Catalysis Today 260 (2016) 95–99

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Control of the surface atomic population of $Rh_{0.5}Pd_{0.5}$ bimetallic nanoparticles supported on CeO_2

Fabiano Bernardi[a,b,*], Michael E. Grass[b], Young P. Hong[b], Rui Chang[b,c], Naila Jabeen[b], Chunjuan Zhang[d], Bryan W. Eichhorn[d], Bora Seo[e], Selim Alayoglu[f], Zahid Hussain[b], Sang Hoon Joo[e,g], Zhi Liu[b,c,h,*]

[a] Departamento de Física, Instituto de Física, Universidade Federal do Rio Grande do Sul (UFRGS), Porto Alegre, RS 91501-970, Brazil
[b] Advanced Light Source (ALS), Lawrence Berkeley National Lab (LBNL), Berkeley, CA 94720, USA
[c] State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, China
[d] Department of Chemistry and Biochemistry, University of Maryland, College Park, MD 20742, USA
[e] Department of Chemistry, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulsan 689-798, Republic of Korea
[f] Department of Chemistry, University of California, Berkeley, CA 94720, USA
[g] School of Energy and Chemical Engineering, Ulsan National Institute of Science and Technology (UNIST), 50 UNIST-gil, Ulsan 689-798, Republic of Korea
[h] School of Physical Science and Technology, ShanghaiTech University, Shanghai 200031, China

ARTICLE INFO

Article history:
Received 23 March 2015
Received in revised form 8 June 2015
Accepted 15 June 2015
Available online 1 August 2015

Keywords:
Strong metal support interaction
Bimetallic nanoparticles
AP-XPS
RhPd
CeO_2

ABSTRACT

$Rh_{0.5}Pd_{0.5}/CeO_2$ 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 H_2 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.

1. Introduction

Strong Metal Support Interaction effect (SMSI) is discovered more than 30 years ago [1] for TiO_2 support. The nanoparticles supported presented an almost complete inhibition of the capacity of chemisorption of H_2 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 $Rh_{0.5}Pd_{0.5}/CeO_2$ [4] and Ni/CeO_2 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 (CeO_2) has been used as a support for metallic nanoparticles with catalytic properties in different kinds of reactions [9].

---

* Corresponding authors at: Advanced Light Source (ALS), Lawrence Berkeley National Lab (LBNL), Berkeley, CA 94720, USA.
E-mail addresses: bernardi@if.ufrgs.br (F. Bernardi), zliu2@mail.sim.ac.cn (Z. Liu).

http://dx.doi.org/10.1016/j.cattod.2015.06.024

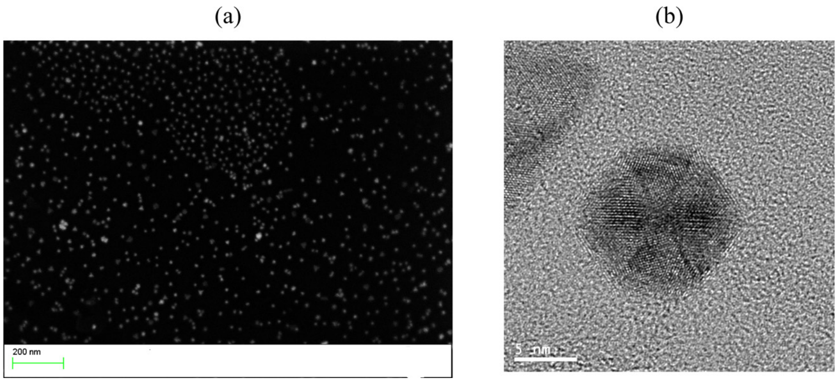

Fig. 1. (a) SEM and (b) HRTEM images of the $Rh_{0.5}Pd_{0.5}$ nanoparticles.

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 $Rh_{0.5}Pd_{0.5}$ 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 $Rh_{0.5}Pd_{0.5}/CeO_2$ nanoparticles subjected to a reduction treatment in H_2 atmosphere by using the APXPS technique. The experiment showed that bimetallic $Rh_{0.5}Pd_{0.5}$ 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 $Rh_{0.5}Pd_{0.5}$ nanoparticles, Pd rich surface of CeO_x covered nanoparticle is even stable during oxidation treatment at 300 °C of the $Rh_{0.5}Pd_{0.5}/CeO_2$ nanoparticles.

2. Experimental

The $Rh_{0.5}Pd_{0.5}$ nanoparticles were synthesized as described previously in [11]. Briefly, $Rh(acac)_3$ (20.0 mg, 0.05 mM), $Pd(acac)_2$ (15.2 mg, 0.05 mM), and poly(vinylpyrrolidone) (PVP, 55*k*, 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 $Rh_{0.5}Pd_{0.5}$ 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 $Rh_{0.5}Pd_{0.5}$ 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 $Rh_{0.5}Pd_{0.5}$ 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_{ph} = 490 eV and E_{ph} = 655 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