

Pr<sup>3+</sup> surface fraction in CePr mixed oxides determined by XPS analysis

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## ABSTRACT

CePr mixed oxides were previously studied as supports for Water Gas Shift catalysts, considering their promising textural and redox properties arising from the presence of a non-stoichiometric oxide. A very small Ce<sup>3+</sup> fraction was observed on those oxides, suggesting that Pr<sup>3+</sup> ion could be responsible for the enhanced activity. Therefore, in-depth XPS analysis is conducted in the present work in order to determine the Pr<sup>3+</sup> fraction by fitting the XPS Pr 3d region. Much higher values of reduced Pr ions than Ce ions were observed, confirming the promoter role of the former.

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## 1. Introduction

Previous studies of CePr mixed oxides for the Water Gas Shift reaction showed an enhanced catalytic activity in samples promoted with Pr, due to a combination of higher surface area and better reducibility [1]. In fact, even a small Pr addition improved sample reducibility and oxygen storage capacity (OSC), both features that are related to the presence of Ce<sup>4+</sup>/Ce<sup>3+</sup> and Pr<sup>4+</sup>/Pr<sup>3+</sup> redox couples. XRD patterns showed that Pr addition expanded the fluorite lattice, by inducing reduction of tetravalent ions, although it was not possible to distinguish between Ce<sup>3+</sup> and Pr<sup>3+</sup>. In line with this observation, Raman spectroscopy and OSC presented evidence of higher concentration of oxygen vacancies in Pr-doped samples. Finally, the theoretical study of density functional theory with Hubbard parameter (DFT + U) suggested that reduction of Pr<sup>4+</sup> was easier than Ce<sup>4+</sup> in these samples [2].

In previous works, XPS spectra of CePr mixed oxides samples were also analyzed. Pr surface content, Ce<sup>4+</sup>/Ce<sup>3+</sup> ratio and a depth analysis were conducted. It was observed that Pr concentration was higher than the expected value, implying surface enrichment in these samples; moreover, the effect was more noticeable as Pr addition increased. Ce<sup>3+</sup> fraction was calculated by fitting the Ce 3d spectrum. It was found that the fraction of cerium reduced ions decreased with Pr content. Besides an angle-variation analysis were also carried out for a bare ceria sample, in order to estimate the Ce<sup>3+</sup> presence depth in CeO<sub>2</sub>. It was concluded that Ce<sup>3+</sup> ions would tend

to occupy the first monolayer, suggesting that they are more stable on the surface of the sample. In CePr samples, the promoter surface enrichment displaced Ce ions from the surface to subsurface sites, explaining the lower Ce<sup>3+</sup> ions fraction observed with Pr addition [2]. This suggests that Pr<sup>4+</sup>/Pr<sup>3+</sup> redox couple would be the main factor responsible of surface enhanced redox properties. In contrast to Ce 3d spectrum, which is well known, the Pr spectrum was less studied, which encourage a further analysis.

Early works on XPS spectra of lanthanide compounds (particularly La, Ce and Pr oxides) were focused in many-electron satellite structure for the 3d and 4d ionizations. Burroughs et al. reported one of the first XPS spectrum of a praseodymium oxide, the 3d region of Pr<sub>2</sub>O<sub>3</sub> sample [3]. Afterwards, Sarma and Rao reported an analysis carried out over a series of lanthanide oxides, including Pr<sub>2</sub>O<sub>3</sub>, and PrO<sub>2</sub> [4]. Both oxides showed similar spectra, with shoulders at the low energy side of the 3d<sub>5/2</sub> peaks centered at 935.0 for PrO<sub>2</sub> and at 932.9 eV for Pr<sub>2</sub>O<sub>3</sub>. These authors also reported the magnitude of spin-orbit splitting, being 17.8 for PrO<sub>2</sub> and 20.7 eV for Pr<sub>2</sub>O<sub>3</sub>. Indeed, both oxides presented very similar features making very complex the identification of peaks corresponding to Pr cations, in case of the simultaneous presence of PrO<sub>2</sub> and Pr<sub>2</sub>O<sub>3</sub> in the same sample.

Bianconi et al. conducted a deep analysis of 3d region of some lanthanide oxides, including PrO<sub>2</sub> [5]. By spectral fitting, in the Pr 3d region (920–970 eV) these authors found three doublets, a shoulder close to 966 eV in the high-energy tail of O 1s Auger peak, and they reported a spin-orbit-splitting energy close to 20.6 eV between 3d<sub>5/2</sub> and 3d<sub>3/2</sub> lines [6]. Ogasawara et al. reduced a Pr<sub>6</sub>O<sub>11</sub> compound at 850 °C for 20 h in order to obtain a reliable Pr<sub>2</sub>O<sub>3</sub> sample. In the 3d region two main peaks were observed, at 925 and 945 eV,

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with two satellites centered at the low energy side of peaks (920 and 940 eV), which were related to  $3d_{5/2}$  and  $3d_{3/2}$  lines respectively [7]. In summary, only a few peak positions are unequivocally accepted, making complex the calculation of  $\text{Pr}^{3+}/\text{Pr}^{4+}$  ratio in the oxides. In fact, the fraction of  $\text{Pr}^{3+}$  ions is seldom estimated and usually Pr reduced ion quantification is performed from the ratio of only one isolated peak to the whole spectrum. An analogue procedure is often employed to determine  $\text{Ce}^{3+}$  fraction, but this method is only recommended if the fraction of reduced ions is higher than 35% [8].

In the present work, an approach to quantify the fraction of  $\text{Pr}^{3+}$  ions by considering all the peaks involved in XPS spectrum is proposed.

## 2. Experimental

CePr mixed oxides samples were the same previously studied in ref. 2, obtained by urea co-precipitation and annealed at 450 °C [2]. Mixed oxides were called CePrX, where X is the percentage atomic ratio (at%) between [Pr] and ([Pr] + [Ce]). XPS measurements were carried out with a multi-technical system (SPECS) equipped with a dual X-ray source of Mg/Al and a hemispheric synthesizer PHOI-BOS 150. Spectra were acquired using Al-K $\alpha$  radiation operated at 200 W and 12 kV. The pressure of the chamber was lower than  $10^{-9}$  mbar. The analyzed region was Pr 3d, between 920 and 990 eV. The binding energies were calibrated using the  $\text{Ce}^{4+}$  ( $u'''$ ) signal at a 916.7 eV as a reference [9]. Background subtraction (Shirley) and peak fitting were performed using a commercial software CasaXPS® v2.3.15.

## 3. Results and discussion

As it was mentioned above, the surface fraction  $\text{Ce}^{3+}$  ions decreased with Pr incorporation in samples, suggesting that  $\text{Pr}^{3+}$  cations should be responsible for the enhanced redox properties. In order to quantify  $\text{Pr}^{3+}$  fraction in CePr mixed oxides samples, XPS Pr 3d spectra are now analyzed.

Usual reported approaches involve the ratio between one solely isolated peak and the whole spectra. Pajaczowska et al. determined the presence of trivalent ions in their mixed Sr-Pr-Ga oxide spectra, by the distinct feature presented by  $\text{Pr}^{4+}$  close to 965 eV [10]. Often, this peak is used to identify the  $\text{Pr}^{4+}$  oxidation state [11], in a similar way as  $u'''$  character is used to quantify  $\text{Ce}^{3+}$  fraction [12]. However, some authors reported that the 965 eV peak might be partially overlapped with the oxygen KLL Auger peak hindering the determination [6,13]. As an alternative, Aragón et al. proposed the application of the intensities of the main peaks of  $\text{Pr}_2\text{O}_3$  and  $\text{PrO}_2$  compounds in  $3d_{5/2}$  lines between 933.2–933.9 eV and 935–936 eV respectively [13]. Sinev et al. reported a fit of Pr 3d spectrum including seven peaks, but only two of them were used to determine  $\text{Pr}^{3+}$  surface fraction [14]. Borchert et al. followed the latter method for several samples, including one of  $\text{Pr}_6\text{O}_{11}$ , and found a good agreement with the theoretical composition ( $\text{PrO}_{1.875}$  stoichiometry was experimentally obtained, instead of the theoretical  $\text{PrO}_{1.833}$ ) [15]. However, to the best of our knowledge, a quantification of  $\text{Pr}^{3+}$  fitting all peaks as is usually carried out for the determination of  $\text{Ce}^{3+}$  in pure ceria samples was not previously attempted [2,16]. This is probably due to the similarity of the features of both Pr oxides ( $\text{PrO}_2$  and  $\text{Pr}_2\text{O}_3$ ), the closeness of peaks, and doublet splitting [4,11,17]. In fact, some authors limited their analysis to the comparison of Pr 3d spectra of several samples in order to estimate  $\text{Pr}^{3+}/\text{Pr}^{4+}$  presence [18,19].

A two-step procedure is proposed: first, we identify  $\text{Pr}^{4+}$  and  $\text{Pr}^{3+}$  peaks; and second, we fit the whole spectrum considering the simultaneous presence of both ions. Afterwards, we calculate

**Table 1**

summary of peak assignment for  $\text{Pr}^{3+}$  and  $\text{Pr}^{4+}$  ions in Pr-containing samples.

$\text{Pr}^{4+}$ peaks (eV)		$\text{Pr}^{3+}$ peaks (eV)		Peak positions
$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	references
966	935.0 929; 933; 946		932.9	[4]
		940; 945	920; 925	[6] <sup>a</sup>
967	935–936		933.2–933.9	[7] <sup>a</sup>
966.1–966.8	945.8–946.4			[13]
953.5; 966.9	933.9	949.8; 973.2	929.5	[15]
	935.5		929.1; 933.4	[18]
953.5; 966.4	933.9	949.8; 973.2	929.5	[19]
		955		[20]
		953		[21]
966–968		953	933	[22]
		953.85	933.75	[23]
967				[24]

<sup>a</sup> values read from figures.

$\text{Pr}^{3+}$  surface fraction from the ratio of their characteristic peaks intensities to the whole spectrum. By the inspection of several published works, it arises that only a few characteristics peaks (listed in Table 1) are reported.

There is a consensus that the peak close to 966 eV, and its spin-orbit partner close to 946 eV, are related to  $\text{Pr}^{4+}$  ion [6,15,18,20,22,24]. Moreover according to some authors, the peak centered between 934 and 936 eV is associated to  $\text{Pr}^{4+}$  [6,13,18,20]. Peak located between 933 and 934 eV is associated to the presence of  $\text{Pr}^{3+}$  [13,19,22,23], as its partner reported at 953–954 eV [22,23]. Finally, the peak usually observed at the lower end of the binding energy of 3d spectra, close to 929 eV, is associated to  $\text{Pr}^{3+}$  ion [18–20]. Besides, in this binding energy range 928–931 eV, it was also reported the presence of a  $\text{Pr}^{4+}$  peak [6] which was taken into account in the spectrum fitting procedure.

It is worth to mention that  $3d_{5/2}$  spectra for  $\text{CeO}_2$  and  $\text{PrO}_2$  present similar features. Bianconi et al. proposed to assign the peaks identified in Pr  $3d_{5/2}$  core level spectrum of  $\text{PrO}_2$  to the same electronic configuration found for peaks in Ce  $3d_{5/2}$  of ceria, which was confirmed by the analysis of Pr  $3d_{5/2}$  XAS spectrum. Similar conclusions were obtained by the comparison of the spectra of Pr  $3d_{3/2}$  and Ce  $3d_{3/2}$  core levels [5,6]. Therefore, data presented in Table 1 and the mentioned similarity between  $\text{CeO}_2$  and  $\text{PrO}_2$  3d spectra would suggest that three doublets (six peaks) are expected for  $\text{Pr}^{4+}$  (hereafter called  $a'''$ - $b'''$ ,  $a''$ - $b''$ ,  $a$ - $b$ ), and two doublets (four peaks) are expected for  $\text{Pr}^{3+}$  (hereafter named  $a'$ - $b'$ ,  $a_0$ - $b_0$ ).

Several features were taken into account in Pr 3d spectra fitting procedure for the three samples studied. The peaks intensities in same doublet were fitted in order to satisfy a 2:3 ratio corresponding to  $3d_{3/2}$ : $3d_{5/2}$  signals respectively. It was considered a similar FWHM for peaks belonging to the same doublet, with values constrained to a difference lower than 15%. Besides, the peaks positions along samples were fitted to be the same in a 0.3 eV gap. In case of  $a'''$ - $b'''$  doublet, it were allowed larger constrains due to  $a'''$  was mounted on low BE side of the strong O KLL Auger peak, hindering the fitting procedure [15]. Then, a maximum difference in FWHM close to 30% was allowed, and the peak positions ( $a'''$  and  $b'''$ ) along samples, were constrained to be same with 0.6 eV range.

From the fitting procedure, doublet splitting close to the values reported in literature for  $\text{PrO}_2$  [6] and  $\text{Pr}_2\text{O}_3$  [5] were found. Results for CePr50, CePr15 and CePr5 samples are shown in Tables 2–4, respectively. As it can be seen, similar peak features are observed for CePr50 and CePr15 mixed oxides. Pr 3d spectrum for CePr5 sample was quite noisy due to the low promoter content, hindering the fitting procedure and this result should be taken as a roughly approximation (Fig. 1).

Results of the fitting procedure are summarized in Table 5 where it can be readily seen that the  $\text{Pr}^{3+}$  surface fraction increases with

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