INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 39 (2014) 18650–18658

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Syngas production by CO_2 reforming of coke oven gas over $Ni/La_2O_3-ZrO_2$ catalysts

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ARTICLE INFO

Article history:
Received 30 October 2013
Received in revised form
21 January 2014
Accepted 5 February 2014
Available online 25 February 2014

Keywords:
Syngas
CO_2 reforming
Coke oven gas
Ni catalyst
Coke deposition

ABSTRACT

Syngas production by CO_2 reforming of coke oven gas (COG) was studied in a fixed-bed reactor over $Ni/La_2O_3-ZrO_2$ catalysts. The catalysts were prepared by sol–gel technique and tested by XRF, BET, XRD, H_2-TPR, TEM and TG–DSC. The influence of nickel loadings and calcination temperature of the catalysts on reforming reaction was measured. The characterization results revealed that all of the catalysts present excellent resistance to coking. The catalyst with appropriate nickel content and calcination temperature has better dispersion of active metal and higher conversion. It is found that the $Ni/La_2O_3-ZrO_2$ catalyst with 10 wt% nickel loading provides the best catalytic activity with the conversions of CH_4 and CO_2 both more than 95% at 800 °C under the atmospheric pressure. The $Ni/La_2O_3-ZrO_2$ catalysts show excellent catalytic performance and anti-carbon property, which will be of great prospects for catalytic CO_2 reforming of COG in the future.

Introduction

As one of the important raw materials for organic chemical industry, methanol has been widely applied in the preparation of varieties of chemicals including formaldehyde, dimethyl ether and ethanediol [1]. With the amounts of fossil fuels available to us are gradually depleting, the use of methanol is an alternative way for us as prospective energy. As a remarkable fuel which can be mixed with gasoline and can provide the environmental carbon neutral, many efforts have focused on the research of methanol [2,3]. In addition, methanol can be considered as an excellent carrier, because it owns a more security when stored and transported. At present, the production of methanol is mainly from syngas, which is composed of H_2 and CO. Previously, syngas is almost exclusively produced by fossil energy, but the research of other ways for syngas preparation has gained much interest due to the increasing awareness of global warming and oil depletion [4,5].

Recently, more attention is paid to coke oven gas (COG) which is regarded as one of the prospective candidates for syngas production [6–9]. COG, a by-product in coke industry, which contains mainly hydrogen (58–60%), methane (23–27%), carbon monoxide (5–8%) and carbon dioxide (less than 3%). While there exists a huge waste of COG generated

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http://dx.doi.org/10.1016/j.ijhydene.2014.02.029

from the coking plants and just let off into the air. Obviously, it causes serious environmental problems, e.g. greenhouse effect and there is a huge waste of energy resources as well. To avoid the issues and find an applicable mean to make use of the high-energy gas, conversion of CH_4 in the H_2-rich gas selectively is of great interest in the future. During the past decades, various methods for producing synthesis gas from COG have been proposed [10,11]. Compared with steam reforming and partial oxidation, CO_2 reforming, also called dry reforming, exhibits certain advantages. First of all, it consumes two greenhouse effect pollutant gases. Meanwhile, if the reaction is performed under suitable ratio of CH_4 and CO_2, a syngas with H_2/CO proportion of nearly 2.0 can be obtained, which is a more suitable proportion for methanol synthesis [6]. What's more, the heat required for the endothermic reaction can be provided from other exothermic processes in the blast furnace [12].

CO_2 reforming of COG is a catalytic reaction. Nowadays, almost all of the efforts have been made to the research of catalysts for CO_2 reforming of CH_4 [13]. There has been a large amount of reported work focused on the reforming process over noble metals catalysts and Ni-based catalysts in recent years [14–16]. Nickel is regarded to be promising active metal due to the economical cost, wide availability and high catalytic activity. However, the major drawback for Ni-based catalysts is the deactivation caused by coke deposition, which will block the active sites on the surface of catalyst and further prevent the reactant gases getting access. Methane cracking and CO disproportionation are two main reasons for deactivation of catalyst [17]. Recently, many studies have paid attention to enhance the anti-carbon property of Ni-based catalysts. In order to improve the stability of Ni-based catalysts, a large number of supports have been widely studied, especially alkaline earth metal and rare earth metal oxides such as ZrO_2 and La_2O_3 [18,19]. Numerous composite oxides supports have been further employed, such as $MgAl_2O_4$, $CaO–ZrO_2$, $CeO_2–ZrO_2$ and others [20–22].

In this work, a series of Ni/La_2O_3–ZrO_2 catalysts synthesized by sol–gel method have been first used in the catalytic CO_2 reforming of COG at 800 °C under atmospheric pressure. The aim of the present study is to investigate the influence of Ni loadings and calcination temperature on the catalytic activity, long-time stability and coke deposition.

Experimental

Catalysts preparation

La_2O_3–ZrO_2 mixed oxides used as support were prepared by the sol–gel method. The raw materials $La(NO_3)_3 \cdot 6H_2O$ (2.31 g), $Zr(NO_3)_4 \cdot 5H_2O$ (34.84 g), citric acid (CA) and ethylenediamine tetraacetic acid (EDTA) were dissolved in distilled water of a molar ratio with total metal ion: EDTA: CA = 1: 1: 1.5 as reported [23,24]. The PH value was controlled at about 9.0 by the addition of ammonia. Then the solution was kept at 95–100 °C with violent stirring until the water was evaporated, and a gel was formed. Followed by drying at 130 °C overnight and the dried solid was calcined in flowing air at 600 °C for 5 h with heating rate of 5 °C min^{-1}.

The mixed oxides obtained were impregnated with an aqueous solution of nickel nitrate for 24 h at room temperature. Then the catalyst precursors were dried at 80 °C until the solution was evaporated and finally calcined in static air at 800 °C for 2 h. Meanwhile, several catalysts were also calcined at 600 °C, 700 °C, 900 °C for 2 h, respectively. The samples were crushed into particles through sieving with 20–40 mesh screens. The Ni mass fraction in the Ni/La_2O_3–ZrO_2 samples was controlled by changing the addition of nickel nitrate. The catalysts were denominated x %Ni/LZ–t ($x = 1, 3, 5, 10, 15$ and $t = 600$ °C, 700 °C, 800 °C, 900 °C), in which x represented the Ni mass fraction in the catalysts and t represented the calcination temperature, respectively. All catalyst particles were reduced at 800 °C for 1 h in a mixture gas of 15 mol% H_2/N_2 before reforming reaction.

Catalysts characterization

The chemical composition of the catalysts was analyzed by Shimadzu Corporation XRF-1800 operated at 40 kV and 95 mA using Rh target.

The BET surface structure of the calcined catalysts was characterized on Micromeritics ASAP 2020 instrument by N_2 physisorption at liquid nitrogen condition. Before measurements, all samples were degassed for 5 h at 300 °C.

XRD pattern of the calcined, reduced and used catalysts was recorded on a Rigaku D/Max-2550 instrument. Data was collected using Cu/Kα radiation with the scanning angle range of 10–90° at the rate of 6° min^{-1} to characterize the phase evolution of the catalysts.

Temperature-programmed reduction (TPR) measurement of the calcined catalysts was performed on Micrometrics AutoChem II 2920 instrument as follows. Before reduction, about 100 mg powder was pretreated under Ar flow for 30 min at 200 °C. Then the temperature was cooled down to 100 °C, and heated to 900 °C at the rate of 10 °C min^{-1} in a 10 mol% H_2/Ar stream with the total flow rate of 30 ml min^{-1}. The amount of hydrogen consumption was monitored by a thermal conductivity detector (TCD). An isopropanol trap was used to remove water generated during reduction.

TEM analysis of the reduced and used catalysts was employed on a JEOL JEM-200CX microscope operated at 100 kV.

The carbon deposition on the used catalysts was analyzed by TG–DSC using a NETZSCH STA 449 F3 thermal analyzer. About 30 mg sample was used for the test. The experiment was carried out by heating from room temperature to 900 °C at a rate of 10 °C min^{-1} in a mixture gas of 10 mol% O_2/N_2 with a total flow rate of 40 ml min^{-1}.

Catalytic activity measurements

The catalytic CO_2 reforming of COG was tested in a fixed-bed quartz tube reactor with the inner diameter of 6 mm. The temperature was controlled by sheathed thermocouple inside the furnace. Before reaction, about 0.5 g of catalyst was reduced in a mixture gas of 15 mol% H_2/N_2 at 800 °C for 1 h. Then the catalytic experiment was carried out at 800 °C by controlling the CH_4:CO_2 ratio to 1:1 which was under stoichiometric condition for the dry reforming of methane and