Superior performance of Ni-W-Ce mixed-metal oxide catalysts for ethanol steam reforming: Synergistic effects of W- and Ni-dopants

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Abstract

The ethanol steam reforming (ESR) reaction was studied over a series of Ni-W-Ce oxide catalysts. The structures of the catalysts were characterized using *in-situ* techniques including X-ray diffraction, Pair Distribution Function, X-ray absorption fine structure and transmission electron microscopy; while possible surface intermediates for the ESR reaction were investigated by Diffuse Reflectance Infrared Fourier Transform Spectroscopy. In these materials, all the W and part of the Ni were incorporated into the CeO₂ lattice, with the remaining Ni forming highly dispersed nano NiO (< 2nm) outside the Ni-W-Ce oxide structure. The nano NiO was reduced to Ni under ESR conditions. The Ni-W-Ce system exhibited a much larger lattice strain than those seen for Ni-Ce and W-Ce. Synergistic effects between Ni and W inside ceria produced a substantial amount of defects and O vacancies that led to high catalytic activity, selectivity and stability (i.e. resistance to coke formation) during ethanol steam reforming.

Keywords: Steam reforming of ethanol; Lattice strain; Oxygen vacancies; Nickel; Ceria; Tungsten; DRIFTS; XRD; XAFS

1 Introduction

Most fuel cell types require hydrogen for their operation and many technologies are under investigation looking for efficient and non-expensive routes for hydrogen generation. Hydrogen production through the steam reforming of ethanol ($\text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 6\text{H}_2$) is receiving a tremendous amount of attention because the ethanol is readily available from energy-renewable sources such as bio-mass [1-3]. On metal/oxide catalysts, the ethanol steam reforming (ESR) process occurs by a complex mechanism involving multiple reactions [2, 4, 5]. It has been postulated that this mechanism requires bifunctional catalysts [3, 6, 7], with the metal component contributing to the C-C and C-H bond scissions and the oxide support promoting the dehydrogenation (or dehydration) reaction as well as the dissociation of H_2O . Then, the adsorbed C-related species (CH_x , C, CO) couple with the adsorbed OH groups or lattice oxygen from the oxide support at the metal-support interface, generating an intermediate which further reforms and dissociates into CO_2 and hydrogen. Deactivation of the metal/oxide catalysts occurs as a consequence of coke formation and metal particle sintering.

The nature of the metal and support directly influence catalytic activity and stability during the ESR process. Expensive noble metals such as Rh, Pt and Ru exhibit good catalytic activity and a relatively good stability, while a metal with a low cost like Ni deactivates due to coke formation [2, 7]. In principle, coke formation on a metal could be prevented by perturbing the electronic properties of the metal through interactions with the oxide support [6, 7], by controlling metal particle size [7, 8] and by enhancing the capacity for oxygen storage and mobility within the oxide support [9]. Mixed-metal oxides are attractive as potential catalysts for the ESR process [2, 6, 7, 9]. The introduction of dopants into the lattice of the oxide support could enhance metal-

support interactions and thereby impact the electronic properties of the metal and oxide to produce surface sites which are very active for the cleavage of the C-C, C-H and O-H bonds present in the reactants [6, 7]. At a structural level, the dopants could impose strain into the lattice of the oxide host [9], inducing in this way the formation of defects that could affect the anchoring of the supported metal on the surface and alter the redox properties of the system leading to a higher mobility of oxygen.

In this study, we investigated the structural and chemical properties of a series of catalysts which contain small nanoparticles of Ni dispersed on $\text{Ni}_x\text{W}_y\text{Ce}_{1-x-y}\text{O}_2$ solid solutions prepared by reverse micro-emulsion methods. As can be seen in Scheme 1, the most stable oxides of Ce, Ni and W adopt very different crystal structures and formal oxidation states (4+, 2+ and 6+, respectively). Furthermore, Ce cations prefer a coordination number of 8, while Ni and W cations adopt a coordination number of 6. Thus, doping of ceria with Ni or W could induce substantial electronic and structural perturbations in the host oxide. Our studies point to synergistic effects when Ni and W are confined inside ceria; effects which make the performance of $\text{Ni}/\text{Ni}_x\text{W}_y\text{Ce}_{1-x-y}\text{O}_2$ catalysts as good or better than that of catalysts containing expensive noble metals such as Rh and Pt [7, 10-12]. This synergistic effect between Ni and W can be important in several areas of chemistry and material sciences in which ceria is widely used [13, 14]. In the Ni-W-Ce ternary system, the addition of tungsten as a stable phase inside the ceria lattice raises several questions: what is the role of tungsten and nickel? How is the bi-metal-oxides interaction compared with a single dopant? Does the oxygen mobility of ceria even more improved as an oxygen storage substrate? To answer these questions, we will first examine the structural and electronic properties of as-prepared $\text{Ni}_x\text{W}_y\text{Ce}_{1-x-y}\text{O}_2$ by means of X-ray Diffraction (XRD), Pair Distribution Function (PDF), X-ray Absorption Fine Structure (XAFS) and Scanning Transmission Electron Microscopy (STEM). Then, the behavior of the $\text{Ni}_x\text{W}_y\text{Ce}_{1-x-y}\text{O}_2$

catalysts under ethanol steam reforming conditions will be investigated by *operando* XRD, XAFS and Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) studies to follow phase evolutions and surface intermediates during the reaction.

2. Experimental

2.1 Sample preparation

References [15, 16] describe in detail the procedure used to prepare the samples. The Ni-W-Ce catalysts were prepared by the use of reverse micro-emulsions with solutions containing n-heptane (organic solvent), Triton-X-100 (surfactant) and n-hexanol (co-surfactant) in amounts similar to those reported previously [15, 16]. The required amounts of ceria nitrate (Aldrich), nickel nitrate (Aldrich) and ammonium tungsten oxide (Aldrich) were dissolved in distilled water and dispersed within already mentioned organic components to form the reverse micro-emulsion. Simultaneously, another micro-emulsion of similar characteristics was prepared containing dissolved in its aqueous phase, the required amount of tetramethyl ammonium hydroxide (TMAH). After 1 h of stirring the two micro-emulsions, the TMAH-containing solution was added to the metal-containing one, and it was left for a period of 24 h with continuous stirring in order to complete the precipitation reaction. The resulting solid was then separated by centrifugation and decantation, rinsed with methanol, and dried overnight at 100 °C. The resulting powder was calcined at 500 °C for 2h in air. Chemical compositions were analyzed by ICP-AES and correspond to the ones mentioned in the sample names within a maximum error of ± 2 at %. No significant amount of impurities was detected by ICP-AES and the other techniques used to characterize the catalysts.

2.2 X-ray diffraction and Pair distribution function (PDF) analysis

In situ time-resolved X-ray diffraction (TR-XRD) experiments in conjunction with mass spectrometry for product analysis were performed at beamline X7B ($\lambda=0.3196\text{\AA}$) of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (BNL). The samples (~ 2.5 mg) were loaded into a silica capillary (0.9 mm ID, 1.0 mm OD) mounted on a flow system [17] to test the ethanol steam reforming activity. The generation of the saturated ethanol vapor or water vapor was achieved by passing He through a bubbler filled with pure ethanol or deionized water. The gas flow rate used in this study, 10 cc/min, was sufficiently low to guarantee that the gases passing through the bubblers reached a vapor saturated state. At 25 °C, the saturated vapor pressure was 0.08 bar for ethanol and 0.03 bar for water. A target EtOH/H₂O molar ratio of 1/6 was achieved by mixing the two vapor gases with an adjustable flow rate for each [18]. The weight-hourly-space-velocity (WHSV), defined as the ratio between the inlet feed (water + ethanol) mass flow rate and the mass of the catalyst, was 10 h⁻¹. A resistance heating coil was placed underneath the capillary, and the temperature was monitored with a type K thermocouple inserted into the capillary next to the sample [17]. The heating process followed a stepped temperature program from room temperature to 450 °C (50°C increment, 10°C/min). A Perkin-Elmer Amorphous silicon detector was used to collect two-dimensional transmission diffraction data, and the powder diffraction rings were integrated using the FIT2D program [19] to obtain the XRD profiles. The lattice parameters and phase fractions were analyzed by the Rietveld method with the aid of the GSAS code [20, 21]. The instrument parameters were derived from fitting of a LaB₆ standard sample. Errors in the calculated oxide lattice parameters by XRD are in the order of $\pm 0.001\text{\AA}$.

PDF analysis is a total elastic scattering technique that takes into account features from both Bragg diffractions and diffuse scattering, so that non-crystalline phases can also be probed. A

PDF profile describes the distribution of all pairs of atoms within a sample as a function of interatomic distances. The PDF data collection in this study was done with the same instruments used for collecting XRD data. A 0.5 mm ID Kapton tube was used as the sample container. Data processing was performed with PDFgetX3 [22]. Errors in the calculated metal-oxygen and metal-metal distances by PDF are in the order of $\pm 0.03 \text{ \AA}$.

2.3 X-ray absorption fine-structure (XAFS)

X-ray absorption spectra of the W $L_{1,3}$ -edges and Ni K-edge were recorded at beamline X19A of NSLS. The sample powders were uniformly spread with a brush over adhesive Kapton polyamide tapes. The X-ray absorption near edge spectra (XANES) or extended X-ray absorption fine structure (EXAFS) spectra were taken repetitiously in the fluorescence-yield mode with a passivated implanted planar silicon (PIPS) detector. The XANES and EXAFS data were then analyzed using the Athena and Artemis programs [23]. Errors in the calculated metal-oxygen and metal-metal distances by EXAFS are in the order of $\pm 0.02 \text{ \AA}$.

2.4 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

DRIFTS data for the $\text{Ni}_x\text{W}_y\text{Ce}_{1-x-y}\text{O}_2$ samples under ESR conditions were collected on a Bruker Equinox 55 FTIR spectrometer equipped with a modified Harrick Praying Mantis DRIFT cell. The gas flow parameters and heating ramp were kept similar to the ones used in the XRD experiments. Details of the instrument can be found elsewhere [24].

2.5 HRTEM and STEM

TEM images were obtained using a JEOL JEM 2100 instrument operating with an acceleration voltage of 200 kV. Sample powders were dispersed as a suspension in deionized water and sonicated for 60s. After being well dispersed, a droplet of suspension was deposited on Holey-Carbon coated Cu grids and allowed to dry before imaging. Electron energy loss spectroscopy

(EELS) was acquired on a Hitachi 2700C operated at 200 kV using a convergence semi-angle of 23 mrad while the collection angle on the EELS spectrometer was 26 mrad.

3 Results and Discussion

3.1 Structural and electronic properties of the Ni-W-Ce catalysts

3.1.1 XRD and TEM

In previous studies, we examined the properties of $\text{Ni}_x\text{Ce}_{1-x}\text{O}_2$ and $\text{W}_y\text{Ce}_{1-y}\text{O}_2$ materials [7,12,14,18]. The concentration of the dopant that could be introduced inside the ceria lattice forming a solid solution was limited: 10-15% in the case of Ni and 20-25% in the case of W. Ni^{2+} replaced Ce^{4+} cations and induced the formation of O vacancies and Ce^{3+} sites [7,14]. On the other hand, W^{6+} cations were present in $\text{W}_y\text{Ce}_{1-y}\text{O}_2$ after creating an O vacancy and replacing two Ce^{3+} centers in the original CeO_2 structure [12]. In principle, two Ce^{4+} cations could be replaced by a $(\text{Ni}^{2+}, \text{W}^{6+})$ pair inside the ceria lattice. In this work, three $\text{Ni}_x\text{W}_y\text{Ce}_{1-x-y}\text{O}_2$ samples with W contents from 0 to 20% were studied: $\text{Ni}_{0.2}\text{Ce}_{0.8}\text{O}_2$, $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ and $\text{Ni}_{0.2}\text{W}_{0.2}\text{Ce}_{0.6}\text{O}_2$, in which W and Ni were doped into ceria simultaneously by using reverse micro-emulsion. The top panel in Fig. 1 shows XRD profiles of the as-prepared samples. All the diffraction patterns for $\text{Ni}_x\text{W}_y\text{Ce}_{1-x-y}\text{O}_2$ samples showed a major contribution from a ceria fluorite-type structure and no peaks attributed to tungsten-related species could be observed in any case, which indicates that there is no crystalline tungsten-related phases in these samples. For the Ni-containing samples, three weak peaks attributed to a NiO phase (marked by red arrows in Fig. 1) were observed and their intensities increased along with the increase of W content. For comparison, Fig. 1 also shows the XRD pattern of a Ni-impregnated sample (20% Ni physically deposited on a W-Ce support, noted as $\text{Ni}_{0.2}/\text{W}_{0.2}\text{Ce}_{0.8}\text{O}_2$), in which the 20% Ni was all present in the crystalline NiO phase. Though

having the same loading of Ni, the three $\text{Ni}_x\text{W}_y\text{Ce}_{1-x-y}\text{O}_2$ samples prepared by reverse micro-emulsion show much weaker NiO peaks than the $\text{Ni}_{0.2}/\text{W}_{0.2}\text{Ce}_{0.8}\text{O}_2$ sample generated by impregnation, suggesting that part of the Ni in the $\text{Ni}_x\text{W}_y\text{Ce}_{1-x-y}\text{O}_2$ samples was incorporated into the ceria lattice. Rietveld refinement provided molar fractions of 7%, 9% and 12% for the NiO phase in $\text{Ni}_{0.2}\text{Ce}_{0.8}\text{O}_2$, $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ and $\text{Ni}_{0.2}\text{W}_{0.2}\text{Ce}_{0.6}\text{O}_2$, respectively. The amount of the Ni embedded in the ceria can be calculated by subtracting the amount of the NiO phase from the total Ni loading, giving 13%, 11% and 8% for $\text{Ni}_{0.2}\text{Ce}_{0.8}\text{O}_2$, $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ and $\text{Ni}_{0.2}\text{W}_{0.2}\text{Ce}_{0.6}\text{O}_2$, respectively (table 1). In contrast to W, Ni was not fully incorporated into the ceria lattice. Moreover, the results show that the Ni solubility limit was reduced by the addition of W. The more W was embedded into the ceria structure, the less Ni was able to accept in its lattice the oxide host.

The bottom panel in Figure 1 shows lattice parameters determined through Rietveld refinement of the XRD data. In general, the introduction of W^{6+} or Ni^{2+} in the ceria produces an expansion in the lattice constant [7, 12, 25]. This expansion has also been observed in calculations with Density Functional Theory (DFT) and is a consequence of differences in the sizes of Ni, W and Ce plus the introduction of oxygen vacancies (Ce^{3+}) in the ceria lattice [7, 12, 25]. The $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ and $\text{Ni}_{0.2}\text{W}_{0.2}\text{Ce}_{0.6}\text{O}_2$ systems have lattice parameters which are larger than that of CeO_2 but smaller than the one seen in $\text{Ni}_{0.2}\text{Ce}_{0.8}\text{O}_2$ [7]. The direction and magnitude of the variations in the ceria lattice constant upon doping is difficult to predict [14, 25-28]. If the dopant cation has the same charge of the original cation (Zr^{4+} or U^{4+} versus Ce^{4+} , for example), one can compare directly the relative sizes of the two cations [9, 28-30]. On the other hand, if the dopant cation has a different charge from the original cation, the situation is much more complex and not only a difference in the relative size of the cations can produce variations in the lattice parameter of ceria [9, 14, 25-27]. A difference in the charge of the cations usually is

accompanied by the formation of oxygen vacancies and Ce^{3+} centers plus variations in local structure. The substantial difference in sizes between Ce^{3+} and Ce^{4+} can overcome or compensate the difference in size between the dopant cations and the Ce^{4+} [9, 14, 25-27]. Thus, in practice, it is very difficult to predict what the doping with W^{6+} or Ni^{2+} will do to the lattice parameters of ceria.

Images of scanning transmission electron microscopy (STEM) for the as-synthesized $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ sample are presented in Fig. 2a-b. The ceria nanoparticles exhibited a size of 4-6 nm which matched well with the particle sizes estimated from XRD (table 1). Fig. 2b-2f shows a STEM image of the sample and the corresponding electron energy loss spectroscopy (EELS) mapping of Ce, Ni and W. As Fig. 2d shows, all the particles presented in Fig. 2c were ceria nanoparticles, no big crystalline particles related to Ni or W were seen. Ni exhibited two types of structures (Fig. 2e): Small NiO clusters (<2nm cluster size) on top of the bulk ceria and mono dispersed cations inside the ceria lattice. In contrast, W was evenly distributed over all the imaged ceria particles, Fig. 2f, indicating that the W was either well mixed into the ceria lattice or formed an amorphous WO_x phase uniformly dispersed covering the surface of all ceria particles. The latter possibility was rejected because disordered shells were not observed on the ceria particles. A corresponding EELS line profile taken across the diameter of a typical ceria nanoparticle provided further evidence of W embedded in the ceria lattice (See SI figure 1).

3.1.2 XAFS and PDF

W L_1 -edge XANES data (Fig. 3) provides information about the oxidation states and local symmetry of the W dopant, obtained from the position of the X-ray absorption edge and the pre-edge peak intensity, respectively. As mentioned above, two Ce^{4+} cations could be replaced

by a ($\text{Ni}^{2+}, \text{W}^{6+}$) pair inside the ceria lattice. Furthermore, the doping of ceria with W^{6+} could involve the formation of an O vacancy and the removal of two Ce^{3+} cations [12]. As shown in Fig. 3, the oxidation state of the as-prepared sample remained the same as a reference WO_3 sample which possessed W^{6+} cations. Yamazoe et al. have studied the pre-edge feature in the W L_1 -edge XANES of various W species with different symmetries (O_h symmetry, distorted O_h symmetry, T_d symmetry) [31]. They reported that regular WO_6 units with O_h symmetry as in Cr_2WO_6 had a trivial pre-edge peak and its intensity increased along when the W symmetry shifted from O_h to T_d . In this study, we used Na_2WO_4 as a reference for a local structure with a typical T_d symmetry characterized by a large pre-edge peak. In comparison, WO_3 which had been proved to have distorted O_h geometry showed a moderate pre-edge peak [31]. Our as-prepared Ni-W-Ce samples all shared similar line-shapes with WO_3 indicating a distorted O_h symmetry for W in these samples, and the distortion might be larger than in the case of WO_3 if one considers the slightly larger pre-edge feature for the as-prepared samples. It is worth noting that the symmetry of the W units was not affected by the addition of Ni. Ni K-edge XANES revealed a +2 oxidation state for Ni in all of the as-prepared samples (see SI figure 2).

W L_3 -edge EXAFS was performed to investigate the coordination numbers and bonding distance between W and its neighboring atoms. Fourier transformed R-space EXAFS data, Fig. 4a, showed a dominant W-O first shell peak. Theoretical fitting of the W-O first shell suggested the coordination number was 6-7, in agreement with W in a distorted octahedral coordination environment (see SI table 1). A second shell at around 3.86 Å could be attributed to W-W bonds, and it is only observed in reference WO_3 but not in any of the W-doped samples. This is a strong indication of a W-Ce solid solution since incorporation of isolated W cations into the ceria lattice would result in no observation of W-W bonding features. A relatively similar phenomenon was also found in the Ni EXAFS (Fig. 4b). The first shell at 2.06 Å could be assigned to Ni-O bonding

(fitting results see SI table 2). For $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$, this first shell peak was broad and the mean square disorder factor was three times larger than the one for $\text{Ni}_{0.2}/\text{W}_{0.2}\text{Ce}_{0.8}\text{O}_2$, which indicates a more distorted first shell for Ni in $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ than in $\text{Ni}_{0.2}/\text{W}_{0.2}\text{Ce}_{0.8}\text{O}_2$. According to the XRD results above, $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ has 9% NiO phase and 11% embedded Ni while $\text{Ni}_{0.2}/\text{W}_{0.2}\text{Ce}_{0.8}\text{O}_2$ had 20% NiO with no Ni embedded to the ceria. It is clear that the broadening feature observed for $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ is owed to the incorporated Ni, whose bonding distances to O is expected to show larger variance than in a crystalline NiO phase. The second shell at around $2.95\text{\AA}$ was attributed to the closest Ni-Ni distance. This shell is strong in the NiO reference and in $\text{Ni}_{0.2}/\text{W}_{0.2}\text{Ce}_{0.8}\text{O}_2$ but shows a dramatic decrease in intensity for $\text{Ni}_{0.2}\text{W}_{0.2}\text{Ce}_{0.7}\text{O}_2$ and even more in $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$. Fitting of this shell gave a Ni-Ni coordination number decreasing from 12 of the bulk NiO to an average of about 7 in $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$. This substantial reduction in the average coordination number of nickel may be a consequence of having very small particles of NiO well dispersed on the ceria [32, 33].

Further structural information came from the PDF data. As shown in Fig. 5a, the addition of W gave rise to the emergence of a W-O peak at $1.76\text{\AA}$ (EXAFS fitting showed to be $\sim 1.78\text{\AA}$) and a small decrease of the Ce-O peak intensity at $2.32\text{\AA}$ due to the reduced Ce-O pairs and concomitant presence of O defects. When there was Ni doping (Fig. 5b), the Ni-O and Ni-Ni correlations showed up at $2.05\text{\AA}$ and $2.95\text{\AA}$, respectively, matched well with the EXAFS fitting of these two bonding distances. The progressive decrease of the Ni-Ni peak intensity confirmed a trend similar to that observed in the Ni K-edge EXAFS.

Thus, on the basis of our XRD, TEM, XAFS and PDF studies, we conclude that W was uniformly embedded into the ceria lattice with a distorted W-O octahedral local structure. Ni was partially

incorporated into the ceria lattice and the remaining Ni formed small NiO clusters over the Ni-W-Ce solid solution.

3.2 Ethanol steam reforming performance of Ni-W-Ce

3.2.1 Activity, selectivity and stability during the ESR reaction

In a previous study, we showed that $\text{Ni}_x\text{Ce}_{1-x}\text{O}_2$ solid solutions have a higher activity and a better stability for the ESR reaction than expensive Rh/CeO₂ catalysts [7]. Here, we will focus on the performance of $\text{Ni}_x\text{W}_y\text{Ce}_{1-x-y}\text{O}_2$ using $\text{Ni}_x\text{Ce}_{1-x}\text{O}_2$ as a benchmark. As shown in Fig. 6, all the samples investigated started to produce a small amount of H₂ when the temperature was raised to around 350°C (300°C for $\text{Ni}_{0.2}\text{Ce}_{0.8}\text{O}_2$), but the activity was not stable over time. Substantial H₂ production was observed as the temperature reached 450°C. Among the $\text{Ni}_x\text{W}_y\text{Ce}_{1-x-y}\text{O}_2$ samples in the lower panel of Figure 6, $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ showed the highest and the most stable catalytic activity compared to the conventional nickel-impregnated sample ($\text{Ni}_{0.2}/\text{CeO}_2$). At 450 C, the ethanol conversion on $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ was 100%. Note that, from 400 to 450°C, the reforming activity of $\text{Ni}_{0.2}\text{W}_{0.2}\text{Ce}_{0.6}\text{O}_2$ remained stable while the activity on $\text{Ni}_{0.2}\text{Ce}_{0.8}\text{O}_2$ decreased slightly. From these activity data, one can find that the W-promoted catalysts showed higher H₂ production than the non W-doped samples. In addition, the solid solution Ni samples (lower panel) were generally more stable during the steam reforming reactions than the conventional Ni-impregnated samples (upper panel).

Showing the best catalytic performance, $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ was also examined for the co-products at the steam reforming reaction conditions (Fig. 7). As the temperature increased, the amount of the produced H₂ and CO₂ tracked each other and stepwise increased as expected for the reforming process. The signal for CH₃ (m/z=15) in the mass spectrum continuously decreased

and became negligible at 450 °C. This signal was mainly a contribution of the reactant ethanol – CH₃ fragment and the product of methane (CH₄) if any. The stepwise decrease of the CH₃ reflected the consumption of ethanol as the temperature increased, while a value close to zero at 450 °C indicated a close to complete conversion of ethanol and no observable production of methane. Nickel particles on supported oxides are well known catalysts for the formation of methane as well as the deactivation by coke deposition [2, 6, 34]. But clearly, the methanation reaction was not a competing reaction path for Ni_{0.2}W_{0.1}Ce_{0.7}O₂ at 450 °C. We also tested the catalytic activity for a long period (24hrs) and the H₂ production remained stable without any sign of deactivation (see SI Fig 3). A small production of CO was observed based on the signal of m/z = 28, which was mainly contributed by both CO and the cracking of CO₂. Calculated CO/CO₂ ratio in the gas fragments at 450 °C was 1:6. No other significant by-products were detected by mass spectrometry. At 450 °C, the Ni_{0.2}W_{0.1}Ce_{0.7}O₂ catalyst exhibited a performance that was better in terms of activity and stability than that found under similar conditions for an expensive Rh/CeO₂ catalyst [7]. However, the small amount of CO produced indicates that the Ni_{0.2}W_{0.1}Ce_{0.7}O₂ catalyst does not have a water-gas shift activity as high as that found on Rh-based catalyst [2, 11].

3.2.2. DRIFTS studies and surface intermediates for the ESR reaction

The *in situ* DRIFTS studies of Figure 8 shows the surface intermediates detected for the ESR reaction on CeO₂, W_{0.1}Ce_{0.9}O₂ and Ni_{0.2}W_{0.1}Ce_{0.7}O₂ as a function of temperature. The most important features appear near 2348 cm⁻¹ as a consequence of the formation of CO₂ from the reforming of ethanol. These features are absent in the case of pure CeO₂ and strong for Ni_{0.2}W_{0.1}Ce_{0.7}O₂. For pure CeO₂ at 25 °C, the dissociative adsorption of ethanol produced ethoxy (CH₃CH₂O) with

features at 1110 and 1050 cm^{-1} for monodentate- $\nu(\text{C-O})$ and bidentate- $\nu(\text{C-O})$ coordinations, respectively [35, 36]. From 150 to 200 $^{\circ}\text{C}$, three peaks corresponding to acetate (CH_3COO^-) started to be resolved at 1550, 1437 and 1343 cm^{-1} which are identified as $\nu_s(\text{COO})$, $\nu_{as}(\text{COO})$ and $\delta_s(\text{CH}_3)$, respectively [2, 37, 38]. In addition, the intensities of the ethoxy CO bands at 1110 and 1050 cm^{-1} decreased and disappeared at 300 $^{\circ}\text{C}$. However, a further increase of the temperature from 300 to 450 $^{\circ}\text{C}$ did not produce a significant change in the IR features or the production of CO_2 . On the $\text{W}_{0.1}\text{Ce}_{0.9}\text{O}_2$ and $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ samples, a transition from acetate to carbonate species ($\nu_{as}\text{-OCO}$ 1467 cm^{-1} and $\nu_s\text{-OCO}$ 1394 cm^{-1}) [2, 39] occurred above 400 $^{\circ}\text{C}$ with simultaneous formation of CO_2 . The acetate $\rightarrow$ carbonate transition is associated with the high activity observed for $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ in Figures 6 and 7. Furthermore, at 450 $^{\circ}\text{C}$, the catalyst has reached a stable structural configuration, as will be explained below using results of XRD and XAFS.

3.2.3 *In-situ* XRD and structural changes

In situ XRD experiments were performed to gain insight into the structural changes of the catalysts during the steam reforming process. Fig. 9a displays a time sequence of XRD profiles for $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ taken during the steam reforming of ethanol. No W-related species were seen through the entire study, indicating that the W-Ce solid solution is stable under the reaction conditions. On the other hand, the NiO clusters identified by the three weak peaks at 7.6 $^{\circ}$, 8.8 $^{\circ}$ and 12.4 $^{\circ}$ remained unchanged till 400 $^{\circ}\text{C}$, at which temperature a clear transition from NiO to metallic Ni was observed. Quantification of the phase transitions as a function of time was plotted in the upper panel of Figure 9b. At first, the catalysts started to be active for H_2 production at 350 $^{\circ}\text{C}$ when metallic Ni was substantially formed. However, one can observe that the appearance of metallic Ni was not accompanied by a similar decrease in the mole fraction of

the NiO phase, which implies that some of the Ni cations inside ceria were reduced and segregated to the surface prior to the reduction of NiO clusters outside ceria crystallites [14]. Then, the NiO phase began to be reduced from 400°C and eventually vanished at 450°C while H₂ production reached its maximum as a consequence of a massively formed metallic Ni phase. Moreover, Rietveld refinement also provided information about the ceria lattice expansion of Ni_{0.2}W_{0.1}Ce_{0.7}O₂ with respect to the reference sample as shown in the lower panel of Fig. 9b. Upon thermal treatment, one can expect a stepwise lattice expansion of ceria lattice coming along with the stepwise heating. However, between 200 and 300 °C, a sharp jump of the lattice constant could be related to the non-thermal expansion resulting from the reduction of ceria from Ce⁴⁺ to Ce³⁺ since Ce³⁺ has a larger atomic radii than Ce⁴⁺ [27, 40]. The formation of Ce³⁺ was regarded as evidence of the creation of oxygen vacancies in the ceria lattice. It is known that ceria will undergo reduction prior to the reduction of NiO during the steam reforming [7, 18, 40], but the substantial reduction in Ni_{0.2}W_{0.1}Ce_{0.7}O₂ is unique among all the Ni-related samples investigated here. The magnitude of the lattice expansion was influenced by the coexistence of W and Ni as dopants: Ni_{0.2}W_{0.1}Ce_{0.7}O₂ had a lattice expansion 1.5 times larger than that of Ni_{0.2}Ce_{0.8}O₂ and 2 times larger than the one for Ni-impregnated ceria (Ni_{0.2}/CeO₂), which implies that the number of oxygen vacancies in the Ni_xW_yCe_{1-x-y}O₂ ternary system was also much larger.

Figure 10a shows the lattice strain of fresh samples derived from XRD profiles by Rietveld refinement [20, 41, 42]. For W-Ce samples without Ni doping, a trend of increasing lattice strain along with increasing W content is observed. However, Ni_{0.2}W_{0.1}Ce_{0.7}O₂ has a much larger strain than Ni_{0.2}Ce_{0.8}O₂ or W_{0.1}Ce_{0.9}O₂. Thus, there is a synergy between Ni and W for the production of strain in the oxide lattice. It is well known that lattice strain is a product of the presence of imperfections and dislocations in the oxide lattice [9, 26, 30, 43, 44]. These defects can act as nucleation centers and enhance the dispersion of reduced Ni on the surface while aiding with

the dissociation of water and ethanol [45,46,47,48]. Time-sequential analysis of the $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ XRD profiles collected during the reforming reaction revealed that its lattice strain varied during the reaction process (figure 10b) and always remained at a very high value. Thus, the concentration of defects and imperfections in this system was always bigger than those on $\text{Ni}_{0.2}\text{Ce}_{0.8}\text{O}_2$, $\text{W}_{0.1}\text{Ce}_{0.9}\text{O}_2$, Ni/CeO_2 or CeO_2 giving the ternary oxide unique catalytic properties. From the viewpoint of selectivity, this may favor the formation of a high concentration of OH groups on the surface [6,13,46] facilitating the reaction of CH_x species with OH to yield CO_2 and H_2 instead of methane and coke.

3.2.4 *In situ* XAFS

Similar experiments were carried out with *in situ* time-resolved XAFS. Notably, since the kapton tube is limited for a maximum temperature of 380°C, a silica tube with 0.1mm wall thickness was used. Several spectra at each temperature were collected and merged to improve the signal-to-noise ratio. Ce L_3 -edge XANES spectra for $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ under steam reforming conditions are displayed in Fig. 11. One can observe that, in pure CeO_2 , the Ce L_3 -edge exhibited two clear peaks for Ce^{4+} , which could be easily distinguished from the single sharp white line of Ce^{3+} at lower photon energy. By comparing with standards for Ce^{3+} and Ce^{4+} , we were able to identify that a significant amount of Ce^{4+} in $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ was reduced to Ce^{3+} from 250°C to 350°C and remained almost unchanged up to 450°C, in good consistency with the *in situ* XRD results for ceria lattice expansion with temperature. In addition, the peak intensity at the Ce^{3+} positions of the sample was apparently more intense than the reference pure CeO_2 at 450°C (blue dash line) under steam reforming conditions, indicating the improved ceria reducibility due to the combined effects of Ni and W as dopants.

Ni K-edge XANES spectra for $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ were also collected under the same conditions. As the temperature increased, the NiO reduction was relatively small from room temperature to 350°C and a substantial reduction took place from 350°C to 450°C. Eventually, some of the Ni still remained oxidized at 450°C inside the lattice of ceria. XRD data at 450 °C showed the NiO phase had been completely reduced to metallic Ni, but provided little direct information about the embedded Ni. The Ni K-edge EXAFS data however are rich in details associated with the NiO→Ni transition (Fig. 12). The intensity of the first two shells around 2.0 and 3.0 Å at 25°C, which corresponds to Ni-O and Ni-Ni distances in NiO respectively, gradually decreased at elevated temperature combined with an increase of the Ni-Ni peak in the metallic Ni phase around 2.6 Å. At 450°C, the metallic Ni-Ni peak was broad and of much lower intensity compared to the one for the Ni foil, which indicates that the newly formed metallic Ni was still present as small clusters (i.e. Ni atoms with a low coordination number) instead of forming large Ni particles [33,49], in agreement with the broad peak feature seen for Ni metal in the corresponding XRD patterns. The extremely small particle size of Ni (or even atomic Ni) gave it a strong adherence to the ceria support, which guaranteed the sufficient supply of OH from the surrounding ceria and also prevented its sintering. Furthermore, small Ni particles in close contact with ceria are electronically perturbed, as shown by experiments of photoemission [7,45] and DFT calculations [34], and do not exhibit the typical methanation activity of bulk nickel [8, 14, 34,50]. Big Ni particles will decompose ethanol into CH_x groups and C atoms [8,50]. As a consequence of this, carbon will be accumulated on the catalysts surface and finally will encapsulate the active sites. This does not occur for the small Ni particles dispersed on Ni-W-Ce.

In situ studies for the W L_1 -edge of $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$ were also performed at the elevated temperature and no changes were found with respect to the line-shape of the fresh sample seen in Fig. 3. Combined with the XRD data that showed no occurrence of any W-related

crystalline phase, this confirms that the W^{+6} cations remained inside the ceria lattice through the entire reaction. Thus, from the *in situ* XAFS studies, we can conclude that the active phase of the catalyst involves small Ni nanoparticles dispersed on a Ni-W-Ce solid solution in which the Ni and W are fully oxidized and part of the Ce^{4+} has been transformed into Ce^{3+} . In previous studies, we have found that this catalyst configuration is active for the water-gas shift reaction [12] and we envision that the system could also be useful for hydrogen/deuterium exchange, olefin hydrogenation, and methane/steam reforming.

4 Summary and Conclusions

We have studied the steam reforming of ethanol over a series of Ni-W-Ce catalysts. A combination of XRD, PDF, TEM and XAFS revealed that W and part of the Ni formed a solid solution with ceria in the $Ni_xW_yCe_{1-x-y}O_2$ catalysts while the remaining Ni was well dispersed on the surface as small NiO clusters. The Ni-W-Ce systems exhibited a much larger lattice strain than those seen for Ni-Ce and W-Ce. Synergistic effects between Ni and W inside ceria produced a substantial amount of defects and O vacancies that led to a high catalytic activity, selectivity and stability for the ethanol steam reforming reaction. At 450 °C, a $Ni_{0.2}W_{0.1}Ce_{0.7}O_2$ catalyst exhibited a performance that was better in terms of activity and stability than that found under similar conditions for an expensive Rh/CeO₂ catalyst.

The reaction pathway leading to the production of CO₂ and H₂ included the formation of ethoxy, acetate and carbonate surface species while the active components of the catalysts most likely were metallic Ni and Ce^{3+} . W- and Ni-doping promoted the formation of Ce^{3+} sites, helping the partial dissociation of water. The formation of a high concentration of OH groups on the catalyst surface facilitated the transformation of CH_x species into CO₂ and H₂ instead of methane and

coke. Furthermore, the presence of defects and imperfections in the $\text{Ni}_x\text{W}_y\text{Ce}_{1-x-y}\text{O}_2$ substrate favored the dispersion of the supported Ni and strong metal-support interactions [7,34,35] that probably modified the chemical reactivity of the admetal.

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Table 1. NiO phase fraction, ceria lattice parameters and particle sizes extracted from XRD.

Catalysts	NiO phase fraction (%)	Ceria Lattice parameters (Å)	Ceria particle sizes (nm)
$\text{Ni}_{0.2}\text{Ce}_{0.8}\text{O}_2$	7	5.410	5.0
$\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$	9	5.405	4.5
$\text{Ni}_{0.2}\text{W}_{0.2}\text{Ce}_{0.6}\text{O}_2$	12	5.404	4.3

Figure Captions

Scheme 1: Crystal structures of CeO_2 , NiO and WO_3

Figure 1. XRD patterns of the as-prepared samples (solid line) and reference samples (dash line).

Figure 2. Selected STEM images (a, b) and EELS mapping (c,d,e,f) of the as-prepared $\text{Ni}_{0.2}\text{W}_{0.1}\text{Ce}_{0.7}\text{O}_2$. The area inside the square displayed in Fig 2b was used for the EELS mapping. The element map was colored to identify and indicate the distribution of corresponding elements: Ce (blue), Ni (green), W (red).

Figure 3. W L_1 -edge XANES spectra of as-prepared samples (solid line) as well as the reference sample (dash line).

Figure 4. R-space EXAFS spectra for the W L_3 -edge (a) and Ni K-edge (b) of the as-prepared catalysts.

Figure 5. PDF spectra of the fresh samples: a) W-O system, b) Ni-W-O system.

Figure 6. H₂ production plots for ethanol steam reforming over a) Ni-impregnated sample, b) Ni_xW_yCe_{1-x-y}O₂ solid solution samples. The samples were held at each isothermal condition for at least half an hour. Catalyst mass= ~ 2.5 mg, a vapor mixture of water and ethanol (molar ratio 6:1) carried by He gas (total flow= 10 ccm/min), WHSV = 10 h⁻¹.

Figure 7. Mass spectroscopic data of the reaction products (H₂, CO₂, CO and CH₄) during the ethanol steam reforming over a Ni_{0.2}W_{0.1}Ce_{0.7}O₂ catalyst. At 450 C, the ethanol conversion on this catalyst was 100%. Catalyst mass= ~ 2.5 mg, a vapor mixture of water and ethanol (molar ratio 6:1) carried by a flow (10 ccm/min) of He gas, WHSV = 10 h⁻¹.

Figure 8. DRIFTS spectra of CeO₂, W_{0.1}Ce_{0.9}O₂ and Ni_{0.2}W_{0.1}Ce_{0.7}O₂ at elevating temperature under steam reforming conditions

Figure 9. a) TR-XRD pattern for Ni_{0.2}W_{0.1}Ce_{0.7}O₂ collected during the ESR process, the NiO and fcc-Ni are marked. b) Sequential Rietveld refinement of the Ni phase fraction (upper panel) and the ceria lattice parameter (lower panel).

Figure 10. a) Rietveld Refinement of the ceria lattice strain for a series of fresh sample with and without Ni loading. b) Sequential Rietveld refinement of the variation of ceria lattice strain under ethanol steam reforming conditions, Ni_{0.2}Ce_{0.8}O₂ and Ni_{0.2}/CeO₂ were chosen as a comparison to the Ni_{0.2}W_{0.1}Ce_{0.7}O₂ catalyst.

Figure 11. Ce L₃-edge XANES spectra collected over Ni_{0.2}W_{0.1}Ce_{0.7}O₂ during ethanol steam reforming reaction at elevated temperatures (solid line). Dash line: reference of Ce³⁺ (Ce(NO₃)₃·6H₂O) at 25°C, reference of Ce⁴⁺ (CeO₂) at 25°C and 450°C under steam.

Figure 12. *In situ* Ni K-edge XAFS spectra of Ni_{0.2}W_{0.1}Ce_{0.7}O₂ under ethanol steam reforming conditions at different temperatures. a) XANES part, b) Fourier transformed R-space of EXAFS part.

TOC graphic

Fig 1

Fig 2

Fig 3

Fig 4

Fig 5

Fig 6

Fig 7

Fig 8

Fig 9

Fig 10

Fig 11

Fig 12