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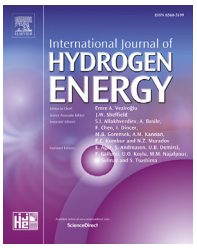

Effects of catalyst preparation parameters and reaction operating conditions on the activity and stability of thermally fused Fe-olivine catalyst in the steam reforming of toluene

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ABSTRACT

An iron-based olivine catalyst synthesized using thermal fusion (TF) was tested in a fixed bed reactor in the steam reforming of a biomass tar model compound. The effects of the catalyst preparation parameters (TF temperature, Fe precursor, Fe-loaded content and olivine support) and reforming reaction operating parameters (reaction temperature and steam to carbon (S/C) molar ratio) on the activity and stability of the TF-olivine catalyst were investigated. The physiochemical properties of the catalyst were analysed, using the following characterizations: X-ray fluorescence (XRF), X-ray diffraction (XRD), Raman spectroscopy, temperature program reduction (TPR) and X-ray photoelectron spectroscopy (XPS). The results showed that a higher TF temperature (1400 °C) promoted the interactions between Fe and olivine supports, part of the Fe was fused into the olivine structure to reorganize a new (Mg, Fe) Fe_2O_4 phase, which resulted in a high H_2 yield and a strong resistance to carbon deposition. Fe_2O_3-olivine showed the best effect for toluene conversion, while Fe/Ni-olivine presented the best performance for carbon resistance. Fe-olivine showed a strong ability to combine hydroxyls, and the yield of H_2 increased with the Fe-loaded content. Toluene conversion increased with the reaction temperature. When the S/C ratio was 1.06, the selectivity of carbon could decrease to 2.71%; meanwhile, the H_2 yield decreased slightly with the increase in the S/C ratio. Finally, the stability of TF-olivine catalyst was tested, and no inactivation was observed in the 48-h continuous catalytic reforming experiment.

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Introduction

The development of alternative renewable energy sources is becoming essential due to the depletion of fossil fuels and the requirement of reducing greenhouse gas emissions. Biomass as the only potential carbonaceous renewable source of energy is attractive. It can be converted and utilized via physical, biological and thermo-chemical processes [1,2]. Gasification is a particularly promising thermo-chemical process for converting biomass into syngas, which can be utilized for the synthesis of value-added chemicals and fuels or for power generation. The raw product of biomass gasification syngas commonly contains H_2, CO, CO_2, CH_4, trace C_2-C_5 hydrocarbons and tars [3–5]. Tar is an awkward by-product that is a mixture of complex polycyclic aromatic hydrocarbons (PAHs) that can be congealed at room temperature. Tar deposition could block gas pipelines, filter elements and power generation assembly [6–8]. In addition, the presence of tar also means a waste of energy and pollution to the environment. Therefore, it is necessary to decrease the tar content to avoid trouble in downstream processes.

One of the best methods to reduce tar concentration, i.e., the use of active and applicable in-bed material as the primary catalyst, has been investigated extensively in Fast Internally Circulating Fluidized Bed (FICFB) and Dual Fluidized Bed (DFB) [9–11]. Compared with a secondary catalytic reactor downstream of the gasifier, the primary catalyst could increase the carbon efficiency and promote more syngas production through tar reforming. Incidentally, it could also simplify downstream cleansing of treatment units [12–14]. A variety of in-bed materials for tar removal have been investigated. Single-component acid catalysts (such as Al_2O_3, SiO_2), alkaline catalysts (such as CaO, MgO) and multi-component natural mineral catalysts (such as dolomite, olivine, zeolites) have been used alone and after metal impregnation as tar reforming catalysts [15–18]. Olivine as a natural mineral shows a slightly lower catalytic activity than calcined dolomite, but its higher mechanical strength is more applicable as a primary catalyst in fluidized bed gasifiers [19,20].

In order to improve the olivine catalytic activities, it is a common method to load an active metal onto the olivine support. The most conventional loading method is fabrication by incipient wetness impregnation (IWI) in the corresponding salt solution. Active metals such as Co, Ce and Ni show good effects on tar reforming but are not frequently used because of their high cost and toxicity [21,22].

In contrast, cheap and nontoxic Fe-based catalyst has been developed and investigated due to the potential effectiveness of the different oxidation states in iron [23,24]. It has been proven that it has active ability for aromatic hydrocarbon (such as toluene, benzene) destruction through acting on the breaking of C–H and C–C bonds. Some studies have demonstrated that free iron (III) oxides on the surface of olivine are significant for tar removal [25–27]. At the same time, iron oxides are also known as promising catalysts for the water gas shift reaction, which can increase the hydrogen concentration and decrease CO production during gasification. The high H_2/CO ratio is beneficial for further applications (such as Fischer-Tropsch synthesis) [28,29].

Olivine catalyst prepared by the IWI method needs a high calcination temperature (~1100 °C) to strengthen the interaction between the active metal and olivine support, which can achieve a balance of activity and stability. In addition to these studies, an alternative method, i.e., thermal fusion (TF) of olivine-loaded metallic Ni catalyst, has been developed, and it presents higher reforming activity and lower carbon deposition rates compared with the catalysts prepared by TI and IWI for both naphthalene and methane [30–32]. The better performance of this catalyst is due to the high calcination temperature (1400 °C), which can strengthen the Ni metal-support interactions by formation of a NiO-MgO solid solution. The high temperature may lead to the exchange of Fe and Mg in the olivine structure and a possible alloying process, which can explain the high carbon resistance of the catalysts.

However, to date, no relevant literature works have reported the effect of iron-based olivine prepared by the TF method on tar destruction. Therefore, this research designs an Fe/olivine catalyst prepared by TF to compare the iron performances to those of nickel catalysts for toluene steam reforming. We investigated the influence of the olivine support, TF temperature, Fe content addition on olivine, Fe precursor, reaction temperature and S/C ratio on toluene-steam reforming. The work mainly focuses on the pivotal surface properties of the catalysts and the metal-support interactions essential for catalyst activity of toluene-steam reforming. These characterizations of TF-olivine were performed by several methods including X-ray photoelectron spectroscopy (XPS) and measurements of physiochemical properties (X-ray diffraction (XRD), X-ray fluorescence (XRF), temperature programmed reduction (TPR) and laser Raman spectroscopy (LRS)).

Experimental section

Catalyst preparation

The olivine catalysts used in this study were minerals from two different locations: Hubei province (HB) and Shanxi province (SX). Each sample was acquired without any chemical treatment and sized to the 380–830 μm range (20–40 mesh) by sieving. Then, the catalysts were calcined at 1400 °C in air for 4 h mixed with quartz sand (60–80 mesh), which was calcined at 1600 °C previously in order to prevent olivine from being fused together. Metallic Fe (5%, 10%, 15% by mass), as either Fe_2O_3 or a mixture of Fe and Ni, was incorporated onto the olivine support using the TF method and calcined at 1200 or 1400 °C by heating in an Ar atmosphere for 4 h. Following this treatment, olivine and quartz sand were separated by screening, and the olivine was used as the tar reforming catalyst.

Characterization techniques

The chemical compositions of TF-olivine catalysts were analysed by X-ray fluorescence (AXIOSmAX-PETRO).

The XRD analysis was characterized using X'Pert-PRO MPD equipment with Cu Kα radiation (λ = 1.54060 Å) at 40 kV and 40 mA at room temperature. XRD measurement was

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