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Improving catalytic activity and stability by in-situ regeneration of Ni-based catalyst for hydrogen production from ethanol steam reforming via controlling of active species dispersion

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ABSTRACT

Nickel is an active component of catalyst for hydrogen production from ethanol steam reforming (ESR). However, Ni based catalyst usually meets severe deactivation due to coking. Normally, Ni catalyst regeneration could be achieved by heating coked catalyst in the oxygen contained atmosphere gas to remove coked carbon by oxidation of carbon. During this regeneration process, dispersed Ni particles are easily segregated because burning of carbon generates huge amount of heat and leads to uncontrollable temperature increase. In this paper, a new regeneration method of Ni catalyst was developed by re-deposition of another portion of Ni on deactivated Ni/SiO₂ catalyst (denoted as catalyst 2) instead of O₂ combustion of the deactivated catalyst (denoted as catalyst 1). H₂-TPR results indicated that the metal-support interaction of catalyst 2 was stronger than that of catalyst 1, leading to higher metal dispersion and smaller Ni particles size over catalyst 2. The H₂ chemisorption and HRTEM results indicated the dispersion of catalyst 2 reached 19.3%, much higher than 9.4% of catalyst 1. The dimension of late-loaded Ni particle was around 9.5 nm, even smaller than that of catalyst 1 (17.5 nm), corresponding to the high catalytic activity and stability of catalyst 2. The ethanol conversion of catalyst 1 and catalyst 2 were 76.5% and 94.6% at 500 °C, respectively. After short term of 20 h test, the ethanol conversion of catalyst 2 still remained, while that of the catalyst 1 decreased to about 40% of initial activity under same reaction condition (T = 550 °C, S/C = 7.5, LHSV = 4.1 h⁻¹ and P = 1 atm.).

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Introduction

Hydrogen is one of promising and clean carriers [1–3]. Presently, H₂ used in industries is largely produced from fossil fuels such as natural gas, liquefied petroleum gas and oil-

derived naphtha, etc [4–21], which produces a large amount of greenhouse gas CO₂. Biomass and biomass-derivatives are renewable hydrogen sources and its reforming is a closed carbon route theoretically because CO₂ could be reused in plant growth cycle [22–28]. Consequently, bioethanol steam

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reforming (ESR) for hydrogen production has received extensive attention because bioethanol is sustainable [29–35], cheap, easy to handle, low in toxicity, and thermodynamically feasible to decompose [36].

In ESR, the catalyst must catalyze the cleavage of C–C, C–H, and O–H bonds, and make the fragments recombining to produce H₂, CO₂ and CO. Noble metals (e.g., Rh, Ru, Pd and Pt) were found to be active components for ESR reaction because of their higher ability to break C–C bonds [37]. Nevertheless, their high costs and relatively low availability impeded the scaled-up usage in catalyst for ESR. For those transition metals, Ni is effective in breaking C–C and C–H bonds and shows high catalytic activity in ESR reaction, however, the main drawback of Ni-based catalysts is the relatively poor stability during reforming, the Ni catalyst goes severe deactivation by carbon deposition [38]. To address the sustainability of Ni-based catalysts, it is necessary to find a new suitable regeneration method to re-use the deactivated Ni-based catalysts.

It was well known that the regeneration of deactivated catalysts should be operated in economic, recyclable and environmental friendly way. Previous studies on catalyst regeneration were mainly involved in removing carbon via carbon burning in the oxygen contained atmosphere [39,40]. Simson et al. [41] studied the regeneration of carbon coked Rh/Pt catalyst after steam reforming of ethanol/gasoline mixtures. They found heat treatment in the air could remove carbon deposits and regenerated the catalyst to initial activity, but the deactivation occurred more quickly than the fresh catalyst. The similar results were reported by Roh et al. [42]. In addition, Sanchez et al. [43] reported the deactivated reforming catalyst could restore its catalytic activity via air combustion but its H₂ selectivity decreased quickly. Meanwhile a small portion of strongly adsorbed carbonaceous could still remain on the catalyst surface, which resulted in the next regeneration cycle of catalyst difficult. There are some other regeneration methods of coked catalyst such as steam and CO₂ treatments. Zhang et al. [44] reported carbon gasification regeneration of the FCC catalyst with steam. This process could produce high-quality syngas simultaneously during catalyst regeneration, but it is energy-consuming way. The use of CO₂ as a mild oxidant had similar results. Bednarczuk et al. [45] reported carbon deposition deactivated Ni/Y₂O₃ and Ni/La₂O₃ catalysts regeneration. In this process, the CO₂ treatment could partially recover their catalytic performance. The above results showed that the deactivated catalysts caused by carbon accumulation could be partly regenerated under the O₂ condition. But they deactivated again more seriously. Under steam and CO₂ conditions, the main problem was producing a large amount of CO, which was main by-product for ESR reaction. Accordingly, in order to solve the above problems, new methods for efficient catalyst regeneration were urgently to be developed and explored.

In this paper, a novel method, the impregnation of 1% Ni to deactivated Ni/SiO₂ directly (catalyst 2) was developed instead of burning of carbon in the oxygen-contained gas. By this new method, later-loaded Ni was dispersed over catalyst in such a highly dispersion state, which made catalyst 2 present high activity and stability for ethanol reforming. The H₂ chemisorption and HRTEM results indicated the dispersion of late-

loaded Ni particle reached 19.3%, much higher than 9.4% of O₂ treatment of the deactivated Ni/SiO₂ catalyst 1. The dimension of late-loaded Ni particle was around 9.5 nm, even smaller than that of catalyst 1 (17.5 nm). The catalyst 2 showed the superior activity, with respect to the catalyst 1 especially at 500 °C. The ethanol conversion of catalyst 1 and 2 were 76.5% and 94.6%, respectively. After short term of 20 h test, the ethanol conversion of catalyst 2 still remained, while that of the catalyst 1 decreased to 40% under same reaction condition (T = 550 °C, S/C = 7.5, LHSV = 4.1 h⁻¹ and P = 1 atm.).

Experimental

Catalyst preparation

1 wt.% Ni/SiO₂ catalyst was prepared by the impregnation method using Ni(NO₃)₂·6H₂O as a precursor. Prior to impregnation, the SiO₂ support (20–45 mesh) was calcined at 600 °C for 6 h in the air. After calcination, its specific area was 431 m² g⁻¹. Then Ni(NO₃)₂·6H₂O was dissolved in the distilled water first, and the solution was mixed with the calculated amount of SiO₂ support. After impregnation, the catalyst precursor was dried at room temperature for 24 h and at 110 °C for another 24 h. Finally, the precursor was calcined at 600 °C for 3 h in a muffle in the air.

The regeneration of the deactivated Ni/SiO₂ catalyst:

- The traditional catalyst regeneration method: After 20 h stability test, the deactivated Ni/SiO₂ catalyst was generated in a He/air (50/50) stream (120 ml/min) heating from room temperature up to 700 °C at 5 °C min⁻¹, maintaining this temperature during 3 h (denoted as catalyst 1).
- A novel catalyst regeneration method: 1 wt.% Ni/(deactivated 1 wt.% Ni/SiO₂) catalyst (denoted as catalyst 2) was prepared by the impregnation method using Ni(NO₃)₂·6H₂O as a precursor. Prior to impregnation, the Ni/SiO₂ catalyst stability experiment was carried out at mild conditions (T = 550 °C, S/C = 7.5, and LHSV = 4.1 h⁻¹) for 20 h during ESR reaction, which was regard as a support. Ni(NO₃)₂·6H₂O was dissolved in the distilled water first, and then the solution was mixed with the preparation of support. After impregnation, the catalyst precursor was dried at room temperature for 24 h and at 110 °C for another 24 h under the inert condition (N₂). Finally, the precursor was calcined at 600 °C for 3 h under the inert condition (N₂).

Catalyst characterizations

H₂ chemisorption over catalysts was performed on the Micromeritics Chemisorb 2750. Prior to H₂ absorption, 150 mg samples were put into the quartz tube reactor, and using He gas purged quartz tube 30 min. These catalysts were reduced in 5 vol.% H₂–He mixture (40 ml/min) at 600 °C for 2 h, then, the sample was cooled to room temperature with He gas flow. After this, opening loop of samples was tested.

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