6:O_2:H_2:He = 10:10:10:70 vol.%) typically employed in studies of gas-phase epoxidation [78]. Oxidation of propene to CO/CO_2, with selectivity >95%, occurred over Au (1 wt%) supported on transition metal oxides (Fe_3O_4, CeO_2 and TiO_2), whereas selective oxidation of propene to oxygenate compounds was the main reaction for Au over oxides of non-transition metals (Si, Mg, Sn). In the case of propane oxidation, the reaction over the same catalysts occurred at least 100 °C higher with measurable conversions obtained above 250–300 °C. Gennequin et al. reported effective propene oxidation to CO_2 in the range 200–400 °C for $Au/Ce_xTi_{1-x}O_2$ (x = 0–0.3) catalysts [79]. Catalytic activity was strongly dependent on the chemical composition and surface area of the support. When a small amount of cerium was added to

TiO_2, the activity increased, the highest propene conversion being obtained on $Au/Ce_{0.3}Ti_{0.7}O_2$. The low surface area and the high gold size (40.9 nm) of Au/TiO_2 were claimed to explain its low activity with respect to the other $Au/Ce_xTi_{1-x}O_2$ catalysts. The conversion of propene was subsequently addressed and compared with that of toluene by the same authors, who investigated the catalytic performance of gold deposited on Ce–Ti mixed oxides prepared by sol–gel and Ce–Ti and Ce–Ti–Zr mesoporous materials [80].

In the latest period, propene oxidation has been investigated by different groups over various catalysts [58,59,81,82]. All studies reported that Au/ceria is the most active catalyst for propene combustion, giving full oxidation into CO_2 at temperature as low as 175–200 °C, depending on gold loadings and pretreatment conditions. Higher temperatures, between 200 and 400 °C, were needed over $Au/CeO_2/Al_2O_3$ catalysts and Au/Al_2O_3 (poorly active). Effective propene oxidation was also achieved over Au/TiO_2 and Au/ZnO below 300–350 °C [59]. A synergism between Pt/Al_2O_3 and Au/TiO_2 was found in the low temperature oxidation of propene/CO mixtures by Kim et al. [70], who reported that the addition of Au/TiO_2 to Pt/Al_2O_3, either as physical mixture or as a pre-catalyst, lowered the light-off temperatures for C_3H_6 oxidation. This was explained considering that Au/TiO_2 favours the oxidation of CO lowering its partial pressure thus reducing the inhibition effect exerted by CO towards the catalytic oxidation of C_3H_6 over Pt/Al_2O_3.

As reported in the literature [28,83,84], alkanes are among the least reactive VOC. C–H bond activation in saturated hydrocarbons is a crucial step in the combustion of these compounds [50]. Differently from C_2H_6 and C_3H_8, CH_4 is characterized by undistorted tetrahedral geometry with equal H–C–H bond angles of 109.47°, being much more stable and therefore the most difficult hydrocarbon to be oxidized [51,72]. It is generally accepted that the breaking of the C–H bond is the rate determining step in methane activation, being catalyzed by the presence over the catalyst surface of both basic and acid sites with suitable strength and geometry [85]. Gold catalysts supported over Co, Ni, Fe, Mn, Cu, Mg and Ce oxides are reported to be much more active than Au/Al_2O_3 [29,51,57,76]. On the other hand, Au particles or the interface Au-support play a key role in the activation of the C–H bond, as demonstrated by Grisel et al. [38,39]. The total oxidation of methane was catalyzed at 750 °C over Au/MgO catalysts with high gold loading (≥5 wt%) containing discrete particles with 5–10 nm diameter and large interface area between Au particles and MgO [86]. Conversion of methane at relatively low temperature (onset in the range 130–150 °C) was reported by Ying et al. [87] for three AURO*lite*™ catalysts (Au/TiO_2, Au/ZnO and Au/Al_2O_3), Au/TiO_2 being the most active. As reported by Grisel et al., the methane oxidation activity of Au/Al_2O_3 was markedly influenced by the preparation method and the gold particle size [38], as well as by doping alumina with transition metals (Cu, Mn, Cr, Fe, Co) and to a lesser extent by Ni and Zn [39]. Some relationship between the oxidation of saturated hydrocarbons (CH_4 and C_3H_8) and the acid/base character of promoters added to Au/Al_2O_3 was found by Gluhoi and Nieuwenhuys [50]. They reported that an oxide with a medium-weak basic character, such as FeO_x, had a more pronounced effect on the activity of Au/Al_2O_3 than a medium-strong or very strong basic oxide, like ZrO_x or BaO, respectively.

Oxidation of isobutane was reported to start at low temperature over highly active Au/CeO_2 catalyst which gives 55% isobutane conversion to CO_2 at 180 °C [88]. Full conversion of such a molecule, however, occurred at much higher temperature, not lower than 450 °C. Deep oxidation of n-hexane was studied by Centeno at al. who obtained 100% conversion at ~370 °C (T_{50} of 305 °C) over Au(2.5 wt%)/CeO_2/Al_2O_3, which was the most active catalyst among investigated Au/Al_2O_3 and $Au/CeO_2/Al_2O_3$ [41] and Au/TiO_2 and Au/TiO_xN_y [42]. Without any catalyst, thermal oxidation or decomposition of n-hexane started above 320 °C reaching only 45% conversion at 360 °C [41]. Cellier et al. [89] reported that gold prepared by DP over P25 or higher surface area TiO_2, synthesized by hydrolysis of titanium isopropoxide, provide complete oxidation of n-hexane at around 350 °C with T_{50} in the 260–280 °C range. They also demonstrated that Au/MnO_2 prepared by DP was much more active than Au/TiO_2 giving 100% hexane conversion at 180 °C. On the other hand, the activity of the pristine γ-MnO_2 oxide was even higher than that of the supported gold catalyst, due to the decrease of surface area of the support after gold deposition.

3.2. Oxygenated VOC

Among oxygenated VOC, alcohols (methanol, ethanol, 2-propanol, n-propanol), aldehydes (formaldehyde), ketones (acetone) and esters (ethylacetate) were reported to be efficaciously oxidized over gold catalysts at low temperature, the reactivity order being: alcohols > aldehydes > ketones > esters > alkanes [28,84].

The low temperature oxidation of methanol and its partial oxidation intermediates was addressed by Haruta et al. over gold supported on reducible oxides [30]. Au/α-Fe_2O_3 was almost as active as alumina-supported Pd and Pt catalysts in the oxidation of CH_3OH, HCHO and HCOOH. Moreover, the activity of gold catalysts was even enhanced by the presence of moisture in the reaction stream. Petrov et al. found that a mixed catalyst consisting of gold (0.2–2.5 wt%) coupled with cobalt oxide supported over CeO_2/TiO_2 was able to totally oxidize methanol, using a reaction mixture 10.5 wt% methanol in air, at temperature as low as 50 °C, exhibiting better performance than a Pt catalyst [76]. Wang and Ro reported that methanol oxidation activity over gold/iron oxide aerogel catalysts was significantly enhanced by increasing gold loadings from 2.4 to 5 wt%, with a decrease of ~60 °C in the T_{50} of methanol conversion [90]. Differently from Minicò et al., who found that the oxidation of methanol over 8.2 wt% Au/Fe_2O_3, produces only CO_2 [37], the oxidation of methanol over Au/Fe_2O_3 aerogel catalysts resulted in a wide pattern of products, such as dimethyl ether, formaldehyde, methyl formate and carbon dioxide. Dimethyl ether was the most dominant product over pure Fe_2O_3 aerogel and its selectivity decreased remarkably on increasing the amount of gold. On the other hand, the CO_2 production enhanced remarkably with increasing gold content.

Sobczak et al. investigated methanol oxidation over AuMCM-41 catalysts [91]. When methanol oxidation was performed over AuVMCM-41 and AuVNbMCM-41 catalysts prepared with H_2SO_4 as pH adjustment agent, the deep oxidation of methanol diminished, the highest selectivity to formaldehyde being observed (52% on AuVNbMCM-41). The high acidity of such materials as well as the interaction among Au, V and Nb reduced the strength of aldehyde chemisorption decreasing its further transformation to formate products [92]. On the contrary, AuVMCM-41 and AuNbMCM-41 prepared by HCl were the most active in the oxidation of methanol to CO_2 in so as the higher basicity enhances CO_2 selectivity.

Bonelli et al. reported that oxidation of methanol occurred at low-temperature (100–150 °C) with high selectivity to CO_2 over Au/FeO_x/SBA-15, prepared by Au–Fe bimetallic carbonyl cluster deposition [93]. The same group [94] also investigated methanol oxidation over FeO_x and Au/FeO_x/ceria catalysts prepared by the same technique. Due to the large excess of oxygen used, CO_2 and H_2O were the only products detected for all catalysts with no significant formation of formaldehyde or formic acid, as intermediates. Catalytic data showed that the presence of iron species on ceria does not significantly affect the methanol oxidation, while Au addition has a strong positive effect on both activity and reducibility of catalysts.

The catalytic combustion of several alcohols (methanol, ethanol, 2-propanol and *n*-propanol) was addressed by Deng et al. over Au/γ-Al_2O_3 catalysts [95]. They reported that methanol was totally

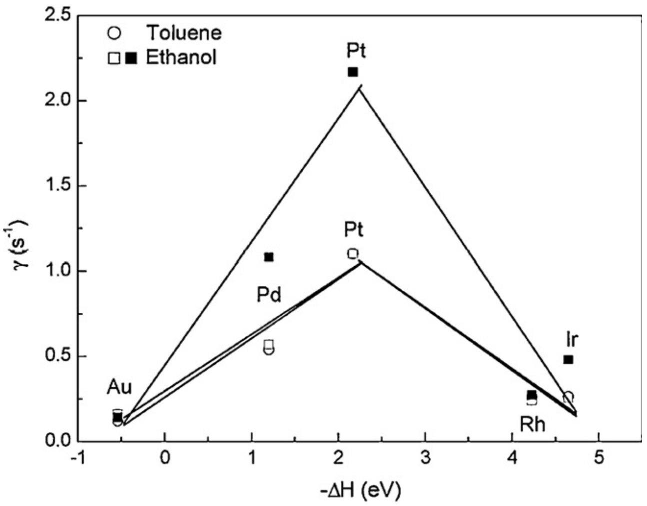

Fig. 12. Volcano-type plot indicating the specific activity at 285 °C in VOC oxidation as a function of oxygen dissociative chemisorption energies on metals. The filled symbols represent the catalysts prepared by incipient wetness impregnation, while the empty symbols represent the catalysts prepared by liquid phase reduction deposition.

Taken from Ref. [74].

transformed into CO_2 and H_2O at 60 °C with alcohol concentrations lower than 18.75 g m^{-3}. When methanol concentration increased, the mineralization temperature also increased, always without other by-products. The temperatures for complete conversion of ethanol, iso-propanol and *n*-propanol with concentration of 2.0 g m^{-3} were higher than for methanol: 155, 170 and 137 °C, respectively, with intermediate oxidation products detected. Complete mineralization of ethanol, iso-propanol and *n*-propanol was instead achieved at 220, 260 and 217 °C, respectively.

Ethanol oxidation was investigated by Santos et al. who confirmed the superior performances of Pt, Pd, Rh and Ir over Au catalysts supported on TiO_2 [74], the following trend being observed independently of the catalyst preparation method: Pt > Pd ≫ Rh ≈ Ir ≫ Au ≫ support. This trend and, in particular, the much lower performance of gold catalysts in comparison with the other noble metals were explained on the basis of the dissociative chemisorption energies of oxygen of noble metals, showing a typical volcano plot (Fig. 12). It was, in fact, suggested that the oxidation of VOC over supported noble metal catalysts involves the dissociative adsorption of oxygen. Oxidation of ethanol, ethyl acetate and toluene was compared by Bastos et al. over exotemplated manganese and cerium oxides loaded with gold (0.75–1.08 wt%) [84]. Over the most active catalysts (Au/CeO_2 and Au/MnO_x) full oxidation of methanol, ethyl acetate and toluene was achieved at around 230, 250 and 300 °C, respectively.

The oxidation of 2-propanol was investigated by Centeno et al. over Au/Al_2O_3 and Au/CeO_2/Al_2O_3 catalysts in the 100–400 °C temperature range [41]. Acetone was formed as intermediate product at low temperature with a maximum at about 230 °C for Au/CeO_2/Al_2O_3 catalysts. Above this temperature complete oxidation of 2-propanol to CO_2 and water occurred, confirming previous results on Au/Fe_2O_3 [35]. Oxidation of 2-propanol over Au/Al_2O_3 catalysts involved also formation of acetone as intermediate, but differently from Au/CeO_2/Al_2O_3 catalysts, two maxima of acetone production were detected (at 160 and 348 °C), complete oxidation to CO_2 being achieved at higher temperature (430 °C) than for Au/CeO_2/Al_2O_3 [41]. The partial oxidation of 2-propanol to acetone at low temperature was confirmed also on Au/TiO_2 and Au/titanium oxynitride catalysts [42]. Among investigated systems, Au/titanium oxynitride showed the highest 2-propanol conversion to acetone, while Au/TiO_2 was the most active for total oxidation to CO_2. The positive role of nitrogen introduction in the anionic network of TiO_2 was claimed for explaining the increased partial oxidation selectivity of TiO_xN_y, while the high deep oxidation activity of Au/TiO_2 was ascribed to the presence on this sample of smaller gold particles.

For Au on alumina- or ceria-coated monoliths it has been demonstrated that the composition of the ceramic foam used as catalyst support has a strong influence on the intermediate products formed during 2-propanol oxidation [96]. Propene, acetone and condensation products of acetone were formed at low-temperature, CO_2 being the main product above 250–300 °C. A dependence of the product distribution (acetone, propene, CO_2) on the catalyst nature was also found by Scirè et al. [97] in the deep oxidation of 2-propanol over gold deposited on different supports (CeO_2, Fe_2O_3, TiO_2, Al_2O_3). Acetone was the intermediate during 2-propanol oxidation and propene was formed over Au/TiO_2 and Au/Al_2O_3, probably due to the acidic nature of these oxides. The effect of moisture contents (500–2200 ppm) on 2-propanol conversion over Au/CeO_2 catalysts was also investigated, pointing out that the activity of 2-propanol oxidation increased slightly with increasing moisture content in the reaction stream [97].

The catalytic oxidation of alcohols and ketones was investigated and compared with that of toluene by the Scirè group over Au/Fe_2O_3 catalysts at different gold loading [35–37]. It was found that gold strongly enhances the rate of VOC oxidation, the higher the gold content the lower the light-off temperature. In particular on the sample with the highest gold content (8.2 wt%) the oxidation of methanol started at about 80 °C reaching a total conversion at 160 °C, while 20% conversion of 2-propanol was observed already at 40 °C. In the case of less reactive acetone and toluene the light-off temperature was 180 and 220 °C, respectively. In the oxidation of ethanol and 2-propanol the formation of intermediate oxidation compounds, acetaldehyde and acetone, respectively, was observed at low-temperature. The absence of intermediate products in the case of methanol oxidation was explained considering that formaldehyde, the intermediate oxidation product, is easily oxidized to CO_2. Also for acetone and toluene oxidation CO_2 was the only product detected probably due to the higher temperature at which the reaction occurs leading to complete oxidation. Similar results were reported by the same research group over Au/ceria catalysts prepared by DP and CP [43,98]. In these papers the observed VOC reactivity orders were 2-propanol > methanol > toluene [43] and methanol > acetone > toluene [98] for both DP and CP series. On the basis of TPD experiments of adsorbed VOC, this behaviour was related to the different degree of interaction between organic molecules and the basic ceria support, alcohols being more strongly adsorbed than ketones and aromatics [43].

Oxidation of formaldehyde has been also widely investigated, as HCHO represents a hazardous chemical widely used to manufacture building materials and household products, being also a secondary product of methanol oxidation. In 1996 Haruta et al. reported that HCHO can be oxidized at temperatures below 100 °C over Au/α-Fe_2O_3 which exhibited high activity as Pd and Pt/Al_2O_3 [30]. Starting from 2005, the oxidation of formaldehyde on supported gold catalysts was more extensively studied. Formaldehyde was effectively removed at 80–100 °C over Au/CeO_2 catalysts, while gold on TiO_2 and CeO_2–TiO_2 mechanical mixture were less active [99]. It was also found that gold deposited over as precipitate ceria was more active than gold over the calcined oxide [99]. A comparative study of the oxidation of HCHO over TiO_2 supported noble metals (Pt, Rh, Pd and Au) was carried out by Zhang et al., the order of activity being: Pt ≫ Rh > Pd > Au [100]. The HCHO oxidation activity of such catalysts was related to their capacities to form formate as intermediate and to decompose it into CO species which are easily oxidized to CO_2. Gold/iron oxide catalysts efficiently oxidized formaldehyde at room temperature and remained active in the presence of moisture, comparing favorably to Pd and

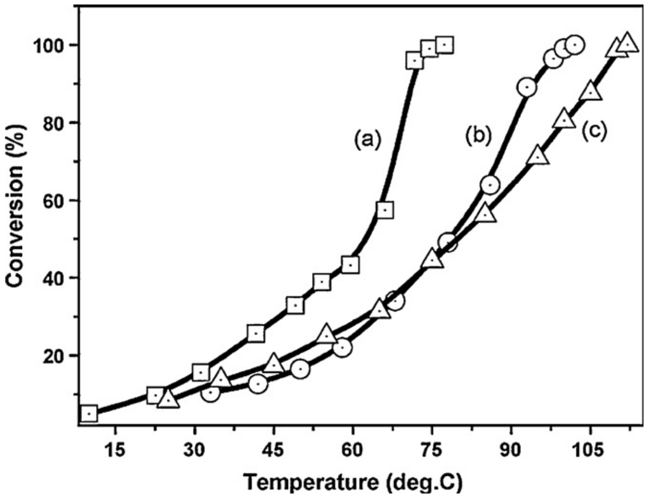

Fig. 13. Comparison of catalytic activity of Au/CeO_2 catalysts with different pore sizes on formaldehyde oxidation, (a) 3DOMAu 1 wt%/CeO_2 (80 nm pore size), (b) 3DOM Au 1 wt%/CeO_2 (130 nm pore size), (c) 3DOM Au 1 wt%/CeO_2 (280 nm pore size).

Taken from Ref. [63].

Pt noble metals [101]. Over the most active sample, containing 7.1 wt% of gold, complete burn off of formaldehyde was achieved at 80 °C. Au/CeO_2 coprecipitated catalysts with low gold content (0.7 and 0.85 wt%), calcined at 300 °C, completely converted HCHO at temperature $\leq$100 °C, the 0.85 wt% Au sample exhibiting the highest activity [102]. Even better performances were achieved on three-dimensionally ordered macroporous Au/CeO_2 catalysts with controlled pore sizes and gold content less than 1 wt% [63,103]. It was found that the Au/CeO_2 catalyst with 80 nm pores displayed 100% formaldehyde conversion at around 75 °C (Fig. 13) [63], much lower than temperatures reported over Au, Ag and Pd supported catalysts [101,102,104,105]. Au/mesoporous Co_3O_4 and Co_3O_4–CeO_2 catalysts, prepared using 2D hexagonal SBA-15 as hard template, showed excellent performances in the HCHO abatement at room temperature. The CO_2 yield was 52.1% over Au/Co_3O_4, the best performing catalyst, while decreased down to 45.5% for Au/Co_3O_4–CeO_2 [106]. Au (1 wt%) catalysts prepared by DP method over ceria, obtained by precipitation with ammonia and using PEG-6000 as dispersant, were also investigated in HCHO oxidation [54]. It was found that the addition of the dispersant during the ceria preparation had a positive effect on the activity. The using of microwave to treat the precipitated support also increased the activity, with the total HCHO conversion temperature decreased to 116 °C. HCHO oxidation was also carried out over Au/ZrO_2-nanocomposite catalysts with low gold content (0.85, 0.73 and 0.06 wt%), prepared by DP method [62]. In line with previous results [102], the higher the gold content the higher was the activity of formaldehyde oxidation to CO_2, the most active sample (0.85 wt% Au) giving full oxidation at 157 °C. Also on Au (0.25–4 wt%)/ZrO_2 catalysts the activity towards HCHO oxidation increased on increasing the gold loading, although this effect was not linear [107]. The possibility of driving formaldehyde oxidation with visible light at room temperature was addressed by Chen et al. using gold catalysts over ZrO_2, CeO_2, Fe_2O_3 and SiO_2 [108], being regarded as advantageous compared to the conventional process, for instance in indoor air purification.

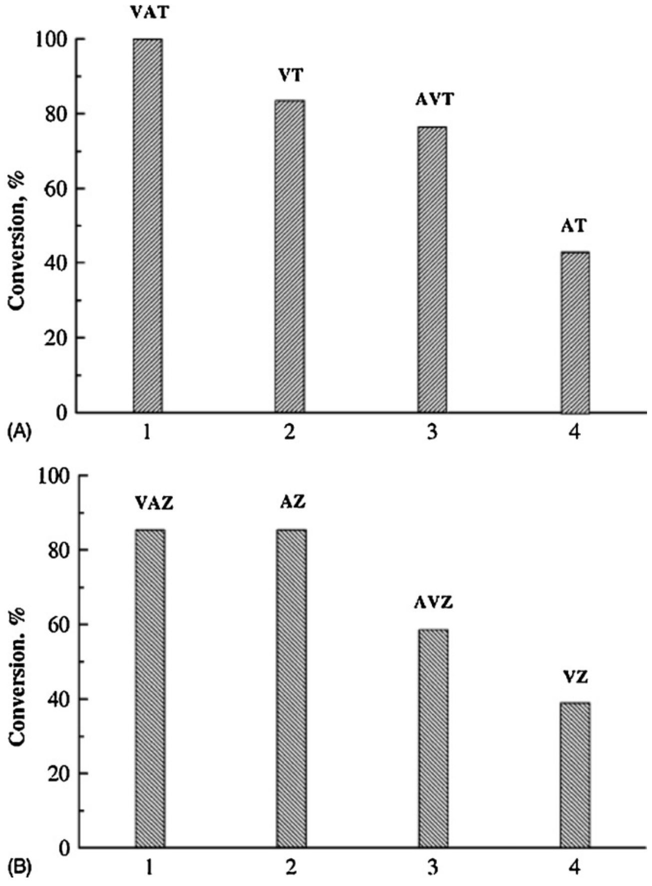

Fig. 14. Catalytic activity in complete benzene oxidation at 275 °C: (A) the catalysts based on mesoporous titania and (B) the catalysts based on mesoporous zirconia.

Taken from Ref. [61].

3.3. *Aromatic hydrocarbons*

The oxidation of aromatic hydrocarbons, such as benzene and toluene, required higher temperatures than aliphatic alkenes, full conversion being achieved between 200 and 300 °C for benzene and between 300 and 450 °C for toluene, depending on the nature of the gold catalyst.

Andreeva et al. reported a benzene conversion of 60% over Au/V_2O_5/ZrO_2 at 250 °C and near 100% on the Au/V_2O_5/TiO_2 at the same temperature, due to a stronger synergistic effect between Au and vanadia over titania [34]. Interestingly in this latter case, the temperature of benzene oxidation was about 150 °C lower than that found over Pd- or Ag-promoted vanadium oxide catalysts [109,110]. The stronger interaction between gold and vanadia supported on titania was confirmed also when mesoporous titania and zirconia were used as supports, 100% benzene conversion being reached at 275 °C on the best catalyst (mesoporous Au/V_2O_5/TiO_2) (Fig. 14) [61]. Furthermore, the same group reported that the temperature for complete benzene oxidation can be further reduced to 200 °C by means of CeO_2 [44]. Comparing the activities of Au/V_2O_5 catalysts supported on ceria–alumina with different ratio, it was found that the activities of the catalysts containing 20 wt% of alumina were higher than those of the corresponding samples containing 10 wt% of alumina, but in any case lower compared to the Au/V_2O_5 catalysts on pure ceria [46]. Substituting vanadia by molybdena, a decreased conversion of benzene was observed in the low-temperature range (150–200 °C) over gold promoted catalysts supported on ceria–alumina [45]. Benzene oxidation was obtained at the lowest temperatures over Au/MoO_3/CeO_2 (near 100% conversion at 180 °C), better performing than Au/V_2O_5/CeO_2 mainly in the 150–180 °C temperature range. In any case both ceria supported samples were more effective in benzene oxidation than the corresponding Au/V_2O_5/TiO_2 and Au/MoO_3/TiO_2 catalysts

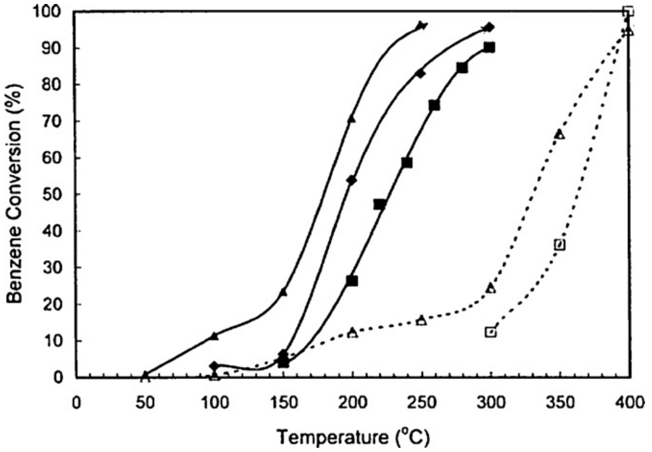

Fig. 15. Conversion for C_6H_6 over the reactivated Au/CeO_2-HS-500 catalyst (full line, filled symbol) and the reference Au/TiO_2 catalysts (dotted line, open symbol) with different reactant composition ■, □, 0.5% C_6H_6 in air, total gas flow rate at 200 ml min^{-1}; ♦, 1% CO and 0.5% C_6H_6 in air, total gas flow rate at 200 ml min^{-1}; ▲, △, 1% CO, 0.5% C_6H_6 and 3% H_2O in air, total flow rate at 200 ml min^{-1}.
Taken from Ref. [56].

[111]. The benzene total oxidation was also addressed by Yang et al., who investigated the catalytic performance of gold/ceria and gold/vanadia/ceria catalysts [112]. The Au (1 wt%) catalyst modified with 2 wt% vanadia on CeO_2 exhibited higher benzene oxidation activity than catalysts with higher vanadia content previously reported [44,111]. Moreover, Yang et al. found that activities of the best performing vanadia promoted Au/CeO_2 samples are similar to those of unpromoted gold catalysts supported on the same ceria with high surface area [112]. When benzene oxidation was performed over $Au/CeO_2/Al_2O_3$ catalysts, full conversion was obtained at 300 °C over the most active sample (2.5 wt% Au), with a T_{50} of 265 °C [41]. Such systems were more active than Au/TiO_2 and Au/TiO_xN_y catalysts successively investigated by the same authors [42]. Della Pina et al. [113] compared the activity of Au catalysts supported on CeO_2, ZrO_2 and $Ce_{0.5}Zr_{0.5}O_2$ to that of Au/TiO_2 and Au/Fe_2O_3 references catalysts supplied by the World Gold Council (WGC). Among the catalysts investigated in that study, total benzene conversion was reached at the lowest temperature (250 °C) over Au/CeO_2, prepared by using ammonia, compared to Au/Fe_2O_3 WGC (290 °C) and $Au/Ce_{0.5}Zr_{0.5}O_2$ (300 °C). The benzene oxidation activity of Au/TiO_2 WGC and Au/ZrO_2 was significantly lower, achieving almost full conversion at around 500 °C [113]. Complete benzene conversion was obtained at 275 °C over high surface area Au (1.5 wt%)/CeO_2 calcined at 300 °C [56], the activity slightly decreasing (90% conversion) by increasing the calcination temperature of ceria to 500 °C. Surprisingly, in the presence of a benzene (0.5 vol.%) and CO (1 vol.%) reaction mixture, the benzene oxidation was enhanced. Adding water vapour (3 vol.%) had further beneficial effect on the activity (Fig. 15). The positive effect of using high surface area mesoporous ceria as support for gold was recently remarked by Ying et al. who reported the high catalytic activity and stability in benzene oxidation over Au/CeO_2 prepared from MCM-48 hard template [64]. Complete conversion of benzene to carbon dioxide was achieved at 200 °C over such high surface area catalyst, which maintained high benzene conversion at 220 °C for 50 h on stream.

Albonetti et al. demonstrated that the presence of gold improves the selectivity of TiO_2 supported FeO_x catalysts towards the complete oxidation of toluene, while the catalytic activity is significantly enhanced as the iron content increases [114]. The catalysts $Fe_{4.5}Au_4$ and $Fe_{6.8}Au_6$, showing the higher fraction of reducible species, resulted to be the most active and selective ones, the extent of interaction between gold and iron oxide species being important for the oxidation activity. Ousmane et al. [58] compared toluene and propene oxidation over Au/CeO_2, $Au/Ce_{7.5}/Al_2O_3$, Au/Al_2O_3 and Au/TiO_2 catalysts and reported full conversion of toluene at temperatures ranging between 230 and 341 °C. Au/CeO_2 was the most active, then the activity decreased in the order: $Au/Ce_{7.5}/Al_2O_3 > Au/TiO_2 > Au/Al_2O_3$. For Au supported over mesoporous titania Hosseini et al. [73] found that toluene oxidation started above 250 °C with ~80% of conversion at 400 °C. Similar results were obtained by Santos et al. for toluene oxidation over Au/TiO_2 [74]. Full toluene conversion was achieved at around 300 °C over Au/CeO_2 and Au/MnO_x catalysts [83]. Similarly, Li and Li [115] reported that Au/CeO_2 catalysts were able to completely convert toluene in the range 250–350 °C depending on the Au content. Iron/gold cluster-derived catalysts showed complete oxidation of toluene between ~330 and 370 °C depending on the Au and FeOx content [116]. Au deposited on Ce–Ti mesoporous oxide was found by Gennequin et al. more active than Au over Ce–Ti–Zr for total oxidation of toluene [80]. Kim and Ahn compared the toluene oxidation activity for Pt–Au catalysts supported on ZnO/Al_2O_3 [117], 80% of toluene conversion being achieved between ~180 and 290 °C, as a function of preparation method and pre-treatment conditions.

While several papers deal with benzene or toluene oxidation over supported gold catalysts, very few investigations have been carried out with BTX mixtures. Recently, BTX oxidation over colloidal gold supported on zinc oxide has been studied by Wu et al. [60]. Au/Al_2O_3 and Au/MgO catalysts prepared by the same method have been used for comparison. The Au/ZnO catalyst exhibited higher activity than gold over Al_2O_3 or MgO. The Au/ZnO oxidation activity towards the three aromatic compounds decreased in the order: benzene > toluene > p-xylene and was governed by different factors such as the adsorption strength of the substrates, the ionization potential of the methyl derivatives and the strength of the weakest C–H bond in the structure. The occurrence of thermal effects was excluded. The high benzene oxidation activity of Au/ZnO was claimed by the same authors in a previous paper where the activity of various metal oxides supported colloidal gold catalysts were compared [118]. In a successive study by the same authors, toluene and p-xylene oxidation was achieved even more efficiently and at lower temperature than Au/ZnO by using Au/Co_3O_4 prepared by gold deposition through a colloidal method [119]. The temperature of 50% of toluene conversion over such Au/Co_3O_4 was 200 °C, being only slightly higher than that (T_{50} = 180 °C) reported by Solsona et al. over gold on high surface area Co_3O_4 [52].

The catalytic abatement of naphthalene, which represents a model molecule of harmful polycyclic aromatic hydrocarbons (PAHs), has been also scarcely investigated. The only study examining the performance of Au catalysts for catalytic oxidation of naphthalene was reported by Solsona et al. [55]. In this case the naphthalene oxidation activity was determined using the % conversion to CO_2, because of the formation of partially oxidized by-products and/or of naphthalene adsorption over ceria. The authors reported that full conversion to CO_2 was obtained between 200 and 325 °C, depending on the preparation method of the ceria support (precipitation with urea or sodium carbonate). Interestingly the most active catalyst was pure ceria (without gold) prepared by deposition-precipitation with urea.

3.4. Cl-VOC, N-VOC and S-VOC

It is known that oxidation of chlorinated hydrocarbons requires special care due to the corrosive effect of hydrogen chloride, which is known to attack the alumina support [31], and therefore alternative classes of catalysts are required [120,121]. For this reason gold catalysts were occasionally used in the oxidation of chlorinated hydrocarbons. At the beginning of 1990s the oxidative decomposition of methyl chloride (CH_3Cl) was studied over different gold supported catalysts by Aida et al. [122]. Au/Co_3O_4 and Au/Al_2O_3 showed the highest activity and stability for the reaction, which was accelerated by the presence of water. The authors investigated over Au/Co_3O_4 and Au/Al_2O_3 catalysts also the decomposition of Freon-12 (CCl_2F_2). In that case, Au/Co_3O_4 showed very low activity, while on Au/Al_2O_3 the conversion curve of CCl_2F_2 was similar to that for CH_3Cl. Some years later, Chen et al. investigated dichloromethane oxidation over Au/Co_3O_4 catalysts with different gold loadings (0.2–10 wt%) [31]. Interestingly, such catalysts were significantly more active at 300 °C than chromia/alumina and 0.5 wt% Pt and Pd alumina catalysts. Dichloromethane was selectively oxidized over Au/Co_3O_4 to CO_2 and HCl, while no by-products (such as $CHCl_3$ or CCl_4) or partial oxidation products (such as CO, Cl_2, $COCl_2$, HCHO) were observed. Comparing the total oxidation of benzene and chlorobenzene over gold catalysts supported on different oxides, Della Pina et al. observed that chlorobenzene conversion curves are shifted to higher temperatures compared to that of benzene [113]. They found that Au/CeO_2, $Au/Ce_{0.5}Zr_{0.5}O_2$, Au/TiO_2 WGC and Au/Fe_2O_3 WGC exhibited not much different performance, 50% chlorobenzene conversion being achieved in the 350–400 °C range (Au/CeO_2 was the most active). Evaluation of the catalytic activity of $Au/Ce_{0.5}Zr_{0.5}O_2$ at 500 °C showed, however, a strong catalyst deactivation with chlorobenzene conversion sharply decreasing after 2 h from 90% to 56%, becoming almost zero after 9 h on stream, thus confirming the limit to the use of Au catalysts in the disposal of chlorinated organic compounds [113]. The oxidation of o-dichlorobenzene was investigated by Albonetti et al. over $Au/FeO_x/TiO_2$ catalysts [114]. Besides CO and CO_2, significant amounts of chlorinated by-products were detected. Moreover, contrary to the high stability shown by the same catalysts during toluene oxidation, a dramatic deactivation of the catalysts occurred with o-dichlorobenzene, confirming conclusions of Della Pina et al. [113]. Oxidative destruction of o-chlorophenol to CO_2 was achieved by Okumura et al. at 150 °C over Au/Fe_2O_3, Au/Fe_2O_3–Pd/SnO_2 and Pt/SnO_2–Au/Fe_2O_3–Ir/La_2O_3 [123], o-chlorophenol conversion ranging between 20% and 60% as a function of the catalyst. Such multi-component Pt/SnO_2–Au/Fe_2O_3–Ir/La_2O_3 catalyst was also successfully applied in the oxidative decomposition of dioxin derivates to CO_2 [68,123].

Nitrogen-containing compounds, such as trimethylamine which is a typical odour-producing compound, have been reported to be efficaciously removed over Au-based catalysts [124]. Gold on ferric oxides and nickel ferrites exhibited the highest oxidation activity owing to their strong affinities to nitrogen [125]. The oxidative decomposition of trimethylamine was found to proceed at temperatures below 100 °C over $Au/NiFe_2O_4$, yielding mostly N_2 and CO_2, while N_2O was mostly produced over Pd and Pt catalysts even at higher temperatures. Efficacious abatement of trimethylamine to carbon dioxide was found to occur also over a binary component catalyst Au/Fe_2O_3–Ir/La_2O_3 able to give complete oxidation at 200 °C [123]. Although the Ir catalyst by itself was much less active for this reaction, it exhibited a boosting effect on the oxidative decomposition of trimethylamine over Au/Fe_2O_3.

The removal of VOC is equally difficult in the case of malodorous S-VOC and requires sulphur-resistant catalysts. To the best of our knowledge, up to now only one study related to the removal of S-VOC over gold catalysts has been reported in the literature [126]. In this paper, the oxidation of CH_3SSCH_3, dimethyldisulfide (DMDS), was investigated over gold deposited on zeolites (MCM-41, HZSM-5 and H-beta) and compared with Au/TiO_2. Titania supported catalysts demonstrated catalytic removal of DMDS at temperature as low as 155 °C with formation of SO_2 (around 35%) and elemental S (around 65%). On the contrary gold/zeolite catalysts were less effective, giving reasonable DMDS oxidation to SO_2 at temperature higher than 290 °C without sulphur formation.

4. Effect of the gold state

4.1. Role of the gold oxidation state

Despite the efforts of many researchers to identify the nature of the active gold species, either ionic or metallic, in the reactions where gold exhibits good catalytic activity, this point still remains a matter of debate. For instance, in the CO oxidation, the most investigated reaction over Au catalysts, oxidized gold species ($Au^{\delta+}$, Au^{1+}, Au^{3+}) were considered more active than Au^0 by several authors [127–131], whereas Prof. Haruta, one of the most expert researcher in the catalysis by gold, disputed the role of oxidic gold on the grounds that most XPS results showed the presence of metallic gold in the most active gold based systems [68]. An intermediate model was proposed by Bond and Thompson [132] involving both Au^0, which adsorbs CO, and Au^{3+}, which activates surface hydroxy groups for reaction with the adsorbed CO to form adsorbed carboxylate.

Also in the case of the VOC total oxidation reaction, the oxidation state of the active gold species is still an unresolved question. First of all, it must be remarked that, due to the preparation/pretreatment conditions of gold catalysts, generally involving a high temperature treatment, most of the authors reported the presence of Au^0, providing no information on the relative activity of oxidized/metallic gold species. The main studies specifically dealing with the effect of the oxidation state of gold will be hereinafter discussed. In summary, the participation of cationic gold in VOC oxidation has been proposed by several authors, whereas a predominant role of gold in the metallic state has been reported by another, less numerous, group. There are also some researchers suggesting that the Au electronic state does not significantly influence the catalytic activity, due to the fact that both metallic and ionic Au has the same activity or the role of gold is secondary to that of the support.

The first authors pointing out the importance of oxidized gold in the VOC combustion were Waters et al. [29], reporting that methane oxidation activity of different Au catalysts supported on metal oxides (Co_3O_4, NiO, MnO_x, Fe_2O_3, CeO_x) increased with increasing the oxidation degree of Au in the oxidized state, probably due to the fact that the oxidation state affects the ability of gold to bind oxygen. Some years later Minicò et al. [37] found that $Au^{\delta+}$ and ferrihydrite are more active compared to Au^0 and hematite respectively. They concluded that the Au state affects the catalytic activity of the Au/iron oxide samples more than that of the oxide support. Centeno et al. [42] found that over Au/TiO_2 the presence of nitrogen in the solids (Au/TiO_xN_y) has a negative role in the total combustion of 2-propanol to CO_2, but a positive one in the partial oxidation to acetone. They suggested that the $Au^{\delta+}$ surface species detected in the Au/TiO_xN_y samples play a determinant role in the partial oxidation mechanism of 2-propanol. The size of gold particles and the state of surface gold species were also found to play a crucial role in the catalytic oxidation of methanol over gold/iron oxide aerogels [90]. In particular, the oxidized gold (Au^{3+}) resulted to be more active than the metallic gold towards the total combustion to carbon dioxide. Liu and Yang [97] proved that, in addition to the effect of the gold particle size, the oxidation state of gold is important for 2-propanol oxidation over Au/CeO_2 catalysts, Au^{+1} species exhibiting higher activity than Au^0. The most active catalyst was, in fact, that one (Au/CeO_2 calcined at 300 °C) containing the highest content of cationic gold species (32% of Au^{+1} and 68% of Au^0) (Fig. 16). Also Cellier et al. [89], found that a thermal pretreatment of Au/TiO_2 at 300 °C with oxygen lead to a more active catalyst towards n-hexane total

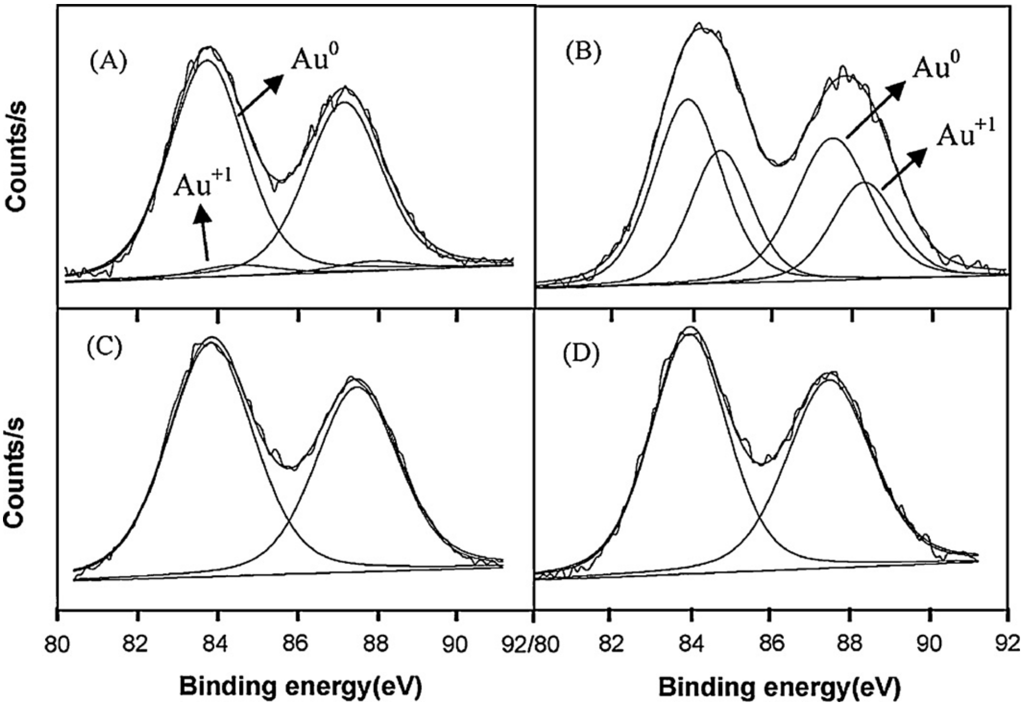

Fig. 16. XPS of Au 4f obtained for 1.6Au/CeO_2 catalysts calcined at (A) 200 °C, (B) 300 °C, (C) 400 °C and (D) 500 °C.
Taken from Ref. [97].

oxidation than an analogous pretreatment with hydrogen. However, in this case this behaviour was not attributed to differences in the oxidation state of gold, since essentially coincident XPS $Au4f_{7/2}$ peaks were recorded after hydrogen or oxygen treatment, but to a better removal of C contaminants obtained upon oxygen treatment. Li et al. [101] proposed that on gold/iron oxide catalysts the gold species with fractional charge ($Au^{\delta+}$) are the active species for the catalytic combustion of formaldehyde, because these species were found to exist in the sample that exhibited the best catalytic performance. It was supposed that HCHO is adsorbed on the surface of Au atoms, being similar to the CO molecules in the CO oxidation reaction, then migrating towards the perimeter of the support oxide (ferrihydrite), responsible for the oxygen activation. Jia et al. [54] also found a positive correlation between the Au^{+1}/Au^0 ratio and the activity of Au/CeO_2 catalysts in the HCHO oxidation, suggesting that Au^{+1} is the active species for HCHO combustion. Shen et al. [102] reported an investigation on the states of gold species in CeO_2 supported gold catalysts, prepared by CP and calcined at 300 °C, used for formaldehyde oxidation. They found that Au/CeO_2 catalyst with highly dispersed metallic gold and small amount of oxidized gold exhibited superior catalytic activity for HCHO oxidation. Interestingly they found that at higher calcination temperatures (700 °C) the mobility of ions increases, Au^{3+} ions entering the lattice of ceria, occupying some sites that are normally occupied by Ce^{4+} ions, resulting in a lattice contraction. Yang et al. [112] reported that the presence of vanadia promoted the catalytic activity of Au/CeO_2 towards benzene combustion in so as the interaction of Au with V_2O_5 on ceria results in the formation of Au^{3+}, regarded as more active compared to Au^0. Analogously the higher activity of the Au/CeO_2 sample calcined at 300 °C compared to the 400 °C calcined one was related to the presence of significant amounts of Au^{3+} species on the sample calcined at 300 °C, which were instead absent in the sample calcined at higher temperature. Ying et al. [88] found that gold is dispersed over Au/CeO_2 samples prepared by DP as Au^0, Au^+ and Au^{3+}. On the basis of ex situ XPS they demonstrated the existence of a correlation between cationic gold and isobutene oxidation activity. The authors proposed that the low temperature activity was closely related to the content of Au^+ (surface gold oxide), with ceria supplying reactive oxygen to adjacent small gold particles, whereas the enhancement of the catalytic activity at high temperature (above 300 °C) was associated with substitutional Au^{3+} reducing the Ce–O bond strength.

The higher activity of Au^0 compared to oxidized Au species was postulated by a lower number of researchers. In particular, Andreeva et al. [45] found that Au/CeO_2, Au/MoO_x/CeO_2, and Au/MoO_x/CeO_2–Al_2O_3 fresh catalysts contained exclusively Au^0, whereas some positively charged gold was present on the AuCeAl catalysts, found to be less active in the benzene oxidation. Delannoy et al. [81] found that for Au/CeO_2 catalysts activation under H_2 at 300 °C leads to more active catalysts towards the propene total combustion than activation in O_2/He at 500 °C. On the basis of XPS and DRIFT experiments they concluded that metallic gold is the active species for the reaction. Lakshmanan et al. [82] came to an analogous conclusion, investigating the oxidation of CO and propene over Au/CeO_2–Al_2O_3 catalysts (1.5–10 wt% CeO_2). They found that the ceria loading and the catalyst activation method govern the oxidative performance by affecting the gold oxidation state, the gold particle size and the distribution of gold on ceria and alumina. The activity of Au/CeO_2–Al_2O_3 was intermediate between that of Au/Al_2O_3 and Au/CeO_2, increasing with the ceria loading for samples activated under H_2 but decreasing if activated under O_2. Characterization results showed that whatever the mode of activation, as the CeO_2 loading increased, the proportion of gold particles on alumina decreased while that on ceria increased, but gold remained unreduced on ceria after calcination under O_2 whereas it was metallic after reduction under H_2. It was concluded that gold on ceria is more active for both CO and propene oxidation when it is metallic than when it is unreduced.

The importance of the coexistence of mixed Au valence states (Au^{3+} and Au^0) was instead proposed by Zhang et al. [63]. They in fact reported that the presence of both Au^{3+} and Au^0 over Au/macroporous ceria catalysts may be the key factor for the enhancement of catalytic efficiency of these catalysts towards formaldehyde oxidation. Similar catalytic performances of oxidized and metallic gold towards HCHO combustion were reported by Zhang et al. [62] over Au supported on mesoporous ZrO_2. They found that Au^{3+} and Au^0 species are able to strongly adsorb HCHO molecules both being active species for the HCHO combustion. The participation of both Au^{3+} and Au^0 in the HCHO combustion was also proposed by Liu et al. in a recent paper [103].

4.2. Role of the size and shape of gold particles

The adsorption properties and reactivity of gold particles have been discussed firstly by Haruta in terms of their size dependency, from bulk to fine particles, clusters and atoms [22]. It was pointed out that, when gold is deposited on metal oxides as hemispherical ultra-fine particles with diameters smaller than 5 nm, it exhibits surprisingly high activity and/or selectivity in the combustion of CO and saturated hydrocarbons, the oxidation–decomposition of amines and organic halogenated compounds, the partial oxidation of hydrocarbons, the hydrogenation of carbon oxides, unsaturated carbonyl compounds, alkynes and alkadienes, and the reduction of nitrogen oxides. In the 1999, Bond and Thompson also stated that the activity of gold is size dependent being higher for very small particles [23].

The unique catalytic nature of supported gold can be explained by assuming that the gold–metal oxide perimeter interface acts as site for activating at least one of the reactants, for example, oxygen. Activation of oxygen on gold nanoparticles, giving rise to peroxospecies, was assumed by Andreeva et al. to explain the synergistic effect manifested in the benzene oxidation reaction over Au catalysts promoted by vanadia (4 and 8 wt%) supported on titania and zirconia [33,34]. The authors confirmed that the strong synergism between nanosized gold and ceria particles is responsible of the enhanced benzene oxidation activity of vanadia-promoted Au–ceria catalysts [44]. Contemporaneously, someone of the same group demonstrated that the presence of small gold particles, causing a strong modification of ceria, played a crucial role in the benzene oxidation activity of gold catalysts on ceria and ceria–alumina promoted by molybdena [45,133].

The important role played in benzene oxidation activity by nanosized gold particles was renewed by Yang et al. over Au/CeO_2 catalysts and Au/CeO_2 promoted by 2 wt% of V_2O_5 [112]. The finding that Au/CeO_2 catalysts prepared from MCM-48 hard template exhibited high catalytic activity and stability in benzene oxidation confirmed the key role of highly dispersed gold species stabilized over high surface area ceria with small particles [64]. Conversely, Au/CeO_2 prepared on nanocrystalline ceria with lower surface area, easily deactivated due to the sintering of gold under reaction conditions [64]. The capacity of highly dispersed small gold particles to weaken the Fe–O and Ce–O bond, thus increasing the lattice oxygen mobility of CP gold/iron oxide catalysts and gold/cerium oxide samples prepared by CP and DP method was invoked by Minicò and Scirè to explain the high activity of these catalysts in the oxidation of 2-propanol, methanol, ethanol, acetone and toluene [35,37,43]. However, by comparing the catalytic data of CP and DP Au/CeO_2 samples, the same authors concluded that the Au particle size is not the only factor governing the VOC oxidation activity of Au/metal oxide catalysts [43], suggesting the important role played also by Au–CeO_2 perimeter. In a further study, indeed, Scirè et al. clearly stated that more active catalysts towards oxidation of methanol, acetone and toluene were obtained when small gold clusters strongly interacting with ceria crystallites are formed [98]. Liu and Yang reported that the activity of 2-propanol oxidation over Au/CeO_2, Au/Fe_2O_3, Au/TiO_2 and Au/Al_2O_3 catalysts decreased for large Au particle size [97]. Santos et al. reported the influence of Au particle size in the oxidation of ethanol and toluene over Au/TiO_2 catalysts in comparison with the particle size effect of other supported noble metals (Pt, Pd, Ir and Rh) [74]. The oxidation of ethanol and toluene on Pt and Pd catalysts supported over titania was found to be structure sensitive, while considering ethanol oxidation over Rh and Au catalysts, the intrinsic activity slightly decreased with the increase of the average particle size of Rh, whereas for gold the effect was negligible. In a successive study on total oxidation of ethyl acetate, ethanol and toluene catalyzed by Au over manganese and cerium oxides prepared by an exotemplating method, Bastos et al. [84] demonstrated that the addition of gold to manganese oxide does not improve the total oxidation of ethyl acetate when large Au particle size (>15 nm) are formed. Conversely, smaller particle size of gold, around 4–11 nm, increased the activity of manganese oxide for the total oxidation both of ethyl acetate and toluene. Moreover, highly dispersed gold deposited over manganese oxide improved the oxidation of toluene towards CO_2, possibly as a result of the oxidation of CO, which was the main by product detected during toluene oxidation over manganese. Total oxidation of ethanol was also enhanced on Au/ceria catalysts containing low Au particle size. The positive role of small Au particles was explained by the authors suggesting a promotional effect of gold in increasing the lattice oxygen donating ability of the oxide.

The catalytic behaviour of multi-component supported catalysts is known to strongly depend on the size of the metal particles and on their reciprocal interactions [22,134]. Accordingly, $Au/FeO_x/TiO_2$ catalysts with small gold nanoparticles were found active for total oxidation of toluene and highly stable under catalytic conditions [114,116]. Moreover, the same authors reported that the optimal gold and iron dispersion, achieved for Au/FeO_x catalysts supported on SBA-15, was as one of the key factors influencing the methanol oxidation activity [93]. Bonelli et al. also attributed the improved methanol oxidation activity of $Au/FeO_x/CeO_2$ catalysts to the formation of small gold metallic nanoparticles anchored on the ceria support together with homogeneously dispersed iron oxide species [94]. The relationship between particle size and catalytic activity for toluene oxidation over bimetallic Pt–Au catalysts was addressed by Kim and Ahn [117]. They found that nanosized gold particles improved the reduction of surface oxygen and then the toluene oxidation, whereas small Pt particles (<5 nm) were poorly active. As reported by Rashkeev et al. [135] the main difference between the behaviour of gold and platinum at the nanoscale is that nanosized Pt binds reactants so strong that the reaction never proceeds at low temperature, while in the case of gold the weaker binding allows the reaction to continue.

Gennequin et al. confirmed the positive role of small Au particles in toluene deep oxidation, showing that gold deposited on mesoporous titania loaded with 20 wt% ceria exhibited the best catalytic activity, thanks to the high dispersion of gold nanoparticles stabilized by interaction with ceria [80]. Similarly, the toluene oxidation activity of Au/CeO_2 catalysts was related by Li and Li to the size of metallic gold particles in strong interaction with the ceria support [115]. Small Au particles as well as the contact perimeter between Au colloids and zinc oxide nanoparticles with abundant oxygen vacancies were also claimed as responsible of the high catalytic activity of colloidal Au/ZnO for benzene, toluene and p-xylene oxidation [119]. Not only the formation of nanoparticles of gold but also a specific interaction with titania was asserted to improve the catalytic behaviour of Au/TiO_2 catalysts with respect to Au/zeolites for dimethyldisulfide (DMDS) oxidation [126].

The positive effect of nanosized gold in enhancing the rate of deep oxidation of n-hexane, benzene and 2-propanol was stated by Centeno et al. over Au/Al_2O_3 and $Au/CeO_2/Al_2O_3$ [41] and Au/TiO_2 and Au/TiO_xN_y [42]. Cellier et al. found a good correlation by plotting the temperatures of 50% (T_{50}) of n-hexane conversion over Au/TiO_2 catalysts against the Au/Ti surface atomic ratio determined by XPS analysis, suggesting that the activity was correlated to the area of exposed gold particles (Fig. 17) [89]. Moreover, the authors

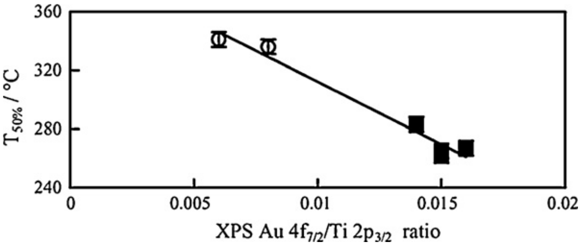

Fig. 17. Temperature of 50% conversion of 125 vppm n-hexane (T_{50}) as a function of the Au4f/Ti2p ratio for Au/TiO_2-IP catalysts prepared by anion adsorption (○) and by deposition–precipitation (■).

Taken from Ref. [89].

envisaged that different dispersion of gold particles on the catalyst surface may involve a different morphology of the exposed particles as well as the presence of different coordinatively unsatured Au surface atoms, as previously stated by Boccuzzi et al. and by Ruff et al. for CO adsorption and oxidation over gold [137,138]. The Au morphology effect on the VOC oxidation activity of Au catalysts dates back to 1998 by Blick et al. who investigated methane oxidation over Au/MgO catalysts [86]. Two-dimensional Au rafts formed over MgO at low gold loading poisoned the methane coupling activity of MgO and no CH_4 oxidation occurred, while discrete three-dimensional Au particles with diameter of 5–10 nm were active for methane oxidation to CO and CO_2.

The role played by ceria in the stabilization of gold nanoparticles was confirmed by Jia et al. who found enhanced HCHO oxidation ability of Au/CeO_2 catalysts with respect to Au/TiO_2 [99]. Shen et al. reinforced that highly dispersed gold catalysts provide more active sites for HCHO oxidation than larger gold crystallites [102]. Hong et al. provided the first comparison of Au catalysts for the removal of CO and HCHO by catalytic oxidation and affirmed that small metallic Au particles are crucial for both reactions [107].

The occurrence of an effect of the Au particle size on the deep oxidation of CH_4, C_3H_6 and C_3H_8 over Au/MO_x/Al_2O_3 (M = Cr, Mn, Fe, Co, Ni, Cu and Zn) catalysts was reported in the papers of the Nieuwenhuys group [38–40,47–50,71]. For CH_4 oxidation over Au/Al_2O_3 and Au/MO_x/Al_2O_3 small Au particles were found to be beneficial for high activity [38]. On the other hand the authors claimed the concomitant importance of the Au/MO_x perimeter interface for CH_4 dissociative adsorption and reaction with activated oxygen [39]. Doping alumina with transition metal oxides, ceria or alkali and alkali-earth metal oxides induced a decrease in the size of gold particles and stabilized them against sintering, improving the performance of supported Au catalysts in the total oxidation of C_3H_6 and C_3H_8 [40,47–49,71]. Gennequin et al. and, one year later, Lamallem et al. also reported that the dispersion of gold is an important factor to obtain high propene oxidation activity over Au/$Ce_xTi_{1-x}O_2$ oxides [79,136]. No clear correlation has been instead observed by Gasior et al. between the Au particle size and the catalytic performance in C_3H_6 and C_3H_8 oxidation over Au dispersed on different oxides of non-transition (Mg, Si, Sn) and transition metals (Fe, Ti, Ce) [78]. Choudhary et al. also reported that the methane combustion activity of gold supported over TiO_2, MgO, Al_2O_3, CoO_x, CeO_2 and Fe_2O_3 catalysts was essentially controlled by the Au-support interactions, Au particle size being not dominating [57].

5. Effect of the preparation method and pretreatment conditions of catalysts

As well known and also discussed in previous chapters the performance of supported Au catalysts are highly dependent on the nature of the support and the size of gold crystallites. The preparation of Au/oxide catalysts is undoubtedly regarded as a key factor strongly affecting the size of gold particles [23,26,139]. As it arises from Table 1, different methods have been reported for the preparation of Au catalysts employed in VOC deep oxidation. In particular deposition–precipitation (DP), first used by the Haruta group [140] using Na_2CO_3, KOH, or NaOH as precipitating agents, and homogeneous deposition–precipitation (HDP) using urea as precipitating agent, were the most used ones, being regarded as proper to give small Au particles mainly located on the support surface, thus leading to very active catalysts [23,26]. Other related deposition techniques such as cluster deposition (CDP), metal colloidal deposition (MCD), liquid phase reduction deposition (LPRD), assisted deposition (ADP) were often used. Moreover other preparation techniques reported were co-precipitation (CP), impregnation (IM), anionic adsorption (AA), exchange techniques (ionic, IE, and direct anionic, DAE), nanocasting and sol–gel. The effect of the preparation method on the physico-chemical properties and the VOC combustion activity of Au/metal oxide catalysts was specifically addressed by several authors, as hereinafter discussed.

Grisel et al. [38] compared the performance towards the CH_4 total oxidation of Au/Al_2O_3 catalysts prepared by impregnation (pore volume and wet) and deposition-precipitation with Na_2CO_3 (DP) or urea (HDP) as precipitating agents. They found that the activity of both catalysts prepared by impregnation was inferior to that of samples prepared by deposition–precipitation, this latter one exhibiting the smallest Au particles. In specific HDP was found to be the best method, leading also to a higher Au loading, due to a slower and more homogeneous pH variation of the solution.

Scirè et al. [43] investigated the catalytic combustion of some representative VOC (2-propanol, methanol and toluene) on gold/ceria catalysts prepared by coprecipitation (CP) and deposition–precipitation with Na_2CO_3 (DP). It was observed that the activity enhancement of ceria by gold was significantly more effective when gold was added by DP than by CP (Fig. 18). It was demonstrated that DP catalysts contain a higher amount of surface gold particles which are also smaller than those found in the CP samples. This result was confirmed by the same research group comparing the deep oxidation of methanol, acetone and toluene over Au/ceria catalysts prepared by CP and DP with KOH, this latter approach providing higher ceria surface area than DP with Na_2CO_3 [98]. Interestingly in this paper the effect of the preparation method was explained considering that on the CP gold system, as a consequence of the much lower solubility product of $Au(OH)_3$ ($K_{sp} = 5 \times 10^{-46}$) compared to $Ce(OH)_3$ ($K_{sp} = 1.6 \times 10^{-20}$), $Au(OH)_3$ is formed before than $Ce(OH)_3$. This should lead to a less intimate mixing of the components [141], thus favoring the aggregation of gold hydroxide in larger particles, partially covered by the cerium hydroxide successively formed. In the presence of the support (DP samples) the extremely low solubility of gold hydroxide leads to the formation of a high number of nucleation centers, which interact with the support, resulting in small gold particles well distributed on its surface.

Andreeva et al. [44] compared the performance of vanadium promoted gold/ceria catalysts prepared by two different deposition-precipitation approaches, the first one (DP) depositing gold on a calcined ceria and the second one (MDP) over a freshly precipitated cerium hydroxyde. They reported that catalysts prepared by DP were more active than those prepared by MDP in so as in this latter method a significant part of gold remained incorporated into the bulk of ceria and therefore the concentration of gold active centers was lower.

Idakiev et al. [61] found that the preparation procedure affects the catalytic activity of Au/V_2O_5 supported on mesoporous titania and zirconia. On both series of catalysts the activity in complete benzene oxidation was higher when the deposition of gold is prior than the vanadia one. This was explained with a more intimate contact between gold and vanadia when the gold is deposited firstly.

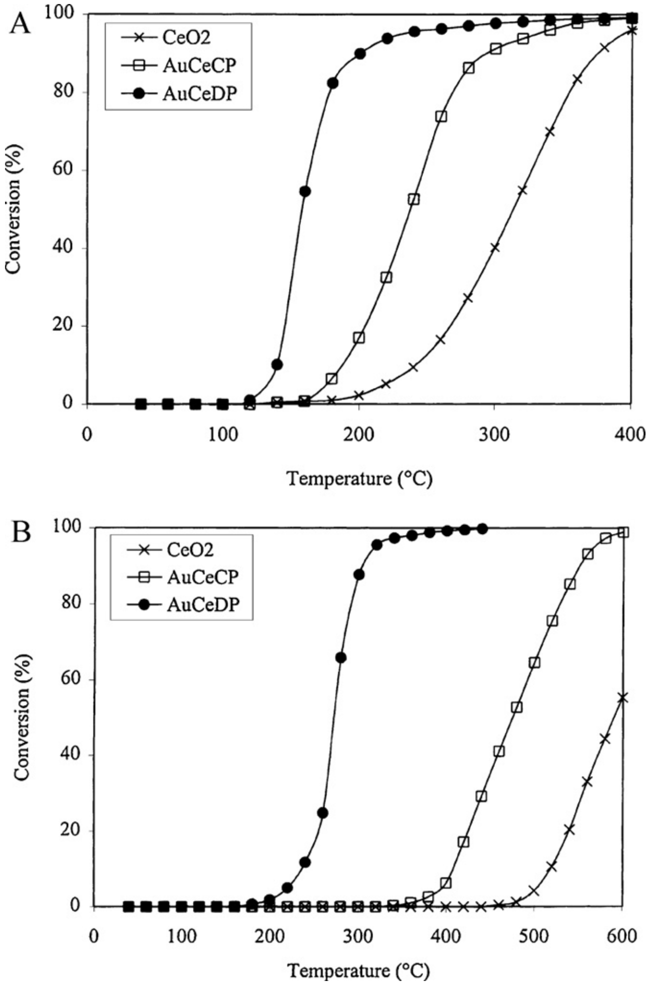

Fig. 18. Conversion of methanol (A) and toluene (B) on Au/CeO_2 catalysts.
Taken from Ref. [43].

Cellier et al. [89] compared the performance of Au/TiO_2 catalysts prepared by DP or anionic adsorption (AA) towards n-hexane oxidation. These two methods differed essentially for the pH of the titania suspension, maintained at 7 for DP and 3 for AA. It was observed that the DP method leads to smaller gold particles and higher gold loadings than AA, then resulting in more active catalysts. It is interesting to note that the difference of gold dispersion was attributed to a different mobility of gold precursors during the thermal post-treatment rather than to a difference in the dispersion of uncalcined samples.

A higher activity in the total oxidation of propane of Au/MnO_x and Au/CoO_x catalysts prepared by CP compared to the corresponding ones prepared by IM was reported by Solsona et al. [51].

Choudhary et al. [57] reported that the Au/Fe_2O_3 catalyst prepared by HDP exhibited much higher methane combustion activity than that prepared by DP with NaOH. Considering that both methods resulted in comparable Au particle size, the better properties of HDP samples were attributed to the higher gold loading provided from this latter method due to the more efficacious electrostatic interaction of the colloidal gold particles (negatively charged in the HDP preparation and positively charged in the DP-NaOH one) with the positively charged metal oxides.

Lamallem et al. [136] found that gold supported on ceria-titania catalysts prepared by HDP resulted in higher propene combustion activity compared to DP with NaOH or Na_2CO_3 and even more to IM ones (Fig. 19). This was related to the higher amount of gold deposited on the oxide and the higher BET surface area of the HDP sample thus favouring the interaction between gold and the support. The very bad properties of the IM catalyst were also related to the presence of high amount of residual chlorine on this sample.

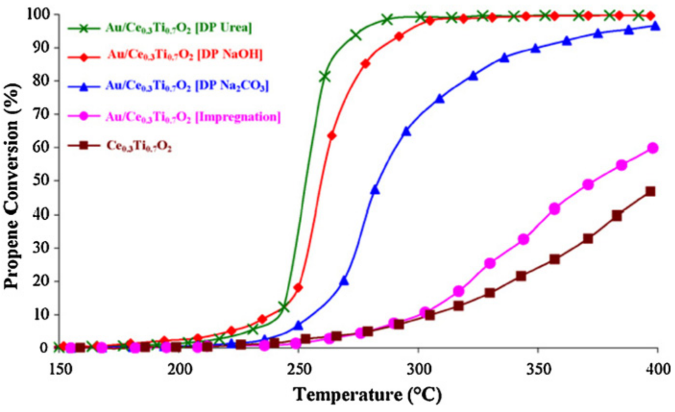

Fig. 19. Propene conversion on $Ce_{0.3}Ti_{0.7}O_2$ and gold-based catalysts prepared by several methods.
Taken from Ref. [136].

Kim and Ahn [117], noted a relevant effect of both the impregnation method used, dip or incipient wetness, and the pretreatment (air or H_2) towards particle size of Pt–Au catalysts supported on ZnO/Al_2O_3 and their activity towards the complete oxidation of toluene. The incipient impregnation technique followed by H_2 treatment resulted in more active catalysts, giving smaller Au particles. This was explained with the negative effect of the chlorine involved in the preparation, which was largely removed by the H_2 pretreatment.

Li and Li [115] compared Au/CeO_2 catalysts, prepared by DP, CP and MCD (metal colloid deposition) in the toluene combustion. They confirmed that DP samples are more active than CP ones, with MCD samples having an activity similar to DP ones. They concluded that the preparation method affects the catalytic activity controlling the gold dispersion, i.e. the size of gold (present as Au^0), which weakens the surface Ce–O bonds adjacent to gold atoms.

Ivanova et al. [72] reported that the preparation of Au/alumina catalysts by a Direct ionic Exchange (DAE) method, followed by washing with ammonia solution produces a strong bonding of the gold complex with the alumina support, resulting in no loss of gold during the subsequent preparation steps, good activity of these catalysts in the C_1–C_3 alkane total oxidation and remarkable resistance to thermal aging at 600 °C in the absence or presence of water.

Santos et al. [74] investigated the effect of the preparation method in the oxidation of CO, toluene and ethanol over titania supported noble metal catalysts. Interestingly a comparison between catalysts prepared by liquid phase reduction deposition (LPRD) and incipient wetness impregnation (IM) revealed that Au-LPRD (4 nm diameter) was far more active than Au-IM (9.1 nm diameter) in the CO oxidation due to the smaller Au particle sizes of the LPDR sample, whereas the difference was significantly less evident in the VOC oxidation, which appeared less affected by the preparation method. In our opinion this behaviour can be well explained considering that the activity of both investigated Au samples in the VOC combustion was quite low (compare 341 °C of T_{50} for ethanol conversion into CO_2 of these catalysts with for instance 200 °C ca. of Au/iron oxide [35]), indicating that TiO_2 is not an efficient support in providing the active oxygen necessary for VOC combustion.

With concern to the influence of the pretreatment of Au/oxide catalysts towards the catalytic performance in the VOC combustion it is possible to state that almost all studies agree with a negative effect of high temperature pretreatments, generally causing an increase in the size of gold clusters and a decrease in the surface area

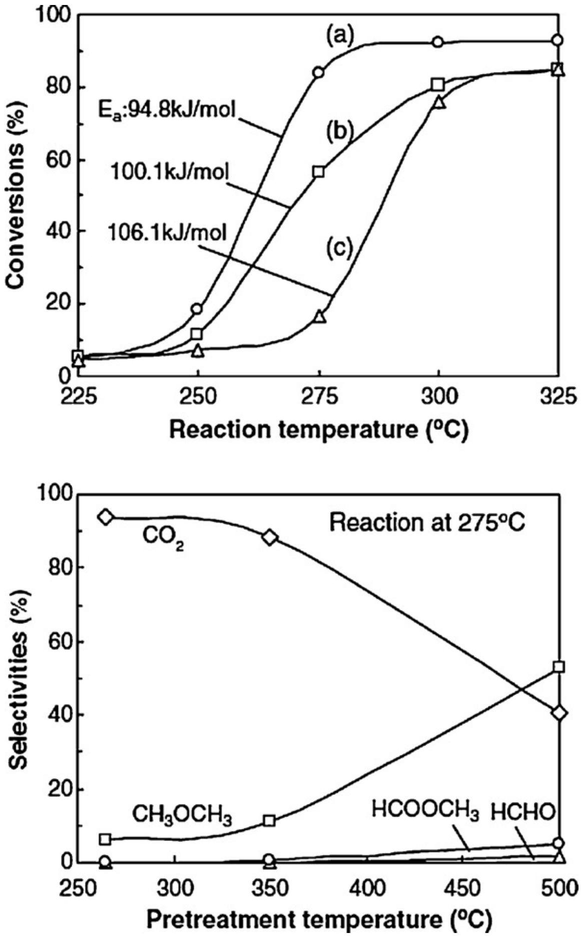

Fig. 20. Effect of catalyst pretreatment temperature on methanol oxidation over 2.4 wt% Au/Fe_2O_3 aerogel, (a) 265 °C, (b) 350 °C and (c) 500 °C. conditions: feed composition $CH_3OH/O_2/N_2 = 2.0/12.7/85.3$ mol%; catalyst contact time 0.1 s. E_a: Arrhenius activation energy estimated based on a first-order model with respect to methanol.

Taken from Ref. [90].

of the catalytic system. This point has been specifically addressed by some researchers. The influence of catalyst pretreatment toward the VOC combustion over Au/iron oxide was investigated by Minicò et al. [37]. They found that higher calcination temperatures lead to growth of gold particle size and reduction of gold from $Au^{\delta+}$ to Au^0, together with a change of the iron oxide phase from ferrihydrite to hematite, resulting in less active catalysts. A similar result was also reported by Wang and Ro [90] over gold/iron oxide aerogels. They, in fact, noted that the catalytic activity towards methanol oxidation decreases significantly with increasing the calcination temperature (from 265 to 500 °C), accompanied with the increase of the activation energy from 94.8 to 106.1 kJ mol^{-1} (Fig. 20). This was attributed to the transformation of gold from Au_2O_3 to metallic Au^0 and to the simultaneous growth of gold particles. Liu and Yang [97] found that calcination temperature has a strong effect on the activity of Au/CeO_2 catalysts towards 2-propanol conversion, with the sample calcined at 300 °C more active than those calcined at higher (400 and 500 °C) or lower temperatures (200 °C). This optimal temperature was ascribed to the fact that at higher temperature the amount of Au^{+1} was considerably lower than at 300 °C, whereas at 200 °C the presence of residual chlorine was detrimental to the activity. Zhang et al. [63] observed a loss of catalytic activity of Au/3DOM CeO_2 catalysts in the HCHO oxidation as a consequence of an annealing treatment at high temperature causing the reduction of Au^{3+} to Au^0. The strong negative effect on the HCHO oxidation activity of a high calcination temperature was also found by Shen et al. [102] which observed a large increase in the size of gold particles, from 2–3 (calcination at 300 °C) to 40–50 nm (calcination at 700 °C), over Au/CeO_2 catalysts prepared by CP.

Lakshmanan et al. [82] reported a significant influence of the catalysts pretreatment showing that for all investigated systems (Au/CeO_2, Au/Al_2O_3 and $Au/xCeO_2$-Al_2O_3) the calcined samples were less active that the reduced ones in propene oxidation, due to the presence on the calcined samples of larger average Au particle size and unreduced gold species.

Solsona et al. [142] also found that the performance of Au/hopcalite catalysts for the total oxidation of propane were affected by the calcination temperature, catalysts treated at the lowest temperature (300 °C) being the most active. This was attributed both to a modification of the hopcalite morphology (decrease of the surface area and increase in the crystallinity) and an increase in the size of Au crystallites with calcination temperature.

6. Kinetics and reaction mechanism

As shown in the previous chapters there is a general agreement that the mechanism of VOC total oxidation over gold supported over reducible oxides is of a redox or Mars–van Krevelen type. Few are, however, the studies directly investigating the reaction mechanism through kinetic experiments or specific techniques (DRIFT, TAP reactor, etc.).

Chen et al. [31] investigated the kinetics of dichloromethane oxidative destruction over Au/cobalt oxide. Over 5% Au/Co_3O_4 the reaction was found to be first order in CH_2Cl_2 and zero order in O_2, with activation energy estimated about 20 kcal mol^{-1}. Grisel et al. [38] reported the Arrhenius plots for CH_4 oxidation over Au/Al_2O_3 catalysts and found that E_a was 140 kJ mol^{-1} over Al_2O_3 and decreased down to 73 kJ mol^{-1} over the most active sample (Au/Al_2O_3 prepared by HDP), value similar to those reported for Pd samples but lower than Pt ones. In a successive investigation over $Au/MO_x/Al_2O_3$ catalysts (M = Cr, Mn, Fe, Co, Ni, Cu and Zn) they discussed [39] the reaction mechanism, suggesting that on Au/Al_2O_3 CH_4 is dissociatively adsorbed on Au or the Au/Al_2O_3 perimeter and reacts with O present at the perimeter and originated from dissociative adsorption of O_2 or dehydroxylation of the alumina surface. Over most of the examined $Au/MO_x/Al_2O_3$ catalysts (M = Mn, Fe, Co, Ni, and Zn), exhibiting similar E_a as Au/Al_2O_3, the improved activity of $Au/MO_x/Al_2O_3$ compared to Au/Al_2O_3 was explained considering a reaction mechanism involving CH_4 activation over Au, with MO_x providing sites capable of supplying active O species. Gluhoi et al. [48] found that the apparent activation energy in propene oxidation decreases after the addition of gold to Al_2O_3, from 90 kJ mol^{-1} (Al_2O_3) to 67 kJ mol^{-1} (Au/Al_2O_3), indicating that gold is the active species in C_3H_6 oxidation. They also suggested that the beneficial role of alkali metal oxides towards the performance of Au/Al_2O_3 in the total oxidation of propene was due to an increase in the concentration of Au active sites in so as the addition of alkali metal oxides to Au/Al_2O_3 was not found to change the E_a. A similar behaviour was also found [50] in methane and propane oxidation over $Au/MO_x/Al_2O_3$ catalysts, with $E_a > 100$ kJ mol^{-1} for MO_x/Al_2O_3 catalysts and 70–80 kJ mol^{-1} for $Au/MO_x/Al_2O_3$ independently from the presence of alkali metal oxides. Zhang and He [100] by means of a DRIFT study proposed a common mechanism for the HCHO combustion over Pt, Rh, Pd and Au supported on TiO_2 (Fig. 21). They suggested that the activity of these systems reflects the capacity of formation of formate species and subsequent decomposition of these formates to CO, which is the rate determining step. Deng et al. [95] reported that the kinetics for the catalytic combustion of methanol over Au/Al_2O_3 catalysts followed quasi-first order reaction with an apparent activation energy

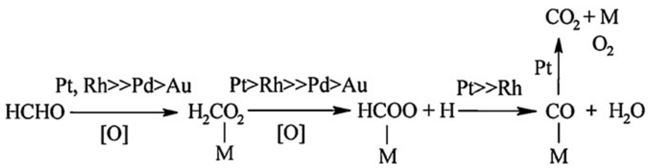

Fig. 21. Reaction scheme of the catalytic oxidation of HCHO on the TiO_2 supported Pt, Rh, Pd and Au catalysts.
Taken from Ref. [100].

of 54.7 kJ mol^{-1}. Ma et al. [106] carried out a DRIFT study suggesting a mechanism for the HCHO combustion over gold supported on mesoporous Co_3O_4 and Co_3O_4–CeO_2 catalysts. They proposed that gold particles of less than 5 nm diameter are embedded or partly entered within the Co_3O_4 or CeO_2 pore walls. Co_3O_4 facets composed mainly of Co^{3+} cations are the active facets for formaldehyde oxidation. Over these sites adsorbed formaldehyde is oxidized into formate. A second attack of surface active oxygen generates bicarbonate species which decomposes into CO_2 (Fig. 22).

Solsona et al. [143] carried out an interesting transient reactor study of the oxidation of propane over Au/CoO_x using the TAP reactor. The authors demonstrated, also using isotopically labelled oxygen, that the reaction occurs via a Mars–van Krevelen mechanism. They, in fact, found that when propane is the only reactant fed to the TAP reactor activity is similar for both CoO_x and Au/CoO_x, whereas when both propane and oxygen are co-fed Au/CoO_x is more active than CoO_x. The positive role of gold, (present as Au^0) on the activity of cobalt oxide was attributed to an increase of the exchange rate of Au/CoO_x oxygen between lattice and surface oxygen, i.e. the reoxidation step, related to a higher concentration of oxygen vacancies (higher oxygen storage capacity). The evidence of a MVK mechanism was confirmed by the same research group by means of an *in situ* DRIFTS study on the oxidation of polycyclic aromatic hydrocarbons over gold/ceria catalysts [55].

Wu et al. [60] also proposed a Mars–van Krevelen mechanism for the benzene total oxidation over Au/ZnO, with a catalytic cycle involving (1) chemisorption of benzene on Au particles, (2) migration of the chemisorbed benzene to the Au–ZnO interface, (3) O_2 activation on the defect sites in the Au–ZnO interface and formation of active oxygen species, (4) reaction between the chemisorbed benzene and active oxygen species at interface. In another study, dealing with the toluene and p-xylene deep oxidation over Au/Co_3O_4 catalysts, the same authors [119] confirmed the MVK mechanism (Fig. 23) and attributed the high activity of Au/Co_3O_4 to a high concentration of superficial electrophilic oxygen species and oxygen vacancies, originated from a strong interaction in the colloidal Au/Co_3O_4 system. In a very recent paper Liu et al. [103], on the basis of FT-IR, TPSR, TPD and TPR measurements, proposed a reaction mechanism for the HCHO oxidation over Au/macroporous ceria involving the participation of both Au^{3+} and Au^0 in the HCHO combustion. They suggested that two distinct processes occur on ionic Au^{3+} and metallic Au^0 (Fig. 24), involving HCOOH and formate as intermediates, carbonate and hydrocarbonate formed being responsible for the catalyst deactivation. Interestingly the process on Au^{3+} showed higher activity than that one on Au^0.

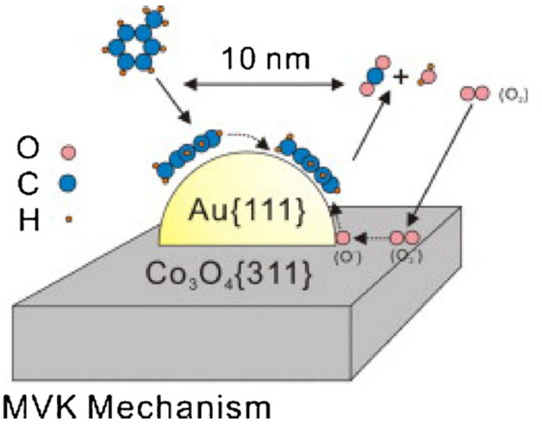

Fig. 23. Proposed MVK mechanism over Au/Co_3O_4 catalysts.
Taken from Ref. [119].

7. Special topics

7.1. Gold based bimetallic catalysts

Only a few reports can be found in the literature regarding the use of gold-containing bimetallic catalysts for the catalytic combustion of VOC.

Miao et al. [144] reported that the activity of Au/Co_3O_4 catalysts towards methane combustion was enhanced by the presence of small amount of Pt (0.2 wt%), with a temperature of 100% conversion decreased by 50 °C ca. On the contrary the presence of Pd had no significant effect. Unfortunately no explanation was provided for the performance improvement of Pt.

Hosseini et al. investigated the promotional effect of gold addition to Pd supported on mesoporous TiO_2 [73] or TiO_2/ZrO_2 [145]. For titania supported catalysts they found [73] that Pd impregnated on Au/TiO_2 exhibits the highest toluene and propene combustion activity, which was higher than corresponding samples supported on conventional titania. The promotional effect of Au was explained with the formation of small metallic particles made up of an Au-

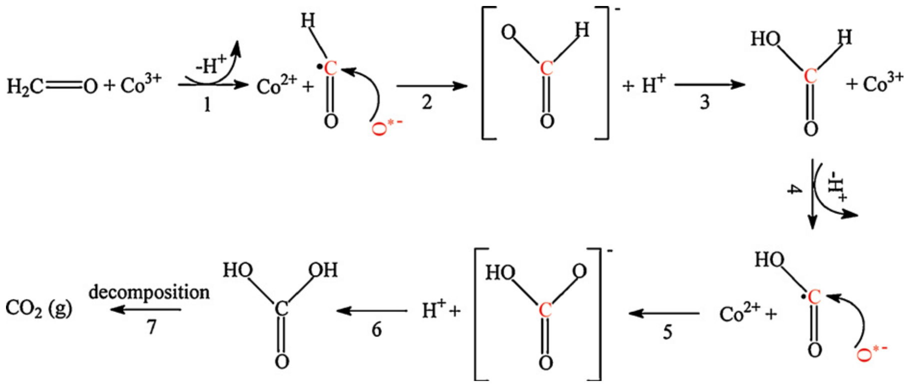

Fig. 22. Microreaction process for formaldehyde oxidation over mesoporous Co_3O_4, Au/Co_3O_4, and Au/Co_3O_4–CeO_2 catalysts at 25 °C.
Taken from Ref. [106].

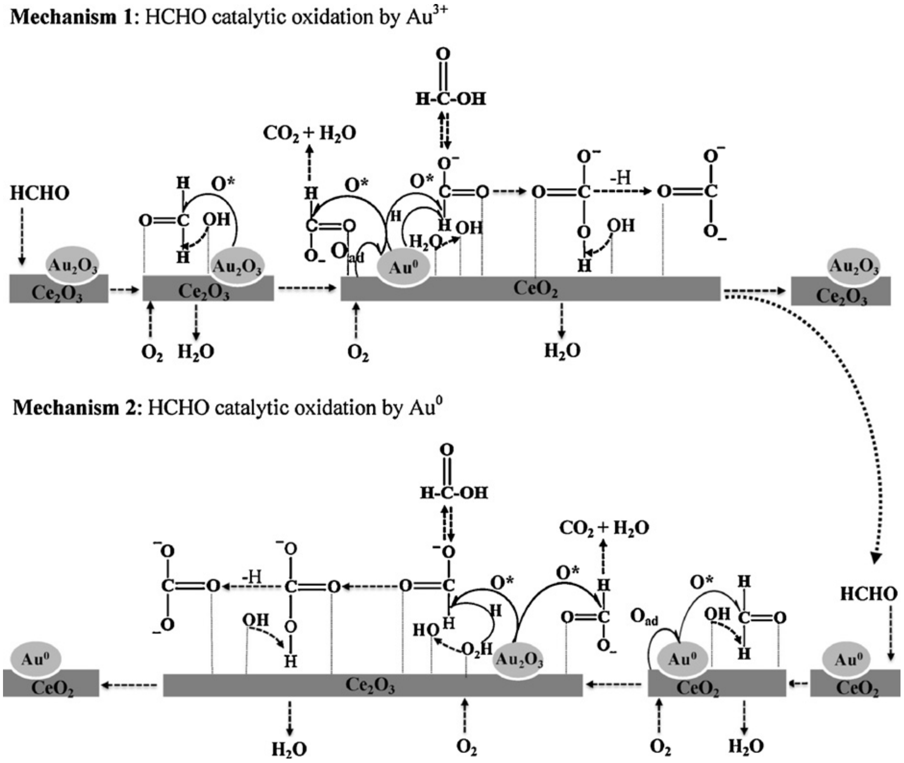

Fig. 24. The proposed catalytic mechanism of 3DOM Au ~ 0.56 wt%/CeO_2 catalyst for enhanced HCHO catalytic oxidation.
Taken from Ref. [103].

rich core with a Pd-rich shell. By operando DRIFT spectroscopy they found a metallic electrodonor effect to the adsorbed molecule, which increases in the same order as the activity for oxidation reactions. In the case of titania/zirconia supported catalysts [145] similar results were observed. Also in this case, in fact, the activity in toluene combustion was higher when the gold was loaded firstly. In this latter case the activity depended also on the Ti:Zr ratio and it was suggested that the weaker adsorption of molecule on the catalyst the higher is the activity for oxidation reaction.

The use of Pt–Au catalysts supported on ZnO/Al_2O_3 was reported in the complete oxidation of toluene [117]. It was found that the coexistence of Pt and Au on ZnO/Al_2O_3 results in a higher activity compared to Pt or Au catalyst only, the highest activity being obtained on the bimetallic Pt–Au catalysts prepared by wetness impregnation and treated in H_2 at 400 °C. A relationship between the Au particle size and the toluene combustion activity was suggested.

The activity and selectivity of mono- (Au) and bimetallic (Au–Pd and Au–Rh) catalysts containing nanoparticles of gold stabilized by different supports (titania, H-ZSM5, H-beta, MCM-41) were investigated in the catalytic combustion of sulphur containing VOC from air [126]. It was found that Au–Pd/TiO_2 and Au–Rh/HZSM-5 were more active and stable than respective monometallic samples in the DMDS removal.

Gold catalysts deposited on a cobalt containing siliceous mesoporous structure, UVM-7, have been recently reported by Solsona et al. [146] in the total oxidation of propane and toluene. The improved activity of the Au–Co bimetallic samples, if compared to gold free cobalt catalysts, was explained on the basis of the enhanced reducibility of some cobalt species in the presence of gold, which facilitates the redox cycle. This high reducibility of cobalt species in the bimetallic samples is probably due to the formation of Co_3O_4 domains at the gold–CoO interface perimeter, which are absent in the gold free cobalt containing UVM-7 catalysts. More interestingly, these catalysts exhibited a high stability during the oxidation of propane and toluene, showing stable activity for at least 50 h and three catalytic cycles.

7.2. Gold-based catalysts for sensors and pollution control devices

A careful choice of supports and preparative conditions makes gold catalysts highly active for the abatement of VOC molecules in air at relatively low-temperature. Moreover, it is particularly advantageous that the oxidation activity of gold is promoted or maintained in the presence of water vapour [56,72,122]. Therefore, gold potential in oxidation reactions results in several applications for air purification and quality control in indoor and outdoor environments, such as office space, submarines, space crafts, automobile and incinerator exhaust gases [24,28,147–149]. To this aim, gold catalysts are employed as air-cleaning devices, for respiratory protection (gas masks), as sensors to detect individual poisonous or flammable gases, as well as deodorisers. The Carrier Corporation (US) has published a patent on Au/TiO_2 coating for photocalytic/thermocatalytic removal of VOC [150]. Meanwhile, Rhodia GmbH has published a patent on Au/CeO_2–ZrO_2 catalysts to be used as filter in cigarettes as well as for treatment of tobacco smoke and polluted air [151]. Union Chemical Laboratories in Taiwan have developed masks for fire fighters based on nanosized (2 nm) gold particles deposited on oxide supports.

Gold-based sensors selective for detection of individual pollutant gases are currently commercialized. Some examples are therein reported. Gold-oxide composites are applied as sensors for hydrocarbons monitoring in automobile exhausts [152,153]. Nanostructured sensing arrays consisting of thin film assemblies of alkanethiolate-monolayer-capped gold nanoparticles have been employed for the detection of volatile organic compounds (VOC) and nitro-aromatic compounds (NAC) [154]. Metal oxide semiconductor (MOX) gas sensors based on ultra-low-power (ULP) consumption micro-machined hotplates containing controlled amount of gold nanoparticles are effective for VOC detection at ppb-level [155]. Gold-doped ZnO nanostructures were used as ethanol sensors, the highest sensitivity, up to 145 ppm, being obtained for 10% Au-doped ZnO sensor [156]. Sakai Chemical Industry Co, Japan has published a patent on binary and ternary-catalysts including Au/Fe_2O_3 for deodorizing exhaust gases from sewage disposal plants, refuse disposal plants, printing and plating factories etc. [157]. Moreover, since 1992 Au/Fe_2O_3 supported on zeolite wash-coated honeycomb has been commercialized as deodorizer in Japanese toilets [24,68].

Osaka Gas Company has found that VOC present in exhaust gases of incinerators can be oxidatively decomposed at low temperature, even 150 °C, over a multi-component catalyst consisting of Au supported on Fe_2O_3–Pt/SnO_2–Ir/La_2O_3 [158–160]. Gold catalysts with low-temperature activity towards CO and hydrocarbons oxidation are suitable for vehicles exhaust gas treatment, especially during the cold start period [161]. In 1999, Yamada corporation patented a multicomponent (Au/MnO_2/CuO/Pd/Al_2O_3) vehicle exhaust-gas purifier [162]. Some years later, Mellor and coworkers formulated a gold based three-way catalyst deposited over a zirconia-stabilized ceria/zirconia/titania and containing CoO_x, Rh, ZnO and BaO as promoters [77]. The high-temperature requirements imposed by gasoline engines limit, however, the use of gold-based catalysts which cannot survive under the drastic experimental conditions typical of PGM-based TWC, unless to be properly stabilized by strong interaction with transition metal oxides. One interesting approach to improve gold thermal stability has been shown by Toyota motor company which as patented mixed Au/La/alkali and alkaline earth metal oxides for automotive exhausts purification [163]. Data for durability at 800 °C has shown constant temperature of 50% of C_3H_6 conversion over such Au promoted catalysts, whereas a standard Au/Al_2O_3 catalyst under the same conditions suffered significant deactivation.

On the other side, temperatures in diesel exhausts are much lower than in gasoline fuelled vehicles (max. 230 °C under European urban driving cycle, whilst max 440 °C under extra-urban driving cycle) [164], therefore gold catalysts could found effective application in diesel exhausts after treatment. Accordingly, at the end of 2007 Nanostellar company announced the development of a diesel exhaust catalyst which uses a first catalytic component based on gold alloyed with palladium as active component for CO oxidation and a second component of platinum/palladium which oxidizes most of the unburned hydrocarbons in diesel exhausts. In early 2011 Nanostellar has started commercial production of such gold/palladium/platinum catalyst which is currently used by one of the four largest European producers of diesel cars [165–168].

8. Conclusions and outlooks

Literature results discussed in previous chapters of this review clearly point out that metal oxide-supported gold systems are receiving growing attention as catalysts for the deep oxidation of VOC, both from academic and industrial point of view. As shown in Fig. 1, this interest significantly boosted in the last years, confirming the prediction of Corma and Garcia, who stated, at the end of their 2008 review on gold catalysts for organic reactions, that "*...it can be anticipated that processes dealing with the complete oxidation of organic pollutants using gold nanoparticles as catalysts will continue to attract attention in the near future*" [26].

Undoubtedly, studies up to now carried out by different research groups allowed to establish that VOC deep oxidation over Au/metal oxide catalysts is governed by both the support and the gold properties, which often amplify their effects due to a synergistic action. Therefore the research mainly focused on the design and obtainment of the most suitable support and/or gold characteristics, aiming to understand how different operative variables, such as preparation techniques, pretreatment and reaction conditions, presence of promoters and/or other substances, can affect support and gold properties and consequently the catalytic performance. Even though the unambiguous distinction of the role of each single parameter towards the VOC combustion performance of Au catalysts is far to be achieved and probably it will remain always matter of debate, we believe that the research in this field has reached by now a satisfactory level of knowledge.

In our opinion not enough attention has been instead devoted to the durability of Au/metal oxide catalysts under reaction conditions. Taking into account the high exothermicity of the VOC combustion and the comparatively low melting point of gold (1064 °C) with respect to other noble metals (for instance 1769 °C of Pt), the poor stability of gold at high temperatures appears as the major drawback for any commercial application of Au/metal oxide catalysts in the environmental protection field, justifying the choice of more expensive noble metals such as platinum and palladium. Therefore, more efforts must be devoted both from academic and industrial researchers in the next future to the development of more stable supported gold systems under deep oxidation reaction conditions. Nevertheless, some encouraging results have been also reported in which performance improvement was sought [39,47–50,64,77].

We also feel that another aspect deserving further research studies is the potential use of supported gold catalysts in the photocatalytic deep oxidation of VOC. The possibility to drive the oxidation of organic contaminants in air at ambient temperature with supported gold nanoparticles appears a great challenge in the catalysis by gold. Au nanoparticles has been, in fact, reported to adsorb visible light intensely because of the surface plasmon resonance effect [108].

Another key question for effective large-scale commercialization of gold catalysts for VOC deep oxidation or other environmental applications is the economic evaluation. Since gold is available on a much larger scale than platinum or palladium, its price has been historically more stable [147]. Accordingly, up to 2004 the price of gold has been relatively constant and much lower than that of platinum [161]. However, due to the increasing demand since 2005 to 2011 the price of gold has shown considerable upward movement, culminating in 1600–1660 US$ per oz [169]. Moreover, the effects of economic and political uncertainty have increased the speculative investment demand for gold. The assumption of a world economic recovery over the next few years is expected to lead to a reduction in speculative demand for gold and, consequently, gold price is forecast to be steady in the next future [170]. Besides, the development of effective and economically advantageous methods for gold recovering from spent catalysts is expected to further boost the investment in gold catalysts [148].

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