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Hydrogen generation from chemical looping reforming of glycerol by Ce-doped nickel phyllosilicate nanotube oxygen carriers

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ABSTRACT

This paper describes the synthesis of a series of xCeNi-PSNT (phyllosilicate nanotube) oxygen carriers (OCs) and presents the effect of Ce loading on the performance in chemical looping reforming (CLR) of glycerol. Various characterization techniques including N_2 adsorption-desorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), H_2 temperature-programmed reduction (TPR), X-ray photoelectron spectra (XPS) and O_2 volumetric chemisorption were employed to investigate the physicochemical properties of the fresh and used OCs. The characterization results demonstrated that the PSNT structure possessed strong confinement effect and that the Ce promotion improved Ni dispersion and the reducibility of NiO particle and isolated Ni ions. The enhanced reducibility significantly shortened the dead time in the fuel feed step, resulting in the high H_2 generation efficiency. The reactivity and stability tests were conducted in a fixed-bed reactor. A Ce/Ni mass ratio of 0.5 was optimized for CLR with an average H_2 yield of 12.5 wt%, an average NiO conversion of 67%, and an accumulated coke deposition of 3.8 wt% in a 10-cycle stability test. The confinement effect of PSNT and Ce promotion both have positive effects on attaining the excellent performance.

1. Introduction

Recently, hydrogen generation using steam reforming has received extensive attention due to its attendant environmental benefits [1,2]. However, the rapid catalysts deactivation arising from coke deposition and sulphides poison is a main challenge in steam reforming. To conquer this problem, researchers have proposed a chemical looping reforming (CLR) process, where the catalysts are regenerated by air [3]. For the fixed-bed reactor configuration, it is performed by alternatively exposing the oxygen carriers (OCs) to reducing condition, where the OCs contact with the fuel to produce hydrogen, and oxidizing condition, where the OCs contact with air to remove coke deposition, by switching the feed gas [4–6]. Furthermore, in a sorption enhanced chemical looping reforming (SE-CLR) process, the oxidation of reduced OCs and coke deposition could provide heat to regenerate the saturated sorbent. Hence, the main issue related with the performance of CLR process lies in the development of the advanced OCs. Adanez et al. [7] have proposed that the excellent OCs should fulfill several characteristics such as high oxygen mobility (OM), high resistance to sintering, high catalytic reactivity and limited cost.

Previously, Mattisson et al. [8] have compared different transition-state metal oxides as the active phase of OCs such as Ni, Cu, Fe and Mn supported on SiO_2 and $Mg_2Al_2O_4$, and the results conclude that Ni-based particles are the most feasible OCs for both chemical looping combustion (CLC) and CLR. Van Sint Annaland et al. [9] further investigated the feasibility of a commercial $NiO/CaAl_2O_4$ catalyst using as a potential OC in low temperature (400–700 °C) CLR applications for hydrogen production. In spite of the excellent reactivity of current Ni-based OCs, the main obstacles for its successful application are the rapid deactivation aroused from metal sintering due to the low Tammann temperature of Ni and insufficient oxygen mobility because of the high activation energy (2.23 eV in CLR) of oxygen anion diffusion of NiO [10,11]. A means of suppressing Ni nanoparticles sintering and improving its dispersion is to confine them in well-defined cavities or channels [12]. The phyllosilicate nanotubes (PSNT) have exhibited excellent thermal stability and uniform pore size distributions, and Gong et al. [13] have reported that the nickel PSNT shows high resistance to coke and sintering due to the confinement effect in an ethanol steam reforming process. Enhancing the oxygen mobility of OCs is a key issue in shorten 'dead time' to improve the hydrogen production

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Table 1
Physical properties of fresh OCs.

Sample	Ni content[a] (wt %)	Ce content[a] (wt %)	BET surface area[b] (m²/g)	Pore volume[b] (cm³/g)	Pore size[b] (nm)	NiO Crystal size[c] (nm)	Dispersion[d] (%)	Microstrain[e] (%)
Ni/PSNT	25.2	–	200.0	0.51	14.2	12.3/15.9	19.3	0.528
0.1CeNi/PSNT	25.3	2.6	170.2	0.43	14.0	9.8	23.5	0.912
0.25CeNi/PSNT	25.9	5.7	162.3	0.32	13.1	9.3	26.1	0.967
0.5CeNi/PSNT	24.7	12.3	120.7	0.25	13.4	5.2/6.1	39.8	1.876
1CeNi/PSNT	24.0	24.2	80.3	0.12	8.1	11.5	31.2	0.751

[a] Determined by ICP-OES.
[b] Determined by N_2 adsorption-desorption.
[c] Determined from Scherrer's equation from the NiO (2 0 0) plane in XRD patterns, before stability test/after stability test.
[d] Determined from H_2 pulse chemisorption.
[e] Determined from the broadening of XRD lines.

efficiency [14]. It has widely accepted that Ce would easily release lattice oxygen under reducing conditions to create anionic vacancies correlated to high lattice oxygen mobility [15]. Tada et al. [16] have demonstrated that the Ceria incorporation is conducive to promote the reduction behavior of Ni-based catalysts.

Therefore, it is of interest to study the effect of combining PSNT with Ce modification on the CLR performance of Ni-based OCs. This work describes the synthesis of a series of xCeNi/PNST OCs and investigates their performance in a CLR process. Various characterization techniques were used including N_2 adsorption-desorption, X-ray diffraction (XRD), transmission electron microscopy (TEM), H_2 temperature-programmed reduction (TPR), X-ray photoelectron spectra (XPS) and O_2 volumetric chemisorption. The activity and stability tests of CLR were conducted in a packed-bed CLR reactor.

2. Experimental

2.1. Preparation of OCs

The synthesis of all the OCs was based on an alkalinity-tuned hydrothermal method [13]. The Ni loading was fixed to 25 wt% for all OCs and the Ce/Ni weight ratios x of the OCs were tuned, i.e., x = 0, 0.1, 0.25, 0.5 and 1. In a typical procedure, 1.649 g of NiCl₂·6H₂O (Aladdin, 99.9%) and a certain amount of CeCl₃·7H₂O (Aladdin, 99.9%) were dissolved in 120 mL deionized water, followed by adding 40 mL Na_2SiO_3 (0.5 mol/L). Then, the mixture was stirred for 10 min, sealed in an autoclave and maintained at 210 °C for 24 h. The precipitates were firstly centrifuged and then washed for several times with deionized water. The obtained solid was dried at 80 °C and calcined at 700 °C for 4 h.

2.2. Characterization and activity tests

XRD was performed with a 2θ range from 10° to 80° by the graphite filtered Cu Kα radiation (λ = 1.5406 Å). The N_2 adsorption-desorption was used to characterize the physical texture of OCs by a Micrometrics Tristar 3000 analyzer at 77 K. The morphology of OCs were obtained from a HRTEM (FEI, Tecnai F30) at 300 kV. H_2-TPR was carried out to detect the metal support interaction (MSI) by a Micrometrics Autochem II device, and a flow rate of 30 mL/min of 10% H_2/N_2 was introduced for reduction. The O_2 volumetric chemisorption was also conducted by the same instrument of TPR. The sample of 0.1 g was first pretreated under an Ar flow of 30 mL/min at 400 °C, and H_2 pulses were injected every 2 min till the maximum reduction, followed by pulsing O_2 every 2 min. The XPS measurement was recorded on a ThermoFisher ESCALAB 250Xi with an Al anode X-ray monochromator. The activity and stability tests were performed in a packed-bed reactor, and the configuration of the reactor is described in our previous studies [17,18]. The OC of 1 g was placed in the middle of the reactor. In the fuel feed step, the mixture of glycerol and water with a steam to carbon ratio (S/

C) of 3 was injected into the evaporator at a flow rate of 4 mL/h. The N_2 as a carrier gas was also introduced into the reactor at a flow rate of 150 mL/min. The reaction temperature was set at 650 °C. In the air feed step, the reaction temperature were same as the fuel feed step, and the air flow rate was 100 mL/min. The reaction durations of fuel feed step and air feed step were 3600 s and 250 s, respectively. The effluents were analyzed by a gas chromatograph (GC, Agilent 7890A) with two detectors. One is a thermal conductivity detector (TCD) with a TDX-01 column using helium as a carrier gas to analyze the species including H_2, CO, CO_2 and CH_4, and the other is a flame ionization detector (FID) with a Porapak-Q column using nitrogen as a carrier gas to measure the concentration of $C_3H_8O_3$, H_2O and CH_3CHO. The calculation method of NiO conversion, H_2 yield, glycerol conversion and steam conversion are shown in ref [19]. The coke elimination amount, Ni conversion and production selectivity are listed below.

$$Coke\ elimination\,(wt\%) = \frac{\int \frac{0.79 \times F_{air} \times y_{co_2}}{y_{N_2}} \times Ar_c\,dt}{m_{cat}} \times 100\% \tag{1}$$

$$F_{Ni \to NiO} = 2F_{O_2} - F_{out,dry} \times (2y_{O_2} + y_{CO} + 2y_{CO_2}) \tag{2}$$

$$S_{H_2} = \frac{3}{7} \times \frac{F_{H_2,produced}}{F_{gly} \times X_{gly}} \times 100\% \tag{3}$$

$$S_j = \frac{F_j \times i}{\sum F_j \times i} \times 100\% \tag{4}$$

where F represents the molar flow rate, Ar_c represents the relative atomic mass of carbon, m_{cat} represents the mass of catalyst, j represents the carbon containing species including CH_4, CO, CO_2, and CH_3CHO, and i represents the number of the carbon atoms in this species.

3. Results and discussion

3.1. Characterization of fresh and used OCs

As shown in Table 1, the Ce doping has a remarkable influence on the physical texture of prepared OCs; e.g., the decreased BET surface area and pore volume, suggesting the successful incorporation of Ce. Additionally, the blockage of the entrances by the Ce doping also contributes to the decease of the surface area and pore volume. In contrast, the active surface of the prepared OCs gradually increased until the Ce/Ni mass ratio reaching 0.5. Zhang et al. [16] have reported that the coexistence Ce in NiCe/SBA-16 would significantly improve the Ni dispersion, and that the positive influence of Ce on controlling the Ni sizes appeared to result from the interaction of Ni-Ce mixed oxide formed. Moreover, it has been demonstrated that Ni crystallites could spread over the CeO_2 at Ni-CeO_2 interface under reducing atmosphere and elevated temperatures and be stabilized by strong MSI, thus improving Ni dispersion [20].

The XRD profiles of fresh is shown in Fig. 1a. All the samples show