Applied Catalysis A: General 489 (2015) 42–50

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Characterization of olivine-supported nickel silicate as potential catalysts for tar removal from biomass gasification

Zhongkui Zhao [a], Nandita Lakshminarayanan [a], Scott L. Swartz [b], Gene B. Arkenberg [b], Larry G. Felix [c], Rachid B. Slimane [d], Chun C. Choi [d], Umit S. Ozkan [a,*]

[a] Department of Chemical and Biomolecular Engineering, The Ohio State University, 140 West 19th Avenue, Columbus, OH 43210, USA
[b] NexTech Materials, Ltd., 404 Enterprise Drive, Lewis Center, OH 43035, USA
[c] Gas Technology Institute, 1500 First Avenue, North, Suite L134, Birmingham, AL 35203-1821, USA
[d] Gas Technology Institute, 1700 South Mount Prospect Road, Des Plaines, IL 60618-1804, USA

ARTICLE INFO

Article history:
Received 6 August 2014
Received in revised form 2 October 2014
Accepted 5 October 2014
Available online 12 October 2014

Keywords:
Olivine
Nickel silicate
Thermal impregnation
Steam reforming
Tar removal
Biomass gasification

ABSTRACT

In this work olivine-supported nickel silicate, which was prepared by thermal impregnation is considered as a potential tar removal catalyst for cleaning the gas stream during biomass gasification. Previous work on Ni-olivine catalysts has shown that these catalysts have good activity for the tar-reforming reaction as well as good stability and tolerance to coking. In this work, various characterization techniques such as X-ray diffraction, X-ray photoelectron spectroscopy, laser Raman spectroscopy, temperature programmed reduction, temperature programmed reaction, and subsequent temperature programmed oxidation are employed to reveal the properties of the catalyst surface and bulk as well as their relationship to catalytic activity. Higher thermal impregnation temperatures produce stronger interactions between the active component and support, leading to better coke tolerance. Relative amounts of reducible Ni, Fe species and surface Mg have an influence on catalytic behavior. Moreover, compared to olivine, the Ni_2SiO_4/olivine catalyst exhibits good catalytic activity for dry reforming, water gas shift, reverse water gas shift and methanation reactions, as well as the steam reforming reaction.

1. Introduction

With the constant rise in petroleum prices, the use of biomass as a potential and promising renewable energy resource, partially replacing fossil fuels via biomass-to-liquid or biomass-to-gas processes has been receiving increasing interest [1]. Biomass gasification is currently a leading option for converting biomass to fuel or chemicals since many of the syngas utilization technologies have already been proven [2]. However, one of the most crucial technical barriers is the effective removal of the tar produced. Tar is a mixture of condensable aromatic compounds [3–5]. The higher molecular weight products of biomass gasification are collectively called tar and are known to be refractory and difficult to remove by thermal, catalytic or physical processes. Tar can also cause problems downstream in the processing clogging coolers, filters and suction channels [6]. Thus, tar removal is one of the major technological barriers to gasification technology. Several technologies are proven for the removal of tar [7–9], and catalytic tar conversion is a technically and economically interesting approach for gas cleaning [10,3,11].

Ni based catalysts [12–20] have been proved to be effective for eliminating tar from biomass gasification gas due to their high tar cracking activity, along with the additional advantages of steam reforming and water gas shift activity, which allows adjustment of the ratio of H_2 to CO in the product gas. However, there are two main limitations for Ni based catalysts: attrition and rapid deactivation by coke formation and sintering [21–26]. Olivine is a naturally occurring mineral with the general formula $(Mg,Fe)_2SiO_4$. Olivine is mechanically hard and attrition resistant, and thus been identified as a potential support material for nickel based reforming catalysts used in fluidized bed gasification processes [27–35].

In our previous work, the thermal impregnation technique has been developed to prepare the robust and coke-resistant olivine-supported nickel catalyst for tar removal [31–33]. In the present paper, a conventional ceramic processing route was employed, by using commercially available equipment and methods for preparing large quantities of the catalyst. Methane steam reforming is used as a model reaction. Various characterization techniques, such as X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), BET, Temperature-programmed reduction (TPR), Laser Raman

---

* Corresponding author. Tel.: +1 614 292 6623; fax: +1 614 292 3769.
E-mail address: Ozkan.1@osu.edu (U.S. Ozkan).

http://dx.doi.org/10.1016/j.apcata.2014.10.011
0926-860X/

Spectroscopy (LRS) have been used to study the catalyst surface and structural characteristics. Temperature programmed reaction experiments of methane steam reforming were performed to investigate the relative activity. Effect of calcination temperature and olivine geographical locations on catalyst nature and properties are also examined. Besides steam reforming, CO_2 dry reforming and water gas shift reaction are also examined since they are important in determining the ratio of H_2/CO, for the downstream utilization of biomass gasification gas.

2. Experimental

2.1. Catalyst preparation

A previously developed thermal impregnation technique [34] was used to prepare Ni_2SiO_4 (SiO_2 and NiO as precursors) and the olivine supported Ni_2SiO_4 catalysts (the synthesized Ni_2SiO_4 and the natural olivines as precursors). The difference is that the precursors were attrition milled for four hours with zirconia in isopropyl alcohol as the milling fluid, and then dried to a powder for initial mixing before calcination. The Ni_2SiO_4 was supported on olivine samples from different geographical locations and the high temperature calcination was conducted at either 1100 °C or 1300 °C.

2.2. Catalyst characterization

Surface area analysis (BET) was performed over both fresh and spent olivine and Ni-doped olivine samples by Kr adsorption at 77 K using a Micromeritics ASAP 2010 instrument. Kr was selected as the adsorbate molecule because of the low surface area of the samples ($<5\,m^2\,g^{-1}$). Before measurement, the samples were degassed under vacuum at 130 °C overnight.

The X-ray diffraction (XRD) patterns were obtained using a Bruker D8 Advance diffractometer with a Braun position sensitive (8°) detector. The spectra were obtained between 2-θ values of 20 and 45° using Cu $K_{\alpha 1}$ radiation (1.5406 nm) at 40 kV and 50 mA. Other experimental parameters were as follows: 0.014367° step size, 0.5 s step time, 1° divergence slit, 0.5° anti-scatter slit, and 0.75 in. detector width. The data were acquired with a 9-sample holder attachment using rotating polypropylene sample holders. Phase identification was done using The International Center for Diffraction Data (ICDD) library.

Laser Raman spectra (LRS) were collected on powdered samples under ambient conditions using a Horiba Jobin-Yvon LabRam HR800 spectrometer with a 633 nm helium–neon laser as the excitation source.

The surface characterization of the samples by X-ray Photoelectron Spectroscopy (XPS) was done with a Kratos Ultra Axis Spectrometer under high vacuum using a monochromatic Al source at 13 kV and 10 mA. The source was used in conjunction with analyzer mode, hybrid lens mode, and a slot aperture setting. The samples were ground into carbon tape and degassed first before being loaded into the analysis chamber. The height optimization for maximum signal was done by using the C 1s peak at 284.5 eV for correction. The charge neutralizer was set to a current of 2.1 A, bias of 1.3 V and a charge of 2.3 V. Each region was scanned 4 times. The deconvolution was performed using XPS Peak 4.1 program. Elemental surface composition was calculated using transmission values and relative sensitivity factors specific for the instrument equipped with an Al source.

The temperature programmed reduction (TPR) experiments were performed with AutoChem II 2920 using a quartz U-shape tube with 100 mg of sample. A pretreatment (30 mL/min He flow with hold at 900 °C for 10 min) was first performed. TPR was conducted with the reductive gas mixture (3 mL/min of H_2 and 27 mL/min Ar) flowing to the reactor as it was heated at a ramp rate of 15 °C/min from ambient to 950 °C, where it was held for 30 min. The TCD was used for quantitative determination of H_2 consumption and was calibrated using standards.

Temperature programmed reaction (TPRxn) experiments with CH_4 and H_2O (steam reforming of methane) were performed on an equal mass basis (100 mg) in a quartz U-tube reactor for the initial activity evaluation. The temperature was measured using K-type thermocouples. The effluent was monitored with a Cirrus RGA mass spectrometer using a Faraday detector. Before performing TPRxn, the reduction pretreatment was carried out. Pretreatment conditions were as follows: 20%H_2/He, 30 mL/min of total flow rate, ramped at the rate of 20 °C/min to 900 °C, and held for 30 min. After the pretreatment, the samples were cooled to ambient temperature in He and then 50 mL/min of the reactant mixture (2%CH_4 and 2%H_2O, He balance) was introduced to the reactor. The temperature was increased from ambient temperature to 900 °C at a ramp rate of 20 °C/min, and then held constant for 30 min. Following the TPRxn experiment, the flow was switched to He and the samples were cooled to ambient temperature in He atmosphere. Then temperature programmed oxidation (TPO) experiments were performed to study coking characteristics. The CO_2 (m/z 44) signal was used to characterize the relative amount of deposited coke. TPO experiment conditions were as follows: 6% O_2/He, 30 mL/min, ramp rate of 20 °C/min to 900 °C, and held for 15 min.

Experiments to probe the reaction network were performed with conditions similar to the TPRxn experiments. The samples (Ni_2SiO_4/olivine, olivine without nickel silicate was also included for comparison) were pre-reduced by using the same conditions as above. Based on the components of the simulated syngas, possible reactions including the Boudouard reaction (10% CO/He), methanation (10% CO and 20% H_2, He balance), CO_2 methanation (15% CO_2 and 20% H_2/He), water gas shift reaction (5% CO and 5% H_2O, He balance), reverse WGS (15% CO_2 and 20% H_2/He), CO_2 dry reforming (15% CO_2 and 5% CH_4, He balance) and CH_4 decomposition (5% CH_4/He) reactions were investigated. The temperature program was a ramp rate of 10 °C/min to 900 °C and a hold time of 15 min. In all cases, the 50 mL/min total flow rate of mixture gas was used.

3. Results and discussion

The olivine supported nickel silicate catalysts synthesized by thermal-impregnation technique were studied in detail. Various characterization techniques were employed to study the nature of the catalyst and the relationship between catalyst structure and properties. In order to compare catalytic activity, the temperature-programmed steam reforming of methane is used as a model reaction. The catalysts are compared based on their calcination temperature as well as the geographical location of the olivine support.

3.1. Comparison of olivine, bulk Ni_2SiO_4 and olivine-supported Ni_2SiO_4

In this section, the structure, nature and catalytic properties of the olivine with and without nickel silicate are discussed. Unsupported nickel silicate was also included for comparison. The olivine used is from Norway until indicated otherwise.

Due to low surface areas of the catalysts, BET experiments were done using Kr as the adsorption molecule. The surface area for Ni_2SiO_4, olivine and Ni_2SiO_4/olivine are 0.7, 0.1 and $2.0\,m^2\,g^{-1}$, respectively. Fig. 1 presents the X-ray diffraction patterns for the three samples. The pattern for Ni_2SiO_4 is also included for comparison. The patterns have been offset for clarity. The olivine sample pattern matches well with the olivine crystal phase and the miller