The Role of Au-Support Interactions in Creation of Catalytic Performance of Au/Ce$_{0.75}$Zr$_{0.25}$O$_2$ in CO Oxidation

I. Dobrosz-Gómez[1], M. A. Gómez García[2], J. M. Rynkowski[3]*

[1]Facultad de Ciencias Exactas y Naturales, Universidad Nacional de Colombia, Sede Manizales, Colombia
[2]G.I.A.N.T., Grupo de Investigación en Aplicación de Nuevas Tecnologias,
Universidad Nacional de Colombia, Sede Manizales, Colombia
[3]Institute of General and Ecological Chemistry, Technical University of Łódź, Żeromskiego 116, 90-924 Łódź, Poland

Abstract

The aim of this work was to obtain more detailed insight into the role of Au-support interactions in the creation of catalytic performance of Au/Ce$_{0.75}$Zr$_{0.25}$O$_2$ in CO oxidation. The Ce$_{0.75}$Zr$_{0.25}$O$_2$ oxide and Au/Ce$_{0.75}$Zr$_{0.25}$O$_2$ catalysts were synthesized, characterized by BET, XRD, HRTEM, AAS, TPR-H$_2$, and tested in CO oxidation. An approximate evaluation of H$_2$ consumption for the surface reduction of the studied samples was estimated, applying the model developed by Johnson and Mooi, based on the qualitative relationship between the magnitude of the capping oxygen and BET surface area.

Introduction

Low-temperature CO oxidation has rapidly become the most intensively studied among the reactions catalyzed by supported Au nanoparticles [1, 2], from both practical and fundamental points of view. Although a great success has been achieved in the synthesis of supported Au catalysts, the origin of their exceptionally high activity in CO oxidation, particularly the role of oxide support and the nature of the active sites, are still ambiguous. It is generally accepted that the catalytic activity of Au-containing systems in CO oxidation depends strongly on the Au precursor, the reaction conditions and first of all the size of gold particles, which is highly sensitive to the preparation and pretreat-

ment procedure [1, 2]. Beside these factors, the importance of oxide support, not only in the stabilization of the active phase dispersion and modification of its electronic state, but also in the activation of reactants, especially oxygen, should be considered [1-3].

During the last several years, CeO$_2$-containing materials are intensively studied both as catalysts and structural and electronic promoters of heterogeneous catalytic reactions due to their unique redox properties, high oxygen storage capacity and high thermal resistance [4]. Undoubtedly, the utilization of CeO$_2$-ZrO$_2$ mixed oxides as one of the key components in the last generation of commercial three-way catalysts (TWCs) [4] constitutes their economically and technologically most important application. However, only a few papers have reported the study of Au supported on ceria-zirconia as catalysts for CO oxidation [5].

*e-mail: jacryn@p.lodz.pl

Previously [5], we presented the relation between the physico-chemical properties of $Ce_{1-x}Zr_xO_2$ (x = 0, 0.25, 0.5, 0.75, 1) supports and the catalytic performance of $Au/Ce_{1-x}Zr_xO_2$ catalysts in CO oxidation. Au/CeO_2-ZrO_2 systems appear to be very promising catalysts in CO oxidation, whose catalytic performance was found to be dependent on Ce/Zr molar ratio. The highest activity was obtained over the $Au/Ce_{0.75}Zr_{0.25}O_2$ catalyst. Consequently, the aim of this work is to obtain more detailed insight into the role of Au-support interactions in the creation of catalytic performance of $Au/Ce_{0.75}Zr_{0.25}O_2$ in CO oxidation. The $Ce_{0.75}Zr_{0.25}O_2$ oxide and a series of $Au/Ce_{0.75}Zr_{0.25}O_2$ catalysts were synthesized, characterized by BET, XRD, HRTEM, AAS, TPR-H_2, and tested in the reaction of CO oxidation. Moreover, an approximate evaluation of H_2 consumption for the surface reduction of the studied samples was performed applying the model developed by Johnson and Mooi [6], based on the qualitative relationship between the amount of the capping oxygen and BET surface area.

Material and Methods

Synthesis

The $Ce_{0.75}Zr_{0.25}O_2$ oxide used as a support for Au was prepared using the sol-gel like method that uses as starting materials zirconium (IV) acetylacetonate [Avocado] and cerium (III) acetyloacetonatehydrate [Sigma-Aldrich], and calcined at 550ºC [5]. Hydrogen tetrachloroaureate (III) trihydrate [Sigma-Aldrich] was used as Au precursor. The catalysts were prepared using the direct anionic exchange (DAE) method of Au species with OH groups of support [5]. The aqueous solution of $HAuCl_4$ was heated up to 70ºC and 2 g of $Ce_{0.75}Zr_{0.25}O_2$ oxide was introduced. After 1 hour of thermostating and vigorous stirring, the suspension was centrifuged. In order to remove residual chlorine from the catalysts, two washing procedures prior to the drying were applied. The solids were suspended in either 4 M ammonia solution at 25ºC or deionized water at 50ºC, stirred for 1 hour and centrifuged again. After drying in an oven at 120ºC overnight, the catalysts were calcined in air at 300ºC for 4h.

Methods

Specific surface area was determined by BET method using a Sorptomatic 1900 apparatus (Carlo-Erba) with nitrogen as an adsorbate. Prior to the measurement, all samples were degassed for 4 hours at 250°C. X-ray diffraction (XRD) patterns were obtained at room temperature using a PANalytical X'Pert Pro MPD diffractometer, operating at 40 kV and 30 mA (Cu K_α radiation). Data were collected in the range 20-70º 2θ with a step size of 0.0167° and step time of 10 s [5].

High Resolution Transmission Electron Microscopy (HRTEM) measurements were carried out using a high resolution microscope EM-002B (TOPCON 200kV) at 10^{-5} Pa

to determine the gold particle size distribution, as described previously [5].

Atomic Absorption Spectroscopy (AAS) analyses were performed with a Solaar M6 Unicam spectrophotometer in order to estimate the amount of Au deposited on support [5].

Temperature Programmed Reduction (TPR-H_2) experiments were carried out by PEAK-4 apparatus equipped with a thermal conductivity detector (TCD). TPR-H_2 experiments were performed using a H_2/He (5 vol. % H_2, 95 vol. % He) gas mixture, with a flow rate of 40 $cm^3 \cdot min^{-1}$, in the temperature range 25-850°C, with a ramp rate 15°C·min^{-1}. Powdered samples of 100 mg were exposed to dry Ar at 250°C for 1 hour before reduction [5].

CO oxidation reaction was carried out at atmospheric pressure in a quartz flow microreactor containing 100 mg of sample in a fixed bed, using a series of mass flow controllers with diluted gases. Before the reaction, a pretreatment in air at 300ºC for 1 hour with a ramp rate of 5ºC·min^{-1} was carried out. The gas mixture containing 1.6 vol. % CO and 3.3 vol. % O_2 was used with a flow of 50 $cm^3 \cdot min^{-1}$, in the temperature range 25-300ºC with a ramp rate 5ºC·min^{-1}. A gas chromatograph fitted with a column containing molecular sieves 5 Å, equipped with TCD detector was used to perform the analysis of both CO and O_2 concentration [5].

The model developed by Johnson and Mooi [6] is based on the qualitative relationship between the amount of the capping oxygen and BET surface area. For this model, the authors considered that the reduction of cubic CeO_2 corresponds to the elimination of one fourth of the surface oxygen ions, and that each ceria crystallite is a cube of n oxygen ions on a side. Therefore, each ceria crystallite contains n^3 oxygen ions and $\frac{1}{2} n^3$ Ce ions. Since the number of capping oxygen ions in a crystallite is:

$$O_c = n^3 - (n-2)^3 = 6n^2 - 12n + 8$$

...and the number of H atoms to reduce half of the O_c ions is:

$$H_c = 2 \cdot O_c$$

...thus, the ratio of hydrogen atoms in the capping peak to the total cerium atoms (H_c/Ce) is [6]:

$$H_c/Ce = 4(6n^2 - 12n + 8)/n^3$$

Results and Discussion

BET data show that the specific surface area of all catalysts is slightly lower or comparable to that of a given support oxide (Table 1).

$Au/Ce_{0.75}Zr_{0.25}O_2$ catalyst prepared without washing shows that real Au content is almost identical to the nominal one (2 wt. %). However, washing the catalysts with either warm water or ammonia leads to a loss of Au, compared to that prepared without the washing stage (Table 1). This loss of Au is attributed to the removal of non-attached

Table 1. Summary of the physico-chemical properties of the studied solids.

Oxide supports/Catalyst denotation (the first number corresponds to the nominal wt. % content of Au)	Surface area[a], [$m^2 \cdot g^{-1}$]	Real gold loading[b], [wt.%]	$D_{oxide\,support}$[c], [nm]	D_{Au}[c], [nm]	Au particle size[d], [nm]	Total H_2 consumption[e], [$mmol \cdot g^{-1}$]	(O_c/Ce)[f], [%]	Activity[g]	
								T_{10}	T_{50}
$Ce_{0.75}Zr_{0.25}O_2$	50	-	7.0 Ce(111)	-	-	1.53	29.7	240	n.d.
$2Au/Ce_{0.75}Zr_{0.25}O_2$ without washing	47	1.98	6.7 Ce(111)	14.6	15.7	1.29	32.7	190	245
$2Au/Ce_{0.75}Zr_{0.25}O_2$ washed with warm water	48	1.84	6.9 Ce(111)	11	11.1	1.12	38.8	90	135
$2Au/Ce_{0.75}Zr_{0.25}O_2$ washed with ammonia	50	1.68	7.2 Ce(111)	n.d.[by XRD]	3.9	0.95	47.2	< 20	35

Determined by: [a] N_2-BET, [b] AAS, [c] XRD, n.d.[by XRD] – Not detectable by XRD, D_{Au} – Average diameter of Au particles estimated by the Scherrer equation using (111) plane, [d] HRTEM; [e] TPR-H_2, [f] (O_c/Ce)% – percentage of oxygen atoms in the capping peak to the total cerium atoms-Johnson et Mooi model; [g] Activity in CO oxidation (CO : O_2 : He = 1.7 : 3.4 : 94.9 vol. %; W/F = 0.12 g·s·cm⁻³), T_{10}, T_{50}, – the temperature at which 10% and 50% CO conversion was obtained, respectively, n.d. – Not detectable in the temperature range 25-300ºC.

gold complexes, simply adsorbed on the support surface due to the deficient quantity of hydroxyl groups which are available for anionic exchange. Moreover, during the washing of the catalysts with ammonia, this effect is strengthened by the replacement of Cl- ligands by OH groups in the exchanged Au species [5].

XRD patterns of both $Ce_{0.75}Zr_{0.25}O_2$ oxide and $Au/Ce_{0.75}Zr_{0.25}O_2$ catalysts (not shown) correspond to a single cubic phase, fluorite-type structure (JCPDS: 03-065-2975). No phase segregation was detected, confirming that ZrO_2 is incorporated into the CeO_2 lattice and forms a solid solution. Simultaneously, a slight shift of the main diffraction peaks characteristic for CeO_2 to higher 2θ values was noticed. This observation indicates that the substitution of Ce^{4+} cation (Ce^{4+} cation radius 0.97Å) with the smaller Zr^{4+} one (Zr^{4+} cation radius 0.84Å) causes lowering of symmetry and a decrease in unit cell parameters [5]. Moreover, compared to the XRD pattern of CeO_2 [5], the main diffraction peaks observed for $Ce_{0.75}Zr_{0.25}O_2$ solid solution become broader. It could be ascribed to the distortion of the cubic phase of fluorite structure due to the incorporation of ZrO_2, resulting in the formation of smaller crystallites (14.2 nm-CeO_2 vs. 7.0 nm-$Ce_{0.75}Zr_{0.25}O_2$). However, for all studied $Au/Ce_{0.75}Zr_{0.25}O_2$ catalysts, a shift of the four main diffraction peaks corresponding to the (101)(110)(200)(211) reflections typical of a face-centered cubic (fcc) cell toward the lower 2θ angles is observed. It could be related to the lattice expansion due to the formation of Ce^{3+} cations, having a bigger radius than Ce^{4+} (1.14Å vs. 0.97Å) [4], suggesting the autoreduction of the catalysts surface during the calcination process [5]. For the catalysts prepared without washing and washed with warm water, Au(111), Au(200) and Au(220) reflections at $2\theta \sim 38.185^\circ$, $2\theta \sim 44.393^\circ$ and $2\theta \sim 64.578^\circ$ were observed (JCPDS:00-004-0784). The average Au particle size is presented in Table 1. For the catalysts washed with ammonia a significant decrease in the

Au particle size was observed, as confirmed by HRTEM studies (Table 1).

The reduction of $Ce_{0.75}Zr_{0.25}O_2$ mixed oxide occurs in one stage with the maximum at 565ºC (Fig. 1a). In the presence of Au particles, the characteristic reduction peak of $Ce_{0.75}Zr_{0.25}O_2$ is shifted toward a lower temperature (Fig. 1a). The observed decrease in the reduction temperature could be related to the activation (dissociation) of H_2 molecule on Au nanoparticles, followed by the migration of dissociated hydrogen species by a spillover process from the surface of the Au particles to the support. However, if the catalyst contains only ionic Au, the surface oxygen reducibility could be intensified through the lattice substitution mechanism [1, 2, 5]. According to those statements, the Au^+ or Au^{3+} ions could fill the vacant Ce^{4+} sites, resulting in oxygen vacancy formations and an increase in oxygen mobility and reducibility. The smaller the Au particle size, the bigger the shift of the reduction peak. Moreover, a considerable decrease in TPR signal intensity for all $Au/Ce_{0.75}Zr_{0.25}O_2$ catalysts is observed. Estimated H_2 consumption strongly depends on Au particle size, with the minimum observed for the catalyst washed with ammonia (Table 1). Considering that washing procedures remove residual chlorine, which is known to inhibit the reducibility of Ce-containing oxides, the catalysts' autoreduction during calcination can occur.

Since the surface area of $Ce_{0.75}Zr_{0.25}O_2$ is smaller than that of CeO_2 (58 $m^2 \cdot g^{-1}$) [5], it could be suggested that the main reduction peak corresponds to a much higher H_2 uptake than that related to surface reduction. It implies that several layers of the mixed oxide contribute to this peak. Applying the model developed by Johnson and Mooi, an approximate evaluation of the H_2 consumption for surface reduction was estimated and is presented in Fig. 1a as the shaded area under TPR-H_2 curves. One can see that H_2 consumption for the removal of surface oxygen is related to the initial part of the reduction peaks. It suggests that
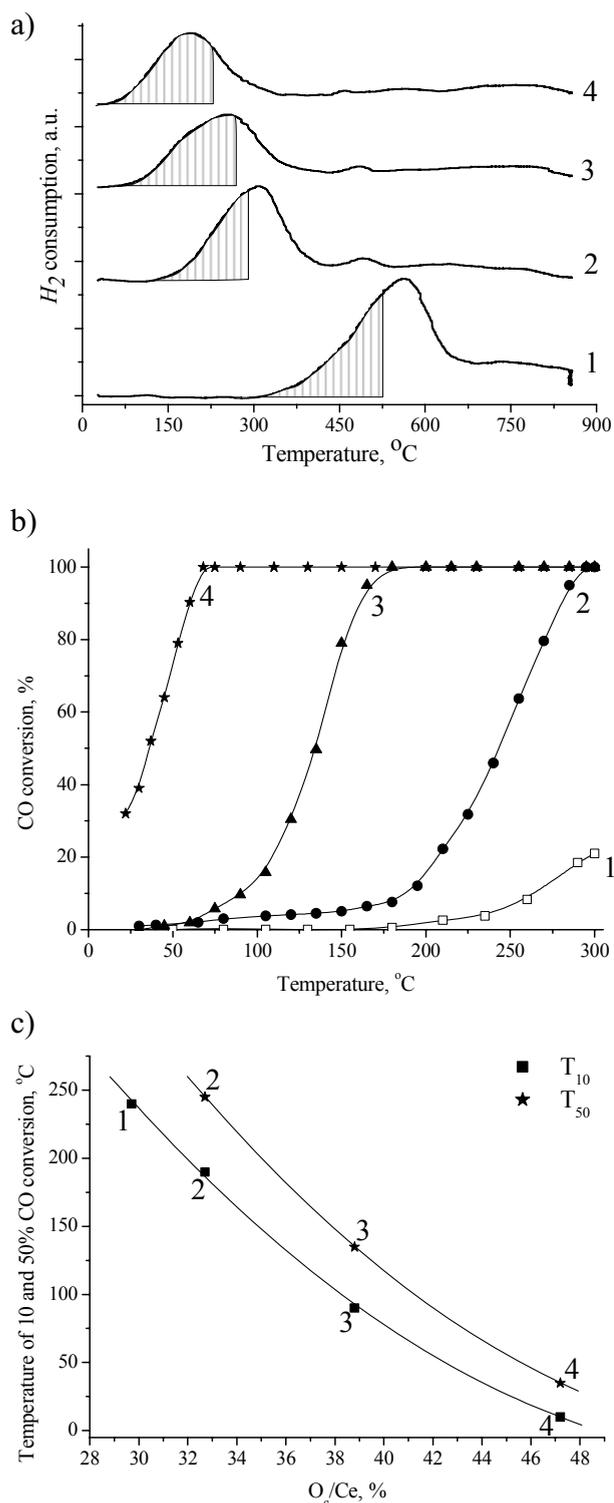
a)

b)

c)

Fig. 1. Characterization of the studied solids: a) TPR-H_2 profiles and H_2 consumption for surface reduction according to Johnson et Mooi model (shadow area), b) the activity in CO oxidation, c) the correlation between the percentage of oxygen atoms in the capping peak to the total cerium atoms (O_c/Ce) and the activity in CO oxidation. Complementary data in Table 1. In all cases: (1) $Ce_{0.75}Zr_{0.25}O_2$ oxide, $Au/Ce_{0.75}Zr_{0.25}O_2$ catalysts: (2) prepared without washing, (3) washed with warm water, and (4) washed with ammonia.

the removal of O_2 from the bulk of mixed oxide takes place also at low temperature. In the presence of Au, the temperature at which the surface capping oxygen can be removed is lower than that observed for $Ce_{0.75}Zr_{0.25}O_2$, due to the spillover of the dissociated atomic hydrogen from the Au particles on the support surface (Fig. 1a). Moreover, for all studied catalysts the H_2 consumption for the removal of surface capping oxygen atoms is higher than that for the oxide support, with the maximum observed for $Au/Ce_{0.75}Zr_{0.25}O_2$ catalysts washed with ammonia (Table 1). It suggests that well dispersed Au nanoparticles can act like a pump, assisting in the oxygen migration from the bulk to the surface of the catalyst. One can see that this process is favoured by high Au dispersion.

Fig. 1b presents a representative series of curves showing the effect of temperature on the CO conversion for the studied samples under stationary conditions. The temperature at which CO conversion reached 10 and 50% (T_{10}, T_{50}) is taken as a measure of catalytic activity (Table 1). CO conversion increases with increasing reaction temperature. The highest activity is observed over the catalyst washed with ammonia.

TPR-H_2 studies show a marked effect of well dispersed Au nanoparticles on the reducibility of $Ce_{0.75}Zr_{0.25}O_2$ support at low temperature. Moreover, the H_2 consumption for the removal of surface capping oxygen atoms is higher than that for oxide support, and strongly depends on Au particle size. One can say 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 (Fig. 1c). These findings indicate the role of both Au particle size and the support redox properties in creation of the catalytic performance of $Au/Ce_{0.75}Zr_{0.25}O_2$ catalysts in CO oxidation. The higher reducibility of the oxide support in the presence of well dispersed Au increases the concentration of surface oxygen vacancies available at low temperature. Such vacancies are potential centres of oxygen activation and can be formed even in the reaction mixture CO + O_2 [3]. It should be noted that in the case of $Ce_{0.75}Zr_{0.25}O_2$ oxide no CO conversion at temperatures below 200ºC was observed. However, in the presence of well dispersed Au their catalytic activity was greatly improved. Considering that CO adsorption was observed on both Au^{3+}, Au^+, Au^0 species and CeO_2 (Ce^{4+}-CO) [7], synergetic effect between the support and Au nanoparticles at the interface could be implied.

Conclusions

The presence of well dispersed Au nanoparticles facilitates the reduction of oxide support. The activity of the studied catalysts strongly depends on the preparation procedure, which determines Au particle size. 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,

indicating the role of both Au particle size and the support redox properties in creation of the catalytic activity of Au/$Ce_{0.75}Zr_{0.25}O_2$ catalysts in CO oxidation. One can imply the synergetic effect between the oxide support and Au nanoparticles at the metal-support interface.

Acknowledgments

References

1. BOND G.C., THOMPSON D.T., Catalysis by Gold. Cat. Rev. – Sci. Eng. **41**, 319, **1999**.

2. HASHMI A.S.K., HUTCHINGS G.J., Review-Gold catalysis. Angew. Chem. Int. Ed. **45**, 7896, **2006**.

3. GRZYBOWSKA-ŚWIERKOSZ B., Nano-Au/oxide support catalysts in oxidation reactions: provenance of active oxygen species. Catal.Today **112**, 3, **2006**.

4. TROVARELLI A. (Ed.), Catalysis by ceria and related materials. ICP, **2002**.

5. DOBROSZ-GÓMEZ I., KOCEMBA I., RYNKOWSKI J.M., Au/$Ce_{1-x}Zr_xO_2$ as effective catalysts for low-temperature CO oxidation. Appl. Catal. B: Environ. **83**, 240, **2008** [and references therein].

6. JOHNSON M. F. L., MOOI J., Cerium dioxide crystallite sizes by temperature-programmed reduction. J. Catal. **103**, 502, **1987**; Erratum: J. Catal. **140**, 612, **1993**.

7. GUZMAN J., CARRETTIN S., CORMA A., Spectroscopic evidence for the supply of reactive oxygen during CO oxidation catalyzed by gold supported on nanocrystalline CeO_2. J. Am. Chem. Soc. **127**, 3286, **2005**.