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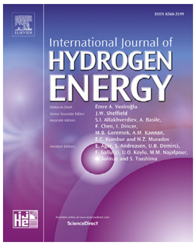

Stability of complex catalyst with NiO@TiO_2 core-shell structure for hydrogen production

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ABSTRACT

Core-shell NiO@TiO_2 and CaO complex catalyst was prepared to improve stability used in the reactive sorption-enhanced reforming (ReSER) process for hydrogen production. NiO@TiO_2 as catalyst component was prepared by synthesizing $Ni(OH)_2$ as core via urea hydrolysis, by coating TiO_2 shell via adsorption phase reaction technique, and was mixed with nano CaO as CO_2 adsorbent to form a complex catalyst. The morphology of NiO@TiO_2 and the complex catalyst were characterized by means of TEM, EDS, XRD and N_2 physisorption measurements. Hydrogen production performance was investigated in a fixed-bed stainless steel reactor. Results showed that the complex catalyst with core-shell NiO@TiO_2 structure has 36 cyclic runs of the ReSER process for hydrogen production, while only nine cycle runs obtained without TiO_2 coated as shell. It was revealed that core-shell NiO@TiO_2 structure could increase the surface area of complex catalyst and promote the separation of NiO core particles. It was also found that the optimum TiO_2 coating time could obtain relative smaller NiO grain. And smaller initial NiO grain in core-shell structure would improve the stability of the complex catalyst.

Introduction

In view of environmental protection and energy structure, hydrogen production from natural gas is a promising process due to the least carbon dioxide emissions. Hydrogen production methods from natural gas include steam methane reforming (SMR) [1], dry reforming of methane (DRM) [2], partial oxidation of methane (POM) [3] and auto thermal reforming of methane (ATRM) [4]. Currently, steam methane reforming (SMR) is the primary process, but it needs to be followed by shift reaction and purification process to obtain high purity hydrogen [5]. Compared to the traditional steam methane reforming (SMR) process, sorption enhanced reforming process (SERP) is a much simpler process that operates in an intermediate temperature range (600–800 °C) and possesses higher methane conversion and higher outlet hydrogen concentration according to Le Chatelier's principle [6–11]. Reactive sorption enhanced reforming (ReSER) process is a potential technique for hydrogen production, which combines steam methane reforming, water-gas shift and CO_2 capture reactions in one reactor by employing a complex catalyst with Ni as catalyst component and nano CaO as CO_2 adsorbent component [12].

Compared to mechanical mixture of Ni catalyst and CO_2 adsorbent, complex catalyst in ReSER process has higher reforming reaction rate but with poor stability [13]. The stability was normally evaluated by the stable reaction-regeneration running cycles. Reaction-regeneration cycle included the reaction step in which CaO carbonated to $CaCO_3$ and the regeneration step in which $CaCO_3$ decomposed to CaO in the complex catalyst. The studies of improving the stability of complex catalyst mainly focused on increasing support surface area and dispersion of nickel by adding the additives and modifying the preparation methods, respectively [14–24]. Additives such as

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ZrO_2 [16] and La_2O_3 [17], were added into NiO–CaO/Al_2O_3 complex catalysts and obtained 20 and 30 stable reaction-regeneration cycles, respectively. Zhang et al. [19] prepared NiO–CaO/Al_2O_3 complex catalyst by hydrothermal precipitation method, and only 10 stable hydrogen production cycles was obtained. Xue [20] obtained 10 stable reaction-regeneration cycles by pretreatment of the nano-$CaCO_3$/Al_2O_3 support of complex catalyst at a high temperature. Satrio et al. [22,23] proposed a core (adsorbent)-shell (catalyst) structural complex catalyst by using a pan-rolling method, but only 3 stable reaction-regeneration production cycles was evaluated. Chen et al. [24] improved core-shell structural complex catalyst (core: CaO–$Ca_9Al_6O_{18}$; shell: nickel deposited on $Ca_5Al_6O_{14}$), that has a 60 stable reaction-regeneration cycles use $Ca_5Al_6O_{14}$ and $Ca_9Al_6O_{18}$ support, but the highest H_2 concentration was 93% and less care the sorption properties of the complex catalyst.

The studies above use Ni as shell. Alternatively, some researchers use Ni as core of core-shell catalyst in methane reforming process without CO_2 adsorption [25–31]. Song et al. [25] prepared a Ni(core)@SiO_2(shell) catalyst through the stöber method, which has a good catalytic activity for hydrogen transfer reactions of hydrocarbons. Lim [26] prepared a Ni(core)@ZrO_2(shell) catalyst via double template emulsion method which has a high activity and stability of methane steam reforming.

On the other hand, consider the functions of NiO and CaO both in the complex catalyst is important. Since the fact of calcium oxide performing the multiple carbonation-calcination cycles during the ReSER hydrogen production process, the different molar volume between CaO (16.7 cm^3/mol) and $CaCO_3$ (36.9 cm^3/mol) leads to structural changes in the complex catalyst [32]. Sun et al. [33] has disclosed that the sintering of CaO caused the changes in the catalyst microstructure and the baring of Ni active sites into CaO affected the activity of complex catalyst. Xu et al. [21] prepared a TiO_2 coated nano CaO/Al_2O_3 to protect the effect of nano CaO from sintering on NiO in the complex catalyst. Results showed that the stability of CO_2 sorption capacity was improved, but deactivation of the complex catalyst still appeared after 13 reaction-regeneration cycles since the growth of nickel crystal during the reaction-regeneration cycles.

In this work, a core-shell construction as NiO(core)@TiO_2(shell) were prepared by adsorption phase technique, and wet mixed with nano CaO to form a new complex catalyst. The performance of protection NiO directly from the influence of CaO in the complex catalyst has been studied. NiO size was controlled by the variation of TiO_2 coating operation conditions. The stability of the complex catalyst was evaluated in a fixed-bed reactor.

Experimental

Preparation and characterization of NiO@TiO_2 and CaO complex catalyst

Preparation of NiO@TiO_2 and CaO complex catalyst

First, the synthesis of nano $Ni(OH)_2$ was carried out by urea hydrolysis approach. Certain mole ratio of $Ni(NO_3)_2$ (analytical reagent, Sinopharm Chemical Reagent Co. Ltd.) and $CO(NH)_2$ (analytical reagent, Sinopharm Chemical Reagent Co. Ltd.) aqueous solution with little polyethylene glycol were mixed in a 3-neck round bottom flask and stirred continuously in water base of 90 °C for set time. Urea hydrolyzed at 90 °C releasing hydroxyl slowly, while $Ni(OH)_2$ generated. After finishing urea hydrolysis reaction and vacuum filtration, nano $Ni(OH)_2$ was washed with deionized water and ethanol.

Then, the preparation of $Ni(OH)_2$ (core)@$Ti(OH)_4$ (shell) was carried out by adsorption phase technique that has been described in the literature [34]. Thin water layer surrounding $Ni(OH)_2$ surface can act as a microreactor and provides the domain for surface coating reaction. Nano $Ni(OH)_2$ was ultrasonic dispersed in ethanol and dehydrated by heat-treated zeolite which was separated before next step to formed a suspension. Certain concentration of $Ti(OC_4H_9)_4$ (analytical reagent, Shanpu Shanghai Chemical Co. Ltd.) ethanol solution was added dropwise to the dehydrated suspension while stirring vigorously. After all of the solution was added, the resulting solution was stirred for 2–8 h at room temperature. Then $Ni(OH)_2$@$Ti(OH)_4$ particles were collected by vacuum filtration and washed by ethanol. Three kinds of $Ni(OH)_2$@$Ti(OH)_4$ particles were prepared under different TiO_2 coating operation conditions of 2 h, 4 h, 8 h, respectively.

At last, wet mixing approach was performed to prepare the complex catalyst. A mixture of $Ni(OH)_2$@$Ti(OH)_4$ as Ni precursor and nano $CaCO_3$ as CaO precursor was ultrasonic dispersed in ethanol, and then alumina sol (10%, Zibo Longao Co. Ltd., China) was added with sufficient mixing. The mixed slurry was dried and ground to a diameter of 0.43–0.85 mm. Material was calcined at 500 °C in air for 4 h and regenerated at 800 °C with 100% N_2 for 15 min.

These NiO@TiO_2–CaO complex catalysts were named ‘Cat1’, ‘Cat2’, ‘Cat3’ according to TiO_2 coating operation time of 2 h, 4 h, 8 h, respectively. The catalyst prepared without TiO_2 coated shell was a NiO–CaO complex catalyst and named ‘Cat4’ in this paper.

Characterization of the complex catalyst

The surface area and pore structures of the sorption complex catalyst were characterized by nitrogen physisorption in liquid N_2 at 77 K using a Belsorp apparatus (BELSORP-mini, Japan). The surface area was calculated according to the Brunauer-Emmett-Teller (BET) formula, and the pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) model. The microcrystallinity of the samples was measured by X-ray diffraction (XRD) on a Rigaku D/MAX-RA X-ray diffractometer (Japan) equipped with a copper anode; the measurement conditions were a voltage of 40 kV, a current of 40 mA, and a diffraction angle 2θ range of 10°–80°.

The morphology of the complex catalyst was characterized by field emission scanning electron microscopy (SEM, SU8010, Hitachi, Japan). The sample was placed on a double-sided conducting resin mounted on a sample holder, coated for 3 min using a gold semi-high-resolution coater and then observed at 3.0 kV. The distribution of the elements on the complex catalyst surface was characterized using energy dispersive spectrometry (EDS) at 26.0 kV.

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