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High catalytic performance of Fe-Ni/Palygorskite in the steam reforming of toluene for hydrogen production

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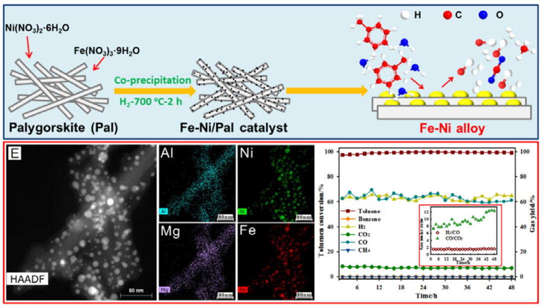
HIGHLIGHTS

- Palygorskite-supported Fe-Ni catalyst with the highly dispersion was prepared.
- Fe_3Ni_8/Palygroskite catalyst showed excellent performance for steam reforming of toluene.
- High H_2 (63%) and CO (60%) yields with stable H_2/CO molar ratio (1.55) were obtained.
- The formation of graphitic carbon was the main reason for the deactivation of the Fe_3Ni_8/Palygorskite catalyst.

GRAPHICAL ABSTRACT



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ABSTRACT

The inexpensive and abundant material, palygorskite, was used as a promising catalyst support to prepare Fe-Ni/Pal catalysts. Catalytic steam reforming of toluene as a biomass tar model compound over these catalysts was investigated in a fixed-bed reactor under different parameters, including reaction temperatures and S/C molar ratios. The stability and lifetime of Fe_3Ni_8/Palygorskite catalyst was evaluated under optimal conditions and its kinetic parameters were determined as well. The fresh and used catalysts were characterized using X-ray diffraction (XRD), H_2 temperature-programmed reduction (H_2-TPR), transmission electron microscopy (TEM), and Raman spectra. The results showed that the Fe_3Ni_8/Palygorskite catalyst with high dispersion was successfully prepared and exhibited superior catalytic performance compared with those of the monometallic catalysts (Fe_3/Palygorskite and Ni_8/Palygorskite) and the bare Palygorskite. Increasing the reaction temperature from 500 °C to 700 °C was beneficial for the toluene conversion and gaseous yields. The catalytic activity of Fe_3Ni_8/Palygorskite varied distinctly with the increase of S/C molar ratio and reached maximum at the the S/C molar ratio of 1.0. The apparent activation energy of 41.55 $kJ\,mol^{-1}$ and the pre-exponential factor of $1.35 \times 10^3\,m^3\,kg^{-1}\,h^{-1}$ were obtained for Fe_3Ni_8/Palygorskite in kinetic studies under optimal reaction conditions, respectively. The carbon deposition analysis of the used catalysts revealed that the formation of graphitic carbon rather than amorphous carbon was the main reason for the deactivation of Fe_3Ni_8/Palygorskite catalysts. When ceased the injection of steam into the reaction system, the graphitic carbon would be accelerating formed on the surface of

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the Fe_3Ni_8/Palygorskite and decreased its catalytic activity for toluene conversion. But owing to the water gas shift reaction, the catalytic activity of Fe_3Ni_8/Palygorskite seemed to recover gradually to its optimum.

1. Introduction

Biomass gasification is a promising method to convert biomass into clean fuels such as H_2, CO, CH_4, and other useful chemicals [1–3]. However, one of the significant problems is the tars formation in biomass gasification. Tars are known to cause several problems due to their condensation such as blocking pipes and filters, forming carbon deposits and deactivating the catalysts [4]. Among the tar conversion technologies, catalytic reforming has been considered as the most effective approach for tar elimination [5].

Various metal-supported catalysts including Ni [6,7], Co [8,9], Fe [10–12], and noble metal-based (such as Rh-based [13,14], and Pt-based [15,16]) systems have been extensively employed for tar removal in biomass gasification. In particular, Ni-based catalysts have attracted much attention because of their high reforming activity and low cost. Nevertheless, the major drawbacks of Ni-based catalysts are their rapid deactivation and low stability due to coke deposition and the sintering of Ni components. Bimetallic catalysts have been found to exhibit better performance than corresponding monometallic systems, probably due to their activity, stability, and coke resistivity [17]. Therefore, some other transition metal additives (Fe, Co, Pd, Ru, Pt) [18–22] and supports [23] have been applied to improve the performance of Ni-based catalysts. Notably, Ni-Fe bimetallic catalysts have been proved to be effective for catalytic reforming of biomass tar, methane, and tar model compounds. Wang et al. [19] investigated the catalytic performance of Ni-Fe/Al_2O_3 catalysts in the steam reforming of biomass tar. The Fe atoms located on the surface of the alloy particles supply oxygen species to react with the carbonaceous intermediates enhancing catalytic activity, catalytic stability, and suppression of coke deposition. Li et al. [24] reported Ni-Fe/α-Al_2O_3 catalysts at a Fe-Ni ratio of 0.5 showed the best catalytic performance. The surface of Ni-Fe alloy particles was assumed to be the active site with high performance. It was also reported that the presence of Ni-Fe alloys can help suppress carbon formation [25].

Recently, extensive research has been focused on the utilization of natural mineral materials as the catalysts or supports due to their low-cost and physicochemical properties [26–28]. Palygorskite (Pal) is a silicate clay mineral with distinctive pore structure and high specific surface area. The chemical formula is $[(Mg_{5-Y-Z}R^{3+}_{y}\square_{Z})(Si_{8-X}R^{3+}_{X})O_{20}(OH)_2(OH_2)_4E^{2+}_{(X-Y+2Z)/2}(H_2O)_4]$, where R^{3+} for Al^{3+} and Fe^{3+}, $\square$ represents octahedral vacancies, and E^{2+} is an exchangeable cation [29]. In the previous work [30–35], the effect of catalyst preparation methods, additive types, and additive loadings on catalytic cracking of biomass tar over Pal-supported catalysts were studied. The results indicated that Pal possessed fair performance as a catalyst and presented excellent properties as a support. The addition of Fe could interact with Ni to form Fe-Ni alloy on the surface of Pal, promoting the catalytic activity of Nix/Pal for tar conversion. Although many researchers have studied the steam reforming of tar (or model compound of tar) over different Ni-Fe catalysts, the Ni-Fe supported on different supports might display different catalytic behaviors. Until now, there is rare studies focus on the utilization of this abundant and inexpensive material as a support to prepare the Ni-Fe/Pal catalysts for steam reforming of biomass tar. Thus, in this present study, we investigated steam reforming of toluene as a model compound of biomass tar over Pal supported Fe-Ni catalysts for H_2 production. The aims are to (i) investigate the effect of steam addition and reaction temperature on the catalytic performance of Fe-Ni/Pal catalysts, (ii) explore the deactivation and regeneration behaviors of Fe-Ni/Pal catalyst, and (iii) promote the functional application of Pal and these promising Pal supported catalysts in biomass utilization.

2. Experimental

2.1. *Catalysts preparation and characterization*

Toluene (Xilong Chemical Co., Ltd, Guangdong Province, China) was selected as a model compound of biomass tar due to its abundance in tar products [36]. Palygorskite clay mineral was collected from Anhui Mingmei Min Chem Co., Ltd. Crown Hill, Mingguang city, Anhui Province, China. Its particle size was less than 0.075 mm after extrusion and crushing. The purification of palygorskite clay following the same procedure in our previous work [31]. The chemical composition of Pal is measured as SiO_2 65.5 wt%, Al_2O_3 5.4 wt%, MgO 14.0 wt%, Fe_2O_3 3.2 wt%, a trace amount of another mineral 0.9 wt% and the ignition loss 11.0 wt% using a Shimadzu XRF-1800 with Rh radiation.

Pal-supported Ni and Fe catalyst (Fe_3Ni_8/Pal, 3, 8 denote the loading content of Fe and Ni in weight percent, respectively) was prepared by co-precipitation. In this work, $Ni(NO_3)_3{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ were chosen as the additive precursors. After co-precipitation, aging, centrifugation, and drying, the obtained samples were crushed and sieved to 0.85–0.425 mm (20–40 mesh) followed by calcination at 600 °C for 2 h in air atmosphere. The Fe_3/Pal and Ni8/Pal catalysts were also prepared by the same procedure and used as the reference samples.

X-ray diffraction (XRD) patterns of catalysts were recorded on D/max-RB between 5 and 70° at a speed of $2^\circ\ min^{-1}$ using a Cu Kα radiation generated at 50 kV and 40 mA. H_2-temperature programmed reduction (TPR) measurements were carried out using a quartz tube reactor with a mass spectrograph (MS, Hiden QIC-20) for detection of H_2. The surface area and pore structure of the catalysts were determined from 13-point BET-N_2 adsorption isotherms using a Novawin 3000e Surface Area and Pore Size Analyzer. Raman spectra of the used catalysts were obtained using a LabRAM HR Evolution by employing the 532 nm line of an argon laser. Transmission electron microscope (TEM) measurements were performed on JEOL-2010 FasTEM with an accelerating voltage of 200 kV. Total carbon deposition on the catalysts was performed on a Jena Multi N/C 2100 TOC/TN analyzer.

2.2. *Experimental system*

Catalytic reaction was performed at atmospheric pressure in a fixed-bed quartz reactor with an inner diameter of 12 mm and a length of 300 mm. A schematic diagram of the experimental system is shown in Fig. S1. Initially, the catalyst (0.5 g) was placed in the middle of the reactor and sandwiched by quartz wool. Prior to the catalytic reaction, the catalyst was in-situ reduced in H_2 ($30\ mL\ min^{-1}$) at 700 °C for 2 h (labeled as Fe_3Ni_8/Pal-raw). Afterwards, the residual H_2 was swapped out from the entire system by the inert carrier gas (Ar) with a flow rate of $100\ mL\ min^{-1}$. The temperature was set to the desired reaction temperature (500–700 °C) and kept for 30 min to achieve steady state. Toluene (3000 ppm) and water (0–2 times toluene concentration) were added by syringe pumps and balanced by argon ($100\ mL\ min^{-1}$). To avoid the condensation of toluene and water vapor, a heater was employed and attached to the gas path. The argon, toluene, and water were well mixed in a static mixer before entering the reactor. In this work, only toluene, benzene, and permanent gases (H_2, CH_4, CO_2, and CO) were analyzed by an on-line Shimadzu 2010 PLUS gas chromatograph equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Toluene conversion and gas yield were calculated according to the following relationships: