

Ceria-zirconia supported gold catalysts*

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This paper presents the most important achievements and conclusions coming from the contributions concerning ceria-zirconia supported Au catalysts for low temperature water gas-shift reaction and low-temperature CO oxidation. The usefulness of CeO₂-ZrO₂ mixed oxides as supports for Au nanoparticles has been reviewed, mainly from the point of view of their contribution to those reactions. A special attention was paid to the active sites of CO oxidation and WGS reaction over Au/ceria-zirconia systems. Some aspects of the reactions mechanisms are also discussed. Ceria-zirconia supported gold catalysts appear to be very promising systems, which have a potential to create a new quality in the catalysis of WGS reaction. Ceria-zirconia mixed oxides also seem to be very promising supports for Au nanoparticles in CO oxidation. They could find a practical application in ambient conditions, especially in air purification systems and a breathing apparatus. It is possible that gold could be usefully incorporated into automobile catalysts, considering that the price of other noble metals is rising rapidly. Their use in this application will, however, require demonstration of adequate stability at operating temperatures.

*This article is dedicated to Professor Roman Lebeda on the occasion of his 65th birthday

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1. INTRODUCTION

It is now fully proved that nanosized particles of gold supported on metal oxides are highly efficient catalysts for numerous reactions, including the low-temperature CO oxidation, also in the presence of hydrogen (PROX), water gas-shift, selective and nonselective oxidation of hydrocarbons, selective reduction of nitric oxide by hydrocarbon in the presence of high concentration of oxygen, organic reactions (selective hydrogenation of α , β unsaturated carbonylic compounds, addition to multiple C-C bonds, selective oxidation by oxygen, selective reductions of nitro groups in the presence of other reducible functions) and many others [1-4]. Furthermore, the recent reversal of market prices of Au with respect to Pt and Rh can drive gold catalysts to commercialisation with an economical advantage.

Various parameters, including the Au precursor, the catalyst preparation method, pre-treatment and catalytic testing conditions, particularly the size of gold nanoparticles (2–5 nm) and the nature of the oxide support, have already been considered as crucial factors influencing the chemistry, structure, and catalytic performance of Au catalysts. The classical impregnation methods, very often used in the preparation of other noble metal catalysts, fail in the case of gold-containing systems. Its application cannot lead to a high dispersion of Au due to its lower melting temperature (1063⁰C) than that of Pd (1550⁰C) and Pt (1769⁰C) and partly because the catalyst precursors are often calcined at low temperatures (below 600⁰C), where chlorine still remains in the metal oxide supports [3-5]. For this purpose, several preparation methods of supported Au catalysts have been developed by many authors, based mainly on the precipitation of a gold precursor at basic pH and its deposition on an inorganic oxide [3]. A main technique is derived from the deposition-precipitation methods as it was originally proposed by Haruta [6]. In this context, an essential role is played by the isoelectric point (IEP) of the oxide support. In general, the oxides having the IEP in the range 6–7, such as TiO₂ (IEP = 6), CeO₂ (IEP = 6.75), ZrO₂ (IEP = 6.7), Fe₂O₃ (IEP = 6.5–6.9) make it possible to obtain active catalysts, while Au supported on both acidic (SiO₂, IEP = 1–2) and basic (MgO, IEP = 12) oxides are usually inactive [5].

Apart from its fundamental role, i.e. dispersing the metal and limiting its tendency to agglomeration, the oxide supports of gold catalysts very often participate in the reaction mechanism, by redox cycling of support metal ions. Such behavior is typical of partly reducible oxides like TiO₂, MnO₂, Fe₂O₃ and primarily of all CeO₂. The ability of cerium to form the reversible existence in +3 and +4 valence states makes it a very good candidate in all applications as a support, where high redox activity is needed. Oxygen storage capacity (OSC) of ceria sealed its importance as the main active component of “washcoat layer” in

TWC catalysts for the removal of automotive exhaust gases from emissions of gasoline engines. Thus, the ceria supported gold systems attracted a lot of attention as the catalysts for low-temperature water gas-shift, carbon monoxide oxidation and PROX reactions. In the last 5 years several tens of relevant papers have been published, most of which being quoted in the papers [7,8]. However, pure ceria is relatively resistant to reduction. At temperatures 400–500°C only a part of surface oxygen (so called “capping oxygen”) is prone to the reduction. The full conversion of CeO₂ to Ce₂O₃ occurs at temperatures much higher than 750°C. At such high temperatures, the sintering of ceria can also take place. Moreover, the oxygen mobility can be reduced due to the ordering of oxygen vacancies. The incorporation of zirconium into the ceria lattice led to the formation of a solid solution which exhibits a lower reduction temperature, better resistance to the sintering, resulting in an improved oxygen storage capacity. The implementation of ceria-zirconia mixed oxides to the TWC converters is considered as one of the major breakthrough points in the development of auto exhaust abatement technology. The decreasing of fluctuations in the air to fuel ratio (A/F) made it possible to sharpen emission control to a great extent. Such unique properties of ceria–zirconia systems seem to make them ideally suited for an application as supports to gold catalysts. Surprisingly, only a few papers concerning Au/Ce_xZr_{1-x}O₂ catalysts [7,9-23], tested mainly in the water-gas shift reaction [9-16] and low-temperature CO oxidation [10,17-23] have been published so far. In this paper the most important achievements and conclusions coming from these contributions have been reviewed.

2. CERIA-ZIRCONIA SUPPORTED GOLD CATALYSTS FOR LOW-TEMPERATURE WATER GAS-SHIFT (WGS) REACTION

Water gas-shift (WGS):



is a process of great importance in applications such as on-board H₂ production via reforming processes for fuel cells. In such an application, a successful low-temperature WGS catalyst will have to possess very high activity in removing carbon monoxide, a poison for membranes in the fuel cell stacks, high selectivity as well as good structural stability under all reaction conditions. The typical low-temperature WGS catalysts (most often Al₂O₃ supported Fe-, Cu-, Cu-ZnO systems) reduce CO concentration to ca. 2000 ppm, achieving equilibrium conversion at about 200°C. However, the desired catalysts for the new generation of Polymer Electrolyte Fuel Cells should operate at much lower temperatures

(ca. 100°C), be resistant to deactivation and nonpyrophoric, in contradiction to the classical catalysts.

Supported gold catalysts have been extensively studied and considered as potential catalysts for WGS reaction. As compared to other platinum group metals, gold based catalysts have shown some of the highest WGS activity. The early works in this area, focused on Au/Fe₂O₃ catalysts, have demonstrated that Au/ α -Fe₂O₃ catalyst presents higher activity than that conventionally used, Cu/ZnO/Al₂O₃ at the temperature below 200°C, under simple WGS conditions [24-25]. However, this catalyst was characterized with poor stability even at moderate temperatures under WGS feeds due to the instability of Fe₂O₃ under reducing conditions [26]. More recent works have shown that Au nanoparticles supported on different metal oxides such as TiO₂ [27], ZrO₂ [28], and CeO₂ [29] present significant WGS activity. As it was proved by Flytzani-Stephanopoulos et al. [29-31], ceria, especially nanocrystalline, shows unique properties as an oxide support, increasing the activity of Au toward CO oxidation. The reported Au-ceria catalysts show good stability in WGS reaction in the full fuel-gas mixture also, which is very important in cyclic start-up and shut-down procedures involving purging with air. However, the resistance to deactivation of ceria supported gold catalysts is not unquestionable, as reported by Kim and Thompson [32]. Its characterization using X-ray photoelectron and infrared spectroscopy indicated that the deactivation was caused primarily by blockage of the active sites by carbonates and/or formates. These species appeared to be formed by CO and H₂, and their formation was facilitated by oxygen deficient sites on ceria [32].

As it was already mentioned, the addition of zirconium into the ceria lattice has a significant effect on both oxygen storage capacity and its stability. The presence of Zr allows the storage and release of oxygen not only from surface layers but also from the bulk lattice structure [20]. Such properties prompted the researchers to investigate ceria–zirconia systems as the oxide supports for gold nanoparticles in low-temperature WGS reaction. Amieiro Fonseca et al. [11] studied gold catalysts containing 0.19–3 wt.% of metallic phase on commercial (Rhodia) CeZrO₄ (Ce : Zr atomic ratio 50:50). To establish the effect of the oxide support on the WGS activity, a series of 2 wt.% Au catalysts supported on different, commercial (CeO₂, TiO₂, ZrO₂) and home made 'FeO(OH)' oxides was prepared. Catalytic tests were performed in a glass microreactor containing 450 mg of sample, using a 5% CO, 30% H₂O and 65% N₂ reaction gas mixture, at a space velocity 40000 cm³.g⁻¹.h⁻¹, in the temperature range 100–300°C. Table 1 presents the effect of the oxide support and Au loading, in the case of CeZrO₄, on WGS activity. Temperatures of 50, 90 and 100% CO conversion were estimated basing on the data provided in [11].

From all tested catalysts, Au/CeZrO₄ shows the highest activity in WGS reaction (the lowest temperature at which the process occurs), with significant (about 20%) CO conversion at temperatures as low as 100⁰C, and its total conversion at ca. 200⁰C. One can see that Au/CeZrO₄ catalysts present significantly higher activity than that of a commercial copper catalyst, characterized with 50, 90 and 100% CO conversion at 174, 193 and 210⁰C, respectively [10].

Tab. 1. Temperatures of 50, 90 and 100% CO conversion over 2 wt.% Au catalysts supported on different oxides and Au/CeZrO₄ catalysts with different Au loading (in details described in [11]).

Conversion temperature	Catalyst							
	Au/FeO(OH)	Au/ZrO ₄	Au/TiO ₂	Au/CeO ₂	2.99wt% Au	1.70wt% Au	0.87wt% Au	0.19wt% Au
T ₅₀	159	170	175	206	125	131	162	199
T ₉₀	177	219	250	282	157	171	210	263
T ₁₀₀	-	-	-	-	194	199	231	-

A higher Au loading, lower temperatures of 50, 90 and 100% CO conversion over Au/CeZrO₄ catalysts were observed. However, the increase in Au loading above 1.70 wt.% does not lead to the further increase in CO conversion. The apparent activation energies of all studied Au/CeZrO₄ catalysts (ca. 28 kJ.mol⁻¹) were significantly lower than that reported for Au/CeO₂ catalyst (ca. 40 kJ.mol⁻¹), due to the promoting role of CeZrO₄ in WGS reaction [11].

The results of X-Ray Photoelectron Spectroscopy (XPS) analysis, together with X-Ray Absorption Near-Edge Structure (XANES) and Extended X-Ray Absorption Fine Structure (EXAFS) have shown that in the as – prepared catalysts, before the catalytic tests, gold prevails in its ionic state. The higher Au loading, the lower amount of gold in the ionic state is observed. The lowest loaded 0.19 wt% Au/CeZrO₄ catalyst contains only Au³⁺ ions, 0.87 wt% Au/CeZrO₄ – 65% Au⁺³ and 35% Au⁺¹ and 1.70 wt.% Au/CeZrO₄ – 57% Au⁺³, 35% Au⁺¹ and 8% Au⁰. However, under full WGS reaction conditions (2.0% CO, 2.5% CO₂, 7.5% H₂O, 8.1% H₂ and 79.9 N₂), even at temperature as low as 100⁰C, gold exists exclusively in the metallic form (Au⁰), conforming rapid and essentially complete reduction of Au³⁺ ions presented in the as – prepared catalyst [13].

The measurements of intrinsic TOF for WGS of the studied catalysts proved that a higher proportion of Au³⁺ in the as – prepared catalyst guarantees higher WGS activity, due to the fact that the reduction of Au³⁺ to Au⁰ takes place under reaction conditions. Thus, one can conclude that monodispersed Au ions are the best precursor state, giving the highest activity of Au/CeZrO₄ catalysts in WGS reaction [33].

Therefore, if the active form of gold in WGS reaction is metallic, what is the point of the beneficial influence of special redox properties of ceria – zirconia oxide support on the catalytic performance of Au/CeZrO₄ catalysts?

Tibiletti et al. [13], basing on XANES and EXAFS experimental results and Density Functional Theory (DFT) calculations, pointed to a model in which metallic gold clusters containing ca. 50 atoms remain in the intimate contact with the oxide support. Part of gold atoms (ca. 15%), placed at the interface with the support, may be located at cerium cation vacancies in the surface of the oxide support. Such gold atoms can carry a small positive charge (Au^{δ+}), which may be very important in the creation of the active site for WGS reaction. It should be pointed out that even in low loading gold catalysts (0.2 wt.%) the fraction of ionic gold, under water gas shift condition, is below the limit of detection by XANES (< 5%). The authors of the quoted paper [13] believe that under WGS reaction conditions, the active form of gold is comprised of small metallic Au clusters, being in a close contact with the oxide support. Such a statement is supported by the results of the combined TPR-H₂ and steady-state TPO-H₂O studies of CeZrO₄, Au/CeZrO₄ and Pt/CeZrO₄ [11]. As it could be expected, both Pt and Au enhanced the reducibility of Ce⁴⁺, shifting the maximum of the TPR profile c.a. 400°C towards a lower temperature. However, platinum appears to be a more effective reduction promoter than gold and enhances the reduction not only of surface, but also of bulk Ce⁴⁺. It is due to the ability of platinum to H₂ adsorption followed by spill-over of hydrogen to the bulk of oxide support. Nevertheless, while Pt is more effective at reducing the bulk Ce at low temperatures, Au appeared to be much more efficient in activating H₂O to oxidize reduced cerium. Therefore, the activity of Au/CeZrO₄ catalysts in WGS reaction at low-temperature may be related to the ability of gold to activate H₂O, to oxidize reduced Ce sites and, as a result, to release H₂. Such consideration may be rationalized by the kinetic expression for WGS reaction over Au/CeZrO₄ catalyst [34]:

$$r = P_{\text{CO}}^{0.75} P_{\text{H}_2\text{O}}^{0.57} P_{\text{CO}_2}^{-0.27} P_{\text{H}_2}^{-0.99}$$

The significant inhibition by hydrogen might indicate its slow reversible release from water molecule [34]. The positive order with respect to CO reflects the weak adsorption of CO on the catalyst. On the other hand, the results of TPR-CO studies suggest that, under reducing conditions, carboneous species are created by CO adsorption on the catalyst which next are decomposed with H₂O and released as CO₂.

Burch [35] proposed a universal mechanism for the forward and reverse WGS reaction. He suggested that depending on the reaction conditions, especially the temperature and H₂O/CO₂ ratio, the dominant mechanism can change from a

redox-type one to that dominated by surface species, like formates, carbonates and carboxylates. At the low-temperature WGS process, where such species have a significant life time on the surface, the final carbonate decomposition step in the mechanism would predominate. At intermediate temperatures, especially in the presence of a large concentration of water, the formate decomposition step in the mechanism would be principal. Finally, at higher temperatures, the redox-type process would be expected to play a crucial role. However, the recent results obtained basing on Operando Drifts data show that the formates are not part of the major reaction pathway over highly active low-temperature WGS Au/CeZrO₄ catalysts [15]. Thus, one can conclude that there is evidence of both “redox-type” and the so-called “associative” (connected with the creation of carbonaceous species) WGS reaction pathway; however, the first of them seems to predominate.

Amieiro Fonseca et al. [11] also studied the influence of both temperature ramp and “the time on stream” on the Au/CeZrO₄ catalysts stability in WGS reaction. Table 2 shows that in all cases some deactivation is observed.

Tab. 2. Temperatures of 50 and 90% CO conversion over 1.70 wt.% Au/CeZrO₄ catalyst, as - prepared, after WGS feed treatment at 200⁰C, after WGS feed treatment at 300⁰C and after ramping to 500⁰C with WGS feed (5% CO, 30% H₂O, 65% N₂) (in details described in [8]).

Conversion temperature	1.70 wt.% Au/CeZrO ₄ catalyst			
	As prepared	50 hrs „time on stream“ in 200 ⁰ C	50 hrs „time on stream“ in 300 ⁰ C	After ramp to 500 ⁰ C with WGS feed
T ₅₀	131	158	223	210
T ₉₀	171	209	300	283

The authors, using different advanced instrumental techniques including Daresbury synchrotron facilities, accurately estimated Au particle size for as - prepared and deactivated samples. After the treatment of the sample with WGS feeds at low temperatures (200⁰C), small gold species (ca. 1 nm) with good interaction with CeZrO₄ support were observed. For this reason, the decrease in activity after such a treatment was relatively low. The increase in the ageing temperature up to 300⁰C led to the significant decrease in activity of Au/CeZrO₄ catalyst. No change in Au particle size was observed, however, the decrease in metal-support interaction was noticed. The treatment of the catalysts at a higher temperature (500⁰C) caused only modest sintering of Au particles. Thus, the authors [11] proposed that the deactivation occurs rather due to the reduction in the number of the Au interface sites, necessary to mediate the WGS reaction, than due to the decrease in Au cluster size. Similar conclusions come from the work of Goguet et al. [12]. Basing on the combined experimental and theoretical

approach, the authors claim that hydrolysis of the interface between the gold and the support reduces the metal – support interaction and causes the metal nanoparticle detachment from the surface. Considering that the intimate contact between the support and the gold is essential for the high WGS activity, such detachment leads to deactivation.

The role of metal – support interface in the creation of catalytic activity of Au/CeO₂-ZrO₂ catalysts in WGS reaction was also studied by Boaro et al. [14]. The possibility of modifying the redox and structural characteristics of zirconia with the insertion of ceria allowed the authors to conclude that the bulk redox properties of the support play a secondary role, while the key parameter for an active WGS catalyst is the nature of metal – support interface. This depends on both the metal particle distribution and the structural and morphological properties of support. It has been found that the synergism between precious metals and support can be designed with an appropriate choice of the catalyst synthesis conditions and the characteristics of support.

In this work [14], WGS activity of gold- and platinum- based catalysts supported on zirconia and ceria–zirconia solid solution has also been compared. At a low temperature, Au catalysts appeared to be more active than platinum containing systems. Interestingly, in the case of Pt catalysts, support composition did not affect significantly the WGS activity. Their activity was mostly influenced by very fine metal particles dispersion. Conversely, the composition of support played a more important role in promoting the activity of Au catalysts. Zirconia appeared to be a very suitable support for gold since it favors the dissociation of water and strongly interacts with gold particles to promote their capacity of adsorption and desorption of reactants involved in the reaction.

In contrast to the authors of the papers discussed up to now, Radhakrishnan et al. [16] found 3.33 wt.% Au/Ce_{0.58}Zr_{0.42}O₂ catalyst merely active in WGS reaction. This catalyst is much less active than any other noble metal catalyst (Pt, Rh, Ru, Pd, Ir) supported on the same oxide support. The authors attribute the discrepancy in their results and those reported in the literature to differences in the synthesis techniques and/or gas compositions and reaction conditions.

However, from the already published, but not very abundant literature, ceria-zirconia supported gold catalysts appear to be very promising systems, which have a potential to create a new quality in the catalysis of WGS reaction.

3. CERIA-ZIRCONIA SUPPORTED GOLD CATALYSTS FOR LOW-TEMPERATURE CARBON MONOXIDE OXIDATION

Carbon monoxide oxidation:



at ambient temperature is a very important reaction for air purification systems and breathing apparatus. The industrial catalyst used at present is hopcalite, a mixed oxide of copper and manganese (CuMn_2O_3) [3,4]. This catalyst is susceptible to deactivation in the presence of water and is unsuitable for a long term use. Moreover, the catalysts active at low-temperature CO oxidation can find a practical application in closed-cycle CO_2 lasers, safety masks and as a material for gas sensors for detection of trace amounts of CO in the air, etc. Carbon monoxide is also one of the main pollutants emitted by gasoline vehicles during the cold-start of engines, since conventional three way catalysts are not efficient at the temperature below 200°C . In order to comply with the new limits imposed by the legislation on pollution control, more efficient catalysts at a low temperature are required. Moreover, these catalysts are expected to be resistant to sintering and sustain its activity at a steady-state working temperature of the exhaust system within cost-effective barriers.

The application of CeO_2 as a component in three-way catalytic converters (TWCs) for the removal of automotive exhaust gases from emissions of gasoline engines is very well established. It relies on the beneficial effect of precious metal – ceria interactions and on the activity of the redox couple $\text{Ce}^{4+}/\text{Ce}^{3+}$ with its ability to change from Ce^{4+} under oxidizing conditions to Ce^{3+} under net reducing conditions and vice versa. Moreover, CeO_2 is known to affect the dispersion of supported metals, promote noble metal reduction and oxidation, store and release oxygen, hydrogen and sulphur, form surface and bulk vacancies. However, pure CeO_2 is characterized by poor thermal stability [36]. As it was already mentioned, introducing foreign cations such as Al^{3+} , Si^{4+} or Zr^{4+} into the CeO_2 lattice to form a solid solution may significantly improve the stability of the surface area and strongly enhance the redox properties of ceria. So far, $\text{CeO}_2\text{-ZrO}_2$ systems have been widely studied in many applications [36-38]. Moreover, due to their high oxygen storage capacity, redox properties, thermal resistance and better catalytic activity at lower temperatures, ceria-zirconia has also been applied as a component of the last generation of commercial TWCs for the treatment of automotive exhaust gases, instead of pure CeO_2 .

Precious metals (Pt, Pd and Rh) supported on different oxides are well-known as efficient oxidation catalysts, widely used for CO oxidation reaction [39-42].

Since the pioneering work of Haruta [43], several research groups have confirmed that CO oxidation can also be successfully catalysed by Au nanoparticles highly dispersed on partly reducible oxides [2-4]. Moreover, Au catalysts appeared to be much more active than the other noble metal catalysts at temperatures below 130°C [2,5]. However, only a few papers have reported the study of Au supported on ceria-zirconia as catalysts for low-temperature CO oxidation [17-23].

Dobrosz-Gómez et al. [21] studied in details the correlations between structural, redox and catalytic properties of Au/Ce_{1-x}Zr_xO₂ catalysts prepared using different synthesis procedures. A special attention was paid to the influence of residual chlorine in the catalysts on their properties and catalytic performance in CO oxidation. A series of Ce_{1-x}Zr_xO₂ (x = 0.25, 0.5, 0.75) solid solutions was prepared by the sol-gel like method, based on a thermal decomposition of mixed propionates. Au/Ce_{1-x}Zr_xO₂ catalysts were synthesized by the direct anionic exchange (DAE) method of gold species with hydroxyl groups of the support [19,44, 45], using hydrogen tetrachloroaurate (III) trihydrate (HAuCl₄·3H₂O) as a gold precursor. To establish the effect of the residual chlorine in the catalysts on their properties and catalytic activity in CO oxidation, three different preparation procedures were used: without washing the residual chlorine and washing with either warm water or ammonia. Catalytic tests were carried out at atmospheric pressure in a quartz flow microreactor containing 100 mg of sample in a fixed bed, using a 1.7 vol.% CO, 3.4 vol.% O₂ and 94.9 vol.% He reaction gas mixture, with a flow of 50 cm³.min⁻¹, in the temperature range 25–300°C, with a ramp rate 5°C.min⁻¹. The effect of the preparation procedure on some physicochemical properties of Au/Ce_{1-x}Zr_xO₂ (x= 0.25, 0.5, 0.75) catalysts is presented in Table 3 (in details described in [21]).

The catalysts as prepared (without washing) showed real Au content almost identical to the nominal one (2 wt.%). However, washing of the catalysts with either warm water or ammonia led to a loss of Au (ca. 5–10% for the catalysts washed with warm water and ca. 10–15% with ammonia) due to the removal of non-attached gold complexes, simply adsorbed on the support surface due to the deficient quantity of hydroxyl groups which are available for anionic exchange.

For the catalysts prepared without washing, irrespective of the oxide used as a support, a non-homogenous distribution of smoothed, mostly spherical or slightly elongated Au particles, in the range of 5–30 nm, was found. Washing of the catalysts with warm water led to the decrease in the Au particle size (5–15 nm). However, Au particles larger than 20 nm were also found due to the incomplete elimination of residual chlorine from the catalysts using warm water as a washing agent. Conversely, washing the catalysts with ammonia significantly improves Au dispersion on the support surface. The presence of spherical Au particles, in the range of 1–5 nm, was observed.

Tab. 3. Characterization data of Au/Ce_{1-x}Zr_xO₂ (x = 0.25, 0.5, 0.75) catalysts obtained using various physicochemical techniques (in details described in [21]).

Catalyst denotation	Real gold loading ^a wt. %	TPR-CO results ^b					Activity in CO oxidation ^c		
		T ⁰ (initial)	Peak I	Peak II	Peak III	CO ₂ formation mmol.g ⁻¹	T ₁₀ °C	T ₅₀ °C	T ₉₀ °C
Without washing									
Au/Ce _{0.75} Zr _{0.25} O ₂	1.98	235	400	520	780	1.24	185	245	280
Au/Ce _{0.5} Zr _{0.5} O ₂	1.98	215	380	520	760	1.18	165	230	265
Au/Ce _{0.25} Zr _{0.75} O ₂	1.98	255	420	575	-	0.79	220	270	295
Washed with warm water									
Au/Ce _{0.75} Zr _{0.25} O ₂	1.84	195	320	530	760	1.06	90	135	160
Au/Ce _{0.5} Zr _{0.5} O ₂	1.86	175	290	500	740	1.02	85	125	145
Au/Ce _{0.25} Zr _{0.75} O ₂	1.83	215	410	570	-	0.71	110	155	190
Washed with ammonia									
Au/Ce _{0.75} Zr _{0.25} O ₂	1.68	85	260	380	740	0.90	< 20	35	60
Au/Ce _{0.5} Zr _{0.5} O ₂	1.74	135	270	400	720	0.87	50	95	120
Au/Ce _{0.25} Zr _{0.75} O ₂	1.71	140	380	-	-	0.67	60	105	125

Determined by: ^a AAS, ^b TPR – CO studies: T⁰ – the temperature at which catalysts reduction starts (the initial reduction temperature), Peak I, II and III – the temperatures at which catalysts reduction occurs (the temperatures of the maxima of the reduction peaks), CO₂ formation – the total quantity of CO₂ formed during the reduction process, ^c Catalytic tests (T₁₀, T₅₀ and T₉₀ – the temperature for 10%, 50% and 90% CO conversion was obtained).

The ToF-SIMS studies of Au/Ce_{1-x}Zr_xO₂ catalysts have confirmed the presence of chloride ions (Cl⁻), also in the surroundings of gold centres (AuCl⁻, AuCl₂⁻, etc.), at the catalysts surface. The intensity ratios of both chloride ions to the total number of ions (Cl⁻/total⁻), AuCl⁻/Au⁻ and AuCl₂⁻/Au⁻ were significantly higher for the catalysts prepared without washing than for those washed with ammonia. For the catalysts prepared without washing the average Au particle size was also much higher, which confirms the role of residual chlorine in the sintering of Au on the support surface. Moreover, for the catalysts prepared without washing, the Cl⁻/total⁻ intensity ratio was higher for Au supported on Ce-rich oxides, due to the different mechanism of chloride ions incorporation into the catalysts. Thus, one can conclude that beside its presence in the exchanged Au species, the chloride ions from the metal precursor can also be incorporated into the ceria lattice either by occupation of an oxygen vacancy (Lewis type sites) or by an exchange of the support OH⁻ groups (Brönsted type sites) [46].

The results of TPR-CO studies [21] have shown a significant effect of the preparation procedure on the reducibility of Au/Ce_{1-x}Zr_xO₂ catalysts (Table 3). As it was mentioned above, washing of the catalysts led to the decrease in the Au particle size. The higher Au dispersion, the lower temperature of Au/Ce_{1-x}Zr_xO₂

catalysts reduction was observed. A non-homogenous dispersion of Au, in the case of the catalysts prepared without washing and washed with warm water, together with the existence of different intermediate phases of CeO₂ [20], allowed the authors to find out that the formation of CO₂ during the reduction of those catalysts at a lower temperature occurs due to two processes. The first one (in the temperature range 200–450⁰C) is related to the reduction of both the oxygen species coordinated around finely dispersed gold particles and the surface capping oxygen of support, strongly anchored with Au. The second one (in the temperature range 430–650⁰C) is related to the reduction of both the oxygen species coordinated around larger gold agglomerates and the support surface layers being not strongly anchored with Au and/or unaffected by Au due to its non-uniform distribution. The removal of residual chlorine with ammonia greatly improved the reducibility of Au/Ce_{1-x}Zr_xO₂ catalysts, compared to those washed with warm water and/or prepared without washing. In the presence of homogeneously dispersed, small gold nanoparticles, the reduction of surface oxygen of ceria-zirconia materials was effectively promoted (Table 3). On the other hand, the bulk reduction of CeO₂ accompanied by the formation of non-stoichiometric oxides of cerium remained almost unchanged.

Irrespective of the preparation procedure, the quantity of CO₂ formed during the Au/Ce_{1-x}Zr_xO₂ catalysts reduction (Table 3) was significantly lower than that observed for the corresponding Ce-Zr mixed oxides [20]. The TPR-CO studies of Ce_{0.5}Zr_{0.5}O₂ oxide impregnated with chloride ions and next washed with warm water or ammonia, as in the case of the catalysts preparation, enabled the authors to confirm that the presence of the residual anionic species (e.g., chlorides from the metal precursor) may also affect the reductive properties of the studied catalysts. They suggested that CeO₂ surface can react with chlorine to form CeOCl or Ce(OH)₂Cl phases that enhance the cerium stability in a low oxidation state [21,47,48]. It explained the lower amount of CO₂ formed during the reduction of both “chlorinated” Ce_{0.5}Zr_{0.5}O₂ oxide and Au/Ce_{1-x}Zr_xO₂ catalysts, prepared without washing and washed with warm water, compared to the Ce-Zr mixed oxides. Interestingly, the quantity of CO₂ formed during the reduction of “chlorinated and next washed with ammonia” Ce_{0.5}Zr_{0.5}O₂ oxide was similar to that estimated for the “untreated” one. This confirmed that a lower amount of CO₂ created during the reduction of ammonia washed catalysts, compared with the oxide supports, was related to the partial reduction of the catalysts surface (catalysts autoreduction) during the temperature treatment. Thus, the removal of residual Cl⁻ with ammonia from the studied materials prevents successfully both the agglomeration of Au particles and the changes in their reducibility. The authors also suggested that the autoreduction phenomenon could be the reason for the change in the catalyst colour during drying and calcination processes from yellow to dark grey and from dark grey to graphite, respectively.

The application of different preparation procedures led to obtain the $\text{Au/Ce}_{1-x}\text{Zr}_x\text{O}_2$ catalysts with different catalytic activity in CO oxidation [21]. According to the literature [5], the residual chloride can affect the activity of Au catalysts in two different ways. It facilitates the agglomeration of Au particles during the heat treatment (calcination step) through the formation of Au-Cl-Au bridges and/or inhibits the catalytic activity by poisoning the active site (the addition of chloride to an active catalyst significantly decreases its activity). In the case of the studied $\text{Au/Ce}_{1-x}\text{Zr}_x\text{O}_2$ catalysts, the removal of chlorine during the washing treatment both inhibited the sintering process of Au and recovered their reducibility [21], leading to the increase in activity of the studied systems. It confirmed the poisoning effect of residual chlorine on the catalytic performance of $\text{Au/Ce}_{1-x}\text{Zr}_x\text{O}_2$ catalysts. The activity of the catalysts both prepared without washing and washed with warm water was increasing in the following order: $\text{Au/Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2 < \text{Au/Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2 < \text{Au/Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$. The series of catalysts washed with ammonia showed the highest activity, the smallest Au nanoparticles and the highest reducibility. Their activity was found to be dependent on Ce/Zr molar ratio in the oxide used as a support for Au, suggesting the importance of the support redox properties in the creation of the catalytic performance of Au/oxide support contacts.

Similarly to the authors of the paper discussed up to now, Wang et al. [49], basing on the XRD and XPS studies, established that highly dispersed Au particles were responsible for better catalytic activity of $\text{Au/Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ catalyst in CO oxidation and that their agglomeration may have negative contribution to the reaction. Moreover, they observed that the addition of Au improved the reducibility of the catalyst due to the weaker bonding of the surface oxygen with ceria-zirconia.

Dobrosz-Gómez et al. [20] have also discussed the relation between the physicochemical properties of the supports and the catalytic performance of $\text{Au/Ce}_{1-x}\text{Zr}_x\text{O}_2$ catalysts in CO oxidation reaction. The usefulness of $\text{CeO}_2\text{-ZrO}_2$ mixed oxides as supports for Au nanoparticles has been studied, from the point of view of their contribution to the reaction. Table 4 presents the effect of the oxide support composition and Au loading, in the case of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$, on the activity of $\text{Au/Ce}_{1-x}\text{Zr}_x\text{O}_2$ catalysts in CO oxidation. Temperatures of 10, 50 and 90% CO conversion were estimated basing on the data provided in [20]. The authors, using AAS and TEM techniques, confirmed the comparable Au content and its dispersion (1–5 nm) on Ce-Zr mixed oxides. However, the significant difference in their activity towards CO oxidation was observed. The activity of $\text{Au/Ce}_{1-x}\text{Zr}_x\text{O}_2$ catalysts was found to be dependent on Ce/Zr molar ratio in the oxide used as a support for Au, increasing in the following order: $\text{Au/Ce}_{0.25}\text{Zr}_{0.75}\text{O}_2 \approx \text{Au/Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2 < \text{Au/Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$. Moreover, in the case of $\text{Au/Ce}_{1-x}\text{Zr}_x\text{O}_2$, at high CeO_2 concentration (75% mol) in the support, the cubic

phase was favoured, whereas both for intermediate (50% mol) and ZrO₂-rich (75% mol) composition, tetragonal one was preferential. Thus, one can see that the presence of a cubic phase in Ce-Zr solid solution improves the catalytic activity of Au/Ce_{1-x}Zr_xO₂ catalysts in CO oxidation.

Tab. 4. Characterization data of Au/Ce_{1-x}Zr_xO₂ (x = 0.25, 0.5, 0.75) catalysts and their oxide supports obtained using various physicochemical techniques (in details described in [20]).

Catalyst denotation	Real gold loading ^a , wt. %	Activity in CO oxidation ^b			TPR-CO results ^c			
		T ₁₀ °C	T ₅₀ °C	T ₉₀ °C	T ⁰ (initial) ^c	Peak I	Peak II	Peak III
Au/Ce _{0.75} Zr _{0.25} O ₂	1.68	< 20	35	60	85	260	380	740
Au/Ce _{0.5} Zr _{0.5} O ₂	1.74	50	95	120	135	270	400	720
Au/Ce _{0.25} Zr _{0.75} O ₂	1.71	60	105	125	140	380	-	-
Au/Ce _{0.75} Zr _{0.25} O ₂	3.31	< 20	25	40	65	220	340	610
Ce _{0.75} Zr _{0.25} O ₂	-	265	345	390	270	460	760	-
Ce _{0.5} Zr _{0.5} O ₂	-	280	355	405	290	500	760	-
Ce _{0.25} Zr _{0.75} O ₂	-	300	385	450	310	530	-	-

Determined by: ^a AAS, ^b Catalytic tests (T₁₀, T₅₀ and T₉₀ – the temperature for 10%, 50% and 90% CO conversion was obtained), ^c TPR – CO studies: T⁰ – the temperature at which catalysts reduction starts (the initial reduction temperature), Peak I, II and III – the temperatures at which catalysts reduction occurs (the temperatures of the maxima of the reduction peaks).

According to the TPR-CO studies, the presence of highly dispersed Au nanoparticles effectively promoted the reduction of the catalysts surface at a low temperature (Table 4). This effect was even more pronounced for the catalyst containing a higher amount of well dispersed Au. The authors observed that the sequence of the decreasing initial temperature of catalysts reduction clearly follows the sequence of increasing activity (Figure 1) and suggested that CO oxidation can be affected by similar factors that influence the reduction process. The highest activity was obtained over the Au/Ce_{0.75}Zr_{0.25}O₂ catalyst. Moreover, its reduction starts at the lowest temperature. Thus, one can see that in the presence of highly dispersed Au nanoparticles, the oxide supports were susceptible to the reduction at a lower temperature and appeared to be responsible for the activity of studied catalysts (Table 4). These findings indicated the role of a support in the creation of the catalytic performance of Au/Ce_{1-x}Zr_xO₂ catalysts in CO oxidation. Higher reducibility of oxide support provided higher concentration of surface oxygen vacancies in the stationary state of the reaction, which can be the centres of oxygen activation. Such vacancies may be formed even in the reaction mixture CO + O₂ exhibiting lower redox potential compared to the oxygen atmosphere [50]. Moreover, the possible

adsorption of CO on Au^{3+} , Au^+ , Au^0 and Ce^{4+} species, observed in the case of Au/CeO_2 catalyst [51], together with the lack of CO conversion over Ce-Zr mixed oxide supports, at temperatures below 200°C (Table 4), enabled the authors to imply the synergetic effect between the support and gold nanoparticles at the interface.

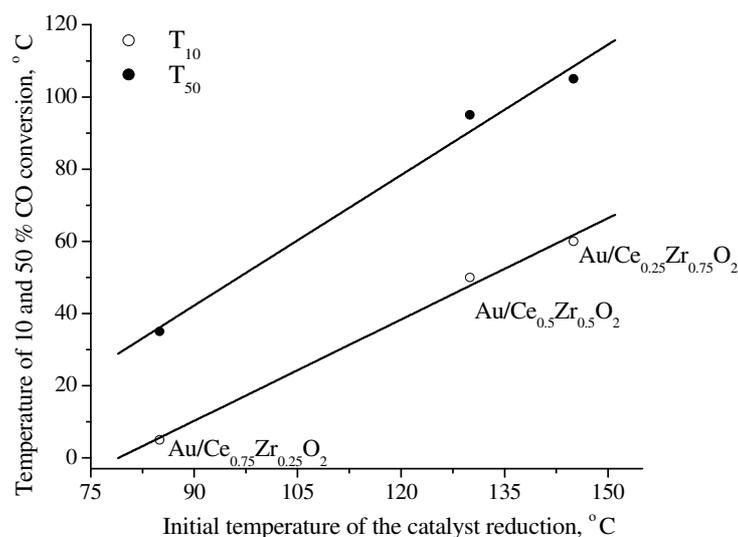


Fig. 1. The correlation between reducibility and the activity of $\text{Au}/\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ ($x = 0.25, 0.5, 0.75$) catalysts in CO oxidation [52].

The reported $\text{Au}/\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ catalyst showed a slight loss of activity (5–8%) during time on stream tests for 5 days performed at 30°C . However, time on stream studies at 60 and 90°C showed a negligible change in activity. This demonstrates good stability of the studied systems in CO oxidation also, which is very important as a function of a gas mixture composition (CO/O₂ ratio). No marked difference in the temperature at which CO oxidation occurs depending on the investigated CO/O₂ ratios over Ce-Zr mixed oxides supported Au catalysts was observed. The authors [20] proposed that the ability to preserve high activity in stoichiometric and lean in O₂ gas mixtures confirms participation of the support in the CO oxidation not only in providing centres for oxygen activation but also as a buffer in releasing-uptaking oxygen through the redox processes realized by $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple.

Moreover, very high activity and stability of $\text{Au}/\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ catalyst in CO/air gas mixture at room and 0°C as well as at the temperature below 0°C allowed the authors to project that the developed systems could find a practical

application in ambient conditions, especially air purification systems and breathing apparatus.

Moreau et al. [17] also studied the influence of “the time on stream” on the Au/CeZrO₄ catalyst stability in CO oxidation. The catalyst (1 wt.% Au nominal content) was prepared by the deposition-precipitation method, using hydrogen tetrachloroaurate (III) trihydrate (10⁻³ M) as a gold precursor. The long-term tests were performed in a continuous flow system, with 50 mg of the catalyst, using 0.49 vol.% CO in synthetic air, with a flow rate of 55 cm³.min⁻¹, at room temperature. They established that Au/CeZrO₄ catalyst shows very slight activity loss during c.a. 2 days. Thus, it was concluded that the incorporation of Zr into the CeO₂ lattice significantly improves the catalyst stability, preventing its deactivation. Moreover, the DRIFT results on fresh and used catalysts enabled the authors [17] to demonstrate that the stability of catalyst was associated with both better retention of surface hydroxyl groups and a minor formation of carbonate/bicarbonate ions near gold particles during reaction.

The papers presented up to now have discussed a number of factors that contribute to wide variations in activities of Au/Ce_{1-x}Zr_xO₂ catalysts in CO oxidation reaction. Apart from the role of size and shape of Au particle, the residual chloride content in the catalysts and the structural and redox properties of the oxide support, the effect of water vapour on catalytic activity of Au/Ce_{1-x}Zr_xO₂ contacts is also evident.

The effect of moisture in the reactant gas on CO conversion over Au/Ce_{0.75}Zr_{0.25}O₂ catalyst has been quantitatively studied in a wide range of concentrations (~0.7 – 6000 ppm) by Dobrosz-Gómez et al. [22]. They noted that at ~0.7 ppm H₂O, CO conversion over Au/Ce_{0.75}Zr_{0.25}O₂ is lower ca. 2 orders of magnitude than that under usual reactant conditions (10 ppm H₂O). However, the presence of moisture generates a positive effect on catalytic activity and wet conditions gave higher CO conversions. The optimum concentration of moisture (200–1000 ppm) for CO oxidation over Au/Ce_{0.75}Zr_{0.25}O₂ has been found. When its concentration was ≥ 2000 ppm, the activity was suppressed due to the blocking of the catalytic active sites or competitive adsorption of moisture and O₂.

Similar conclusions come from the work of Moreau et al. [17], in which the role of hydroxyl groups in the mechanism of CO oxidation over Au/CeZrO₄ catalyst was discussed. Basing on DRIFT analysis, they confirmed that the presence of some OH groups is essential to obtain high activity in CO oxidation. However, their existence in excess could be the reason for Au/CeZrO₄ deactivation.

The thermal pretreatment of Au/Ce_{0.75}Zr_{0.25}O₂ catalyst in dry He (even at a temperature as low as 100°C and/or 200°C) also suppressed its catalytic activity, as reported by Dobrosz-Gómez et al. [22]. The significant decrease in CO

conversion (ca. 50%) at 30°C over Au/Ce_{0.75}Zr_{0.25}O₂ catalyst was observed. However, the loss of activity was completely restored by the exposition of the catalysts to the moisture/He stream (6000 ppm H₂O) at room temperature. Thus, one can conclude that the observed deactivation takes place due to the dehydroxylation of Au-OH species on the catalyst surface. On the other hand, for as-prepared Au/Ce_{0.75}Zr_{0.25}O₂ catalyst precursors (dried at 120°C), tested in CO oxidation without further pretreatment, CO conversion at 30°C was about 2 times higher than that for the catalysts calcined at 300°C. Considering that uncalcined samples contain some quantities of both physis- and chemisorbed water, its promoting effect on the activity at a low temperature could be expected. Thus, it was suggested that the activity of the studied Au catalysts in CO oxidation depends on the amount of moisture adsorbed on the catalyst rather than on its content in the feed stream, which suggests that the reaction involves water-derived species on the catalysts surface.

Therefore, Dobrosz-Gómez et al. [22] pointed to a model in which CO oxidation over the studied contact occurs by the reaction between CO adsorbed mostly on Au nanoparticles and oxygen adsorbed and activated on the oxygen vacancies of Ce_{0.75}Zr_{0.25}O₂ surface. The oxygen vacancies can be either distant from the Au particles, in which case the active oxygen species would migrate by a spill-over towards the active Au centres with chemisorbed reactant or situated at the periphery of the Au particles [50]. Moisture, when present, might activate O₂ molecules on the oxygen vacancies of the support surface and/or modify the electronic state of Au. The perimeter interfaces appear to act as major active sites, whereas the support surface as a moisture reservoir.

A detailed insight into the effect of Au/Ce_{0.75}Zr_{0.25}O₂ catalyst pretreatment in H₂ stream on its activity, mostly from the point of view of the active sites for CO oxidation, was examined by the same authors [22]. The catalyst pre-reduction at 200°C led to the increase in CO conversion from 20% to 60%, compared to sample pre-heated in air stream. However, the contact pre-reduced at higher temperature (290°C) appeared to be less active in CO oxidation than that pre-reduced at 200°C. On the other hand, the activity of the pre-reduced catalysts was still higher than that observed over the unreduced ones. Moreover, the observed increase in activity was relatively stable in time (no deactivation after a few hours of reaction), independently on the applied reduction temperature. According to the authors [22], such an effect could be related to the reduction (“cleaning”) of oxide species on the surface of the Au particles rather than to the reduction of the support. However, only partial pre-reduction of Au³⁺ ions to Au⁰ atoms (pre-reduction at a lower temperature - 200°C) can lead to the increase in CO conversion Au/Ce_{0.75}Zr_{0.25}O₂ catalyst. The presence of a higher amount of Au⁰ atoms, after the reduction at a higher temperature (290°C), made the catalyst less active in CO oxidation. It has shown that both metallic and oxidized gold

species are responsible for the catalytic oxidation of CO over Au/Ce_{0.75}Zr_{0.25}O₂ catalyst.

Similar conclusions come from the works of Wang et al. [49] and Moreau et al. [17], in which the presence of both Au⁰ and Au³⁺ is required to obtain high activity over Au/Ce-Zr catalysts. They considered that Au⁰ adsorbed CO, while Au³⁺ cemented the metallic particle on the support and activated surface hydroxyl groups, which next can react with the adsorbed CO to form carboxylate. Moreover, they suggested that the progressive reduction of Au³⁺ can also cause catalyst deactivation.

The highest increase in CO conversion, from 20% to 95%, compared to sample pre-heated in air stream, was observed over Au/Ce_{0.75}Zr_{0.25}O₂ pretreated in H₂/H₂O gas mixture at 200^oC, as reported by Dobosz-Gómez et al. [22]. This confirmed that the presence of metallic Au atoms on the catalysts surface is not the only condition that needs to be met to guarantee high activity in CO oxidation. The authors suggested that the additional presence of H₂O during the pretreatment in H₂ prevented the complete reduction of Au, remaining its part in a cationic state with a hydroxyl ligand and/or change the content of water-derived species, which may activate O₂ molecules, aiding their dissociation. It resulted in the significant increase in activity. Those statements allowed the authors to imply that moisture can both enhance the dissociation of O₂ molecules adsorbed on the oxygen vacancies and modify the electronic state of gold. Next, the activated oxygen can rapidly react with CO adsorbed on the metallic Au particles.

The role of metal – support interactions in the creation of catalytic performance of Au/Ce_{0.75}Zr_{0.25}O₂ catalysts in CO oxidation was also studied by Dobosz-Gómez et al. [23]. A series of Au/Ce_{0.75}Zr_{0.25}O₂ catalysts, prepared using different synthesis procedures, was characterized by different structural, morphological and catalytic properties. An approximate evaluation of the H₂ consumption for the surface reduction (“capping” oxygen) of the studied samples was estimated applying the model developed by Johnson et Mooi [53], based on the qualitative relationship between the magnitude of the capping oxygen and BET surface area. They observed that the sequence of the increasing percentage of oxygen atoms in the capping peak to the total cerium atoms (O_c/Ce) clearly follows the sequence of increasing activity of the studied catalysts, confirming the role of both Au particle size and the redox properties of support in creation of the catalytic activity of Au/Ce_{0.75}Zr_{0.25}O₂ catalysts in CO oxidation. It has been found that the synergism between precious metals and support can be designed with an appropriate choice of the catalyst synthesis conditions and the characteristics of the support.

Ceria-zirconia mixed oxides appear to be very promising supports for Au nanoparticles in CO oxidation. So far, only a few papers have reported the

studies of Au/Ce_{1-x}Zr_xO₂ systems as catalysts for CO oxidation. However, basing on the already published literature, one can see that they could find a practical application in ambient conditions, especially air purification systems and breathing apparatus. It is possible that gold could be usefully incorporated into automobile catalysts, considering that the price of other noble metals is rising rapidly. Their use in this application will, however, require demonstration of adequate stability at operating temperatures.

4. CONCLUSIONS

In this paper the most important achievements and conclusions, coming from the contributions concerning ceria-zirconia supported Au catalysts for low temperature water gas-shift reaction and low-temperature CO oxidation, have been reviewed. They can be summarized as follows:

- High activity of Au/Ce_{1-x}Zr_xO₂ contacts in low-temperature WGS reaction and CO oxidation is displayed by gold particles with an optimum size of 3–5 nm.
- The oxide support can modify the electronic properties of nanosized gold particles and this interaction defines the precise nature of the structure and properties at the gold/support interface.
- The choice of the catalyst preparation method should guarantee a good contact between gold and the support, high gold dispersion and uniform distribution on the surface.
- The consideration of various aspects of the reactions mechanisms is of great significance for assistance in the design and selection of highly active catalysts.
- Ceria-zirconia supported gold catalysts appear to be very promising systems, which have a potential to create a new quality in the catalysis of WGS reaction.
- Ceria-zirconia mixed oxides are very effective supports for Au nanoparticles in CO oxidation. They have a potential to be practically applied in ambient conditions, especially in air purification systems and breathing apparatus. It is possible that gold could be usefully incorporated into automobile catalysts, considering that the price of other noble metals is rising rapidly. Their use in this application will, however, require demonstration of adequate stability at operating temperatures.

5. REFERENCES

- [1] G. J. Hutchings, M. Brust, H. Schmidbaur, *Chem. Soc. Rev.*, 37, 1759 (2008).
- [2] A. Corma, H. Garcia, *Chem. Soc. Rev.*, 37, 2096 (2008) and references therein

- [3] G. C. Bond, D. T. Thompson, *Cat. Rev. – Sci. Eng.*, 41 (3-4), 319, (1999).
- [4] A. S. K. Hashmi, G. J. Hutchings, *Angew. Chem. Int. Ed.*, 45, 7896, (2006).
- [5] I. Dobrosz, I. Kocemba, J. Rynkowski, *Pol. J. Chem. Tech.*, 7, 27 (2005) and references therein
- [6] M. Haruta, *Catal. Today*. 36, 153, (1997).
- [7] S. E. Collins, J. M. Cies, E. del Rio, M. López-Haro, S. Trasobares, J. J. Calvino, J. M. Pintado, S. Bernal, *J. Phys. Chem. C*, 111, 14371 (2007).
- [8] G. Avgouropoulos, M. Manzoli, F. Boccuzzi, T. Tabakova, J. Papavasiliou, T. Ioannides, V. Idakiev, *J. Catal.*, 256, 237 (2008).
- [9] G. C. Bond, D. T. Thompson, *Appl. Catal. A: Gen.*, 302, 1 (2006).
- [10] D. T. Thompson, *Top. Catal.* 38, 231 (2006).
- [11] A. Amieiro Fonseca, J. M. Fisher, D. Ozkaya, M. D. Shannon, D. Thompsett, *Top. Catal.* 44, 223 (2007).
- [12] A. Goguet, R. Burch, Y. Chen, C. Hardacre, P. Hu, R. W. Joyner, F. C. Meunier, B. S. Mun, D. Thompsett, D. Tibiletti, *J. Phys. Chem. C*, 111, 16927 (2007).
- [13] D. Tibiletti, A. Amieiro Fonseca, R. Burch, Y. Chen, J. M. Fisher, A. Goguet, C. Hardacre, D. Thompsett, P. Hu, D. Thompsett, *J. Phys. Chem. B*, 109, 22553 (2005).
- [14] M. Boaro, M. Vicario, J. Llorca, C. de Leitenburg, G. Dolcetti, A. Trovarelli, *Appl. Catal. B: Environ.*, 88, 272, (2009).
- [15] F. C. Meunier, A. Goguet, C. Hardacre, R. Burch, D. Thompsett, *J. Catal.*, 252, 18 (2007).
- [16] R. Radhakrishnan, R. R. Willigan, Z. Dardas, T. H. Vanderspurt, *AIChE*, 52, 1888 (2006).
- [17] F. Moreau, G. C. Bond, B. van der Linden, B. M. M. Silberova, M. Makkee, *Appl. Catal. A: Gen.* 347, 208 (2008).
- [18] I. Dobrosz, M. A. Gómez-García, I. Kocemba, W. Maniukiewicz, J. M. Rynkowski, *Pol. J. Environ. Stud.*, 14(IV), 231 (2005).
- [19] I. Dobrosz, I. Kocemba, J. M. Rynkowski, *Pol. J. Environ. Stud.*, 15 (6A), 32 (2006).
- [20] I. Dobrosz-Gómez, I. Kocemba, J. M. Rynkowski, *Appl. Catal. B: Environ.*, 83, 240 (2008).
- [21] I. Dobrosz-Gómez, I. Kocemba, J. M. Rynkowski, *Appl. Catal. B: Environ.*, 88, 83 (2008).
- [22] I. Dobrosz-Gómez, I. Kocemba, J. M. Rynkowski, *Catal. Lett.*, 128, 297 (2009).
- [23] I. Dobrosz-Gómez, I. Kocemba, J. M. Rynkowski, *Pol. J. Environ. Stud.*, in press
- [24] D. Andreeva, V. Idakiev, T. Tabakova, A. Andreev, *J. Catal.*, 158, 354 (1996).
- [25] D. Andreeva, *Gold Bull.* 35/3, 82 (2002).
- [26] A. Venugopal, M. S. Scurrill, *Appl. Catal. A: Gen.*, 258, 241 (2004).
- [27] V. Idakiev, Z.-Y. Yuan, T. Tabakova, B.-L. Su, *Appl. Catal. A: Gen.*, 281, 149 (2005).
- [28] V. Idakiev, T. Tabakova, A. Naydenov, Z.-Y. Yuan, B.-L. Su, *Appl. Catal. B: Environ.*, 63, 178 (2006).
- [29] Q. Fu, H. Saltsburg, M. Flytzani-Stephanopoulos, *Science*, 301, 935 (2003).
- [30] W. Deng, M. Flytzani-Stephanopoulos, *Angew. Chem. Int. Ed.*, 45, 2285 (2006).
- [31] Q. Fu, W. Deng, H. Saltsburg, M. Flytzani-Stephanopoulos, *Appl. Catal. B: Environ.*, 56, 57 (2005).
- [32] C. H. Kim, L. T. Thompson, *J. Catal.*, 230, 66 (2005).
- [33] Amieiro A. Fonseca, J. M. Fisher, D. Thompsett, WO Patent 2005/087656 22 Sept 2005
- [34] G. C. Bond, C. Louis, D. T. Thompson, "Catalysis by Gold", Catalytic Science Series, Vol. 6., Imperial College Press, 2006, p. 280.
- [35] R. Burch, *Phys. Chem. Chem. Phys.*, 8, 5483 (2006).
- [36] A. Trovarelli, (ed.), *Catalysis by ceria and related materials*, Imperial College Press, 2002.
- [37] A. Trovarelli, *Catal. Rev. Sci. Eng.*, 38, 440 (1996).
- [38] M. A. Gómez-García, V. Pitchon, A. Kiennemann, *Env. Int.*, 31, 445 (2005) and references therein.

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- [39] A. Martorana, G. Deganello, A. Longo, A. Prestianni, L. Liotta, A. Macaluso, G. Pantaleo, A. Balerna, S. Mobilio, *J. Solid State Chem.*, 177, 1268 (2004).
- [40] L. F. Chen, G. González, J. A. Wang, L. E. Noréna, A. Toledo, S. Castillo, M. Morán-Pineda, *Appl. Surf. Sci.*, 243, 319 (2005).
- [41] J. A. Wang, T. López, X. Bokhimi, O. Novaro, *J. Mol. Catal. A*, 239, 249 (2005).
- [42] P.-X. Huang, F. Wu, B.-L. Zhu, X.-P. Gao, H.-Y. Zhu, T.-Y. Yan, W.-P. Huang, S.-H. Wu, D.-Y. Song, *J. Phys. Chem. B*, 109, 19169 (2005).
- [43] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.*, 2, 405 (1987).
- [44] I. Dobrosz, K. Jiratova, V. Pitchon, J. M. Rynkowski, *J. Mol. Catal. A: Chemical*, 234, 187 (2005).
- [45] S. Ivanova, C. Petit, V. Pitchon, *Appl. Catal. A: General*, 267, 191 (2004).
- [46] C. Force, J. P. Belzunegui, J. Sanz, A. Martinez-Arias, J. Soria, *J. Catal.*, 197, 192 (2001).
- [47] F. Le Normand, L. Hilaire, K. Kili, G. Grill, G. Maire, *J. Phys. Chem.*, 92, 2561 (1988).
- [48] L. Kepinski, M. Wolcyrz, J. Okal, *J. Chem. Soc. Faraday Trans.*, 91, 507 (1995).
- [49] S.-P. Wang, T.-Y. Zhang, X.-Y. Wang, S.-M. Zhang, S.-R. Wang, W.-P. Huang, S.-H. Wu, *J. Mol. Catal. A: Chemical*, 272, 45 (2007).
- [50] B. Grzybowska-Świerkosz, *Catal. Today*, 112, 3 (2006).
- [51] J. Guzman, S. Carrettin, A. Corma, *J. Am. Chem. Soc.*, 127, 3286 (2005).
- [52] I. Dobrosz-Gómez, PhD Thesis, 2007
- [53] M. F. L. Johnson, J. Mooi, *J. Catal.*, 103, 502 (1987); *Erratum: J. Catal.*, 140, 612, (1993).