Control of the surface atomic population of Rh_{0.5}Pd_{0.5} bimetallic nanoparticles supported on CeO₂

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ABSTRACT

Rh_{0.5}Pd_{0.5}/CeO₂ bimetallic nanoparticles were subjected to reducing and oxidizing atmospheres at different temperatures and characterized by means of the Ambient Pressure X-Ray Photoelectron Spectroscopy (AP-XPS). The surface atomic population is calculated for all cases. By using a high temperature pre-treatment at 480 °C in H₂ atmosphere, it was possible to control the surface atomic population with Pd atoms frozen at the skin layer even in an oxidizing atmosphere, which is not observed without high temperature pre-treatment (Rh atoms at the skin layer). The change of the Rh/Pd surface segregation behavior after the high temperature pre-treatment is attributed to the geometrical factor of Strong Metal Support Interaction (SMSI) effect, i.e., the occurrence of the ceria capping layer around nanoparticles.

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1. Introduction

Strong Metal Support Interaction effect (SMSI) is discovered more than 30 years ago [1] for TiO₂ support. The nanoparticles supported presented an almost complete inhibition of the capacity of chemisorption of H₂ and CO [2]. The reason for the SMSI effect can be attributed to either an electronic or geometrical factor, both dependents on the temperature employed during the reduction treatment. The geometrical factor occurs due to the migration of functional groups from the support covering the metallic nanoparticles during the reduction process. In this way, the functional groups can block some catalytic active sites of the nanoparticles, which is detrimental for the final nanoparticles properties

observed. In some cases, it is possible also the creation of new catalytic active sites, enhancing the catalytic properties of the nanoparticles [2]. Therefore, the SMSI effect can be used to modify the surface properties of the catalyst. Since the thickness of the oxide capping layer around the nanoparticles can be as thin as 1 nm, by using the geometrical factor of the SMSI effect is possible also to bring the nanoparticle/support interface to a region accessible by conventional XPS (due to the surface sensitivity of this technique).

In the literature, the study of the SMSI effect has been performed mainly by using the High Resolution Transmission Electron Microscopy (HRTEM) technique [3]. Recently, several works regarding the observation of the SMSI effect on Rh_{0.5}Pd_{0.5}/CeO₂ [4] and Ni/CeO₂ nanoparticles [5] were performed by using the Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) technique. The APXPS technique allows to obtain the XPS characterization of the nanoparticles under real conditions (high temperature and pressure) [6–8].

Ceria (CeO₂) has been used as a support for metallic nanoparticles with catalytic properties in different kinds of reactions [9].

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Fig. 1. (a) SEM and (b) HRTEM images of the $\text{Rh}_{0.5}\text{Pd}_{0.5}$ nanoparticles.

Since ceria is a reducible support there is the existence of the Strong Metal Support Interaction effect (SMSI) when the metallic nanoparticles supported on ceria are subjected to a reduction treatment. Since the oxidation state of CeO_{2-x} ($0 < x < 0.5$) is strongly dependent on the temperature and oxygen pressure [10], the use of *in situ* measurements is important in order to have a complete understanding of the phenomenon.

In the last few years, researchers have also dedicated great effort to control the surface atomic population of bimetallic nanoparticles [11–15]. The reason is that the metallic atoms at the surface play a fundamental role in the catalytic processes. By changing the surface atomic population it is possible to control catalytic properties such as activity and selectivity. In the literature there are theoretical works reporting the tendency for segregation of transition metal impurities to the surface of transition metal hosts [16]. This prediction works well to bulk samples that can behave in a distinct way of the nanoparticles [17].

In the previous work [11,12], it was demonstrated that it is possible to control the surface atomic population of $\text{Rh}_{0.5}\text{Pd}_{0.5}$ bimetallic nanoparticles by using of alternating gaseous atmospheres. For an oxidizing atmosphere, the surface atomic population is composed mainly of Rh atoms, while in a reducing atmosphere it is composed mainly by Pd atoms. The driving force for the segregation and preferential oxidation of Rh at the surface is the higher stability of Rh oxide compared to Pd oxide [11]. Studies like these showed an interesting way of engineering the surface of nanoparticles for catalysis. They also highlighted the strong interplay between the nanoparticles and its gaseous atmospheres and unstable nature of nanoparticle under realistic conditions.

In this report, it is observed the geometrical factor of the SMSI effect for the $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$ nanoparticles subjected to a reduction treatment in H_2 atmosphere by using the APXPS technique. The experiment showed that bimetallic $\text{Rh}_{0.5}\text{Pd}_{0.5}$ nanoparticles are covered with a thin layer of CeO_x using a high temperature (480°C) thermal pre-treatment in a H_2 atmosphere. It induces a new nanoparticle configuration composed of a Pd-rich surface. Unlike the uncovered $\text{Rh}_{0.5}\text{Pd}_{0.5}$ nanoparticles, Pd rich surface of CeO_x covered nanoparticle is even stable during oxidation treatment at 300°C of the $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$ nanoparticles.

2. Experimental

The $\text{Rh}_{0.5}\text{Pd}_{0.5}$ nanoparticles were synthesized as described previously in [11]. Briefly, $\text{Rh}(\text{acac})_3$ (20.0 mg, 0.05 mM), $\text{Pd}(\text{acac})_2$ (15.2 mg, 0.05 mM), and poly(vinylpyrrolidone) (PVP, 55k, 111 mg, 1 mmol) were added to 1,4-butanediol (20 mL) with vigorous stirring in a round bottom flask. The flask was evacuated, and heated to 50°C for 10 min and maintained at that temperature for 20 min. Subsequently, the mixture was heated to 220°C for 20 min and

maintained for 1.5 h under N_2 atmosphere. When the reaction was complete, an excess of acetone was poured into the solution at room temperature to form a cloudy black suspension, which was separated by centrifugation at 4000 rpm. The resulting black product was collected by discarding the colorless supernatant. The precipitated $\text{Rh}_{0.5}\text{Pd}_{0.5}$ nanoparticles were washed with acetone once, and were redispersed in ethanol.

TEM (Transmission Electron Microscopy) and SEM (Scanning Electron Microscopy) studies showed that this procedure leads to the formation of 10 nm average diameter $\text{Rh}_{0.5}\text{Pd}_{0.5}$ nanoparticles. Fig. 1 shows the (a) SEM image and the (b) HRTEM image of the sample studied. The CeO_2 film was sputtered on an YSZ (yttria-stabilized zirconia) substrate in accordance to the method described in [18]. Monolayers of bimetallic $\text{Rh}_{0.5}\text{Pd}_{0.5}$ nanoparticles on CeO_2/YSZ samples were then prepared by using the Langmuir-Blodgett (LB) method as described in [12].

For the APXPS measurements, the sample was initially submitted to a thermal treatment at 200°C in a mixed atmosphere of 100 mTorr H_2 + 100 mTorr O_2 during 1 hour. This treatment was performed to remove the PVP capping layer existing at the surface of the nanoparticles, which is remaining from the nanoparticles during synthesis process. After that, the sample was submitted to five subsequent processes: (i) reduction at 300°C with 100 mTorr H_2 , (ii) oxidation at 300°C with 100 mTorr O_2 , (iii) reduction at 480°C with 100 mTorr H_2 , (iv) oxidation at 300°C with 100 mTorr O_2 and (v) reduction at 300°C with 100 mTorr H_2 . In this paper, the step (iii) will be named as high temperature pre-treatment. APXPS spectra from the Rh 3d, Pd 3d, Ce 4d, O 1s and C 1s core levels were acquired during the five steps described above at photon energies of $E_{\text{ph}} = 490 \text{ eV}$ and $E_{\text{ph}} = 655 \text{ eV}$ at the Advanced Light Source at Berkeley [19,20]. The spectra were obtained after the sample had already reached a steady state. The peak intensities of these spectra were used to determine the surface atomic fractions of the two elements (Rh and Pd) after calibration using the photoionization cross section corresponding to the x-ray energies used [21].

We also would like to point out that the PVP capping is mostly removed after 300°C with 100 mTorr O_2 treatment. However, the role of the polymer capping agent, PVP, cannot be completely disregarded. More detailed discussions can be found in the previous reports [17].

3. Results

Fig. 2 shows the Rh 3d (a) and Pd 3d (b) core levels APXPS spectra during every step of the thermal treatment employed ((i)–(v) described in experimental section). For comparison purposes, all the spectra are presented with the same y scale. It is observed the presence of the Rh^0 and Pd^0 components after all reduction treatments ((i), (iii) and (v) steps). When exposed to an oxidizing

Fig. 2. APXPS measurements at (a) Rh 3d and (b) Pd 3d core levels for the reduction and oxidation treatments described ((i)–(v)). The vertical lines indicate the binding energies of the observed components.

atmosphere ((ii) and (iv) steps) it is observed the presence of Rh–O and Pd–O components as expected. The Rh 3d / Pd 3d intensity ratio corresponds to the presence of Pd (Rh) atoms at the skin layer of the nanoparticles before the high temperature pre-treatment employed for reducing (oxidizing) atmospheres. Moreover, there is an apparent change on this ratio for the same treatments after the high temperature pre-treatment employed.

In order to investigate in more details the surface atomic population during all thermal treatments employed, Fig. 3 shows the Rh and Pd atomic fraction at the skin layer ($\lambda = 0.4$ nm) calculated using APXPS measurements with $E_{ph} = 490$ eV. Before the high temperature pre-treatment employed, the measurements show Pd atoms at the skin layer during reduction treatment at 300 °C with a Pd fraction around 80%. During the oxidation treatment, still before the high temperature pre-treatment, there is an inversion on the atomic population at the surface and the results show a Rh rich layer with a Rh fraction of around 60%. This behavior was observed previously for the same Rh_{0.5}Pd_{0.5} nanoparticles [11,12]. During the high temperature reduction pre-treatment at 480 °C the Pd fraction at the surface is kept at around 80% as the previous case. However,

Fig. 3. Rh (red points) and Pd (blue points) fractions at the skin layer ($\lambda = 0.4$ nm) of the nanoparticles as a function of the thermal treatment employed and calculated using the intensities at the Rh 3d and Pd 3d core levels. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

after the high temperature reduction pre-treatment, it is clear from the APXPS data that the Pd fraction at the surface is higher than the Rh fraction even in the presence of an oxidizing atmosphere. In both cases after the high temperature pre-treatment, reduction and oxidation, the Pd fraction at the surface region is maintained at around 80% in both cases, which means that Pd atoms are frozen at the surface after this high temperature reduction pre-treatment.

The geometrical factor of the SMSI effect can be identified by calculating the (Rh + Pd)/Ce intensity ratio, which can be obtained from the APXPS measurements. Fig. 4 shows a comparison for this ratio for the different reduction and oxidation treatments employed. The ratio was calculated by considering APXPS measurements at photon energies of $E_{ph} = 655$ eV (for Rh 3d and Pd 3d intensities) and $E_{ph} = 490$ eV (for Ce 4d intensity). The reason for taking into account different photon energies is to keep approximately the same kinetic energy of photoelectrons coming out from Rh 3d, Pd 3d and Ce 4d core levels. In this way, it is possible to probe the same depth of the sample for all elements. Moreover, since the sample is inserted in a gaseous atmosphere, the same kinetic energy ensures the same photoelectron attenuation from the gas. Since the XPS is a surface sensitive technique, the decrease of this ratio

Fig. 4. The (Rh 3d + Pd 3d) to Ce 4d ratio obtained from the APXPS data as a function of the gaseous treatment employed. The Rh 3d + Pd 3d to Ce 4d ratios drop from 1.8 to 0.6 after the high temperature H₂ pre-treatment. This is a strong evidence for the SMSI effect, where nanoparticles are covered by a thin layer of ceria and Pd atoms are frozen at the surface of the nanoparticles.

Fig. 5. Proposed model for the surface atomic population during different thermal treatments employed. The circles blue (red) colored indicates a nanoparticle with a Pd (Rh) rich surface atomic population. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

is characteristic for the encapsulation of the nanoparticles by functional groups from the support. The (Rh + Pd)/Ce ratio is around 1.8 before the high temperature pre-treatment and it goes to around 0.6 after the reduction in H_2 atmosphere at 480°C . The subsequent oxidation and reduction treatment does not change this ratio significantly, indicating that a thin CeO_x layer is grown on the $\text{Rh}_{0.5}\text{Pd}_{0.5}$ nanoparticles and the CeO_x capping layer is kept at the surface of the nanoparticles in these steps.

The XPS spectra at the Pd 3d and Rh 3d core levels presented in Fig. 2 shows the existence of Rh-O and Pd-O components during the oxidation treatments. After the high temperature pre-treatment, the oxidation treatment induces a high fraction of Rh ($\sim 95\%$) and Pd ($\sim 80\%$) atoms oxidized. Recently it was observed in the literature, for Pt-Au/ CeO_2 bimetallic nanoparticles, that oxygen atoms are released from the CeO_2 support during reduction treatment in H_2 at $T > 520\text{K}$ and it oxidizes Pt atoms present at the surface of the nanoparticles [22]. It can be discarded in this work since it is observed functional groups from the support on top of $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$ nanoparticles at 480°C and essentially no oxidation for both Rh ($\sim 7\%$ of Rh-O) and Pd ($\sim 1\%$ of Pd-O) atoms during this high temperature pre-treatment in H_2 atmosphere. Then, the explanation for the oxidation of Rh and Pd atoms after the high temperature pre-treatment, where the nanoparticle is covered on top by functional groups from the support, is that oxygen atoms can penetrate into the capping layer and interact with the nanoparticles. The analogous behavior is observed for the reduction treatment after the high temperature pre-treatment, where a low fraction of the Rh-O ($\sim 5\%$) and Pd-O ($\sim 10\%$) components is observed. In other words, although the nanoparticles are protected by the capping layer from the high temperature pre-treatment, the Rh and Pd atoms present at the surface of the nanoparticles are still interacting with the gaseous atmosphere (O_2 or H_2).

Although in the literature [23] it was observed the formation of strong Pd-O-Ce bonds during reduction treatment at 500°C for Pd/ CeO_2 nanoparticles, it is discarded as the reason for the Pd freezing at the surface since no shift in the binding energy is observed at the Pd 3d core level. In fact, the high temperature pre-treatment changes the Rh segregation behavior under oxidizing atmosphere suggesting the modification of the surface due to the capping layer covering the nanoparticles. In this way, it is possible to modify the surface atomic population by means of the SMSI effect. Using this tool, it is possible to create a new atomic configuration at the surface of the $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$ nanoparticles submitted to the oxidation process.

Fig. 5 shows the model proposed for the surface atomic population observed. Before the high temperature pre-treatment, the Pd/Rh switching in the surface atomic population agrees

with that observed previously [11,12]. The high temperature pre-treatment promotes the migration of functional groups from the support to the surface of the nanoparticles. After that, the nanoparticles are still interacting with the gaseous atmosphere and consequently change their oxidation state, although the surface atomic population does not change anymore. This result here can be used to explain the behavior of RhPd supported on different type of ceria (nanoshaped CeO_2 cubes and CeO_2 rods) in the ethanol steam reforming (ESR) reaction toward the production of hydrogen [24]. It was shown that at $650\text{--}700\text{K}$ the hydrogen yield follows the trend $\text{RhPd}/\text{CeO}_2\text{-cubes} > \text{RhPd}/\text{CeO}_2\text{-rods} > \text{RhPd}/\text{CeO}_2\text{-polycrystalline}$, whereas at temperatures higher than 800K the catalytic performance of all samples is similar and close to the thermodynamic equilibrium [24]. This behavior can be understood as that the RhPd nanoparticles at higher temperature are all covered with thin layer of ceria with similar Pd skin layer at the interface.

4. Conclusions

In conclusion, we have studied the surface atomic population of bimetallic nanoparticles, $\text{Rh}_{0.5}\text{Pd}_{0.5}$ on a CeO_2 support, exposed to thermal treatments in reducing and oxidizing atmospheres at different temperatures by using the APXPS technique. The results point out to a switching between a Rh (Pd)-rich skin layer for oxidizing (reducing) atmospheres. However, if the thermal treatments in these atmospheres are performed after a high temperature pre-treatment (480°C) in H_2 atmosphere, the switching between Pd and Rh atoms does not occurs anymore. In this case, Pd atoms are frozen at the surface of the nanoparticles, independent of the reducing or oxidizing atmosphere employed during the thermal treatment. It is explained due to the geometrical factor of the SMSI effect occurring after exposing the system to the high temperature pre-treatment in H_2 atmosphere. These changes of the surface atom switching behavior may lead to the catalytic property changes of the RhPd catalysts under different environments. Pd atoms can now stay at the shell under oxidizing conditions. Future tests should be performed to correlate the surface segregation observed here with the possible changes on the catalytic activity.

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References

- [1] S.J. Tauster, S.C. Fung, R.L. Garten, Strong metal–support interactions. Group 8 noble metals supported on titanium dioxide, *Journal of the American Chemical Society* 100 (1) (1978) 170–175.
- [2] S.J. Tauster, Strong metal–support interactions, *Accounts of Chemical Research* 20 (11) (1987) 389–394.
- [3] S. Bernal, J.J. Calvino, M.A. Cauqui, J.M. Gatica, C. López Cartes, J.A. Pérez Omil, J.M. Pintado, Some contributions of electron microscopy to the characterisation of the strong metal–support interaction effect, *Catalysis Today* 77 (4) (2003) 385–406.
- [4] N.J. Divins, I. Angurell, C. Escudero, V. Pérez-Dieste, J. Llorca, Influence of the support on surface rearrangements of bimetallic nanoparticles in real catalysts, *Science* 346 (6209) (2014) 620–623.
- [5] A. Caballero, J.P. Holgado, V.M. Gonzalez-delaCruz, S.E. Habas, T. Herranz, M. Salmeron, In situ spectroscopic detection of SMSI effect in a Ni/CeO₂ system: hydrogen-induced burial and dig out of metallic nickel, *Chemical Communications* 46 (7) (2010) 1097–1099.
- [6] M. Salmeron, R. Schlögl, Ambient pressure photoelectron spectroscopy: a new tool for surface science and nanotechnology, *Surface Science Reports* 63 (4) (2008) 169–199.
- [7] D.E. Starr, Z. Liu, M. Haevecker, A. Knop-Gericke, H. Bluhm, Investigation of solid/vapor interfaces using ambient pressure X-ray photoelectron spectroscopy, *Chemical Society Reviews* 42 (13) (2013) 5833–5857.
- [8] X. Liu, W. Yang, Z. Liu, Recent progress on synchrotron-based in-situ soft X-ray spectroscopy for energy materials, *Advanced Materials* 26 (46) (2014) 7710–7729.
- [9] A. Trovarelli, Catalytic properties of ceria and CeO₂-containing materials, *Catalysis Reviews: Science and Engineering* 38 (4) (1996) 439–520.
- [10] M. Mogensen, N.M. Sammes, G.A. Tompsett, Physical, chemical and electrochemical properties of pure and doped ceria, *Solid State Ionics* 129 (1–4) (2000) 63–94.
- [11] F. Tao, M.E. Grass, Y. Zhang, D.R. Butcher, J.R. Renzas, Z. Liu, J.Y. Chung, B.S. Mun, M. Salmeron, G.A. Somorjai, Reaction-driven restructuring of Rh–Pd and Pt–Pd core–shell nanoparticles, *Science* 322 (5903) (2008) 932–934.
- [12] F. Tao, M.E. Grass, Y. Zhang, D.R. Butcher, F. Aksoy, S. Aloni, V. Altoe, S. Alayoglu, J.R. Renzas, C.-K. Tsung, Z. Zhu, Z. Liu, M. Salmeron, G.A. Somorjai, Evolution of structure and chemistry of bimetallic nanoparticle catalysts under reaction conditions, *Journal of the American Chemical Society* 132 (25) (2010) 8697–8703.
- [13] F. Bernardi, M. Alves, A. Traverse, D. Silva, C. Scheeren, J. Dupont, J. Morais, Monitoring atomic rearrangement in Pt_xPd_{1–x} (x = 1, 0.7, or 0.5) nanoparticles driven by reduction and sulfidation processes, *The Journal of Physical Chemistry C* 113 (10) (2009) 3909–3916.
- [14] F. Bernardi, G. Fecher, M. Alves, J. Morais, Unraveling the formation of core–shell structures in nanoparticles by S–XPS, *The Journal of Physical Chemistry Letters* 1 (6) (2010) 912–917.
- [15] D.O. Silva, L. Luza, A. Gual, D.L. Baptista, F. Bernardi, M.J.M. Zapata, J. Morais, J. Dupont, Straightforward synthesis of bimetallic Co/Pt nanoparticles in ionic liquid: atomic rearrangement driven by reduction–sulfidation processes and Fischer–Tropsch catalysis, *Nanoscale* 6 (15) (2014) 9085–9092.
- [16] A.V. Ruban, H.L. Skriver, J.K. Nørskov, Surface segregation energies in transition–metal alloys, *Physical Review B* 59 (24) (1999) 15990–16000.
- [17] M.E. Grass, M. Park, F. Aksoy, Y. Zhang, M. Kunz, Z. Liu, B.S. Mun, Effect of O₂, CO, and NO on surface segregation in a Rh_{0.5}Pd_{0.5} bulk crystal and comparison to Rh_{0.5}Pd_{0.5} nanoparticles, *Langmuir* 26 (21) (2010) 16362–16367.
- [18] C.J. Zhang, M.E. Grass, A.H. McDaniel, S.C. DeCaluwe, F. El Gabaly, Z. Liu, K.F. McCarty, R.L. Farrow, M.A. Linne, Z. Hussain, G.S. Jackson, H. Bluhm, B.W. Eichhorn, Measuring fundamental properties in operating solid oxide electrochemical cells by using in situ X-ray photoelectron spectroscopy, *Nature Materials* 9 (11) (2010) 944–949.
- [19] M.E. Grass, P.G. Karlsson, F. Aksoy, M. Lundqvist, B. Wannberg, B.S. Mun, Z. Hussain, Z. Liu, New ambient pressure photoemission endstation at Advanced Light Source beamline 9.3.2, *Review of Scientific Instruments* 81 (5) (2010).
- [20] D. Ogletree, H. Bluhm, G. Lebedev, C. Fadley, Z. Hussain, M. Salmeron, A differentially pumped electrostatic lens system for photoemission studies in the millibar range, *Review of Scientific Instruments* 73 (2002) 3872.
- [21] J.J. Yeh, I. Lindau, Atomic subshell photoionization cross sections and asymmetry parameters: 1 [less-than-or-equals, slant] Z [less-than-or-equals, slant] 103, *Atomic Data and Nuclear Data Tables* 32 (1) (1985) 1–155.
- [22] C.-W. Liu, Y.-C. Wei, K.-W. Wang, Surface condition manipulation and oxygen reduction enhancement of PtAu/C catalysts synergistically modified by CeO₂ Addition and N₂ treatment, *The Journal of Physical Chemistry C* 115 (17) (2011) 8702–8708.
- [23] Y. Matsumura, W.-J. Shen, Y. Ichihashi, M. Okumura, Low-temperature methanol synthesis catalyzed over ultrafine Palladium particles supported on cerium oxide, *Journal of Catalysis* 197 (2) (2001) 267–272.
- [24] N.J. Divins, A. Casanovas, W. Xu, S.D. Senanayake, D. Wiater, A. Trovarelli, J. Llorca, The influence of nano-architected CeO_x supports in RhPd/CeO₂ for the catalytic ethanol steam reforming reaction, *Catalysis Today* 253 (2015) 99–105.