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# Enhanced catalytic performance of Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst modified with CaZrO<sub>3</sub> nanoparticles in steam-methane reforming

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## ABSTRACT

Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts containing CaZrO<sub>3</sub> nanoparticles as a promoter were prepared by sequential impregnation for H<sub>2</sub> production from steam-methane reforming. The effects of different loadings of CaZrO<sub>3</sub> nanoparticles from 0 to 15 wt% on the catalytic performance of Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts in steam-methane reforming were studied. The Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts containing 15 wt% CaZrO<sub>3</sub> nanoparticles provided the highest H<sub>2</sub> yield due to facilitative steps of enormous steam adsorption-dissociation at the sites of oxygen vacancies on the surface of CaZrO<sub>3</sub> nanoparticles. The existence of facilitative steps created additional H<sup>+</sup> and OH<sup>-</sup> enhancing both H<sub>2</sub> yield and the gasification of deposited carbon, respectively. The tests of steam-methane reforming at low S/C ratio of 1/3 for 97 h revealed that the catalytic performance of CaZrO<sub>3</sub>-modified Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts was higher than that of the unmodified Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Interestingly, at high S/C ratio of 3 excessive steam adsorption at the oxygen vacancies on CaZrO<sub>3</sub> nanoparticles resulted in highly competitive adsorption between steam and methane decreasing CH<sub>4</sub> dissociation. The results suggested that in the steam-methane reforming, optimum S/C ratios for the CaZrO<sub>3</sub>-modified Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalysts were relatively lower than those for the unmodified Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst due to excellent steam adsorption-dissociation capability for CaZrO<sub>3</sub> nanoparticles.

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## Introduction

H<sub>2</sub> production has recently been given special attention due to the utilization of H<sub>2</sub> as clean fuel in fuel cell technologies in

addition to the increasing demands for ammonia and methanol syntheses, hydrogenation and refinery [1–3]. At present, H<sub>2</sub> is commercially produced through steam-methane reforming (SMR) since it is the economical method and

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methane is extractable from natural gas which is abundant in nature [3]. Recent remarkable efforts to boost SMR have continuously been made in both reactor design and catalyst performance, although SMR has been successfully-utilized technology in industrial production [4–9]. The efforts are to make the better understanding and effective control of reaction mechanisms, carbon formation and sulfur poisoning resulting in lower cost plants [10]. Additionally, the recent major aims have been to adaptation to emerging H<sub>2</sub> economy such as micro-reformer coupled with low-temperature fuel cell technologies [11,12].

In the pragmatic production of SMR, Ni/Al<sub>2</sub>O<sub>3</sub> catalyst is typically used due to its two main advantages, i.e. low cost and high catalytic activity. Although it offers the practical advantages, the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst still possesses low catalytic stability compared with noble metals such as Pt, Pd, Ru, Rh and Ir [13–15]. The improvement in catalytic stability of the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst is a challenge for industrial use. In order to alleviate the issue resulting from carbon formation on the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst, the revision of reduction in the deactivation of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in SMR was carried out in this work. Urasaki et al. [16] pointed out that lattice oxygen in the perovskite supports of Ni catalysts showed beneficial effects on methane dissociation and carbon gasification due to its transportation to CH<sub>x</sub> fragments and inactive carbon, respectively. The perovskite supports, especially for LaAlO<sub>3</sub> and SrTiO<sub>3</sub>, indicated repeatedly releasing and regenerating oxygen atoms in their structure leading to advantages of both the high catalytic activity and stability.

In addition, the balance between the methane dissociation and the carbon gasification played a key role in the SMR process. Zhang et al. [17] showed that NaCeTi<sub>2</sub>O<sub>6</sub> perovskite-supported Ni catalysts created the proper balance resulting from the basicity of Na<sup>+</sup> sites and being oxygen ion-conductor of perovskite oxide. In addition to the balance, it was found that the incorporation of Ce in the Ni/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by sequential impregnation created Ce<sup>3+</sup>/Ce<sup>4+</sup> ions on ceria surface enhancing the adsorption–dissociation of steam [18]. A study also reported that oxygen storage capacity under redox condition of Ce in the solid solution of Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub> used as the support of Ni provided high methane conversion and stability in SMR [19].

From the previous literature, the addition of perovskite particles as promoter to the Ni/α-Al<sub>2</sub>O<sub>3</sub> catalyst might particularly be beneficial for adsorbing water and then supporting both the catalytic activity and stability of Ni in SMR [20]. In this case, the addition of perovskite particles in small amount was not responsible for high cost, compared with using them as only support. The perovskite structure (ABO<sub>3</sub>) can typically be prepared from various oxides of A and B sites for example LaNiO<sub>3</sub>, BaFeO<sub>3</sub>, SrTiO<sub>3</sub>, BiMnO<sub>3</sub> etc [21]. Interestingly, the combination of Ni metal and perovskite support created complex metal-support interaction depending greatly upon the reducibility of perovskite [22]. Their combination led to strong resistance to Ni oxidation in steam reforming reaction of hydrocarbon [23]. Furthermore, the specific surface area of perovskite support and Ni-perovskite interface dominated the exchange of lattice oxygen through redox cycle during steam reforming [24]. Moreover, the lattice oxygen of perovskite

support promoted the oxidation of toluene intermediate at their perimeter [25].

In this work, CaZrO<sub>3</sub> nanoparticles were utilized as the promoter by means of mixing together with the Ni/α-Al<sub>2</sub>O<sub>3</sub> catalyst by sequential impregnation. According to phase diagram of CaO–ZrO<sub>2</sub> system, CaZrO<sub>3</sub> can be prepared from mixing CaO and ZrO<sub>2</sub> at 1:1 mole ratio and their subsequent calcination at temperatures higher than 500 °C [26]. From variously practical point of view on appropriate promoter of Ni/α-Al<sub>2</sub>O<sub>3</sub> catalyst, it should be noteworthy that CaO was also highly beneficial for sorption enhanced reforming of methane as CO<sub>2</sub> sorbent [27–30]. It was a fact that the co-existence of CaO and CaZrO<sub>3</sub> from well-designed preparation offered synergetic effects in the production of high purity H<sub>2</sub> from sorption enhanced steam methane reforming [31].

In order to achieve the preparation of CaZrO<sub>3</sub>-modified Ni/α-Al<sub>2</sub>O<sub>3</sub> catalysts, CaZrO<sub>3</sub> particles were first calcined at 800 °C to ensure their stability for reforming tests at 700 °C. The loading percentages of CaZrO<sub>3</sub> nanoparticles into the Ni/α-Al<sub>2</sub>O<sub>3</sub> catalyst were varied from 0 to 15 wt% because useful interaction resulting from their perimeter might offer outstanding performance [32]. Additionally, S/C ratios at 1/3, 1 and 3 were employed in testing SMR over the CaZrO<sub>3</sub>-modified Ni/α-Al<sub>2</sub>O<sub>3</sub> catalysts. Using the low S/C ratio of 1/3 allows for energy savings in SMR, although SMR thermodynamic equilibrium is satisfied at S/C ratio of ~3. In addition, the low S/C ratio can be coupled with emerging applications such as power-to-gas system [33] and Pd membrane for H<sub>2</sub> purification [34]. The long-term tests of SMR over CaZrO<sub>3</sub>-modified Ni/α-Al<sub>2</sub>O<sub>3</sub> catalysts at S/C ratio of 1/3 for 97 h were conducted and compared with those over the typical Ni/α-Al<sub>2</sub>O<sub>3</sub> catalyst to evaluate their catalytic performance. The S/C ratio of 1/3 was employed to rapidly accelerate the deactivation of catalysts. Therefore, their performance, especially for stability, was able to clearly compare within 97 h.

## Experimental

### Catalyst preparation

The method of sequential impregnation was used to prepared Ni/α-Al<sub>2</sub>O<sub>3</sub> catalysts modified with CaZrO<sub>3</sub> at different loading percentages. Commercial α-Al<sub>2</sub>O<sub>3</sub> powder (AMS-9, Sumitomo Inc., Japan) with BET surface area of 7.85 m<sup>2</sup>/g and average pore diameter of 15.96 nm was used as support. The α-Al<sub>2</sub>O<sub>3</sub> powder was impregnated in the mixed solution of Ca(N-O<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (Sigma-Aldrich), and ZrO(NO<sub>3</sub>)<sub>2</sub>·H<sub>2</sub>O (Sigma-Aldrich) at 1:1 mole ratio of CaO:ZrO<sub>2</sub> to form CaZrO<sub>3</sub> nanoparticles after calcination. The mixtures were dried overnight in air at 90 °C and then calcined at 800 °C for 1 h. The calcined powder was subsequently impregnated in the solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Merck) before drying overnight in air at 90 °C and then calcination at 700 °C for 1 h.

Each prepared catalyst contained 10 wt% Ni. The modified catalysts were named N5CZA, N10CZA, and N15CZA following the variation in CaZrO<sub>3</sub> amounts at 5, 10 and 15 wt%, respectively. The unmodified catalyst (10 wt% Ni/α-Al<sub>2</sub>O<sub>3</sub>) named NA was also prepared by the impregnation method for comparison with the modified Ni catalysts.

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