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NANOMATERIALS

Influence of the support on surface rearrangements of bimetallic nanoparticles in real catalysts

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Catalysts used for heterogeneous processes are usually composed of metal nanoparticles dispersed over a high-surface-area support. In recent years, near-ambient pressure techniques have allowed catalyst characterization under operating conditions, overcoming the pressure gap effect. However, the use of model systems may not truly represent the changes that occur in real catalysts (the so-called material gap effect). Supports can play an important role in the catalytic process by providing new active sites and may strongly affect both the physical and chemical properties of metal nanoparticles. We used near-ambient pressure x-ray photoelectron spectroscopy to show that the surface rearrangement of bimetallic (rhodium-palladium) nanoparticles under working conditions for ethanol steam reforming with real catalysts is strongly influenced by the presence of a reducible ceria support.

The structure of heterogeneous catalysts is dynamic and depends on the composition of the surrounding environment. Thus, both their surface structure and composition may be modified when the gaseous conditions change, in order to adapt their electronic properties and geometry to the new surrounding environment. Some structures and active phases only exist under reaction conditions and can differ from those identified under ultrahigh-vacuum (UHV) conditions (1, 2). Thus, the study of catalytic systems under real operating conditions is essential to identify the active species at work, because the restructuring driven by the environment may induce strong changes in both the properties and behavior of catalysts (3, 4). The advent of several in situ surface-sensitive techniques has allowed the characterization of surfaces under controlled atmospheres that can closely reproduce the working conditions of these systems (5). In this work, we used synchrotron-based ambient-pressure x-ray photoelectron spectroscopy (AP-XPS) to monitor both the surface restructuring and chemical state of two systems: (i) unsupported model $\text{Rh}_{0.5}\text{Pd}_{0.5}$ nanoparticles (NPs) and (ii) $\text{Rh}_{0.5}\text{Pd}_{0.5}$ NPs supported on CeO_2 powder (which constitutes a real catalyst). Both systems were exposed to reducing, oxidizing, and ethanol steam reforming (ESR) conditions to produce hydrogen. Three photon energies were chosen (670, 875, and 1150 eV) in order to perform a depth-profile study of both systems to infer the environment-induced rearrangement and the development of a core-shell structure.

RhPd NPs were first studied by AP-XPS at the Advanced Light Source (Berkeley, USA) in a seminal work by Tao *et al.* under NO , O_2 , H_2 , and $\text{NO} + \text{CO}$ environments to investigate the surface rearrangement of this bimetallic system in relevant reactions applied to pollution abatement (6). These authors used unsupported model NPs about 15 nm in diameter and found that a core-shell structure developed under the reducing and oxidizing environments tested. This finding showed that surface rearrangements in bimetallic systems occurred under different

atmospheres, although no support was used. At the same time, the RhPd system shows excellent performance in ESR ($\text{C}_2\text{H}_5\text{OH} + 3 \text{H}_2\text{O} \rightarrow 6 \text{H}_2 + 2 \text{CO}_2$) when supported over CeO_2 (7, 8). This reaction represents a very attractive route to obtain hydrogen from both a renewable and widespread source (bioethanol) without net CO_2 emissions and is currently being intensively researched (9, 10).

The synergic effect exerted by the support on the catalytic performance of metal NPs has been extensively studied, and immense effort has been made to elucidate the exact mechanisms involved in the metal-support interaction (11–16). Nonetheless, most of the fundamental work has been conducted in model systems such as single crystals, thin films, or isolated NPs. These systems lack some important features found in real catalysts, such as a high surface area, different types of defects, exposed planes and anchoring sites, the presence of reactive hydroxyl groups, the ability to activate certain reactants, etc., which all play an important role in the catalytic processes. We overcame this problem by directly studying a $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$ real catalyst pellet in the AP-XPS experiments. By combining the results obtained from the AP-XPS studies with bench catalytic tests in a model system (unsupported $\text{Rh}_{0.5}\text{Pd}_{0.5}$ NPs) and in our real catalytic system ($\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$), we showed that the CeO_2 support exerts a prominent role on the surface rearrangement of the bimetallic NPs, which in turn has a strong effect on the catalytic performance. The CeO_2 support is crucial for the ESR reaction, not only for activating the water molecule and avoiding carbon deposition because of its remarkable oxygen storage-release capability (17–19), but also by

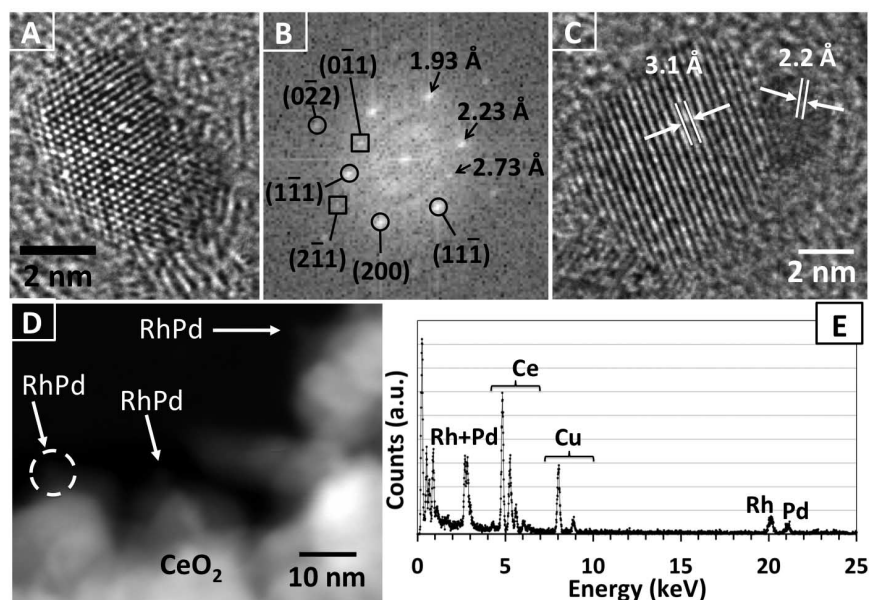


Fig. 1. The characterization of the unsupported $\text{Rh}_{0.5}\text{Pd}_{0.5}$ NPs and the $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$ catalyst by TEM techniques revealed the presence of isolated alloy NPs. (A) HRTEM image of a representative $\text{Rh}_{0.5}\text{Pd}_{0.5}$ NP as prepared. (B) Fourier transform image of the NP shown in (A). (C) HRTEM image of the $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$ catalyst. (D) STEM image of the $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$ catalyst. (E) EDX spectrum recorded in the region encircled in (D) (the Cu signal is due to the TEM grid).

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altering the oxidation states together with the surface reorganization of the noble metal atoms under reaction conditions.

The model $\text{Rh}_{0.5}\text{Pd}_{0.5}$ NPs were prepared by using a variation of a previously published procedure (20), followed by an extraction process

with dodecanethiol in toluene (21, 22). Figure 1A shows a representative high-resolution transmission electron microscopy (HRTEM) image of a model $\text{Rh}_{0.5}\text{Pd}_{0.5}$ NP. The mean diameter of the model $\text{Rh}_{0.5}\text{Pd}_{0.5}$ NPs determined by TEM analysis was 4 ± 1 nm. Rh and Pd were alloyed; the Fourier transform (FT) image (Fig. 1B) shows reflections at 1.93 and 2.23 Å that can be indexed to the (200) and (111) planes of a RhPd alloy, respectively, and reflections forbidden by selection rules in face-centered cubic Rh and Pd [(011) and (211) planes] (23). The $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$ catalyst (3 weight % metal) was prepared by incipient wetness impregnation from a toluene solution containing the model $\text{Rh}_{0.5}\text{Pd}_{0.5}$ NPs followed by calcination at 573 K for 6 hours. Figure 1C shows a HRTEM image of a $\text{Rh}_{0.5}\text{Pd}_{0.5}$ NP supported on a CeO_2 crystallite. The pre-formed $\text{Rh}_{0.5}\text{Pd}_{0.5}$ NPs were well dispersed on the ceria support and maintained their original size. The respective interplanar spacings measured for CeO_2 and for the metal NPs (Fig. 1C) closely match the theoretical values of CeO_2 (111) at 3.12 Å and Pd-Rh (111) at 2.25 to 2.20 Å. The bimetallic nature of the metal particles was confirmed by energy-dispersive x-ray spectroscopy (EDX) on individual nanoparticles. Figure 1E shows the EDX analysis performed on the region encircled in Fig. 1D, which corresponds to a scanning transmission electron microscopy (STEM) image of the sample. All of the NPs analyzed showed Rh and Pd signals consistent with an atomic Rh/Pd ratio of 1.0 ± 0.2 .

As expected, the catalytic performance of $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$ for ESR was superior to that of the model $\text{Rh}_{0.5}\text{Pd}_{0.5}$ NPs (22) (fig. S1). At 1050 K, at a steam-to-carbon ratio (S/C) of 3 and space velocity of 2.04×10^{-4} ml of liquid/(milligrams of catalyst \times minutes), the amount of hydrogen produced by $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$ doubled that achieved by the model $\text{Rh}_{0.5}\text{Pd}_{0.5}$ NPs (28 versus 15 ml/min). In addition, the product distribution obtained was notably different in both systems. Following (7), the ESR over noble metals supported on reducible oxides follows three steps: (i) ethanol decomposition ($\text{C}_2\text{H}_5\text{OH} \rightarrow \text{H}_2 + \text{CO} + \text{CH}_4$); (ii) water-gas shift (WGS, $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \text{CO}_2$); and (iii) methane steam reforming (MSR, $\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow 3 \text{H}_2 + \text{CO}$). The much higher CO_2 concentration attained by the $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$ than that obtained by the unsupported NPs (15.9 versus 1.8% at 1050 K) shows promotion of the WGS reaction (step 2) by CeO_2 , as already reported (24). In the case of the unsupported NPs, the lack of WGS promotion was confirmed by the presence of large quantities of CO in the reformat stream (31.1 versus 12.3% for $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$). Additionally, methane concentration was lower in the case of the real catalyst (11.0 versus 14.7% for the model NPs), indicating that MSR (step 3) also took place to a greater degree in the presence of the CeO_2 support. These two effects led to higher hydrogen production for the $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$ system than for the model NPs, thus demonstrating the essential role of the ceria support for ESR. After ESR performance, field emission scanning electron microscopy (FESEM) and HRTEM showed RhPd NPs of similar size, 6 ± 1 nm, in both samples (fig. S2).

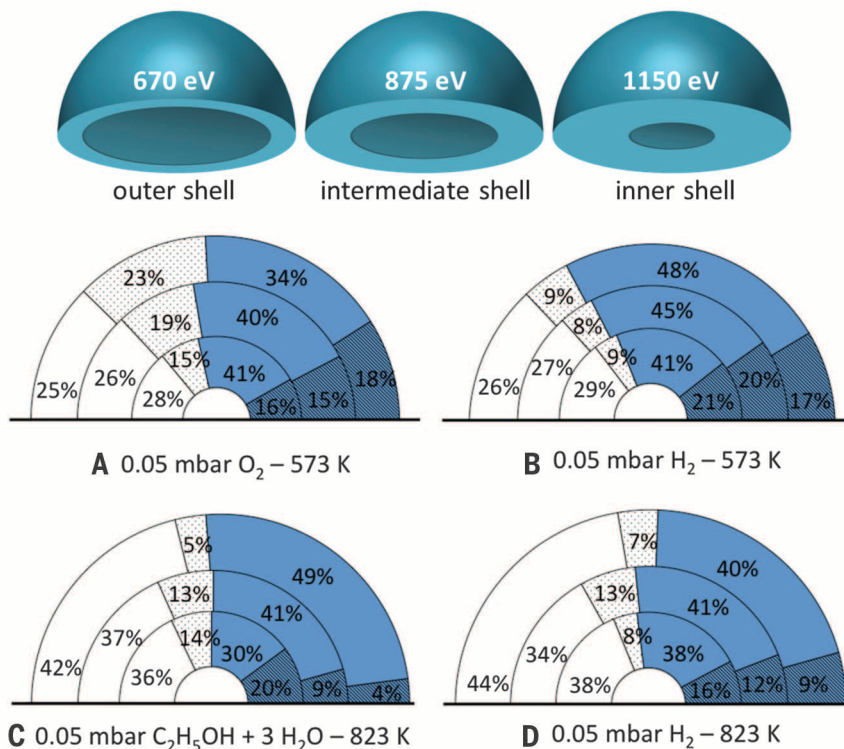


Fig. 2. Atomic fractions of Pd and Rh calculated for the model $\text{Rh}_{0.5}\text{Pd}_{0.5}$ NPs. The top row shows the three different volumes sampled. Semicircles below show the atomic fractions of Pd (depicted in blue) and Rh (depicted in white), where the dashed regions correspond to the oxidized fraction of each metal. The outer semicircle corresponds to the atomic fractions obtained with $h\nu = 670$ eV, the intermediate semicircle corresponds to $h\nu = 875$ eV, and the inner semicircle corresponds to $h\nu = 1150$ eV. (A to D) show the different gaseous environments.

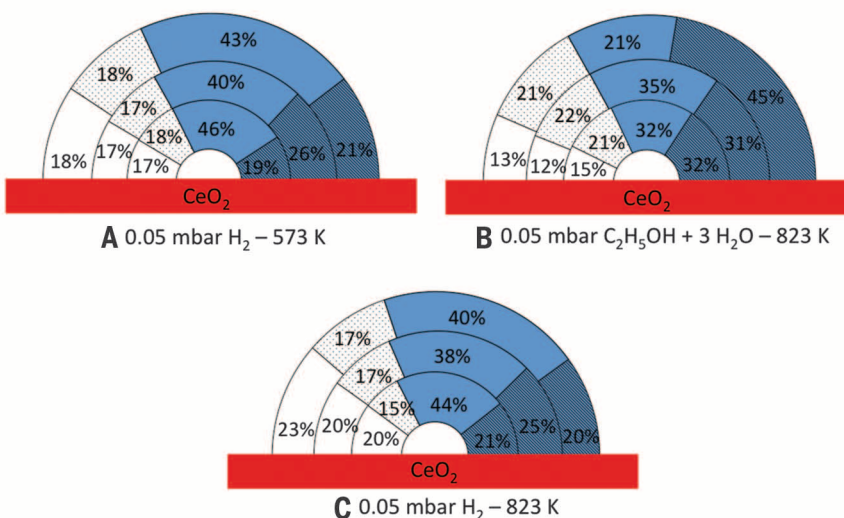


Fig. 3. Atomic fractions of Pd and Rh calculated for the $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$ catalyst. Semicircles show the atomic fractions of Pd (depicted in blue) and Rh (depicted in white), where the dashed regions correspond to the oxidized fraction of each metal. The outer semicircle corresponds to the atomic fractions obtained with $h\nu = 670$ eV, the intermediate semicircle corresponds to $h\nu = 875$ eV, and the inner semicircle corresponds to $h\nu = 1150$ eV. (A to C) show the different gaseous environments.

The AP-XPS experiments were carried out at the CIRCE beamline of the ALBA synchrotron light source (25), at a sample pressure of 0.05 mbar. The sequence was as follows: (i) O₂ at 573 K, (ii) H₂ at 573 K, (iii) ethanol and water (S/C = 3) at 823 K, and (iv) H₂ at 823 K. Three different photon energies ($h\nu$) of 670, 875, and 1150 eV were used in each case to obtain XP spectra of Rh 3d, Pd 3d, O 1s, C 1s, and Ce 3d (the latter excited only by $h\nu = 1150$ eV). The chosen photon energies account for inelastic mean free paths (IMFPs) of Rh 3d and Pd 3d photoelectrons of ~0.7, 0.9, and 1.2 nm, respectively (26), which allowed us to perform a depth-profile study of the Rh_{0.5}Pd_{0.5} NPs. For a spherical Rh_{0.5}Pd_{0.5} NP 4 nm in diameter, the volumes defined by these IMFPs from the exterior surface represent approximately 25, 34, and 44% of their total volume, respectively (22).

Figure 2 shows the percentage atomic ratios between Rh and Pd, together with their oxidation states calculated from the XP spectra recorded for the model Rh_{0.5}Pd_{0.5} NPs under the different gaseous environments tested and the three photon energies monitored (22). In each figure, the three regions shown symbolize the results obtained for each sampling depth. During the first treatment (calcination at 573 K, O₂ atmosphere, Fig. 2A), the model NPs showed a Pd/Rh ratio near unity and did not show substantial differences at the different depths studied. The Pd atomic fraction in the outer region (excited at 670 eV) was 0.52 ± 0.03 , whereas for the inner region (excited at 1150 eV), it was 0.57 ± 0.03 . Pd was highly reduced at all depths with concentrations of metallic Pd of 65 to 72%. Rh was also reduced in all the layers, but to a lesser extent (51 to 65%). For both metals, oxidation increased toward the NP surface.

Upon reduction with H₂ at 573 K (for catalyst activation, see Fig. 2B and fig. S4), Pd segregated toward the surface, with a Pd atomic fraction of about 0.65 ± 0.03 . This result fully agrees with the work of Tao *et al.* (6), where a migration of Pd atoms toward the surface during H₂ exposure was also reported. At the same time, Rh experienced a strong reduction, and ~75% of both metals was present in the metallic state. After H₂ activation of the sample, we studied the ESR process by dosing ethanol and water directly inside the analysis chamber at 823 K. Under ESR (Fig. 2C), the NPs restructured as Rh atoms migrated toward the surface; again the atomic ratio of Rh and Pd was ~1:1. Furthermore, the outer region of the Rh_{0.5}Pd_{0.5} NPs further reduced, and approximately 90% of Rh and Pd was found in their metallic state, which is ascribed to the reducing effect of the hydrogen generated during the ESR reaction at 823 K. This effect was corroborated by studying the Rh_{0.5}Pd_{0.5} NPs under pure H₂ at the same temperature (Fig. 2D and fig. S5). At this temperature, the noble metals did not undergo substantial changes as compared with the previous ESR environment.

A different scenario results when the model Rh_{0.5}Pd_{0.5} NPs are supported on CeO₂ (Fig. 3). For the real Rh_{0.5}Pd_{0.5}/CeO₂ catalyst, the reduction treatment at 573 K resulted in a Pd-rich

surface with Pd atomic fractions of about 0.65 (Fig. 3A and fig. S4). This value is similar to that found for the unsupported NPs under the same environment (Fig. 2B). However, under ESR conditions at 823 K, there was no migration of Rh or Pd. The atomic fraction of both noble metals remained approximately constant at the same values as in the previous reducing treatment for all depths; for the unsupported NPs, surface Pd enrichment that occurred during catalyst activation was reversed during the ESR reaction. Most importantly, both metals became more oxidized (Fig. 3B), whereas for unsupported NPs, the metals were predominantly reduced (Fig. 2C). Furthermore, Pd developed a core-shell structure of oxidation states, as seen in Fig. 4 as a large oxidized Pd component in the outer shell of the Rh_{0.5}Pd_{0.5}/CeO₂ catalyst. Taking into account that the region sampled at 670 eV corresponds only to the outer shell, whereas the region sampled at 875 eV corresponds to the weighted contribution of the outer shell and the intermediate shell, the strong decrease of the Pd oxidation fraction observed in the 875-eV region of the sup-

ported NPs indicates that the Pd oxidation is strongly confined to the NPs surface. It is likely that the activation of water by CeO₂, as deduced from the catalytic results, creates -OH groups at the catalyst surface, thus leading to the oxidation of the outermost layers of the NPs. This remarkable difference indicates that the interaction of the metal NPs with the ceria support plays a key role in reactions catalyzed by the RhPd alloy NPs by limiting the reorganization of the metals under reaction conditions ("quenching effect") and by providing active oxygen atoms to the metals at the surface of the NPs. Figure 4 shows the Pd 3d, Rh 3d, and O 1s XP spectra recorded for both the model Rh_{0.5}Pd_{0.5} NPs and the Rh_{0.5}Pd_{0.5}/CeO₂ catalyst under ESR conditions at 823 K. The photoemission lines of the noble metals of the real catalyst contain, in all cases, an additional component with respect to the unsupported NPs at ~308.7 and 337.8 eV for Rh 3d_{5/2} and Pd 3d_{5/2}, respectively, which is ascribed to the metal-support interaction discussed above (27). The O 1s spectra of the Rh_{0.5}Pd_{0.5}/CeO₂ showed three spectral features: the component at low binding energy

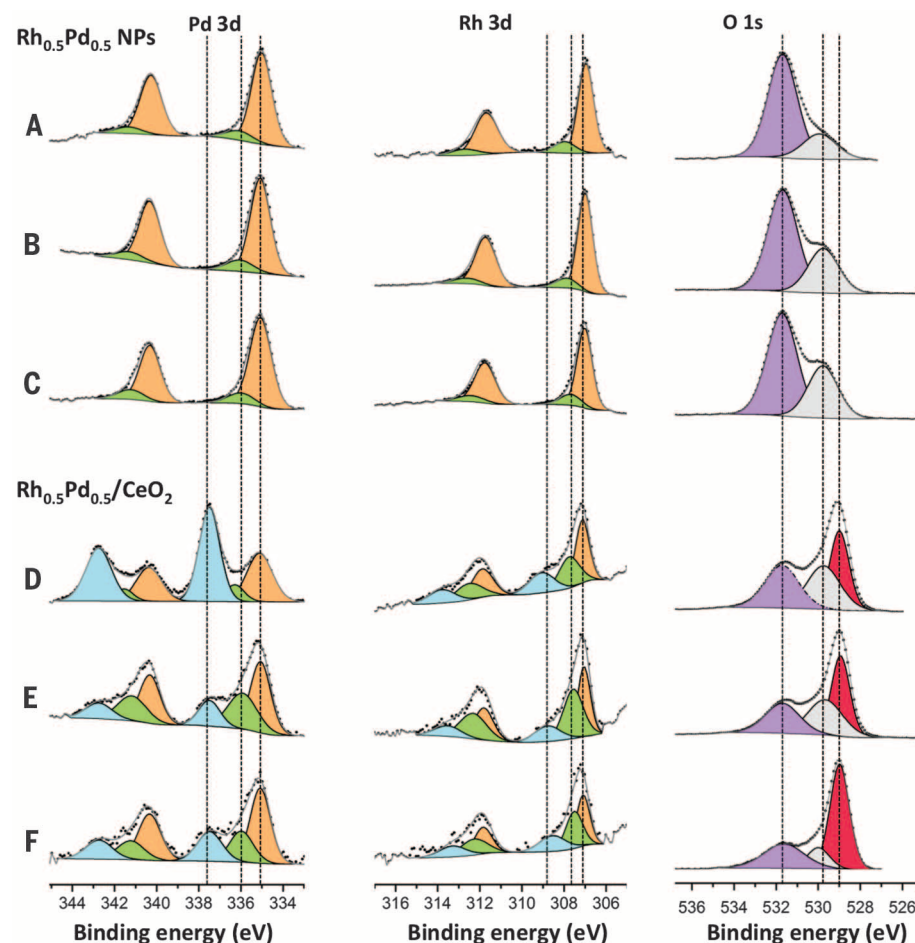


Fig. 4. Ambient pressure x-ray photoelectron spectra of Pd 3d, Rh 3d, and O 1s. The spectra were recorded for both the model Rh_{0.5}Pd_{0.5} NPs (A to C) and the Rh_{0.5}Pd_{0.5}/CeO₂ catalyst (D to F) under ESR conditions at 823 K. The photon energies used were 670 eV [(A) and (D)], 875 eV [(B) and (E)], and 1150 eV [(C) and (F)]. The sample pressure was 0.05 mbar. The O 1s regions in (B), (C), (E), and (F) correspond in kinetic energy scale to the metal regions in (A), (B), (D), and (E), respectively.

(529.1 eV) has been ascribed to O-Ce, the component at 530 eV to O-metals (Rh and/or Pd), and the component at 531.8 eV to -OH groups present on the surface of the catalyst (Fig. 4, D to F, O 1s) (28, 29). The ratio between the area of the O-Ce peak and the -OH peak increases as the photon energy increases; i.e., as the sampling depth increases, which highlights the sensitivity to different depths of the chosen photon energies and the presence of the -OH groups on the surface of the $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$ catalyst. The same trend is observed for the unsupported NPs, where the ratio between the O-metal peak and the -OH peak also increases when the photon energy is increased (Fig. 4, A to C, O 1s). In this case, the O 1s high-binding-energy component could be related to hydroxyl groups interacting with water molecules (30), because they almost do not participate in the ESR reaction (fig. S1), and the -OH groups do not affect the oxidation state of the metals (Fig. 2 C), because the inner shells are the most oxidized ones.

Finally, the oxidation state of both metals in the $\text{Rh}_{0.5}\text{Pd}_{0.5}/\text{CeO}_2$ catalyst very nearly recovered the values of the first reducing treatment at lower temperature (Fig. 3A) during the reduction with pure H_2 at the reaction temperature (823 K, Fig. 3C and fig. S5), unlike the model NPs, and again this points to the stabilizing effect of the ceria support. Analysis of the oxidation state of cerium (performed only with $h\nu = 1150$ eV, fig. S3) reveals variations depending on the gaseous environment and temperature (22). Under H_2 and 573 K, the $\text{Ce}^{3+}/\text{Ce}^{4+}$ atomic ratio was 0.63. The ratio decreased to 0.58 during the ESR reaction at 823 K, in accordance with the oxidation experienced by the noble metals, and it strongly increased up to 0.83 under H_2 at 823 K.

In the absence of a support, the model NPs were more strongly reduced for all the environments tested, and the reduction temperature affected the amount of metallic phase found in Rh and Pd. Compared with the unsupported NPs, the capability of CeO_2 as a support to activate water and to donate oxygen atoms determined the oxidation states of the noble metals under the same reaction conditions. In addition, the interaction between the ceria support and the metal nanoparticles prevented reorganization of the Rh and Pd atoms. We have thus demonstrated the pivotal role of the metal-support interaction in the reorganization of metal atoms in supported bimetallic catalysts under operating conditions and shown that this effect has a strong influence on the catalytic performance. Keeping this in mind, it should be noted that AP-XPS studies (and other studies) carried out on unsupported model systems may not provide reliable information on supported real catalysts. For this reason, it is very important to also take into account the influence of the support in spite of the experimental difficulties often encountered.

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SUPPLEMENTARY MATERIALS

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Materials and Methods
Figs. S1 to S5
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EARLY SOLAR SYSTEM

Early accretion of water in the inner solar system from a carbonaceous chondrite-like source

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Determining the origin of water and the timing of its accretion within the inner solar system is important for understanding the dynamics of planet formation. The timing of water accretion to the inner solar system also has implications for how and when life emerged on Earth. We report in situ measurements of the hydrogen isotopic composition of the mineral apatite in eucrite meteorites, whose parent body is the main-belt asteroid 4 Vesta. These measurements sample one of the oldest hydrogen reservoirs in the solar system and show that Vesta contains the same hydrogen isotopic composition as that of carbonaceous chondrites. Taking into account the old ages of eucrite meteorites and their similarity to Earth's isotopic ratios of hydrogen, carbon, and nitrogen, we demonstrate that these volatiles could have been added early to Earth, rather than gained during a late accretion event.

Hydrogen is vitally important in cosmochemical and geochemical processes. For example, water (H_2O) plays a critical role in plate tectonics on Earth (1) and has likely shaped the surface of Mars (2). Despite the abundance of water on Earth and evidence of

water on the Moon, Mars, and the asteroid 4 Vesta (2–4), these planetary bodies are often thought to have accreted dry (5–8). This prompts two key questions: Where did the water come from? And when was it present in the inner solar system? The answers may reveal information about accretion processes in terrestrial planets. Additionally, the extent and importance of lateral water transport throughout the history of the solar system are debatable (9, 10).

The source of water in planetary bodies can be investigated by measuring the ratio between the isotopes of hydrogen (deuterium, D or ^2H , and hydrogen, ^1H) because different regions of the

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