An experimental investigation on the deactivation and regeneration of a steam reforming catalyst

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ABSTRACT

The effectiveness and the deactivating behavior of a Ni-based catalyst were studied in the presence of H_2S during a steam reforming in order to investigate the effect of the sulfur poisoning during the process, and the physical properties of the samples were characterized through BET, XRD, TPR, and TEM. Methane gas with different levels of H_2S was subjected to the steam reforming reaction over the Ni-based catalyst in a small laboratory-scale evaluating device. Initially, the steam reforming reactions were carried out without H_2S in the feeding stream. Then various concentrations of H_2S, in the range of 20—150 ppm, were introduced to the feeding gas, and the catalytic activity was characterized in terms of the methane conversion. Tests were carried out at the atmospheric pressure in the temperature from 700 °C to 900 °C. The results show that the deactivating behavior of the catalyst strongly depended on the operating temperature and the H_2S concentration. After performing the poisoning studies, the regeneration of the catalyst was studied by the H_2S removal, the temperature enhancement or the steam treatment. It was found out that the poisoning at the low temperature was not recoverable by remove H_2S from the feeding stream. However, the poisoning at high temperature was easily reversed by the removal of H_2S. The activity of the sulfur poisoned catalyst can be well regained by the method of the steam treatment and Ni particles on the surface of regenerated catalyst have an average particle size about 12.1 nm.

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1. Introduction

The steam reforming is one of the most important methods in the production of hydrogen in industry [1—6]. It is a strongly endothermic reaction and is favored a high temperature and a low pressure. The reforming process is industrially operated at a high temperature above 700 °C over the nickel-alumina based catalysts [7,8]. The nickel-based catalysts are efficient but are sensitive to poisons such as sulfur [9,10]. Therefore, it usually requires a sulfur removal process upstream. When exposed to sulfur present in the reforming fuels, the catalysts adsorb the sulfur on its surface, causing a partial or complete loss of activity in the industrial steam reforming process [11,12]. The deactivation of the steam reforming catalysts due to the sulfur poisoning is a significant barrier to commercialize the hydrogen technologies.
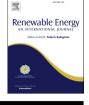
There are few studies on the sulfur poisoning of the steam reforming catalyst during the industrial applications. The catalytic performance of a model steam reforming has been determined in some previous studies [13—19]. The application of these results in an industrial reforming process still require the avoidance of the poisoning effect of some components present in the real complex stream. A Ni/La_2O_3 catalyst via a wet impregnation method for dry reforming of methane was shown that La_2O_3 derived from the $La_2O_2CO_3$ precursor maintained its initial morphology upon thermal treatment and could highly disperse Ni particles [15—17]. Most of the transition metals lose reforming activity in the presence of H_2S and other sulfur containing compounds. The deactivating rate is faster when the H_2S concentration is higher [20—25]. In principle, it is possible to regenerate the sulfur-poisoned reforming catalyst by removing the retained sulfur [26—29]. The regenerating process can be performed by the treatment of hydrogen, but its driving force is extremely small. The reversibility of a methane steam reforming has been reported at a temperature of 700—900 °C. If the operation temperature is below 700 °C, the regenerating reaction is irreversible [30—35].

The objective of this study was to investigate the deactivation

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and regeneration of a steam reforming catalyst during the sulfur poisoning. A Ni-based steam reforming catalyst was prepared and its performance in the presence of H_2S was tested by experiments. According to some reports [13–17], the deactivation of Ni/Al_2O_3 due to the sulfur poisoning is instantaneous, but its regeneration is a slow process. Some research groups have carried out researches on the deactivation and regeneration of the Ni catalyst during the steam reforming of model biogas [7–14]. Srinivas [13,14] reported that the deactivation and regeneration of Ni-based catalysts were studied during steam reforming of biogas containing ppm levels of H_2S. The regeneration methods, such as a sequential steam, steam-air, a steam-hydrogen treatment, and a high reaction temperature are ineffective to completely recover the activity of the sulfur-poisoned catalysts. In this study, the Ni-based catalysts with cerium additive were prepared by a simple impregnating method, which have better activity and stability in the presence of H_2S during a steam reforming. And we investigated the regeneration of the catalyst by the removal of H_2S, the temperature enhancement or the steam treatment techniques.

2. Experimental section

2.1. Catalyst preparation

$Ni(NO_3)_2 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, α-Al_2O_3 and the modified cement were used in the present study. All other chemicals were of the chemical reagent grade and used directly in the industrial production. The Ni-Ce steam reforming catalyst was prepared by a conventional impregnation method. Initially, the industrial α-Al_2O_3 powder with a certain amount of modified cement was produced to the special α-Al_2O_3 support (four hole rings with the average length of 16 mm, the outside diameter of 16 mm, and the hole diameter of 4 mm) after ball milling, pressing and molding. And then the α-Al_2O_3 support was calcined in air at 950 °C for 6 h to remove any volatile components present. The Ni-Ce catalyst supported on the α-Al_2O_3 was prepared by a wet impregnation method using nickel (II) nitrate hex-hydrate and cerium (III) nitrate hex-hydrate as precursors. Measured amount of metal precursors equivalent to the desired Ni (13 wt%) and Ce (1 wt%) loading was first dissolved in the distilled water of volume equal to or slightly over the total pore volume of the support. After impregnation, the wet samples were subsequently dried overnight at 120 °C and followed by the calcination at 750 °C for 6 h in the presence of air.

2.2. Catalyst characterization

The surface area and pore size distribution of the steam reforming catalysts were analyzed by a N_2 adsorption-desorption technique with a Quanta Chrome-Autosorb-1C Sorptometer. The BET surface area data were collected from a multipoint BET analysis of the nitrogen adsorption isotherms.

X-ray diffraction (XRD) patterns of fresh and used catalysts at wide ($2\theta = 10°$–$90°$) angles were measured by a Bruker D8 advanced X-ray diffractometer, with a Cu Kα radiation source ($\lambda = 0.15406$ nm) at 40 kV and 40 mA.

Temperature Programmed Reduction (TPR) experiments were performed in a gas flow system by the quartz tube reactor with an online TCD detector. A sample which is about 0.20 g loaded in a quartz tube reactor was maintained by a carrier gas with a N_2 flow of 40 ml/min at 120 °C for 0.5 h. Then each run was carried out at a heating rate of 10 °C/min from 80 °C to 980 °C under a hydrogen (5% H_2/N_2) flow of 40 ml/min. The hydrogen consumption was monitored by a mass spectrometer and the reduction curve of the sample was recorded by the recorder.

Transmission electron microscopy (TEM) was performed by using a JEM 2010 electron microscope at an accelerating voltage of 200 kV to examine the sample morphologies.

2.3. Steam reforming experiments

A scheme of the experimental set-up used to conduct steam reforming of methane was shown in Fig. 1. A quartz reactor tube was used to exclude the effect of reactor materials. The temperatures of the pre-heater and the reactor were maintained by the single-zone tube furnaces equipped with the temperature controllers. A K-type thermocouple was placed at the center of the catalyst bed to record and control its temperature. 1.5 g of the catalyst (50–60 meshes) was loaded into a tubular quartz reactor (10 mm outside diameter and 1 mm wall thickness). The catalysts were reduced and activated in a flowing H_2 gas of 30 ml/min at 750 °C for 2 h previously. Before the reaction starts, water was fed into a vaporizer by a metering pump. The water vapor and the raw material gas, methane or hydrogen, were mixed and pre-heated to 250 °C in a pre-heater. And then the pre-heated reagents were fed into the reactor. The steam reforming reaction was conducted at a steam to methane ratios of 3.0 with a CH_4 flow of 40 ml/min, and at the reaction temperature of 700 °C, 800 °C and 900 °C. The reactants and the reaction products of the outlet after condensing and separating were analyzed on line by gas chromatography. The methane steam reforming reactions were performed until reached a steady state. After reaching a steady state, H_2S was introduced into the reactor. The steam reforming reactions were conducted in the presence of H_2S and the samples were collected every 30 min until reaching a new steady state. The catalytic performance of catalysts was evaluated by the methane conversion rate in Eq. (1).

$$CH_4 \text{ conversion rate } (\%) = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100\% \qquad (1)$$

3. Results and discussions

3.1. Physical properties of catalysts

The Surface area and pore size distribution values of Al_2O_3 carrier, calcined catalyst sample, fresh reduced catalyst sample, spent poisoned catalyst sample and regenerated catalyst sample were showed in Table 1. The surface area of Al_2O_3 carrier calcined at 950 °C was 41.6 m^2/g. The calcined and reduced samples showed the lower surface area and pore volume compared to Al_2O_3 carrier, for the pore were occupied by the active ingredient and additive. The surface area and pore volume of poisoned sample was significantly lower than the fresh reduced sample. However, the surface area and pore volume of regenerated sample could be recovered to the fresh reduced sample.

Fig. 2 shows that XRD patterns of Al_2O_3 carrier, calcined catalyst sample, fresh reduced reforming catalyst sample spent poisoned reforming catalyst sample at 700°Cwith 150 ppm H_2S and regenerated catalyst sample after sulfur poisoning by steam treatment method. The characteristic peak of Al_2O_3 was observed in all samples at $2\theta = 37.8°$, $45.3°$, $67.2°$. The characteristic peak of $NiAl_2O_4$ at $2\theta = 45.5°$ was observed in calcined catalyst sample, fresh reduced reforming catalyst sample, used poisoned catalyst sample and regenerated catalyst sample, indicating its existence of stronger metal-support interaction. The calcined sample showed three diffraction peaks at $2\theta = 37.2°$, $43.3°$, $62.8°$, which indicating the presence of NiO. The Ni peaks were observed at $2\theta = 44.5°$, $51.9°$, $77°$ in fresh reduced sample, spent poisoned sample, and regenerated sample. No characteristic peaks corresponding to NiS