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Trends in the CO oxidation and PROX performances of the platinum-group metals supported on ceria

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ABSTRACT

PGM–CeO_2 (PGM = Pt, Pd, Ir, Rh, Ru) catalysts were prepared by one-step solution combustion synthesis (SCS) and characterized by elemental analysis, N_2 volumetry, aberration-corrected HRTEM, X-ray diffraction, and CO-DRIFTS. The samples, consisting of 2–6 nm metal nanoparticles supported on mesoporous ceria, were tested in CO oxidation in absence and presence of hydrogen (PROX). To our knowledge, this work presents the first comparison of all the platinum-group metals (except Os) for these reactions in the same conditions. The as-prepared SCS catalysts are active in CO oxidation and a reducing treatment has no significant effect on their performances. While the best catalyst in H_2-free CO oxidation is Rh–CeO_2, the addition of a high hydrogen excess decreases the Rh catalyst activity but enhances the CO oxidation rate on all other systems, including alumina-supported metals employed as reference catalysts. The resulting PROX turnover frequencies (Pt > Pd > Rh > Ir > Ru) follow the trends predicted by published density-functional-theory calculations considering the $CO_{ad} + O_{ad}$ elementary reaction as the rate-determining step. Pt–CeO_2 is not only the most active but also the most selective catalyst, reaching near 100% CO_2 at low temperature (*ca.* 100 °C). The alumina-supported catalysts appeared less active than their ceria-supported counterparts in both reactions. The effect of heating/cooling cycles on the reaction kinetics was also investigated. Whereas the Pt, Pd and Ir ceria-supported catalysts were stable throughout PROX cycles, Rh and Ru ones exhibited apparently chaotic behaviors above *ca.* 200 °C, which are proposed to be induced by favorable CO dissociation and methanation pathways and/or variable metal oxidation states.

1. Introduction

Beyond the prototypical catalytic oxidation of CO, the preferential oxidation of CO in hydrogen excess (PROX) has been proposed as a viable process to remove CO impurities from reformate hydrogen, in order to feed onboard proton-exchange-membrane fuel cells with pure hydrogen and thereby avoid the Pt anode poisoning by CO [1–3]. PROX has been widely studied over platinum-group metals (PGMs, *i.e.* Pt, Pd, Ir, Rh, Ru, and Os) supported on non-reducible oxides (typically Al_2O_3), and coinage metals supported on reducible oxides (typically CuO/CeO_2). Conversely, the combination of PGMs with reducible oxides has been much less studied, although reducible oxides are known to act as PGM promoters in PROX [3]. Due to its excellent redox properties, ceria is extensively used in heterogeneous catalysis, where it can act as an oxygen buffer for oxidation reactions [4]. The three-way catalytic converter for gasoline-powered automotive engines is the best known catalytic application of ceria. It typically consists of a monolith washcoated with a ceria-zirconia/alumina film containing Pt, Pd, and Rh nanoparticles, which are active for catalyzing CO/hydrocarbon oxidation and NO_x reduction. Both for CO oxidation and PROX, ceria has proved its superiority over any other simple oxide as a PGM support, especially at low temperatures [5–7]. This is explained by the existence, in addition to the standard Langmuir–Hinshelwood mechanism which proceeds on the metal only, of a second mechanism involving oxygen from ceria at the metal/ceria interface [5,8].

To the best of our knowledge, there has been no report to date comparing, under the same conditions, the PGM/ceria series in CO oxidation or PROX. Only Mariño et al. [6] compared Pt, Pd, and Ir on various oxides, including ceria, showing the following hierarchy between the studied metals in terms of PROX

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Table 1
Characteristics of the samples.

Sample name	Metal content (wt%)[a]	Metal particle size (nm)[b] fresh/reduced	Mean ceria crystallite size/lattice parameter (nm)[c]	Surface area (m^2/g)[d]
CeO_2	0	–	24/0.54134	28
$Pt–CeO_2$	0.98	ND/4.0 ± 1.3	27/0.54123	17
$Pd–CeO_2$	0.31	ND/6.5 ± 1.9	27/0.54137	35
$Ir–CeO_2$	0.93	2.1 ± 0.7/3.4 ± 1.1	26/0.54147	29
$Rh–CeO_2$	0.73	4.6 ± 1.8/4.7 ± 1.5	39/0.54136	12
$Ru–CeO_2$	1.01	2.8 ± 1.1/3.1 ± 1.3	23/0.54138	20

ND = not determined.
[a] Determined by ICP-OES.
[b] Determined by TEM (the "reduced" samples were heated to 400 °C in H_2 flow).
[c] Determined by XRD Rietveld refinements for as-prepared catalysts.
[d] Determined by N_2 adsorption volumetry (BET) for as-prepared catalysts.

performances: Pt > Ir ≫ Pd. Rh and Ru-based catalysts have been rarely studied for PROX. Galletti et al. [9] investigated a Rh/CeO_2 catalyst, and Chen et al. [10] studied a Ru/Al_2O_3 catalyst modified by ceria–terbia mixed oxide. $Ru(Ce_{0.8}Tb_{0.2}O_2)/Al_2O_3$ performs well, whereas Rh/CeO_2 is not compelling for PROX. Oh and Sinkevitch [11] compared various commercial catalysts for application of PROX to fuel cells and reported that Ru/Al_2O_3 and Rh/Al_2O_3 are more selective than Pt/Al_2O_3.

In this paper, we compare all the PGMs (except Os, which forms a highly toxic oxide in ambient air) supported on ceria for CO oxidation and PROX. In addition to metal benchmarking for each reaction, we emphasize the strongly metal-dependent (positive or negative) effect of hydrogen on CO oxidation activity. Moreover, we also assess the support effect using a commercial Pt/Al_2O_3 catalyst as reference and previous results for Pd/Al_2O_3 and Ir/Al_2O_3. For catalyst preparation, we have used solution combustion synthesis (SCS), which consists in the fast and self-sustained combustion of a pre-heated aqueous solution of a metallic salt (usually nitrate) and an organic fuel (typically glycine) [12]. Unlike for mixed oxides, SCS has been very scarcely used for the preparation of noble metals/oxides combinations [9,13–15]. Here, this method has been employed to prepare a PGM/ceria series with the objective of maximizing the metal dispersion and the metal–oxide interaction, while limiting metal-dependent nanoparticle size issues inherent to conventional impregnation methods.

2. Experimental

2.1. Catalyst preparation

A series of CeO_2 and $PGM–CeO_2$ powders (see Table 1) was prepared by solution combustion synthesis (SCS), using ceric ammonium nitrate, CAN [$(NH_4)_2Ce(NO_3)_6$, Sigma–Aldrich, 99.99%] as both ceria precursor salt and oxidizing agent. The PGM precursors were: $H_2PtCl_6{\cdot}6H_2O$ (Strem Chemicals, 38–40% Pt), $Pd(NH_3)_4Cl_2{\cdot}H_2O$ (Sigma–Aldrich, 98%), $(NH_4)_2IrCl_6$ (Strem Chemicals, 99%), $RhCl_3$ (Sigma–Aldrich, 38–40% Rh), and $RuCl_3$ (Sigma–Aldrich, 38–42% Ru). Glycine ($C_2H_5NO_2$, Sigma–Aldrich, 99%) was used as fuel. The CAN:glycine:PGM precursor mixture composition was chosen in order to obtain stoichiometric proportions of oxidizer and fuel (*i.e.*, with the oxidizing/reducing valence ratio of the redox mixture equal to 1) [16] and reach the desired metal loading (1 wt%). Table 1 shows the actual loadings.

Practically, a borosilicate beaker (300 cm^3) containing a mixture of CAN (5.00 g), glycine (1.82 g), PGM precursor, and 30 mL deionized water was introduced into a muffle furnace (Carbolite ELF 11/6) maintained at 350 °C. At the point of complete dehydration (5–10 min), the solution started boiling and foaming, and ignition took place after a few seconds with rapid evolution of a large quantity of gases. This yielded a voluminous solid product within a few minutes. The powder color ranged from pale yellow (CeO_2) to brown-gray ($PGM–CeO_2$).

2.2. Catalyst characterization

The metal amounts were determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Activa instrument from Horiba Jobin Yvon). In order to dissolve them completely, the samples were treated with a mixture of H_2SO_4, *aqua regia* and HF at 250–300 °C.

Isotherm determination was performed by N_2 adsorption volumetry at −196 °C (ASAP 2010M instrument from Micromeritics). Specific surface areas were derived using the BET method. Prior to the measurements, the powders were outgassed at 300 °C for 2 h in vacuum.

The crystalline structure was analyzed at RT and ambient atmosphere using a Bruker D8 Advance A25 diffractometer (CuKα radiation at 0.154184 nm) equipped with a Ni filter and 1-D fast multistrip detector (LynxEye, 192 channels on 2.95°). The diffractograms were collected at 2θ with steps of 0.02° from 4° to 80° for a total acquisition time of 32 min and from 20° to 85° for a total acquisition time of 110 min. Phase identification was performed using the Diffrac.Eva software (Bruker) and the ICDD-PDF4+ database. The lattice parameters and the crystallite sizes were determined using the Rietveld method (Fullprof code).

The local sample microstructure was examined by high-resolution transmission electron microscopy (TEM) and scanning transmission electron microscopy-high angle annular dark field (STEM-HAADF) using a FEI Titan G2 aberration-corrected ETEM (in high-vacuum mode) operated at 300 kV with 1 Å best resolution. The samples were crushed in ethanol and the solution was ultrasonically stirred before dropping it on a holey carbon-covered copper TEM grid, followed by drying. In some cases, a standard reducing pretreatment consisting in heating the as-prepared samples to 400 °C (5 °C min^{-1}, 2 h plateau) in pure H_2 flow (3–7 L h^{-1}, 1 atm), was applied. This temperature was found high enough for reducing all the metals while avoiding an extensive reduction of ceria, which can be detrimental for the catalytic performances [17]. For example, CO oxidation tests performed after reduction at 500 °C on $Pt–CeO_2$ showed a slight decrease in activity as compared to the 400 °C reduction case (not shown).

Infrared spectroscopy of adsorbed CO was performed using a Thermo Nicolet 6700 FTIR spectrophotometer equipped with an *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) chamber (Harrick HVC-DRP cell) and a high-sensitivity MCT detector. The cell was connected to a gas handling system allowing for *in situ* treatments with several gases at temperatures up to 500 °C. About 30 mg of the powder sample were placed into the cell sample holder and pretreated under He flow (40 mL min^{-1}, 1 atm) at 300 °C for 1 h. CO was pre-adsorbed by exposing the sample kept at 50 °C to a flow of 1% CO in He for 15 min. Then