One-Pot Polyol Synthesis of Pt/CeO₂ and Au/CeO₂ Nanopowders as Catalysts for CO Oxidation

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The facile one-pot synthesis of CeO₂-based catalysts has been developed to prepare a relatively large amount of nanopowders with relevant catalytic activity towards CO oxidation. The method consists of a two-steps process carried out in ethylene glycol: in the first step, 5 nm well-crystallized pure CeO₂ is prepared. In a subsequent second step, a salt of a noble metal is added to the CeO₂ suspension and the deposition of the noble metal on the nanocrystalline CeO₂ is induced by heating. Two catalysts were prepared: Pt/CeO₂ and Au/CeO₂. The as-prepared catalysts, the thermally treated catalysts, as well as the pure CeO₂, are characterized by XRD, TGA, XPS, FTIR, HR-TEM, STEM, particle size distribution, and N₂-physisorption. In spite of the identical preparation protocol, Au and Pt behave in a completely different way: Au forms rather large particles, most of them with triangular shape, easily identifiable and dispersed in the CeO₂ matrix. In contrast, Pt was not identified as isolated particles. The high resolution X-ray diffraction carried out on the Pt/CeO₂ thermally treated sample (500 °C for 1 h) shows a significant CeO₂ lattice shrinkage, which can be interpreted as an at least partial incorporation of Pt into the CeO₂ crystal lattice. Moreover, only Pt²⁺ and Pt⁴⁺ species were identified by XPS. In literature, the incorporation of Pt into the CeO₂ lattice is supported by first-principle calculations and experimentally demonstrated only by combustion synthesis methods. To the best of our knowledge this is the first report where ionically dispersed Pt into the CeO₂ lattice is obtained via a liquid synthesis method. The thermally treated Pt/CeO₂ sample revealed good activity with 50% CO conversion at almost room temperature.

Keywords: CeO₂ Nanoparticles, Polyol Synthesis, CO Oxidation, Pt Dispersion, Au Nanoparticles.

1. INTRODUCTION

Carbon monoxide (CO) is produced worldwide in about a billion of tons per year from fossil fuel combustion.^{1,2} Since it is highly toxic and an ozone precursor, CO depollution by its oxidation to inert CO₂ with O₂ is a task of paramount relevance. The conversion is kinetically inhibited as a gas phase reaction^{1,4} but readily accessible via heterogeneous catalysis, where the chemical species CO and O₂ are able to be adsorbed on a solid catalyst surface. Noble metals supported on oxygen-deficient metal oxide materials represent ideal synergistic catalysts for CO

oxidation, since they are able to provide chemisorption centers for both CO and O₂ on highly dispersed noble metals and on surface oxygen vacancies of the metal oxide, respectively. The contact points between the noble metal and metal oxide, most probably, are the active catalytic centers.³ Thus, the metal oxide is not merely a support but actively involved in the catalytic process: the nature of these bi-phasic points are essential for efficient catalysts in terms of activity, selectivity, working temperature and stability. Noble metals, e.g., Au, Pd, and Pt, supported on metal oxides such as TiO₂, ZrO₂, CeO₂, Al₂O₃, Fe₂O₃, Co₃O₄, SiO₂, NiO, zeolites and mixtures thereof have been proved as catalytically active materials

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for CO oxidation.^{5–14} Among the metal oxides, CeO₂ was regarded as one of the most active and versatile component due to its remarkable redox properties.^{15,16} A large number of oxygen vacancies may be compensated by Ce³⁺ species, offering a material with significant oxygen mobility and oxygen storage capacity (OSC) even at elevated temperatures.^{17,18}

To meet practical needs, catalysts are often required to work at relatively high temperatures, such as for the oxidation of automotive exhaust gases. Under these conditions, dispersed metals tend to minimize their surface energy by sintering, resulting in the loss of bi-phasic points and thus of catalytic activity.^{19–30} Among a number of combinations, the Pt/CeO₂ system has been found to be highly active and stable^{31–34} for a wide range of applications.^{35–43} Here, the strong Pt–CeO₂ interaction inhibits the migration of Pt clusters or particles on the CeO₂ surface (anti-sintering properties) even during reactions at elevated temperatures.^{22,23,44} Au-based catalysts, on the other hand, have been intensely studied especially for their unique activity at low temperatures.⁴⁵

Catalysts are often prepared by deposition of the noble metal on a metal oxide support. Most of the literature deals with commercially available supports. In other more detailed papers, the metal oxide support is prepared in laboratory as well.⁴⁶ For instance, CeO₂ can be prepared via soft-chemical routes,⁴⁷ with the aim to obtain a material with tailored properties such as high surface area⁴⁸ or defined morphology.⁴⁵ Similarly, the deposition of the noble metal can be carried out according to several methodologies, including the chemical reduction of inorganic precursor salts on the metal oxide support suspended in water^{45–47} or organic solvents.⁴⁸

Recently, Meher et al.⁴⁷ have shown a method to synthesize CeO₂ according to a surfactant-assisted hydrothermal method. The hydrothermal synthesis was carried out for 24 h to obtain an intermediate product, which is then transformed to CeO₂ upon calcination. In a subsequent step the noble metal (0.5 wt.% Pt) was deposited either by conventional impregnation or by ethylene glycol reduction (EGR). The second deposition method leads to a highly dispersed Pt catalyst which is able to promote 100% CO conversion at $T < 100$ °C (50% conversion at $T = 56$ °C).

In a previous work, the one-pot synthesis of Pt@CeO₂ multicore@shell catalysts has been described in detail.⁴⁶ The method allows preparing 3.4 g L⁻¹ of Pt/CeO₂ catalyst (10 wt.% Pt). The complex thermal-resistant structure is obtained under protective atmosphere and 100% CO conversion is reached at $T = 145$ °C (50% conversion at about 125 °C). The complex structure is formed provided that an appropriate CeO₂/Pt-ratio is maintained, limiting the flexibility of the prepared formulation.

A third interesting paper deals with ionically dispersed Pt species into CeO₂ lattice prepared by the combustion synthesis methods.³² The authors claim that noble metal ions act as efficient catalytic centers for a number of reactions.

Inspired by these three papers and with our experience on metal and metal oxide^{49,50} nanoparticle synthesis, we developed our own facile high-throughput one-pot synthesis method for noble metal/metal oxide catalyst preparation. Our method is carried out in an open reactor vessel filled with ethylene glycol (EG), which allows the preparation of about 8.5 g L⁻¹ of CeO₂-supported nanocatalysts by a sequence of two heating steps. The first step promotes the crystallization of pure nano-CeO₂ from cerium(III) nitrate hexahydrate Ce(NO₃)₃ · 6H₂O. After cooling down to room temperature, an aqueous solution of the desired noble metal precursor is added. A second heating run favors the noble metal reduction on the CeO₂ in suspension. The entire one-pot procedure can last for less than two hours, including cooling cycles. The protocol has been tested for the preparation of Pt/CeO₂ and Au/CeO₂ but it is neither limited to these noble metals nor to CeO₂ as the only support material. The results show a completely different dispersion behavior of the two metals in the CeO₂ matrix. The characterization and the catalytic activities of the as-prepared as well as annealed catalysts are presented.

2. EXPERIMENTAL DETAILS

2.1. Materials

Chemical reagents including cerium(III) nitrate hexahydrate (Ce(NO₃)₃ · 6H₂O, >99.0%), ethylene glycol (EG, puriss. p.a > 99.5%) and sodium hydroxide (NaOH, >98%) were obtained from Sigma-Aldrich and used as received without further purification. For the preparation of Au catalysts, a precursor solution of hydrogen tetrachloroaurate (HAuCl₄) was prepared by dissolving 1.081 g Au (99.99%) in a mixture of hydrochloric acid (HCl, 37%, Sigma-Aldrich) and nitric acid (HNO₃, 65%, Sigma-Aldrich) in a 3:1 volume ratio (*aqua regia*), which was diluted with milliQ water to a final Au concentration of 21.43 mg mL⁻¹. An aqueous solution of hydrogen hexachloroplatinate(IV) (H₂PtCl₆, 8% in H₂O) was obtained from Sigma-Aldrich and used as received without further purification as precursor for the deposition of Pt nanoparticulate catalysts. Reagent grade ethanol and acetone were used for powder washing purposes and obtained from VWR. Cordierite was used to dilute the catalyst for catalytic tests.

2.2. Preparation of CeO₂ Nanopowders by Polyol-Mediated Synthesis

In a typical synthesis, a fixed amount of the Ce precursor salt (4.16 g, 10 mmol of Ce(NO₃)₃ · 6H₂O) and sodium hydroxide (1.14 g, 30 mmol of NaOH) were each dissolved in 100 mL of EG at 120 °C, respectively.

After that, both solutions were cooled to room temperature (RT). A colloidal dispersion of CeO₂ nanoparticles (NPs) was precipitated by mixing both solutions and 10 mL of milliQ water under vigorous stirring after heating the mixture to 160 °C for 30 min. During this time,

the color of the liquid changed from white to grey-purple. After the cooling, the suspension was sonicated (Sonics-VibraCell, VCX130, 130 W / 20 kHz) at 100% power for 1 min in order to break down loose agglomerates and to evenly disperse the NPs for the following polyol-mediated reductive deposition-precipitation of noble metal on the CeO₂ nanoparticles.

2.3. Deposition-Precipitation of Noble Metal on CeO₂ by Ethylene Glycol Reduction (EGR) Method

The noble metal (Au or Pt) was deposited on the CeO₂ according to the following procedure. An appropriate amount of the noble metal precursor solution (HAuCl₄ or H₂PtCl₆) was added under vigorous stirring to the slurry containing dispersed CeO₂ in order to achieve a total loading of 6 wt.% of noble metal. The mixture was heated up to 180 °C for 30 min which leads to the reduction of the noble metal ions by EG. The deposition-precipitation of metallic Au on CeO₂ can be easily followed by the color change of the suspension to crimson red, whereas the completion of the reduction of the Pt⁴⁺-species gives rise to a black suspension. The final products were collected by centrifugation. In order to completely remove EG and byproducts, the solids were washed twice in ethanol and once in acetone by redispersing the solids via sonication (100% power, 1 min). Finally, the catalysts were dried at RT overnight. For the catalytic tests, the materials were either used as prepared or thermally treated (TT) in air for 1 h at 500 °C (heating rate 2.5 K min⁻¹). The total noble metal content of the catalyst was determined by chemical analysis (ICP-MS).

2.4. Characterization

For screening purposes, X-ray powder diffraction (XRD) patterns were collected with a Bruker D8 Advance diffractometer (Cu K α radiation) in the range 15–90° 2 θ ($\Delta^2 2\theta = 0.019$), while cell parameters and crystallite sizes were calculated from high resolution XRD patterns collected using 25 keV synchrotron radiation at the MS-X04SA beamline (SLS-PSI),⁴⁹ using 0.3 mm capillaries. Cell parameters and phase quantifications were calculated by Rietveld refinement using GSAS (profile function #4)⁵¹ and the ICS database.⁵²

High-resolution transmission electron microscopy (HRTEM), scanning transmission electron microscopy (STEM), electron diffraction (ED) and energy-dispersive X-ray (EDX) spectroscopy data were obtained with a JEOL 2200FS TEM/STEM microscope equipped with a Gatan Digiscan system and operated at 200 kV. The microscope provides a point-to-point resolution of 0.23 nm (TEM mode) and a spatial resolution of 0.16 nm (STEM mode). The samples for TEM characterization were dispersed in *i*-propanol and a drop of the suspension was deposited onto either carbon-coated or holey-carbon-coated copper grids allowing the solvent to evaporate in air. In addition, for the STEM data acquisition, some

samples were gently plasma cleaned with an Ar (75%)/O₂ (25%) plasma for a few seconds to remove hydrocarbon contamination.

Specific surface area (SSA) (BET method⁵³) and pore size distribution (BJH method,⁵⁴) were determined by N₂-physisorption using a Micromeritics Tristar II 3020 working at liquid nitrogen, after evacuation of the sample at 110 °C for 24 h. The BET equivalent diameter (d_{BET}) was obtained using the relation (1):

$$d_{\text{BET}} = \frac{6}{\rho_{\text{XRD}} \text{SSA}} \quad (1)$$

where ρ_{XRD} is the density measured from lattice parameters and 6 is the geometrical factor for spherical or cubic particles.

Fourier transform infrared (FTIR) measurements were performed using a Bruker Hyperion 3000 microscope coupled to a Bruker Vertex70 v Interferometer. Solid samples were deposited on a single ZnSe optical window and measured in transmission mode with 15x Schwarzschild objectives. Liquid samples (e.g., EG as reference measurements) were pressed between two ZnSe optical windows and measured as a thin film in transmission mode with 15x Schwarzschild objectives. The blades of the confocal apertures of the microscope were set at 46 × 50 μm^2 for solid samples and at 110 × 100 μm^2 for liquid samples. The interferometer was operated in the mid-infrared region using a Ge Multilayer beamsplitter supported on KBr. Mirrors were scanned at 40 kHz up to a resolution of 4 cm⁻¹. 500 forward-backward double sided interferograms were collected for background and sample over the range 400–8000 cm⁻¹, phase corrected with the Mertz method and apodized with a Blackman-Harris 3–Term function and a zero-filling factor of 2.

Thermogravimetric analysis (TGA) was carried out with a Mettler Toledo TGA/SDTA 851e in the temperature range 25–950 °C (heating rate 5 K min⁻¹) under Ar/O₂ (20% O₂, 15 mL min⁻¹).

Catalytic activity data for CO oxidation were obtained in a quartz tube plug flow reactor ($d_i = 6$ mm) that was loaded with a specific amount of catalyst (3.6 mg of metal, Pt or Au) mixed with cordierite, firmly fixed between two quartz wool plugs. A thermocouple was inserted at the middle of the catalyst bed and the catalytic tests were carried out in the temperature range 298–673 °C (heating rate 5 K min⁻¹). A gas flow of 3% O₂ with 1000 ppm CO (100 mL min⁻¹, balance N₂) was introduced in the quartz tube ($GHSV = 28000$ mL g_{metal}⁻¹ min⁻¹). The out-flowing gases were monitored using a Thermo Scientific Antaris IR spectrometer. Conversion data are reported as $X_i = 100 \cdot (C_{\text{CO}}^{\text{in}} - C_{\text{CO}}^{\text{out}}) / C_{\text{CO}}^{\text{in}}$.

Chemical analysis was performed with an Agilent 7700x ICP-MS after digestion of the samples and dilution in milliQ water, using external standard calibration. For the Au/CeO₂ samples, 20 mg of powders were dissolved in

solutions consisting of 3 mL of concentrated HCl (30%) and 1 mL HNO₃ (65%). For the Pt/CeO₂ samples, 20 mg of powders were dissolved in 1 mL of concentrated HCl (30%) and 3 mL HNO₃ (65%). In order to perform a complete dissolution of the samples, a high-pressure microwave digestion unit was used. The digested samples were diluted with a two step process in water solution (milliQ water, 3% HCl, and 1% HNO₃) with a total dilution factor of about 2.5×10^6 . Calibration and blank solutions were prepared by diluting (single-element) standard solutions down to a range of concentrations between 0 and 20 ppb ($\mu\text{g L}^{-1}$). The same acidic matrix containing 3% HCl and 1% HNO₃ was used for the preparation of the calibration and sample solutions.

Particle size distributions were measured with an X-ray disc centrifuge (Brookhaven Instrument, BI-XDC) in water after sonication (Sonics-VibraCell, VCX130, 130 W/20 kHz) of the suspension for 3 min at 100% power.

X-ray Photoelectron Spectroscopy (XPS) measurements were performed using a VG ESCALAB 220iXL spectrometer (Thermo Fisher Scientific) working with an Al K α source and a magnetic lens system. The spectra were recorded in constant analyzer energy mode at pass energy of 30 eV for high resolution acquisition of core levels. The XPS binding energy was calibrated using the Ag 3d_{5/2}, the Cu 2p_{3/2} and the Au 4f_{7/2} peaks after Ar ion sputtering of the samples surface. The data was evaluated using the Advantage software (v. 4.43, Thermo Fisher Scientific). Background subtraction has been performed according to Shirley.⁵⁵

3. RESULTS AND DISCUSSION

3.1. Characterization of CeO₂ Nanopowders

The synthesized CeO₂ NPs have been characterized as reference material. The HRTEM images, the XRD pattern (a) and the N₂-physorption hysteresis of the as-prepared CeO₂ powders are shown in Figures 1, 2(a) and 3, respectively. Table 1 summarizes the relevant characteristic data. The crystallite sizes estimated from the HRTEM images (d_{TEM}) are in excellent agreement with the sizes calculated from the diffraction pattern (d_{XRD}) and from the SSA

Figure 1. HRTEM image of the as prepared CeO₂.

Figure 2. X-ray diffraction patterns collected at the MS X04SA beam line at the energy of 25 keV ($\lambda = 0.4965$ nm). (a) as prepared CeO₂; (b) Pt/CeO₂; (c) Pt/CeO₂ (TT); (d) Au/CeO₂ (TT); (e) Au/CeO₂. The peak positions of Au, Pt and CeO₂ are shown below the patterns.

Figure 3. N₂-physorption hysteresis of pure CeO₂ (inset: pore size distribution).

(d_{BET}). The hysteresis loop in Figure 3 matches the H1-type,⁵⁶ fingerprint of interparticle capillary condensation. Since the particles are not close-packed (Fig. 1), the pore size distribution (Fig. 3, inset) is rather large (20 nm) compared to the crystallite size (5 nm). According to the

Table I. Summary of the properties of pure CeO₂.

Sample	SSA (BET) (m ² g ⁻¹)	Density (XRD) (g cm ⁻³)	Lattice param. <i>a</i> (Å)	<i>d</i> _{XRD} (nm)	<i>d</i> _{HET} (nm)	<i>d</i> _{TEM} (nm)
As prepared	169 (±5)	7.09 (7)	5.441 (0)	4.7 (±1)	5.0 (±0.5)	5 (±2)
Thermal treatment@500 °C for 1 h	123 (±5)	7.20 (0)	5.413 (9)	14 (±2)	6.9 (±0.5)	5–10

t-plot,⁵⁷ no micropores are revealed, in agreement with the highly ordered crystalline structure (Fig. 1).

Figure 4 shows the thermogravimetric analysis. The sample loses about 1.5 wt.% in the temperature range 25–105 °C due to the adsorbed water. At about 155–160 °C an abrupt weight change (about 9 wt.%) occurs as a consequence of the rapid combustion of organic residues, as confirmed by the intense exothermic simultaneous differential thermal analysis (SDTA) signal. FTIR analysis (not shown) has revealed characteristic bands of ethylene glycol on the as-prepared dried powders. In the temperature range 160–950 °C a smooth weight loss (about 7 wt.%) occurs with limited SDTA signals that could be assigned both to residual intragranular carbon combustion (exothermic) and lattice O₂ release (endothermic) with creation of oxygen vacancies. As a consequence of the thermal treatment at 500 °C for 1 h the SSA decreases to 123 m² g⁻¹ (Table I) and no significant change in the pore size distribution has been detected.

The particle size distribution of the CeO₂ dried powders, re-dispersed in water is shown in Figure 5. The average volumetric size, *d*_{V50%} (where *d*_{VY%} is the diameter corresponding to the Y% of the cumulative volumetric distribution) is about 29 nm and the distribution span, (*d*_{V90%} – *d*_{V10%})/*d*_{V50%}, is about 3.5. The bimodal distribution reveals the presence of agglomerates, formed during the drying procedure. The calculated average agglomeration factor (*F*_{ag} = *d*_{V50%}/*d*_{HET}) is about 6.

It can be concluded that the method allows producing well-crystallized loosely-packed CeO₂-NPs with an average particle size of 5 nm. As a consequence of thermal treatment at 500 °C for 1 h, crystal growth occurs and 25%

of the surface area is lost, although the overall pore structure is conserved. The as-prepared powders form agglomerates of an average size of 29 nm upon drying at room temperature.

3.2. Pt/CeO₂ and Au/CeO₂ Samples Characterization

The chemical analysis carried out on Pt/CeO₂ and Au/CeO₂ samples confirms that the concentrations of noble metals are in agreement with the dosed amount of noble metal in the preparation procedure (about 6 wt.% in the as-prepared samples Pt/CeO₂ and Au/CeO₂). The thermally treated samples show a noble metal concentration coherent with the weight loss of CeO₂ (Fig. 4). This data are reported in Table II.

X-ray diffraction patterns of the Pt/CeO₂ and Au/CeO₂ samples are reported in Figure 2. It can be seen that for Pt/CeO₂ samples, no peaks related to Pt appear. Coherently, several HRTEM images were accurately examined but the lattice fringes of Pt (111) (0.23 nm) were not identified in both Pt/CeO₂ and Pt/CeO₂(TT) samples (Fig. 6). The Pt/CeO₂ (TT) sample was also investigated by bright-field (BF) (Fig. 7(a)) and high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) (Fig. 7(b)). The intensity of the HAADF-STEM images approximately scales with the square of the atomic number *Z* and with the thickness of the sample. Thus, because of its favorable atomic-number contrast it should be possible to distinguish the Pt from the CeO₂ nanoparticles. Indeed, high contrast spots are detected in the HAADF-STEM image of

Figure 4. Thermogravimetric analysis of the pure CeO₂ sample. The blue line is the weight change (%) and the red line is the SDTA signal (°C).

Figure 5. Particle size distribution of the pure CeO₂ sample after drying and re-dispersion in water. The blue line is the differential volumetric distribution and the red line is the cumulative volumetric distribution.

Table II. Summary of the Pt/CeO₂ and Au/CeO₂ sample properties. (TT = Thermally treated).

Sample name	Noble metal	Thermal treatment	Noble metal content from ICP (wt.%)	Noble metal content from XRD (wt.%)	CeO ₂ crystallite size (nm)	CeO ₂ lattice param. <i>a</i> (Å)	Noble metal crystallite size (nm)
Pt/CeO ₂	Pt	As-prepared	6.3 (±0.5)	—	6 (±1)	5.435 (1)	—
Pt/CeO ₂ (TT)	Pt	500 °C/1 h	5.0 (±0.5)	—	9 (±1)	5.365 (3)	—
Au/CeO ₂	Au	As-prepared	6.4 (±0.5)	5.9 (±0.5)	5 (±1)	5.436 (6)	74 (±5)
Au/CeO ₂ (TT)	Au	500 °C/1 h	5.3 (±0.5)	5.4 (±0.5)	15 (±2)	5.414 (9)	86 (±5)

Figure 7(b). These spots might be associated to dispersed Pt nanoparticles (≈ 1 nm), as also confirmed by the presence of homogeneously distributed Pt by EDX analysis (Fig. 7(c)). No electron diffraction rings or spots attributable to Pt are revealed in the ED image (Fig. 7(d)), in agreement with the XRD patterns.

It can be concluded that Pt may be incorporated in the CeO₂ lattice and/or is decorating the CeO₂ particle surface with clusters of size below the detection limits of the instruments used for the material characterization. The value of crystal lattice parameter *a* (Table II) for Pt/CeO₂(TT) supports the hypothesis of Pt incorporation in the CeO₂ lattice: since Pt²⁺ and Pt⁴⁺ are smaller than Ce⁴⁺, a crystal lattice contraction is expected by replacement of Pt for Ce (Pt_{Ce}). The as prepared samples (Pt/CeO₂, Au/CeO₂ and pure CeO₂) show an average lattice parameter (*a*) of 5.437(6) Å, while thermally treated samples (Au/CeO₂ (TT), pure CeO₂(TT), and in agreement with the work of Nagai⁵⁸) show an average value of 5.414(1) Å. This contraction can be explained by crystal defect segregation and lattice relaxation processes. The crystal lattice parameter measured for Pt/CeO₂(TT) is significantly smaller (*a* = 5.365(3) Å). Thus, the incorporation of Pt into the crystal lattice is plausible. The incorporation occurs only because of the thermal treatment, since Pt/CeO₂ shows the same lattice parameter of the pure material. Moreover, the thermally induced CeO₂ crystal growth is affected by the presence of Pt. Pure CeO₂ and Au/CeO₂ samples grow from 5–6 nm to 14–15 nm as a consequence of the thermal treatment, while the Pt/CeO₂

(TT) sample shows significant crystal growth inhibition with a size of 9 nm. This inhibition may be related to the influence of defects induced by the presence of Pt in the CeO₂ lattice (Pt_{Ce}²⁺, Pt_{Ce}⁴⁺) and oxygen vacancies V_O[•] (as compensation defect). The CeO₂ crystal growth inhibition may be attributed to the formation of associations between the dopants ions and oxygen vacancies.^{59–61}

The possibility to incorporate noble metal into a metal oxide lattice is supported by DFT modeling⁶² and experimentally demonstrated for Pt,³² Cu,⁶³ and Pd⁶⁴ into CeO₂ and Pt into TiO₂.⁶⁵ All the aforementioned solid solution samples were prepared by the combustion synthesis method. To the best of our knowledge, this is the first report where the incorporation of Pt into the CeO₂ lattice is obtained via liquid synthesis method, in combination with a mild thermal treatment. In order to support these findings, Pt/CeO₂ and Pt/CeO₂ (TT) samples were analyzed by XPS. Figure 8 shows the photoelectron spectra of the Pt 4f_{7/2-5/2} core level region. For metallic Pt with zero oxidation (Pt⁰) the spin orbit 4f_{7/2} and 4f_{5/2} peaks are located at 71.0 and 74.3 eV, for Pt²⁺ at 71.7 and 74.9 eV, and for Pt⁴⁺ at 74.0 and 77.2 eV.³² Thus, the energy difference between Pt²⁺ and Pt⁴⁺ 4f_{7/2} peaks is about 2.3 eV. This difference is coherent with our best fitting and it is supporting the presence of both ionic Pt-species in the samples. In the as prepared sample the amount of Pt²⁺ is about 73%, while it corresponds to about 48% in the thermally treated sample. Combining the XRD and XPS analyses, it can be concluded that in the as-prepared sample, Pt ionic species, mainly as Pt²⁺, are incorporated on

Figure 6. HRTEM images of the sample Pt/CeO₂ (TT).

Figure 7. (a) BF-STEM and (b) HAADF-STEM images, (c) energy-dispersive X-ray (EDX) spectra and (d) electron diffraction (ED) pattern collected on sample Pt/CeO₂ (TT).

the CeO₂ surface, while upon mild thermal treatment in air, Pt²⁺ is partially oxidized to Pt⁴⁺ and it diffuses into the CeO₂ lattice. A more detailed investigation by X-ray Absorption Spectroscopy (XAS) is currently in progress.

A completely different scenario can be depicted for the Au/CeO₂ samples (Au/CeO₂ and Au/CeO₂(TT)). Here, Au

crystallites are distributed in well-defined particles, most of them with triangular shape (Figs. 9 and 10), for which the chemical composition was confirmed by EDX analysis (not shown). The calculated Au crystal size for the as-prepared and thermally treated samples is about 80 nm, in rough agreement with the TEM images. The CeO₂

Figure 8. XPS of Pt(4f) core level region of (a) Pt/CeO₂ (b) Pt/CeO₂(TT). The blue lines refer to the Pt²⁺ (dashed line 4f_{7/2}, continuous line 4f_{5/2}); the red line refers to Pt⁴⁺ (dashed line 4f_{7/2}, continuous line 4f_{5/2}), the black line is the best fitting of the experimental data (crosses).

Figure 9. (left) BF-STEM and (right) HAADF-STEM images of sample Au/CeO₂.

crystallite sizes increase as a consequence of the thermal treatment from 5 to 15 nm, in agreement with the pure CeO₂. The EDX analysis, performed on thick CeO₂ aggregates but in distinct distance from the isolated Au particles, does not detect any Au contribution. Moreover, within the experimental incertitude, the XRD analysis confirms that Au is in form of isolated crystalline particles only, as shown by the agreement between the chemical analysis (overall amount) and the diffraction patterns (Rietveld refinement, Fig. 11). Accordingly, the CeO₂ crystal lattice parameter is not affected by Au, confirming that the noble metal is not incorporated. In conclusion, Au does not show a strong interaction with CeO₂ and isolated Au large crystals dispersed in the CeO₂ matrix are formed. Similar results have been recently obtained in our laboratory for Au/TiO₂ catalysts.

Figure 12 shows the results of the catalytic tests for CO oxidation. The Pt samples show better catalytic activity than the Au samples, in agreement with their much better dispersion of the noble metal in the CeO₂ matrix.

It is worth noting that the thermal treatment has an opposite effect on the catalytic properties: for Pt/CeO₂

Figure 11. Rietveld refinement of the XRD pattern collected on sample Au/CeO₂ (TT).

samples, 50% CO conversion is obtained at 32 and 97 °C for samples Pt/CeO₂(TT) and Pt/CeO₂, respectively, while 50% CO conversion is obtained at 201 and 276 °C for samples Au/CeO₂ and Au/CeO₂(TT), respectively. This result has to be discussed in parallel with the incorporation of

Figure 10. (left) BF-STEM and (right) HAADF-STEM images of sample Au/CeO₂ (TT).

Figure 12. CO conversion (X_i) against measured temperature for sample (a) Pt/CeO₂ (TT); (b) Pt/CeO₂; (c) Au/CeO₂; (d) Au/CeO₂ (TT).

Pt into the CeO₂ lattice: once Pt is incorporated, superior activity is shown. On the other hand, Au samples do not show any solubility into the CeO₂ lattice and the detrimental effect of thermal treatment could be related to a partial re-crystallization and/or crystal growth of Au particles. Despite of the rather large Au crystals, the Au/CeO₂ catalysts show an acceptable activity at relatively high temperature.

4. CONCLUSIONS

The polyol-based preparation method described in this paper allows the facile one-pot synthesis of a relatively high amount of catalyst in a rather short time. The protocol has been tested for the preparation of Pt/CeO₂ and Au/CeO₂. The resulting catalysts have been tested for CO oxidation activity.

The pure CeO₂ has been completely characterized and consists of 5 nm well-crystallized material; the deposition of the noble metals does not affect the CeO₂ particle size, morphology, or crystallinity.

The relevant finding of this experimental work is that the two classes of catalysts show radical microstructural differences, reflected by the catalytic properties. In the case of Pt/CeO₂ the noble metal is incorporated—at least partially—into the CeO₂ crystal lattice upon thermal treatment at 500 °C and excellent catalytic properties are obtained (50% CO conversion at almost room temperature). Because of the dilution of the noble metal into a refractory matrix (CeO₂), relevant temperature resistant properties are expected for this class of materials. This is the first report where ionically dispersed Pt into CeO₂ lattice is obtained by a liquid synthesis method.

In the case of the Au/CeO₂ catalyst, rather large (80 nm) well-faceted Au crystals are formed. The thermal treatment has a slight negative effect on the catalytic activity but despite the rather large Au crystals, an acceptable activity at relatively high temperature is maintained. Improvements

in the direction of a much finer dispersion of Au in/on the CeO₂ matrix are required for this class of materials.

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