

# In situ spectroscopic detection of SMSI effect in a Ni/CeO<sub>2</sub> system: hydrogen-induced burial and dig out of metallic nickel

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In situ APPEES technique demonstrates that the strong metal support interaction effect (SMSI) in the Ni-ceria system is associated with the decoration and burial of metallic particles by the partially reduced support, a phenomenon reversible by evacuation at high temperature of the previously absorbed hydrogen. The strong metal-support interaction (SMSI) effect, a phenomenon widely studied for more than 30 years,<sup>1</sup> is characterized by a strong change in the physical and chemical properties of metal particles dispersed over reducible oxides. The more important signature of the SMSI effect is the almost complete inhibition of hydrogen chemisorption capacity, with modifications of the catalytic performance of the metal/oxide system.<sup>2</sup> Evidence of the structural changes brought by SMSI has been obtained by high resolution electron microscopy imaging, which shows decoration of the metal particles with oxide moieties of the support after reduction in hydrogen at high temperature.<sup>3</sup> Particularly, in titania supported systems, it has been well established how upon high temperature reduction in hydrogen ( $T \geq 500$  °C), oxide moieties from the support migrate over the metallic particles, blocking the surface and modifying its adsorption and catalytic properties.<sup>4</sup> It has also been stated that modifications of the electronic properties of the metal particles occur before the migration of support can be detected. This is the case for supports such as CeO<sub>2</sub>, where the electronic effects related with SMSI are already important after reduction in hydrogen at 500 °C, even though decoration of metallic particles is only detected by TEM after hydrogen treatment at

$T > 700\text{ }^{\circ}\text{C}$ .<sup>5</sup> Several explanations have been proposed to explain this apparent disagreement, including that of Munuera et al.,<sup>6</sup> who more than 20 years ago proposed for that metal-titania systems hydrogen plays an essential role in SMSI through the formation of hydride-like entities of the partially reduced support, which account for a high mobility of the phases involved, as well as for the partial reversibility of the effect. This interpretation is especially relevant as most of the characterization techniques, including XPS and electron microscopies are usually used in vacuum conditions, after elimination of adsorbed and absorbed hydrogen. The recent development of ambient pressure photoemission spectroscopy (APPEs) allows for a different approach to the study of this effect. The APPEs spectrometer used in our study is located in beamline 9.3.2 of the Advanced Light Source in Berkeley, CA, USA.<sup>7</sup> The spectrometer consists of a chamber connected to a differentially pumped electrostatic lens system that focuses the electrons emitted by the sample into the focal plane of a hemispherical electron energy analyzer, reducing the pressure from the Torr range, in the vicinity of the sample, down to about  $10^{-10}$  Torr in the analyzer. In this work, photoemission spectra of the Ce4d, C1s, O1s and Ni3p levels were recorded using photon energies which produce photoelectrons emitted approximately with the same kinetic energy (300–350 eV), thus, ensuring the same analysis depth for all the elements. The in situ XPS experiments were performed with Ni nanoparticles supported on a CeO<sub>2</sub> thin film. The nickel particles of about 10–15 nm in diameter, prepared following published methods described in ref. 8, were deposited on the ceria support using the Langmuir-Blodgett (LB) method.<sup>9</sup> The cerium oxide support was prepared by electron beam evaporation.<sup>10</sup> Fig. 1 shows SEM images of the nickel particles before (top) and after (bottom) being deposited in the CeO<sub>2</sub> support. As can be seen, when deposited in the ceria support, the nickel nanoparticles of about 10–15 nm appear isolated or form small islands. In the APPEs chamber, the sample was first heated in vacuum at 120 °C to clean the surface from physisorbed water and other contaminants. After that it was heated to 500 °C in 1 Torr of hydrogen and the chamber was subsequently

evacuated at the same temperature. The treatment was carried out for 30 min. Fig. 2 shows the Ce4d region spectra of the original sample, after hydrogen reduction at 300 and 500 °C, and finally, after evacuation at 500 °C. These spectra were obtained in operando conditions, i.e., at the same temperature and in the presence of gas, as indicated in the figure. According to the literature,<sup>11</sup> the spectrum of the original sample corresponds to a fully oxidized Ce(IV) oxide phase, characterized by the features between 105 and 130 eV, labeled A to E. The peak at 103 eV corresponds to the Si2p signal from silicon oxide impurities in the nozzle<sup>7</sup> that communicates the reaction chamber with the analyzer, which can be used as an internal reference for normalization and energy calibration. While no important changes can be observed during hydrogen treatment at 300 °C, upon reduction at 500 °C the Ce4d spectrum shows the characteristics of a partially reduced CeO<sub>2-x</sub> phase.<sup>12</sup> Finally, the evacuation of

the hydrogen absorbed by the support during the reduction treatment produces only minor effects in the Ce4d signal, although the small decrease of the intensity peak A could be related to an even more reduced CeO<sub>2-x</sub> phase, which is also consistent with the decrease of the O1s signal observed during this treatment (not shown). The evolution of the Ni3p and C1s signals during these treatments are presented in Fig. 3. It shows how the partially oxidized metal particles in the original sample (B.E. at 70 eV) are completely reduced to the metallic state upon hydrogen reduction at 300 °C (peak centered at 68

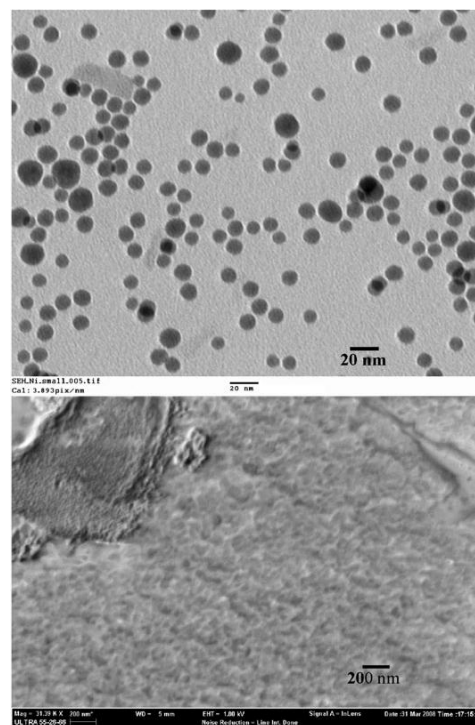


Fig. 1 (top) SEM image of the Ni nanoparticles. (bottom) SEM image of a nanoparticle island deposited on the ceria support.

eV). Interestingly, during the treatment at 500 °C in hydrogen the intensity of the Ni3p signal decreases substantially, an effect that parallels the partial reduction of the cerium oxide support, shown in Fig. 2. These facts imply that no nickel particles are now located at the surface of the sample. According to the previous literature on the SMSI effect the virtual disappearance of nickel from the surface of the support can be explained by the mobilization of the metallic and/or the partially reduced cerium oxide species, that cover the metallic particles. It is worthy of note that although SMSI electronic effects in CeO<sub>2</sub> supported systems have been previously observed after reduction in hydrogen at 500 °C, no decoration has been detected by electron microscopies at this temperature.<sup>12</sup> This apparent contradiction can be explained by analyzing the Ni3p spectrum obtained after evacuation of the Ni/ceria system at 500 °C (Fig. 3). As shown, after evacuation the intensity of this Ni3p signal is almost recovered. The elimination of hydrogen species adsorbed/ absorbed during reduction reverses the migration of paths of the nickel and/or ceria phases. So, as suggested previously for titania systems,<sup>6</sup> it seems from our results that hydrogen, adsorbed during surface reduction of the cerium oxide,<sup>13</sup> plays a role in the migration of the nickel and/or cerium oxide phases, probably through the formation of hydride-like species. It is worth noting that the C1s signal, also shown in Fig. 3, undergoes changes in intensity similar to that observed for the Ni3p signal. The first treatment with hydrogen at 300 °C produces an important decrease in the intensity of the signal, mainly due to the hydrogenation and elimination of contaminants from the surface. Although the further reduction in intensity after the hydrogen treatment at 500 °C could be explained similarly, the increase in intensity observed by evacuating at 500 °C suggests that other effects are working on it. As the nickel particles and the carbon impurities are both initially located at the surface of the ceria thin film used as support, these findings also support the idea that it is the cerium oxide rather than the metal that preferentially migrates onto the nickel nanoparticles and carbon impurities. Related with these results, we have recently shown that on Ni/ceria powder catalysts the catalytic performance in

methane reforming and the shape of the nickel metallic particles are both dependent on the reductive nature of the gas mixture.<sup>14</sup> In that work we also found that the nickel particles are flattened after hydrogen reduction at high temperature, which also contributes to increase the stability of the catalysts in the dry reforming reaction of methane. Our APPEs findings clearly demonstrate that this behaviour must be related with the strong metal support interaction induced by hydrogen in these systems. The drawing in Scheme 1 illustrates the structural changes induced in the Ni/ceria system after the hydrogen and evacuation treatment. At 300 °C the nickel particles are reduced to the metallic state, while at 500 °C, the hydrogen partially reduces the ceria support, completely covering the nickel particles. By evacuation at the same temperature, the nickel appears at the surface of the system. According to previous results,<sup>14</sup> the nickel particles also change their shape, appearing more flattened after the high temperature reduction treatment, which also facilitates the burial process. In conclusion, we have shown how by hydrogen reduction at high temperature, the ceria phase is partially reduced. This is accompanied by the loss of the Ni XPS signal. This result provides strong evidence that ceria moieties migrate onto the nickel particles. This migration, related to the SMSI effect, is reversible by evacuation of the hydrogen at the same temperature, showing that the hydrogen species participate in the process, probably through the formation of a hydride-like phase with the partially reduced

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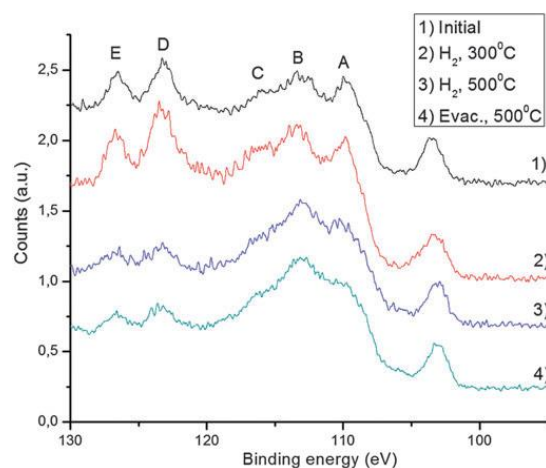


Fig. 2 Ce4d spectra of the Ni/ceria system submitted to reduction and evacuation treatments.

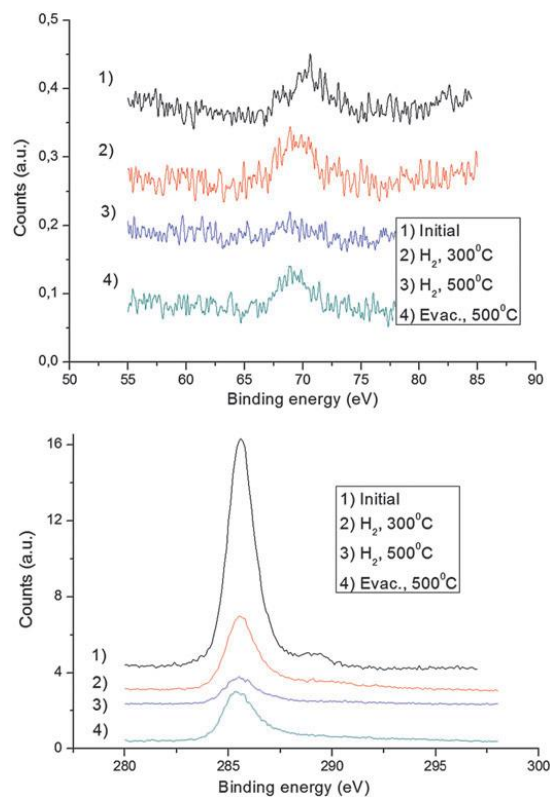
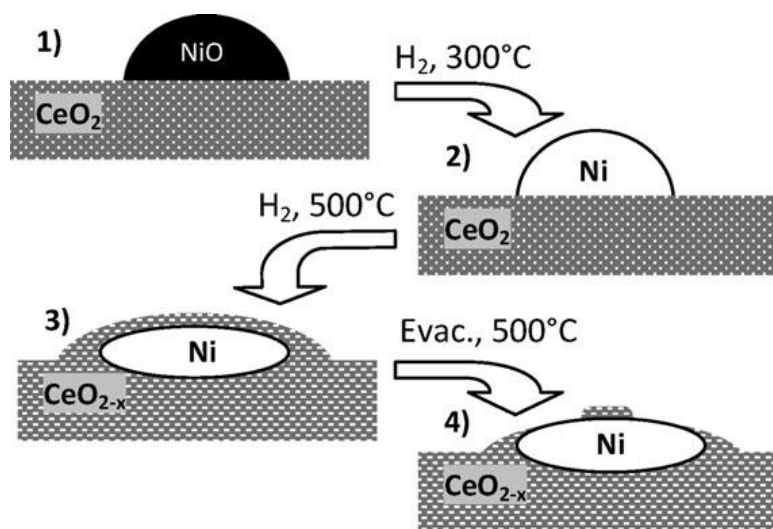


Fig. 3 (top) Ni3p and (bottom) C1s spectra of the Ni/ceria system submitted to reduction and evacuation treatments.



Scheme 1 Schematic evolution of the Ni/ceria system submitted to reduction and evacuation treatments

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