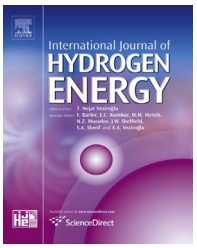
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2016) 1–14

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Effect of support on hydrogen production from chemical looping steam reforming of ethanol over Ni-based oxygen carriers

Kaiqiang Wang [a], *Binlin Dou* [a,b,*], *Bo Jiang* [a], *Qian Zhang* [a], *Min Li* [a], *Haisheng Chen* [c,**], *Yujie Xu* [c]

[a] *School of Energy and Power Engineering, Key Laboratory of Ocean Energy Utilization and Energy Conservation of Ministry of Education, Dalian University of Technology, 116023, Dalian, China*

[b] *School of Energy and Power Engineering, University of Shanghai for Science and Technology, Shanghai, 200093, China*

[c] *Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing, 100190, China*

ARTICLE INFO

Article history:
Received 22 April 2016
Received in revised form
29 July 2016
Accepted 31 July 2016

Keywords:
Chemical looping steam reforming
Oxygen carriers
Support structure
Fixed-bed reactor

ABSTRACT

The Ni-based oxygen carriers (OCs) with different supports including alloy Ni/Al_2O_3, lamellar Ni/MMT, mesoporous Ni/Al-MCM-41 and mesoporous Ni/SBA-15 were synthesized. The effect of support on hydrogen production from chemical looping steam reforming (CLSR) of ethanol was investigated in a fixed-bed reactor. The oxygen carriers were characterized by some techniques, including N_2 adsorption–desorption, XRD, TEM, ICP-OES, H_2 pulse chemisorption, H_2-TPR, and TG-DTG. It was observed that Ni/SBA-15 exhibited most efficient confinement effect followed by Ni/Al-MCM-41, Ni/MMT and Ni/Al_2O_3 via: 1) small nickel particle size and high dispersion as well as strengthened metal-support interaction; 2) sintering resistance due to spatial restriction of support; 3) anti-coke capability derived from small nickel particles and ordered diffusion routes for reactants and products. In addition, the silica supported OCs were conductive to promote water gas shift (WGS) reaction but the supports containing Al atoms were prone to coke deposition due to the formation of acid sites. The 'dead time' and oxygen transfer capacity reflected that the redox performance of oxygen carriers was listed in the following order: Ni/SBA-15, Ni/Al-MCM-41, Ni/MMT and Ni/Al_2O_3. Ni/Al-MCM-41 exhibited excellent activity in initial cycle of CLSR but the collapse of the Ni/Al-MCM-41 structure for its weak thermo stability leaded to the deactivation and sintering of active phase. The Ni/SBA-15 and lamellar Ni/MMT OCs exhibited superior activity and stability but the performance of Ni/Al_2O_3 OCs was mediocre.

* *Corresponding author*. School of Energy and Power Engineering, Key Laboratory of Ocean Energy Utilization and Energy Conservation of Ministry of Education, Dalian University of Technology, 116023, Dalian, China.

** *Corresponding author*.

E-mail addresses: bldou@dlut.edu.cn (B. Dou), chen_hs@mail.etp.ac.cn (H. Chen).

http://dx.doi.org/10.1016/j.ijhydene.2016.07.261

Introduction

The demand for hydrogen which is regarded as a bridge to sustainable energy is expected to increase concerning the energy security and environmental issues related to the usage of fossil fuels [1–3]. And it is vital to find out an efficient method for large-scale industrial hydrogen production owing to the application of hydrogen in high-efficiency energy conversion devices such as fuel cells and H_2 internal combustion energies [4–7]. Steam reforming (SR) or enhanced-sorption SR of hydrocarbons and oxygenates derived from biomass with or without chemical looping has been the dominant industrial process for efficient hydrogen generation in recent years [8–13]. Among the hydrocarbons and oxygenates, ethanol is considered as an important candidate attributing to several advantages: high H element content, less hazardous, handling and transport safely, mature technology for ethanol production from biomass sources [12,14,15]. In addition, when ethanol is utilized in gasoline as a liquid fuel, a significant fraction of cost comes from the separation of ethanol and water via distillation [16].

Chemical looping steam reforming (CLSR) is considered as an efficient method for hydrogen production [17]. In the CLSR process, the oxygen carriers (OCs) are reduced and oxidized in a cyclic manner to convert hydrocarbons into gaseous products. During the reduction step, the fuel feed is oxidized into gaseous products by obtaining lattice oxygen from OCs rather than air or pure oxygen. What followed is water gas shift reaction when steam is fed, achieving higher hydrogen purity of gas products. In the subsequent oxidation step, the oxidation of reduced OCs and carbon deposition occurs, releasing a large amount of heat [8]. Thus, the CLSR process could achieve heat balance without addition of external heat by obtaining heat from hot OCs coming from the air feed step in a fluidized bed reactor [8,18–20]. Comparing with conventional steam reforming process, the major advantages of CLSR process are that it overcomes the influence of carbon deposition and achieves autothermal condition [21,22]. In addition, the CLSR process utilizes air for the heat-generating oxidation reactions rather than pure oxygen from a costly air separation unit, which differs from the conventional partial oxidation or conventional autothermal reforming processes [23]. The oxygen carriers perform two crucial functions when the process is carried out in a fixed-bed reactor [24]: oxygen transfer via redox cycles and steam reforming catalyst in its reduced form. Thus, catalytic and redox performance of OCs are crucial for efficient hydrogen production. The fixed-bed reactor is chosen attributing to that it simplify the scalability and that it is feasible to evaluate the performance to OCs [25].

Numerous metal oxides have been investigated as OCs for CLSR process [12,22,25], and the Ni-based oxygen carriers are considered as promising candidates for its low-cost, high oxygen transfer capacity and superior activity [26–28]. However, the maintenance of high activity and stability still remains grand challenge [25,29]. It was also observed that the particle size had a great effect on the catalytic activity and coke resistant ability [30–32]. Consequently, it is crucial to improve the performance of Ni-based OCs via effective strategies. There is a consensus that the support of catalysis plays a significant role in catalytic and redox performance. An effective way of improving Ni dispersion, suppressing the aggregation and controlling the particle size is to accommodate them in various supports such as alumina, lamellar or mesoporous silica which offer dispersion surface areas for active phase [33]. The utilization of conventional metal oxides as a support such as Al_2O_3 is in favor of enhancing the anti-sintering capacity via synergistic effects [34–37]. Moreover, the supports with lamellar or mesoporous structure are considered as an excellent host to disperse or confine nanoparticles for their large surface area and spatial restriction on the metal particles to hamper their sintering [38–42]. Beyond that, the ordered channels of mesoporous silica molecular sieve MCM-41 and SBA-15 provide valid diffusion routes for turnover of the reactants and resultants. Strawhecker et al. [43] illustrated that montmorillonite (MMT) exhibited lamellar structure with coexistence of exfoliated and intercalated MMT layers. And Li et al. [44] revealed that montmorillonite-supported Ni nanoparticles exhibited excellent catalytic activity and stability and anti-sintering ability in ethanol steam reforming process. It has been verified that Ni/MCM-41 was highly efficient for the conversion of renewable biomass resource with very low coke deposition, meanwhile, the influence of Ni content in relation to the particle size distribution and coke deposition was investigated [45]. Li et al. [46] have illustrated that ceria-promoted Ni/SBA-15 catalysts showed excellent properties such as high activity, long-term stability, good anti-sintering and coke resistance ability in ethanol steam reforming process. Moreover, the silica support could effectively improve water gas shift (WGS) activity rather than methanation attributing to multilayer-induced dissociation of water on the silica surface and the enhanced reaction of adsorbed hydroxyls with CO, which is conductive to achieve high selectivity towards hydrogen in ethanol steam reforming [47,48]. In general, the properties of support affects the performance of supported nickel catalysts strongly in the catalytic reforming reactions [35,49,50].

However, the influence of different support structure has barely been investigated comprehensively over Ni-based OCs in CLSR process in a fixed-bed reactor. Following the above considerations, we synthesized a group of Ni-based OCs with different support structure, including Ni/Al_2O_3, Ni/MMT, Ni/Al-MCM-41 and Ni/SBA-15, The properties of OCs were studied using N_2 adsorption–desorption, X-ray diffraction (XRD), inductively coupled plasma optical emission spectroscopy (ICP-OES), transmission electron microscopy (TEM), H_2 pulse chemisorption, H_2-temperature programmed reduction (H_2-TPR) and thermogravimetric analysis (TGA). The effect of support morphological structure on the catalytic and redox performance of OCs was evaluated in CLSR process.

Experiment

Oxygen carrier preparation

The conventional Ni/Al_2O_3 alloy OCs were prepared by co-precipitation method with a rising pH technique [9]. The Ni/MMT OCs with a lamellar structure were synthesized by an ultrasound assisted cation exchange impregnation method

Please cite this article in press as: Wang K, et al., Effect of support on hydrogen production from chemical looping steam reforming of ethanol over Ni-based oxygen carriers, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.07.261