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# Effect of rare earth (RE – La, Pr, Nd) metal-doped ceria nanoparticles on catalytic hydrogen iodide decomposition for hydrogen production

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## ABSTRACT

In this work, high surface area rare earth (RE = La, Pr, and Nd) metal-doped ceria ( $\text{CeO}_2$ ) nanocatalysts have been synthesized by the citric-aided sol-gel method for hydrogen-iodide decomposition in thermochemical water-splitting sulfur-iodine (SI) cycle for hydrogen production. This sol-gel method allows the insertion of rare earth metal  $\text{M}^{3+}$  ions into the  $\text{CeO}_2$  material. Incorporation of rare earth metals created a different synergistic effect between RE and Ce components such as increase of oxygen mobility, oxygen vacancy, and thermal stability of the  $\text{CeO}_2$  material. These doped- $\text{CeO}_2$  materials were characterized by various physicochemical techniques, namely, XRD, BET, ICP-AES, TEM, TGA, and RAMAN spectroscopy. XRD and TEM studies revealed 5–10 nm particles of the RE- $\text{CeO}_2$  material. Shifting of peaks and increase in lattice parameter values confirmed the formation of Ce-RE solid solutions (XRD and Raman). Incorporation of dopants resulted in an increase in the specific surface area (BET), thermal stability (TGA), and oxygen vacancy concentration (Raman). Among different dopants,  $\text{CeO}_2$ -L (La-doped  $\text{CeO}_2$ ) material exhibits the highest specific surface area, thermal stability, and oxygen vacancy concentration, and smallest crystallite size. The catalytic activity of doped- $\text{CeO}_2$  materials is explored for hydrogen-iodide decomposition. The order of catalytic activity is as follows:  $\text{CeO}_2 < \text{CeO}_2\text{-N}$  (N = Nd)  $< \text{CeO}_2\text{-P}$  (P = Pr)  $< \text{CeO}_2\text{-L}$  (L = La).  $\text{CeO}_2$ -L shows higher catalytic activity and stability in comparison to the pure  $\text{CeO}_2$  material. It also showed an excellent time-on-stream stability for 35 h. The apparent activation energy of  $\text{CeO}_2$ -L,  $\text{CeO}_2$ -P, and  $\text{CeO}_2$ -N was found to be 48.9, 54.8, and 61.4  $\text{kJ mol}^{-1}$ , respectively. The effect of iodine on hydrogen iodide conversion was also studied over a  $\text{CeO}_2$ -L catalyst. Thus, RE-doped  $\text{CeO}_2$  catalysts show a lot of potential of generating hydrogen from hydrogen iodide in the SI cycle.

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## Introduction

Cerium dioxide ( $\text{CeO}_2$ ) is one of the rare earth metal oxides which have been used for different variety of applications.

Due to its unique properties, it finds applications in gas sensor, glass-polishing materials, solid electrolyte, sunscreen, catalyst/support, environmental chemistry and medicine [1–4]. It exhibits excellent activity in various catalytic reactions such as three-way catalysis (TWCs) for removal of

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toxic exhaust gases from automobiles, hydrogen-iodide decomposition for hydrogen generation, low-temperature CO oxidation, water-gas shift (WGS) reaction, and NO<sub>x</sub> reduction due to its high oxygen storage/release capability and fast redox cycle, Ce<sup>3+</sup> to Ce<sup>4+</sup> [5–10]. This is related to the surface defects of the materials. Cerium has an electronic configuration of [Xe] 4f<sup>2</sup> 6s<sup>2</sup> which shows that it has two common valence state of Ce (III) and Ce (IV). Because of this possibility, it can change its oxidation state from (III) to (IV) and vice-versa easily. This is due to lower potential energy barrier to electron density distribution and somewhat similar energy of 5d and 4f states between Ce (III) and Ce (IV) [11]. When the oxygen amount starts decreasing from CeO<sub>2</sub> material, there is formation of oxygen vacancies. In stoichiometric CeO<sub>2</sub>, oxygen exhibits an oxidation state of –2 and a large amount of oxygen vacancies can be expected when Ce (IV) changes to Ce (III) in order to maintain electro-neutrality [12,13]. To enhance these unique properties, suitable doping is required to achieve physical and chemical application. Doping in CeO<sub>2</sub> lattice can change its electronic properties and makes it applicable for other sophisticated applications.

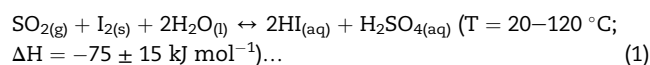
CeO<sub>2</sub> has a fluorite (CaF<sub>2</sub>) structure with space group *Fm3m*. This fluorite structure consists of fcc unit cell of cations and anions occupying the octahedral interstitial sites. Its colour is pale yellow due to charge transfer of Ce(IV)-O(II) whereas CeO<sub>2-δ</sub> (0.5 > δ > 0) is blue and turns black-greyish [14]. CeO<sub>2</sub> possesses few defects depending on the partial pressure of oxygen. Defects in CeO<sub>2</sub> such as oxygen vacancy control its chemical and electronic properties. CeO<sub>2</sub> tend to form more oxygen vacancies when it is present at nano scale. In this regime, it acts as a catalyst itself with large surface area to volume ratio and produces unique properties. Carrettin et al. [15] showed that the CeO<sub>2</sub> of 3–4 nm particle size supported Au produced an increase of two order magnitude of activity as compared to Au supported on bulk CeO<sub>2</sub> for CO oxidation. This indicates that the properties of a support can be modified by taking it into the nano regime and changing an inactive support to an active one. It shows that the reactivity of CeO<sub>2</sub> can be tuned by controlling its size. CeO<sub>2</sub> nanoparticles also exhibit some different properties as compared to the bulk CeO<sub>2</sub> such as pressure-induced phase transformation, increase in electronic conductivity, size-induced lattice relaxation, and the shift in UV–vis and Raman spectra [16–22].

Two possible ways to enhance the structural, morphological, and redox properties of CeO<sub>2</sub> are: (a) by deposition of precious metal nanoparticles on the surface of CeO<sub>2</sub> and (b) by doping or incorporation of metals into the lattice of CeO<sub>2</sub> material. The second way is more suitable as it generates more defects (Ce<sup>3+</sup>, oxygen vacancies etc.) by the expansion or contraction of cell volume. Doping or incorporation with rare earth metals such as La, Pr, and Nd into CeO<sub>2</sub> lattice can result into oxygen vacancies and oxygen mobility and thus further improved the catalytic activity of CeO<sub>2</sub> in many catalytic reactions [23–26]. Recently, Singhania et al. [27] showed that the addition of Pd into ceria lattice resulted in an increase in the number of oxygen vacancies and consequently enhance the catalytic activity. Similarly, Zhang et al. [28,29] reported the incorporation of Ni and Pt into CeO<sub>2</sub> lattice which resulted into larger oxygen vacancies, smaller particle size, larger specific

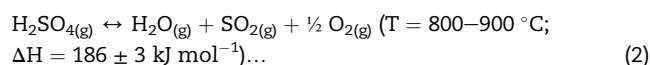
surface area, better thermal stability and dispersion and improved the catalytic activity. The ionic radii of La<sup>3+</sup> (1.15 Å), Pr<sup>3+</sup> (1.13 Å), and Nd<sup>3+</sup> (0.99 Å) are close to the ionic radius of Ce<sup>4+</sup> (0.97 Å). Because of comparable ionic radii of these rare earth metal ions, there is a possibility to incorporate these into CeO<sub>2</sub> lattice which might create a different synergistic effect between the rare earth metals and Ce components and result in better catalytic activity than CeO<sub>2</sub> alone. Different CeO<sub>2</sub>-metal oxides have been prepared by various methods such as sol-gel, solution combustion, hydrothermal, solvothermal, microemulsion, hydrolysis, co-precipitation, electrochemical, impregnation, and thermal-decomposition [30–35]. Among these methods, sol-gel is quite simple, time-saving and produces pure homogeneous materials.

Hydrogen-iodide decomposition is an important part of thermochemical water-splitting sulfur-iodine (SI) cycle in which a large quantity of hydrogen is produced without any release of green-house gas [3,6,27]. The SI cycle consists of the following reactions [35–38]:

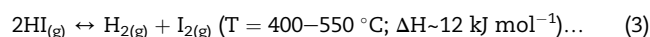
#### Bunsen reaction:



#### Sulfuric-acid decomposition:



#### Hydrogen-iodide decomposition:



#### Net reaction:



The net reaction of the SI cycle is the decomposition of water into hydrogen and oxygen only. Hydrogen-iodide decomposition is a slow equilibrium-limited reaction. Thus, a highly active and stable catalyst is required along with some thermal energy which can generate large quantities of hydrogen from hydrogen iodide in the SI cycle. Different supports such as activated carbon, carbon nanotubes, graphite, carbon molecular sieves, zirconia, ceria and  $\gamma$ -alumina and catalysts such as Ni, Pt, Pd, Ru and Ir have been reported for hydrogen-iodide decomposition [39–44]. Among different supports, CeO<sub>2</sub> has been chosen as it is non-toxic, inexpensive, and abundant and has unique physicochemical properties. In nano regime, it acts as a catalyst or support.

In the present paper, different rare earth metals (La, Pr and Nd) have been doped into CeO<sub>2</sub> material by simple sol-gel method and their catalytic activities are explored for hydrogen-iodide decomposition. As far the author knows, these studies are not explored before using the RE-doped CeO<sub>2</sub> materials for hydrogen-iodide decomposition. The RE-doped CeO<sub>2</sub> materials are also tested for long time-on-stream stability of 35 h. These doped-CeO<sub>2</sub> materials are also characterized by BET, XRD, ICP-AES, TEM, TGA, and RAMAN techniques.

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