

Effect of Additives on Catalytic Cracking of Biomass Gasification Tar over a Nickel-Based Catalyst

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Abstract: The palygorskite-supported nickel (Ni/PG) catalysts were modified by loading with several additives (Fe, Mg, Mn, and Ce) by incipient wetness impregnation. The effect of the additives and their content on the catalytic activity of Ni/PG and H₂ yield in tar cracking was investigated. The catalysts were characterized by X-ray diffraction and transmission electron microscopy. The content of the additives affected the catalyst activity and the selectivity in tar cracking. Fe was the best species for promoting the performance of Ni/PG both in tar conversion and H₂ yield. Increasing the Fe loading amount over the Ni/PG catalyst was favorable for tar removal.

Key words: biomass gasification; tar; supported catalyst; palygorskite; nickel; additive; carbon deposition; tar removal

Technologies for utilizing renewable energy have attracted the attention of many governments and corporations due to the shortage of world energy and greenhouse effects caused by the emission of CO₂. Biomass energy is a topic of research because of its widespread sources and renewability. Among the biomass conversion processes, biomass gasification and power generation are the most promising. However, a major issue in biomass gasification is how to deal with the tar formed in the product gas, which would cause problems to the process equipment and the engines and turbines used in the application of the produced gas when it condenses. Thus, the removal of tar components (condensable hydrocarbons, which includes benzene, phenol, naphthalene, other oxygen-containing hydrocarbons, and complex PAH) from the product gas before it condenses is necessary [1]. It has been suggested that the catalytic cracking of gaseous tar species is the most promising technology by the adoption of active catalysts [2,3]. For the catalytic cracking of benzene, phenol, naphthalene, and other tar model compounds, there are two main series of catalysts: noble metal-based catalysts (Rh, Ru, Pd, etc.) [4–6] and transition metal-based (Ni, Co, Cu, etc.) catalysts [7–10]. The Ni-based catalysts are the only one close to the noble metal-based catalysts in activity, but it is much cheaper. Thus, Ni-based catalysts are regarded as

the best potential option for a tar catalyst although it often suffered from deactivation and sintering at high temperatures. Therefore, it is crucial to explore a new catalyst to avoid catalyst sintering and reduce the use of noble metals.

Recently, a catalyst modified by a small amount of a metal additive has caught the attention of researchers [11–13]. Additives added into Ni-based catalysts can improve the stability, selectivity, dispersion of active components, and coking resistance. Wang et al. [14] investigated the promotional effects of Ce, La, and Ca on the catalytic performance of Ni/ α -Al₂O₃ and Ni/ γ -Al₂O₃ catalysts. The results indicated that Ce was the best promoter among the three promoters tested and the effect of Ce loadings on the catalytic performance was investigated. Yang et al. [15] studied the promotional effect of Ce on the catalytic performance of 8%Ni/ γ -Al₂O₃. It was found that the addition of Ce decreased the activation energy of CH₄ and improved the resistance to carbon deposition of the catalyst. In addition, the effect of Ce loading on Ni/CeO₂-Al₂O₃ catalytic carbon dioxide reforming of methane was investigated by Wang et al. [16]. The results showed that a large amount of promoter generally decreased catalytic activity because of the coverage of active sites. The total oxidation of C₃H₆ was investigated over Au/Al₂O₃ and the effect of additives (Ce, Mn, Co, and Fe) on

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Au/Al₂O₃ was investigated by Gluhoi et al. [11]. The results indicated that the most active catalyst contained Ce, which was attributed to the lattice oxygen of the oxide. Yu et al. [17] investigated the effect of Ni-Fe/attapulgite on the steam reforming of apricot stone pyrolysis tar for hydrogen-rich gas. The results showed that the Ni-Fe/attapulgite catalyst had excellent low-temperature activity and coking resistance. The effect of MgO on Pt/Ni/CeO₂/Al₂O₃ catalytic reforming of biomass pyrolysis tar was investigated by Nakamura et al. [6]. The results showed that MgO played a crucial role in decreasing the reduction temperature of NiO, improving the dispersion of Ni and sintering resistance and enhancing the stability and catalytic activity of Pt/Ni/CeO₂/MgO/Al₂O₃.

Various additives and their loading have a significant impact on the resistance to sintering and carbon deposition, improving the stability and dispersion of the active component and catalytic activity of the catalyst. Palygorskite-supported Ni (Ni/PG) catalysts developed in our previous work have showed outstanding potential in the catalytic cracking of biomass tar but suffered from the above problems to some degree [18]. In this work, efforts were made on the modification of the Ni/PG catalyst by the loading of several additives (Fe, Mg, Mn, and Ce) to evaluate the influence of the additives on a 6%Ni/PG catalyst for the cracking rice husk gasification tar.

1 Experimental

1.1 Catalyst preparation

Palygorskite (PG) clay used was sampled from Crown Hill, Mingguang city, Anhui province, China. Its particle size was less than 0.074 mm after extrusion, cutting, and crushing. The contents of SiO₂, Al₂O₃, MgO, Fe₂O₃, and FeO in PG clay were 65.52%, 5.36%, 13.93%, 3.19%, and 0.42%, respectively. The specific surface area, pore volume, and maximum pore diameter were 228.5 m²/g, 0.41 ml/g, and 2.8 nm, respectively. PG was impregnated with metal salts by pore volume wetness impregnation. Ni(NO₃)₂·6H₂O (29.7 g), Fe(NO₃)₃·9H₂O (43.3 g), and 86 ml deionized distilled water were put in a 150 ml beaker. The mixed liquor was poured into 88 g PG clay after they were dissolved. The beaker was washed twice with 10 ml deionized distilled water. Then the compound was stirred for 20 min. After stirring, the impregnated samples were aged at room temperature overnight, dried at 378 K, cooled to room temperature, and ground and sieved to obtain particles of 20–40 mesh. The catalysts were finally calcined in an air flow at 773 K for 2 h and in a H₂ flow at 773 K for 1 h. After that, a 6%Fe-6%Ni/PG catalyst was obtained. The catalysts with different Fe loadings and including Mg, Mn, and Ce additives were also prepared using the same method.

1.2 Catalyst characterization

Powder X-ray diffraction (XRD) analysis of the catalysts

was performed on a Rigaku D/Max-rB diffractometer using Cu K_α radiation at 40 kV tube voltage and 100 mA tube current. The XRD patterns were taken in the range of 2θ = 5°–70° at a scan speed of 4°/min in an apparatus. Transmission electron microscopy (TEM) was performed on an H-800 apparatus.

1.3 Catalyst activity

Biomass tar derived from a rice husk gasification power plant was used as the raw material. The tar consisted of 79.2% C, 5.3% H, 1.6% N, 7.4% O, 5.3% ash, and a small amount of Cl and S. The fixed experimental conditions were temperature 973 K, reaction time 20 min, catalyst 10 g, tar concentration 0.45 g/min, and carrier gas (N₂) flow rate 80 ml/min. The rice husk gasification tar was pumped into the reactor with a peristaltic pump and the time was recorded from the first drop. The catalyst activity for catalytic cracking was evaluated by tar conversion, H₂ yield, and carbon deposition. The reference [19] is generally regarded as the standard for tar collecting and analysis, but in this work, granular activated carbon (GAC) was used for collecting unreacted tar and byproducts. The definition of tar conversion was $X(\text{tar}) = (m(\text{tar}1) - m(\text{tar}2))/m(\text{tar}1) \times 100\%$, where $m(\text{tar}1)$ and $m(\text{tar}2)$ represented the amount of tar pumped into the reactor and tar collected in the filter, respectively.

The noncondensable gases including hydrogen, nitrogen, carbon monoxide, and methane were collected by a gas collection bag, measured by a wet test meter, and analyzed by a gas chromatograph (GC-7890T) equipped with a C2000 column and a thermal conductivity detector (TCD) using argon as the carrier gas. The H₂ yield was calculated by $X(\text{H}_2) = m(\text{H}_2)/m(\text{H}_1) \times 100\%$, where $m(\text{H}_2)$ and $m(\text{H}_1)$ represented the mass of hydrogen contained in the catalytic cracking gas and hydrogen from reacted tar, respectively.

The amount of total carbon deposited on the catalyst was analyzed on a Multi N/C 2100 analyzer.

2 Results and discussion

2.1 Effect of additives and additive loading on 6%Ni/PG catalyst activity

The effects of Fe, Mg, Mn, and Ce on 6%Ni/PG catalyst catalytic cracking of biomass gasification tar are shown in Fig. 1. Only 64% tar conversion was observed over 6%Ni/PG. The addition of additives played a different role in tar conversion. Among the additives, the addition of Mg, Mn, and Ce improved the catalyst activity in catalytic cracking of tar with low additive loading. However, the promotion became weak with increasing additive loading. Especially, the addition of Ce even decreased the catalyst activity in the catalytic decomposition of tar when the Ce loading was more than 6%. These results indicated that the promotion by Mg, Mn, and Ce on the

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