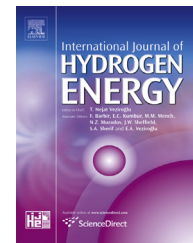


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Nickel supported on iron-bearing olivine for CO₂ methanation

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ABSTRACT

Calcined olivine supported nickel catalysts (Ni/olivine) were prepared by incipient wetness method and used for CO₂ methanation. To investigate the structure-activity relationships of the catalysts, the structure of the olivine during calcination and that of the Ni/olivine after calcination and reduction were illustrated by means of powder X-ray diffraction, temperature programmed reduction, Mössbauer spectroscopy and BET surface area measurement, and the CO₂ methanation were evaluated by using Ni/olivine with different calcination temperatures of the olivine, Ni loadings, calcination and reduction temperatures of the catalyst. It was found that the FeO_x phase formed on the surface of the calcined olivine was extracted from the olivine during its calcination, laying the base for the interaction between the surface FeO_x and the NiO supported. The Ni–Fe alloy as the effective active component was formed on the calcined olivine containing mainly (Mg_xFe_{1-x})₂SiO₄ and the thermal induced FeO_x phase, from the reduced NiO and the partially reduced FeO_x during the reduction of the Ni/olivine. The unreduced FeO_x between the active phase Ni–Fe alloy and the olivine body, as the very support of the Ni–Fe alloy, plays an important role in CO₂ methanation. With 6 wt.% Ni/olivine prepared under optimized condition as catalyst, at temperature of 400 °C and a H₂/CO₂ mole ratio of 6.0 and an hourly space velocity of 11,000 h⁻¹, the CO₂ methanation achieved 98% CO₂ conversion with 99% selectivity to CH₄. The Ni/olivine with strong resistance to coke deposition and abrasion could be a promising methanation catalyst, especially for fluidized bed operation.

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Introduction

Synthetic natural gas (SNG) could be produced by catalytic CO/CO₂ methanation from syngas of various origins [1–5]. Among variety of methanation catalysts, the supported nickel catalysts are predominant because of their good activity and selectivity and, important for commercial application, relative lower cost [6–9]. The activity and stability of nickel catalysts vary with support materials, promoters and preparation methods

[8,10–14]. Specifically, the supports with different specific surface area, thermostability, acidity and basicity, redox property and potential support-metal interactions could greatly influence the catalytic activity of supported catalysts [15–17]. The catalytic performance of nickel supported on Al₂O₃, SiC, SiO₂, MgAl₂O₄, Ce_xZr_{1-x}O₂, rice husk ash, etc. has been studied [8,10,11,13,15,16]. It was found that the lattice mismatch between the small Ni⁰ particles and the support γ-Al₂O₃ leads to the formation of an additional thin interface composed by mixed Ni–NiC_x or Ni₃C in Ni/γ-Al₂O₃, which could result in the

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detachment of the Ni-particles from the support during methanation of biomass-derived synthesis gas [18]. Nickel supported on SiC and MgAl₂O₄ shows better resistance to coke formation and sintering compared with Ni/γ-Al₂O₃ because of less acidity of the support and moderate interactions between the support and Ni [8,10]. Support matching with the supported metal was suggested to be a key factor in developing supported nickel catalyst with excellent stability [19]. Besides, the activity and stability of the supported catalysts could be improved by the supports via electronical modification and strong metal-support interaction (SMSI) [16,20,21], characterized by reducible supports and reduction treatment under high temperature (typically above 723 K). Based on the reducible nature of CeO₂ and TiO₂, M/CeO₂ and M/TiO₂ catalysts exhibiting some sort of SMSI effect were widely studied and used in various applications [22–25]. Catalytic methanation of carbon dioxide by active oxygen material Ce_xZr_{1-x}O₂ supported Ni–Co catalyst was reported by Hongwei Zhu et al. [16]. It was suggested that modifications of the structural and redox properties of the support could affect the catalytic performance, in particular, the active oxygen site of Ce_xZr_{1-x}O₂ can considerably improve the catalytic activity.

Compared to the traditional Ni-based catalyst, bimetallic Ni₃Fe or NiFe alloy were predicted to be more active and cost-effective than the traditional Ni-based catalyst for methanation by the DFT calculations [6,26,27]. Experimental works focused on this topic were also reported [15,28,29]. A.L. Kustov et al. found that bimetallic catalysts with compositions 25Fe75Ni at low metal loadings and 50Fe50Ni at high metal loadings were efficient for CO methanation [28]. Dharmendra Pandey et al. have systemically investigated the catalytic activities of Ni–Fe bimetallic catalysts for CO₂ hydrogenation and they found that Ni and Fe in the ratio of 3:1 supported on Al₂O₃, ZrO₂, TiO₂ and SiO₂ showed a higher CH₄ yield compared to the supported Ni catalysts [15,29]. Both works suggested that the Ni–Fe alloy formed in the Ni–Fe supported catalysts was effective for CO/CO₂ methanation.

Natural olivine with high attrition resistance and good catalytic activity for tar reforming was widely studied in dual bed gasification of biomass [30–34]. It contains (Mg_xFe_{1-x})₂SiO₄ as the main phase and small quantities of MgSiO₃ and FeO_x species [35–37]. The interactions between supported NiO and (Mg_xFe_{1-x})₂SiO₄ might lead to NiO–MgO solid solution formation [36], which was reported to be helpful in enhancing Ni species dispersion and stability of the Ni/olivine [36,38,39]. More importantly, the olivine could be a source of Fe for the supported bimetallic Ni–Fe catalysts. Through high temperature calcination, the iron in the bulk could partly be migrated to the surface of the calcined olivine in the form of FeO_x, thus, the redox property of olivine in regards of the iron oxides is controllable. In this way, calcined Fe-bearing olivine could be a potential support behaving in a different way from the inert supports, by providing suitable iron source for the formation of active site (Ni–Fe) and affecting its catalytic activity resulting from the distinctive metal-support relationship as well. Calcined olivine supported nickel (Ni/olivine) has been studied as a cheap steam-reforming nickel-based catalyst [35,36,40] and Ni–Fe alloys were achieved during reduction of the catalyst [36]. However, the calcination temperatures of Ni/olivine were generally as high as 1100 °C–1400 °C to enhance

the stability in these works. As a result, the NiO grafted with the support or integrated into olivine structure could hardly be reduced at a temperature well below 910 °C [36,41,42] and predictably has little catalytic activity for CO₂ methanation [43]. Ni/olivine or Ni–Fe/olivine prepared for methanation hasn't gained enough attention yet.

In the present work, olivine supported nickel catalyst and its activity for CO₂ methanation are reported. Thermal transformation of olivine and Ni/olivine during calcination and reduction has been illustrated by means of powder X-ray diffraction (XRD), temperature programmed reduction (TPR), Mössbauer spectroscopy, X-ray fluorescence (XRF) and BET surface area measurement. The effects of calcination temperature of the olivine, Ni loading, calcination and reduction temperature of the catalyst, and reaction temperature on the catalytic performance of the catalyst have been studied. The structure-activity relationships and the method for catalyst optimization are then proposed.

Experimental

Catalyst preparation

A natural occurring olivine received from the Chinese city of Yichang was used as catalyst support after calcination at different temperatures (600, 800, 1000 or 1200 °C) for 4.5 h. The Ni/olivine catalysts were prepared by impregnation of the calcined olivine (0.38–0.83 mm) with an aqueous solution of nickel nitrate by the incipient wetness method. Prior to impregnation, the supports were dried at 105 °C for 1 h. The impregnated supports were then dried at room temperature overnight, and heated in air up to different temperatures (350, 600 or 900 °C) with a heating rate of 3 °C/min and kept at the final temperature for 4.5 h. The prepared Ni/olivine catalysts were denoted as x Ni/y-olivine-z, where x (wt.%) represented the mass ratio of Ni to olivine in the finished catalyst, y the calcination temperature (in °C) of olivine and z the calcination temperature of impregnated catalyst. According to the results of XRF analysis, the content of Ni loading fits well within 12% accuracy of that aimed for in the catalyst preparation procedure. As an example, the composition of the 3 Ni/1000-olivine-350 by XRF analysis is given in Table 1. Here 3.28 wt.% NiO in catalyst equals to 2.66 wt.% Ni. A commercial catalyst M-849H provided by Dalian Catalytic Engineering Technology LTD. was used for comparison in this work. As shown in Table 2, it contains 47.33 wt.% NiO and equals to 37.18 wt.% Ni loading.

Catalyst characterization

Specific surface areas measurements of the supports and catalysts were carried out using BET method on the basis of

Table 1 – Composition of 3 Ni/1000-olivine-350 by XRF analysis (wt.%).

| MgO | SiO ₂ | Fe ₂ O ₃ | Al ₂ O ₃ | CaO | NiO |
|-------|------------------|--------------------------------|--------------------------------|------|------|
| 45.87 | 40.65 | 8.28 | 0.96 | 0.96 | 3.28 |

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