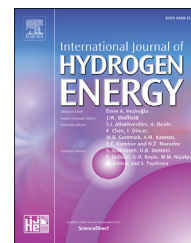


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# Ni/Y<sub>2</sub>B<sub>2</sub>O<sub>7</sub> (B=Ti, Sn, Zr and Ce) catalysts for methane steam reforming: On the effects of B site replacement

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## ABSTRACT

In this study, a series of Y<sub>2</sub>B<sub>2</sub>O<sub>7</sub> compounds with a fixed Yttrium cation A site but with different B (B=Ti, Sn, Zr and Ce) sites have been synthesized and used to support Ni for methane reforming for hydrogen production. By replacing the B site with Ti, Sn, Zr and Ce cations in sequence, the r<sub>A</sub>/r<sub>B</sub> ratios of the resulted Y<sub>2</sub>B<sub>2</sub>O<sub>7</sub> compounds become smaller. As a consequence, the crystalline structures of the compounds become less ordered with the transformation of the bulk phase from well-ordered pyrochlore (Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>) to less ordered pyrochlore (Y<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>) and subsequently to defective fluorite (Y<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Y<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub>). XPS results have revealed that on the surfaces of Ni/Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Ni/Y<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub>, higher O/(Y + B) atomic ratios can be achieved than on the other two catalysts, indicating the presence of more abundant oxygen species, which is beneficial to remove the carbon deposits. In comparison with Y<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Y<sub>2</sub>Ce<sub>2</sub>O<sub>7</sub>, the supported Ni or Ni<sub>3</sub>Sn<sub>2</sub> active sites have stronger interaction with Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> and Y<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> supports, which anchors the active sites tighter on the supports and suppresses its aggregation effectively, thus obtaining catalysts with larger active metallic surface areas and better thermal stability. As a result, the stability and coking resistance of the catalysts can be enhanced. For the reduced Ni/Y<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub>, Ni<sub>3</sub>Sn<sub>2</sub> alloy has formed, which improves the coking resistance of the catalyst but degrades its activity significantly. On Ni/Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> catalyst, which possesses the largest amount of active surface oxygen species, the strongest Ni interaction with the support can also be obtained, therefore, it exhibits the highest activity, stability and strongest coking resistance among all of the catalysts.

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## Introduction

With the growing demands for energy, worldwide concerns regarding the energy security and environmental issues

related to the use of fossil fuels are created [1–3]. Hydrogen, a clean energy, has been considered as the most promising energy carrier and as an important “raw material” in chemical industries and refineries for many years [4,5]. Among different routes for large scale industrial hydrogen and syngas

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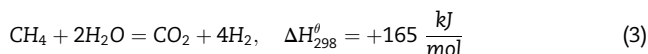
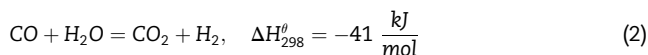
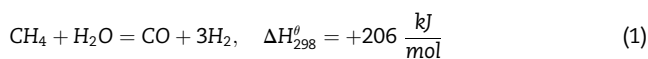
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production, hydrocarbons steam reforming, primarily methane steam reforming (MSR), has been the preferred one [1,6]. The three main reactions taking place during MSR are listed here [7,8]:



Generally, the industrial process of MSR needs to be performed around 800 °C and 15–30 bar over suitable catalysts because Reaction (1) is highly endothermic [9]. It has been found that the group VIII metals, such as Fe, Co, Ni, Pt, Pd, Ru, and Rh, can be used as the active components for this reaction [3,10]. However, the application of noble metals in MSR is restricted by their high price and scarcity, though they exhibit excellent performance and potent coking resistance [11,12]. In comparison, Ni-based catalysts are more preferred considering their high initial activity and low costs. However, Ni-based catalysts deactivate easily due to severe coking and sintering of active Ni species during the high temperature reforming processes [13–15]. Therefore, there is still a great necessity to design and develop catalysts with potent resistance to both coking and the sintering of the active sites for large-scale H<sub>2</sub> production as a new energy source [3]. It was found previously that a support with high thermal stability, mobile oxygen species and a certain surface area can anchor the Ni active sites even at high temperature, thus improving the reaction performance and coking resistance of a Ni-based catalyst [9,16–18].

Over recent years, pyrochlore compounds, typically with an A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> stoichiometry formula, have attracted attention in catalysis field because of their excellent thermal stability, superior oxygen ion conductivity and inherent oxygen vacancies in the structures [19–21]. Usually, in the cubic pyrochlore structure, the eight-coordinated A site is occupied by a tetravalent rare-earth cation with a larger radius and the six-coordinated B site is occupied by a tetravalent transition metal cation with a smaller radius [22,23]. From another point of view, the structure of pyrochlore can be envisioned as interpenetrating networks of BO<sub>6</sub> octahedra and A<sub>2</sub>O chains of distorted cubes, indicating the presence of two types of lattice oxygen anions with different chemical environments in its structure, namely six 48f oxygen anions and one 8b oxygen anions [24]. Specifically, a 48f oxygen anion is coordinated to two A and two B sites, and an 8b oxygen anion is coordinated to four A sites according to former publications about the detailed crystallographic structure of pyrochlores with different elements [25]. One-eighth of the 8b site oxygen anions are absent in the cubic structure of a pyrochlore compared with a strict cubic fluorite structure (AO<sub>2</sub>), which results in A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> compounds containing inherent 8a oxygen vacancies [26]. Due to this 8a site vacancies, it is possible to form Frenkel defects by migrating an oxygen anion onto the 8a site from an occupied 8b or 48f site [25]. A number of previous studies have testified that the phase stability of A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> is primarily determined by the radius ratio of the A and B site

cations. Indeed, when the r<sub>A</sub>/r<sub>B</sub> ratio is in the range of 1.46–1.78, an ordered pyrochlore structure can be achieved. Whereas, when the r<sub>A</sub>/r<sub>B</sub> ratio is less than 1.46, it inclines to crystallize as a disordered fluorite with oxygen anion defects [22,26,27]. As a consequence, the A and B cations tend to distribute in the A and B sites randomly in the defective fluorite structure, resulting in more disordered and mobile 8a oxygen vacancies [27–29], which are believed to be favorable to a redox reactions involving oxygen migration [19,21,30,31].

Except for the superior thermal stability of A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> supports, this oxygen mobility is also believed to be favorable for the elimination of carbon deposits on the Ni active species and improve the stability of the catalysts during the high temperature reforming processes [1,32–34]. Therefore, A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> compounds have been investigated as catalysts for reforming processes both in theoretical calculation and experimental work. For example, Pakhare and co-workers [35,36] elucidated the surface reaction kinetics, the rate limiting steps and microkinetic model of Rh-substituted La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> pyrochlore catalysts in dry reforming of methane by DFT simulation. Spivey and co-workers [37–39] found that La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> partially substituted by Ru, Rh, Pt or Ni cations at Zr site lead to the formation of more active oxygen species, which contributed to the reaction performance and coking resistance of the catalysts in methane reforming. In addition, Peppley et al. [40] observed metallicly dispersed ruthenium in the pyrochlore matrix for Ru-substituted pyrochlore, which improved its catalytic activity in the VOCs autothermal reforming processes. Lee and co-workers [41] also found that Ru-substituted pyrochlore exhibits high activity and stability in ethanol steam reforming, which was ascribed to the metal-metal interaction between La and Ru. However, these reports mainly focused on investigating partially substituted pyrochlores used for reforming reactions directly. So far, only a few studies about loading metals on pyrochlore supports for reforming reactions can be found. Mizuki and co-workers [42] found that NiO<sub>x</sub>/Ce<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> showed high activity and stability in MSR. More recently, our group found that Ni supported on Y<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> support prepared by glycine-nitrate combustion method exhibited superior activity and anti-coking ability for MSR [9]. Additionally, it is also revealed by our group that Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> showed excellent coking resistance for MSR. While the activity on Ni/La<sub>2</sub>Sn<sub>2</sub>O<sub>7</sub> is low, Ni/La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> possesses much higher activity than the traditional Ni/Al<sub>2</sub>O<sub>3</sub> catalyst [16]. This indicates that A<sub>2</sub>B<sub>2</sub>O<sub>7</sub> pyrochlores with different structures and properties could be prepared by tuning A or B sites, thus obtaining catalysts with different performance for methane reforming.

Therefore, with the purpose to understand the relationship between the pyrochlore structure and its reaction performance in reforming reaction, and to develop catalysts with potential industrial applications, in this work, Y<sub>2</sub>B<sub>2</sub>O<sub>7</sub> pyrochlores with a fixed Yttrium A site but with different B site cations have been prepared by co-precipitation method and used as supports for Ni for MSR. It has been found that pyrochlore supports with different structures and reaction performance can be prepared by replacing the B site with different cations, among which Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> exhibits the best performance. The relationship between the reaction

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