Effect of Promoters on Steam Reforming of Toluene over a Ni-Based Catalyst Supported on Coal Gangue Ash

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ABSTRACT: The exploration of high-value-added materials using inorganic solid waste is a very important contribution to sustainable development. Coal gangue ash (CGA) as a solid waste was chosen as catalyst support. Five low-cost catalysts modified by different promoters (Co, Ce, Fe, Mn, and Mo) were prepared using a co-impregnation method. The toluene steam reforming tests were carried out at 800 °C under S/C = 2 (steam-to-carbon mole ratio). Catalyst characteristics were evaluated using X-ray diffraction (XRD), the Brunauer–Emmett–Teller (BET) method, temperature-programmed reduction (TPR), and Raman spectroscopy. The results showed that most promoters could interact with a Ni active compound and enhance the toluene conversion and H2 yield. The Mo-Ni/CGA-1d (1d means the acid pretreatment time) catalyst performed the best catalytic activity, and corresponding toluene conversion and H2 yield was equal to 92.6 and 62.3%, respectively, and it should be due to the formation of Mo-Ni alloy. Meanwhile, the Mo-Ni/CGA-1d catalyst exhibited higher stability during the runtime of 300 min compared with the Mn-Ni/CGA-1d catalyst, which can be attributed to the formation of the Mo2C structure with high-carbon-resistance ability. This is perhaps because the dissociation of CO2 or H2O on the Mo2C structure surface is beneficial to the production of free oxygen species, which can accelerate the removal of carbon deposition on the catalyst surface.

1. INTRODUCTION

Recently, the lack of fossil fuel is increasingly becoming a global concern. Biomass conversion, as well as utilization, has been regarded as one of the most promising solutions to satisfy the increasing energy demand. Thermochemical conversion of biomass by gasification is an attractive process to produce syngas (a mixture of hydrogen and carbon monoxide), which can be used to produce liquid hydrocarbons and oxygenates.1,2 However, the presence of tar in syngas remains a significant barrier to limit the further development and commercialization of biomass gasification technology. The tar mainly is a mixture of condensable aromatic hydrocarbons such as single-to-polyaromatic aromatic hydrocarbons (PAHs). Cleaning the final syngas is hence essential. Among all different cleaning technologies, the use of catalysts to destroy the by-product tars should be the most interesting solution. There is no need to remove tars in downstream flows, and the energy efficiency is improved due to the conversion of tars into useful producer gas.3 Due to the complexity of tar components, including toluene, benzene, naphthalene, phenol, glycerol, PAH etc., many researchers select toluene as a tar model due to its stable aromatic structure apparent in tar forming processes,4–6 which is also adopted in this work.

Catalytic reforming is one promising technique for tar conversion during biomass gasification. The catalysts being employed are responsible for both purification and compositional adjustment of the product gases to improve production efficiency while not damaging downstream application. It is known that Ni-based catalysts are active in tar reforming, and the effects of supports, additive oxides, and other metals on the catalyst performance have been widely investigated. Previous reports suggested that the Al2O3 was widely used as a catalyst support due to its high mechanical strength, tuneable textural properties, and availability.7–10 In addition, natural mineral (olivine and dolomite),11–13 zeolite,14 zirconia,15 magnesium oxide,16 silica,16 etc. also were selected as carriers by many researchers. However, Ni is very active for the undesired methanation and coke formation reactions, and it has low activity for the desired water-gas shift reaction.17

Therefore, the modification of Ni-based catalysts by incorporating metal or metal oxide promoters has been widely studied in literature to increase their activity, reducibility, stability, and regenerability in the reforming of biomass tar. Mn, especially, has a high redox potential and improves
catalytic activity and coking resistance. The presence of a Ce promoter in the Ni/Al2O3 catalyst could enhance the H2 selectivity due to its unique properties resulting from the synergistic effect of the Ce promoter and preparation methodology for synthesizing Ce-doped-meso-Al2O3. The La promoter was proved to that could reduce the active metal size and suppress the sintering and coking of Ni/sepiolite catalysts due to the strong metal—support interaction. Alkaline-earth metals (MgO and CaO) have been incorporated into Ni/Al2O3 catalysts to reduce the acidity of Al2O3 support and decrease the coke formation rate, and MgO favors H2O adsorption and OH mobility on the surface, enhancing coke gasification. Alkali-earth-metal Ba also could improve the catalytic performance due to the electron donation from Ba to Ni on the Ba/Ni/LaAlO3 catalyst. Comparing with Ce and Zr promoters, the Fe-doped catalyst had higher catalytic activity and stability because of its high dispersion of active sites and accessibility of reactants to active sites. Meanwhile, the addition of Fe increased the amounts of lattice oxygen and adsorbed oxygen on the surface of the Ni/Al2O3 catalyst, and the lattice oxygen could oxidize the carbon deposited or intermediates on adjacent Ni atoms to inhibit the formation of coke deposited and adjust the syngas composition. Adnan et al. investigated the effect of incorporation of the Fe and Co on the Ce-ZrO2 catalyst during toluene reforming. They found that the Fe-Co/Fe-ZrO2 catalyst exhibited excellent performance due to the promotion of water-gas shift reaction, while the Ce-ZrO2 catalyst promoted CO2 reforming of methane. The performances of Ni–Co/Al2O3 catalysts with the optimum composition were much higher than the corresponding monometallic Ni and Co catalysts in terms of the catalytic activity, the resistance to coke formation, and the catalyst life in the steam reforming of biomass tar. It should be attributed to the synergistic effect between Ni and Co due to the formation of alloy. Similar results also obtained by Li et al. Mo-Ni catalysts have been extensively studied in literature as active and stable hydrodesulphurization catalysts. More recently, Mo-Ni catalysts were evaluated during hydrocarbon reforming and its resistance of coking during reforming has been observed; however, the addition of Mo to Ni had a negative impact on catalyst activity in some cases. According to above results, one or part of the metals (Co, Ce, Fe, Mn, and Mo) was popular to use as promoters due to their better performance improvement for relative catalysts in many studies. However, the difference of the effect of these promoters on catalyst activity is not clearly established in literature. Therefore, these popular metals (Co, Ce, Fe, Mn, and Mo) were selected as catalyst promoters to contrast their performance in this study.

Meanwhile, the catalysts that have been reported in tar reforming still face a great challenge to meet the actual requirements including low cost and high catalytic activity. To reduce the catalyst cost, some residual ashes from combustion or municipal solid waste incineration were paid more attention in the catalyst field in recent years, because the main constituents of these residual ashes are SiO2, Al2O3, Fe2O3, and CaO, which are common carrier materials. Wang et al. investigated the performance of the Ni/coal-ash catalyst during the typical bio-oil model compound reforming process, and they found that the Ni/coal-ash catalyst was comparable with other commercial Ni-based steam reforming catalysts. The performance of biomass tar decomposition over calcined coal gangue and γ-Al2O3 was contrasted using phenol as a model compound, and the results indicated that the performance of coal gangue was lower than γ-Al2O3, which may be due to the high content of SiO2 in gangue. Moreover, three combustion ashes (coal ash, refuse-derived fuel (RDF) ash, and waste tyre ash) were chosen as catalyst supports by Al-Rabbi et al. and corresponding catalysts after Ni loading were tested by the raw gas form wood pellet pyrolysis. They found that only a small influence of Ni addition to the combustion ashes in terms of the total gas yield, but the hydrogen yield increased obviously after Ni addition. It suggests that the combustion ashes performed better for catalytic performance due to the high metal content in them, and the loading of Ni is beneficial to the gas reforming. The coal bottom ash including the elements like Si, Fe, Al, Ca, and Mg can be used as a catalyst in biomass gasification. The Fe2O3 can improve the tar reduction in the product gas whereas CaO assists to capture CO2 in the gasification process. Tian et al. studied the catalytic activity of coal bottom ash for fuel gas production and tar elimination. They found that the existence of coal bottom ash could remarkably decrease the tar content to 0.97 g/Nm3. Above studies indicated that some solid wastes could be used as catalyst supports or catalysts and exhibited good catalytic performance under certain conditions.

It is known that coal gangue ash (CGA) is the major solid reject material that is produced in the coal mining and washing process. Due to increasing production and without effective treatment and disposal, CGA not only occupied lands but also polluted the water body, air, and farmland. The major oxides are SiO2, Al2O3, and Fe2O3 in CGA, implying that the CGA has great potential to be used as catalyst support. The reuse of CGA not only can reduce the negative effects caused by wastes themselves, such as occupation of land and pollution of the environment, but also can achieve the reutilization of wastes and reduce the catalyst cost.

To relieve environmental pressure and satisfy the demand for high-value-added utilization of coal gangue ash, we have studied the performance of Ni/CGA catalysts without promoters and optimized the condition of CGA acid pretreatment in previous work. The aim of this work is to further improve the catalytic activity of the Ni/CGA catalyst. Therefore, we prepare a series of catalysts modified by different promoters (Co, Ce, Fe, Mo, and Mn) and deeply investigate the effect of promoters on catalytic performance under the toluene steam reforming process. Finally, the catalytic performance stability of part catalysts with better activity was evaluated.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. The raw coal gangue ash (CGA) was obtained from a power plant in Henan province, China. First, the raw CGA was placed in a muffle furnace calcining for 2 h at 800 °C to remove residual carbon. Then, the calcined CGA was impregnated in nitric acid solution (2 mol/L) (solid-to-liquid ratio = 60 g/L) and stirred to remove some substances; the acid pretreatment condition was optimized for 1 day for CGA support as in previous work. Subsequently, the mixture was filtered using a vacuum filter, washed to neutral using deionized water, followed by drying for 24 h at 105 °C, and then calcined for 2 h at 500 °C. After above processes, the CGA after acid pretreatment was chosen as catalyst support. The catalyst with 15 wt % Ni and promoter Co (Co:Ni = 1:3, mole ratio) was prepared by co-impregnation; Ni(NO3)2·6H2O and Co(NO3)2·6H2O dis-
solved in ethanol followed by mixing with the CGA support after acid pretreatment. The precursor was stirred for about 12 h at ordinary temperature. Then, the resulting uniform mixture was heated to 80 °C with stirring until the complete evaporation of ethanol solvent, followed by drying at 105 °C for 24 h and calcining at 500 °C for 2 h in static air. The thermal-treated catalyst was crushed and sieved to obtain required particles with a size in the range of 0.25−0.43 mm. Then, other catalysts with different promoters (Ce, Fe, Mo, and Mn) also were prepared by the same method as above. These catalysts were named as M-Ni/CGA-1d (M: Ni = 1:3, mole ratio), with M representing Co, Ce, Fe, Mo, and Mn, and 1d representing the acid pretreatment time of raw CGA support. Meanwhile, the Ni/CGA (15 wt % Ni) was also prepared to compare with M-Ni/CGA-1d catalysts.

2.2. Catalyst Characterization. The chemical composition of CGA support was analyzed by using an XRF (X-ray fluorescence spectrometer (AxiosmAX Petro, PANAlytical B.V., Holland)). It uses 160 mA current, 4 kW full-power excitation, and five spectroscopic crystals to improve the detection effect of light elements. Before analysis, the samples should be pressed to pieces.

The X-ray diffraction (XRD) pattern of the fresh and spent catalysts was obtained by using an X′Pert Pro X-ray diffractometer (MPD, Holland) employing a Cu Kα radiation source operating at 40 kV and 40 mA. Data were collected over the 2θ range of 5−80° using a scan rate of 0.0167°. Meanwhile, Scherrer’s equation was used to calculate the mean size of metal particle.

The surface area and pore structure of the support and fresh catalyst were measured using Quantachrome apparatus (SiMP-10, America) by N2 adsorption−desorption at −192 °C. Before the measurement, all the samples were degassed at 150 °C for about 12 h. The specific surface area was calculated from the isotherm using the Brunauer−Emmett−Teller (BET) method. The pore distribution, average pore diameter, and cumulative volumes of samples were obtained by the Barret−Joyner−Halenda (BJH) method from the desorption branches of the N2 isotherm.

H2−TPR (temperature-programmed reduction) was conducted on a Quantachrome Chemstrat instrument (America). The power samples (50 mg) were outgassed at 200 °C for 1 h under flowing Ar to remove any moisture and impurities. After cooling to 50 °C, a flow rate of 10 mL/min of 10 vol % H2−Ar was introduced. Then, the temperature was increased to 1000 °C at a rate of 10 °C/min.

To better understand the type of carbon on the catalyst surface, some spent catalysts were analyzed by using Raman spectroscopy (HORIBA Jobin-Yvon, France) with a spectral resolution of less than 1 cm−1. The laser line at 532 nm of a He−Cd laser was used as an excitation source.

2.3. Catalyst Test. The schematic diagram of toluene steam reforming system used for the toluene steam reforming is shown in Figure 1. The continuous-flow fixed-bed reactor was made of quartz with a 25 mm inner diameter and 800 mm length. The mass of catalyst used was 4 g, and the sizes of all catalysts particles were in the range of 0.25−0.43 mm. To reduce the catalyst, 50 vol % H2/Ar was introduced for 1 h at 700 °C with a rate of 300 mL/min. After reduction, the toluene (0.2 mL/min) and water (0.5 mL/min) were simultaneously injected to the reactor by metering pumps (steam to carbon mole ratio (S/C) = 2). Under above reaction conditions, the weight hourly space velocity (WHSV) was 2.6 h−1. The reaction temperature was 800 °C, and the nitrogen was selected as carrier gas during the reforming process with a rate of 200 mL/min. The reaction products were then passed through a cold trap to collect the condensable substances. The production of syngas was sampled with a gas trap and analyzed by gas chromatograph (Agilent, 7890A, America).

The toluene conversion (Xt), H2 yield (YH2), and gas production rate were calculated as follows

\[
X_t(\%) = \frac{n_{\text{CH}_2}}{7 \times n_{\text{toluene in}}} \times 100
\]

\[
Y_{\text{H}_2}(\%) = \frac{\text{moles of H}_2}{\text{moles of H}_2 \text{ in stoichiometric potential}} \times 100
\]

\[
\text{gas production rate (μmol/min)} = \frac{V_{\text{gas}}}{V_{\text{Ni}}} \times n_{\text{Ni in}}
\]

where n (μmol/min) is the molar flow rate of each gas, V (vol %) is the volume content in syngas.

The major reactions that can occur during toluene steam reforming are as follows:

Steam reforming

\[
\text{C}_7\text{H}_8 + 7\text{H}_2\text{O} \rightarrow 7\text{CO} + 11\text{H}_2
\]

\[
\text{C}_7\text{H}_8 + 14\text{H}_2\text{O} \rightarrow 7\text{CO}_2 + 18\text{H}_2
\]

Water gas shift (WGS)

\[
\text{CO + H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2
\]

Hydroalkylation

\[
\text{C}_7\text{H}_8 + \text{H}_2 \rightarrow \text{C}_8\text{H}_{16} + \text{CH}_4
\]

Methane steam reforming

\[
\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2
\]
Methane dry reforming
\[
\text{CH}_4 + \text{CO}_2 \leftrightarrow 2\text{CO} + 2\text{H}_2
\]  
(9)

Boudouard reaction
\[
\text{CO}_2 + \text{C} \leftrightarrow 2\text{CO}
\]  
(10)

Coke gasification
\[
\text{C} + \text{H}_2\text{O} \leftrightarrow \text{CO} + \text{H}_2
\]  
(11)

3. RESULTS AND DISCUSSION

3.1. Catalyst Characterization.

3.1.1. Chemical Composition.

The composition analyses of CGA before and after acid pretreatment are shown in Table 1. This table shows that the CGA mainly consisted of SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}, which were common carriers for catalysts. The presence of Fe\textsubscript{2}O\textsubscript{3} could play an important role of a promoter in relative catalysts. After acid pretreatment, the contents of CaO and SO\textsubscript{3} decreased rapidly, resulting in the increase of the SiO\textsubscript{2} content. The existence of sulfur could lead to the deactivation of Ni-based catalysts by adsorbing on the surface of Ni crystallites during the reaction.\textsuperscript{37} Therefore, the effect of sulfur on catalyst activity could be minimized by the acid pretreatment process because the SO\textsubscript{3} content was almost zero. The content of Fe\textsubscript{2}O\textsubscript{3} rose to 6.59 wt %, which means that the Fe element was difficult to convert to the ion state in acid solution. It implies that there is a strong interaction between Fe\textsubscript{2}O\textsubscript{3}, Al\textsubscript{2}O\textsubscript{3}, and SiO\textsubscript{2}. In addition, a slight decrease of the Al\textsubscript{2}O\textsubscript{3} content was found, which attributed to the dissolution of a small amount of Al\textsubscript{2}O\textsubscript{3} during the acid pretreatment process. The sum of SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} content was more than 86 wt %, and Fe\textsubscript{2}O\textsubscript{3}, K\textsubscript{2}O, TiO\textsubscript{2}, CaO, MgO, and Na\textsubscript{2}O were also detected in CGA-1d support. Therefore, the analysis of CGA chemical composition indicated that it has great potential to be used as catalyst preparation.

3.1.2. XRD.

XRD patterns of the catalysts before and after reduction are shown in Figure 2. Figure 2a indicates that the crystal phases of quartz, Fe\textsubscript{2}O\textsubscript{3}, gismondine, and magnetite were found in CGA-1d and the diffraction peaks of CaSO\textsubscript{4} were not observed. It confirmed that the removal of sulfur was very thorough. After the loading of the Ni active compound, the major diffraction peaks of crystal phases in CGA-1d support were still visible, which means that the loading of Ni has a little effect on the structure of CGA-1d. The peaks of the crystalline NiO phase could be observed for Ni/CGA-1d catalysts at 2\theta = 37.2°, 43.1°, and 62.8°, corresponding to (111), (200), and (220) diffraction of cubic NiO (PDF 73-1519), respectively.\textsuperscript{38} The peaks of spinel NiAl\textsubscript{2}O\textsubscript{4} were not observed because the calcined temperature (500 °C) of Ni/CGA-1d catalysts was far lower than the formation temperature (500 °C) of Ni/CGA-1d catalysts was far lower than the formation temperature (800 °C) of spinel NiAl\textsubscript{2}O\textsubscript{4} as reported.\textsuperscript{39} After the addition of metal promoters, the Co-Ni/CGA-1d catalyst exhibited other obvious diffraction peaks at 2\theta angle of 31.2° and 36.7°. It could be assigned to Co\textsubscript{3}O\textsubscript{4} or CoAl\textsubscript{2}O\textsubscript{4} due to their similar diffraction peaks. Generally, spinel CoAl\textsubscript{2}O\textsubscript{4} could be formed at higher temperature than 700 °C,\textsuperscript{40} and Wang et al.\textsuperscript{41} did not found the existence of CoAl\textsubscript{2}O\textsubscript{4} spinel in the Co-Fe/Al\textsubscript{2}O\textsubscript{3} catalyst after calcined at 500 °C. Therefore, these peaks should be attributed to the formation of Co\textsubscript{3}O\textsubscript{4} taking into the low calcination temperature (500 °C) and the low reduction temperature (350 °C) in the TPR profiles. For the Mn-Ni/CGA-1d catalyst, the peak at 2\theta = 36.6° was assigned to NiMnO\textsubscript{4}, which indicated that the MnO\textsubscript{2} could interact with NiO. It was consistent with the Mn-Ni/Al\textsubscript{2}O\textsubscript{3} catalyst as reported.\textsuperscript{13} The promoters on other catalysts (Ce-Ni/CGA-1d,
could be assigned to Fe-rich Fe-Ni alloy (Fe0.94Ni0.06), but the position of Ni basically no shift for Ce-Ni/CGA-1d and Mn-

the addition of promoters, it could be seen that the peak among all catalysts around 2°

Fe2O3, MoO3, NiMnO3, and Co3O4 were disappeared (Figure 2b), indicating a marked reduction of NiO and relative oxidative promoters. Only the promoter Ce was still in the CeO2 phase at 2° = 28.6°, 33.1°, 47.5°, and 56.3° and without the formation of CeAlO3, which is a consequence of solid-state reaction between Ce2O3 and Al2O3. Osorio-Vargas et al. related these CeO2 peaks to the fluorite structure, identified by planes (111), (200), (220), and (311), and they attributed the good segregation of CeO2 on the Al2O3 to this phase. For the Mo-Ni/CGA-1d catalyst, a strong interaction occurred between the metals Mo and Ni, and a Mo−Ni alloy (PDF: 48-1745) was formed with the 2θ angles at 40.9°, 43.2°, 43.9°, and 45.4°.

To further discuss the differences of the metal Ni diffraction peak among all catalysts around 2θ = 44.5°, the X-ray patterns of all catalysts supported on CGA-1d after reduction in a narrow range of 2θ are shown in Figure 2c. In the case of the Ni/CGA-1d catalyst, the Ni peak position was shifted to a smaller angle and it was in the middle of the α-Fe and Ni peak position. It implies the formation of part α-Fe-Ni alloy. After the addition of promoters, it can be seen that the peak position of Ni basically no shift for Ce-Ni/CGA-1d and Mn-Ni/CGA-1d catalysts. The shoulder peak of Ce-Ni/CGA-1d could be assigned to Fe-rich Fe-Ni alloy (Fe0.94Ni0.06), but the shoulder peak of Mn-Ni/CGA-1d may be assigned to the Mn-Ni-Fe alloy, which was attributed to the interaction between NiMnO3 and Fe2O3 during reduction. The diffraction peak between Ni and Co positions should be assigned to Co-Ni alloy. For the Fe-Ni/CGA-1d catalyst, only one peak was observed at 2θ = 44.2°, which was only slightly shift to a smaller angle comparing with the Ni° peak. According to previous reports, the shift was interpreted to result from the creation of defect sites in the metallic Ni phase by Fe species, thus resulting in the formation of a Ni-rich Ni−Fe alloy with a face-centered-cubic (fcc) structure. Therefore, this peak could be assigned to Ni-rich FeNi3 alloy because the mole ratio of the loading quantity of promoter Fe and Ni was 1:3.

Moreover, the Scherrer’s equation was employed to estimate the mean crystallite size at the full width at half-maximum of the main (200) peak.

\[
\text{crystallite size} = \frac{(k \times \lambda)}{(\beta \times \cos \theta)}
\]  
(12)

The cubic phase structure with a k of 0.89 was selected for calculation, while \( \lambda = 0.1542 \) nm. \( \beta \) and \( \theta \) were the peak full width at half-maximum and position of the prominent peak, respectively. According to Table 2, it was found that the crystallite size of Ni° was 73.9 nm on the Ni/CGA-1d catalyst. After the addition of Ce, Fe, and Mo metal promoters, the crystallite size of Ni° decreased sharply. Especially for the Mo-Ni/CGA-1d catalyst, corresponding crystallite size of Ni° was only 27.7 nm, this behavior is mainly due to the addition of Mo that can inhibit the enrichment of the Ni° particle by the obvious Mo-Ni alloy formation. It should be one of the reasons for its best catalytic performance. However, the crystallite size of Ni° increased after the addition of Co and Mn metal promoters, which should be due to sintering of Co3O4 and NiO for the Co-Ni/CGA-1d catalyst, and the formation of NiMnO3 for the Mn-Ni/CGA-1d catalyst. The interaction between these active compounds resulted to the smaller \( S_{\text{ BET}} \) surface area for Co-Ni/CGA-1d and Mn-Ni/CGA-1d catalysts and is shown in Table 3. Above results indicate that the introduction of metal promoters can affect the interaction between active compounds, and the formation of some active species can affect the catalytic performance during tar steam reforming.

3.1.3. Bet. The textural properties including the surface area, pore volume, and average pore size of support and all catalysts are all deduced from the \( N_2 \) adsorption−desorption data and are shown in Table 3. It could be found that the surface area of CGA-1d was 18.34 m²/g, which was larger than that of the Ni/CGA-1d catalyst. It should be due to the blockage of partial mesopores after Ni loading. Thereafter, comparing with the Ni/CGA-1d catalyst, the surface areas of Mn-Ni/CGA-1d, Co-Ni/CGA-1d, and Mo-Ni/CGA-1d catalysts reduced after the incorporation of Mn, Co, and Mo promoters. It can be considered that the structural properties of these catalysts were changed by the formation of Mn-Ni-Fe, Co-Ni, and Mo-Ni alloys. However, the Ce-Ni/CGA-1d catalyst had the highest surface area due to without any interaction between CeO2 and NiO. For the Fe-Ni/CGA-1d catalyst, its surface area was almost no difference with the Ni/CGA-1d catalyst. It should be attributed to the atomic rate of Fe and Ni promoters that was exactly equal to that of Fe-Ni alloy (FeNi°), which perhaps inhibit the enrichment of Ni° particles during reduction. In terms of pore volume, all catalysts exhibited higher pore volume than support, which should be attributed to the formation of mesopores between 5 and 30 nm caused by the arrangement of active compounds. Figure 3 depicts the isothermal curves and pore size distribution over support and all prepared catalysts. As show in Figure 3a, the support and all catalysts were exhibited the IV-type Langmuir adsorption isotherm, which was assigned to the mesoporous structure. Moreover, the mesopores in the 3−5 nm range dominate all catalysts, and the some mesopores in the 5−30 nm range were also observed (Figure 3b). It claimed the change of the pore volume for all catalysts. Meanwhile, the number of mesopores between 3 and 5 nm for Co-Ni/CGA-1d

| catalyst | CGA-1d | Ni/CGA-1d | Co-Ni/CGA-1d | Ce-Ni/CGA-1d | Mn-Ni/CGA-1d | Mo-Ni/CGA-1d | Mn-Ni/CGA-1d (after reduction) | Mo-Ni/CGA-1d (after reduction) |
|----------|--------|-----------|--------------|--------------|--------------|--------------|-------------------------------|-------------------------------|
| \( s_{\text{ BET}} \) (m²/g) | 18.34  | 13.39     | 10.89        | 15.62        | 7.21         | 11.41        | 13.54                         |                               |
| pore volume (cm³/g) | 0.023  | 0.033     | 0.024        | 0.038        | 0.026        | 0.042        | 0.029                         |                               |
| average pore diameter (nm) | 3.74   | 3.78      | 4.17         | 3.75         | 4.27         | 3.79         | 3.84                          |                               |
and Mn-Ni/CGA-1d was less than other catalysts, which may be caused by the interaction between Co$_3$O$_4$ and NiO as well as NiO and MnO$_2$, respectively. Especially for the Mn-Ni/CGA-1d catalyst, the blockage was worst because some mesopores could be blocked during the rearrangement of Ni and the bonding of the Ni-Mn process. It may be the main reason leading to the increase of the average pore diameter and decrease of the SBET surface area. In addition, the surface area of the Mo-Ni/CGA-1d catalyst was not the highest, but its pore volume was higher than all other catalysts with the value of 0.042 cm$^3$/g. It was attributed to the higher number of mesopores than other catalysts, and the increase of mesopores could promote the diffusion and adsorption of reactants during reforming. It may be one reason for the highest catalytic performance over the Mo-Ni/CGA-1d catalyst comparing with other catalysts.

3.1.4. TPR. The reducibility of support and all catalysts were investigated by H$_2$-TPR. The H$_2$-TPR profiles are presented in Figure 4. The CGA-1d support exhibited a very weak signal peak (490 °C) of hydrogen reduction, and its corresponding H$_2$ consumption was only 8.64 cm$^3$/g (Table 4). According to the chemical composition of CGA support, this should be related to the reduction of Fe$_2$O$_3$ in a weak interaction with Al$_2$O$_3$ or SiO$_2$. After the loading of Ni and metal promoters, the intensity of H$_2$ consumption peaks increased sharply due to the reduction of active compounds. After the load of active compounds, all samples showed weak peaks between 450 and 500 °C except for the Mo-Ni/CGA-1d catalyst. This peak was ascribed to the reduction of Fe$_3$O$_4$, derived from CGA support.

Figure 4. TPR profiles of the as-prepared catalyst.

On the other hand, The Ni/CGA-1d and Ce-Ni/CGA-1d catalysts gave one H$_2$ consumption peak at about 360 °C with similar H$_2$ consumptions (54.59 and 59.17 cm$^3$/g, respectively). It should be attributed to the reduction of NiO particles, which had been confirmed through XRD characteristic. One H$_2$ consumption peak was also observed for Fe-Ni/CGA-1d catalysts at 345 °C, but its H$_2$ consumption increased to 72.36 cm$^3$/g, which was higher than the Ni/CGA-1d catalyst due to the reduction of introduced promoter Fe species. It indicated that the NiO and promoter Fe species were simultaneously reduced and the H$_2$ consumption peak was shifted to lower temperature. Therefore, the promoting effect of the Fe addition on Ni/CGA-1d is not due to the increase of the active sites, but it suggests that the synergy between Ni and Fe can promote the reaction. Indeed, Ni and Fe easily form solid solutions. The absence of an alteration of the main phases on CGA-1d support confirms that the promoter Fe species on the Fe-Ni/CGA-1d catalyst are more inclined to form the strong interaction with Ni particles instead of interacting with CGA-1d support. The Co-Ni/CGA-1d catalyst had two H$_2$ consumption peaks below 400 °C. The major peak corresponding to the reduction of NiO was shifted to low temperature (342 °C) because the presence of Co promotes the reduction of Ni species. The shoulder peak at 250 °C should represent the reduction of NiO, which was complete. It implied that the H$_2$ consumption peak (480 °C) with a larger peak area should be ascribed to the simultaneous reduction of MoO$_3$, NiO, and Fe$_2$O$_3$, which was the main reason for the formation of Mo-Ni alloy observed by XRD. It suggests that the cleavage of the Ni−O bond on the Mo-Ni/CGA-1d catalyst is more difficult to achieve due to the existence of Mo, which is contrary to the results as reported by Claude et al. It should be due to the different Ni species formed during catalyst preparation. Although Claude et al. indicated that the better reduction of Ni species caused by the addition of molybdenum on the Ni-Mo/γ-Al$_2$O$_3$ catalyst, the
Ni species was in the form of NiAl2O4 with a higher reduction temperature than 800 °C. Therefore, relative results indicate that the promoter Mo can affect the reducibility of Ni species in different forms. In addition, the H2 consumption peak (700 °C) with a smaller peak area was attributed to the reduction of MoO3 with a high interaction between Mo species and CGA support. Above results indicated that the Mo-Ni/CGA-1d catalyst exhibited the highest reduction temperature comparing with other catalysts. This implies that the degree of the interaction between active compounds was higher on the Mo-Ni/CGA-1d catalyst than other catalysts, and it promoted the formation of Mo-Ni alloy. It should be the key factor for the best performance over the Mo-Ni/CGA-1d catalyst during toluene reforming.

3.2. Catalyst Test. 3.2.1. Effect of Different Promoters on Catalytic Performance. The effect of different promoters on Ni-based catalysts performance is shown in Figure 5. The performance was evaluated for 60 min at 800 °C. Figure 5a indicates that the toluene conversion and H2 yield were 77.2 and 49.5% over the Ni/CGA-1d catalyst. After the addition of different promoters (Co, Ce, Fe, Mo, and Mn), the toluene conversion and H2 yield increased in different degrees. These observations suggest the acceleration of the toluene cracking and the steam reforming reaction rate in the presence of these promoters. It appeared that the Mn-Ni/CGA-1d and Mo-Ni/CGA-1d catalysts showed the best catalytic performances. The corresponding toluene conversion and H2 yield were 89.1 and 61.9% over the Mn-Ni/CGA-1d catalyst, whereas relative values were up to 92.6 and 62.3% over the Mo-Ni/CGA-1d catalyst, and they increased by 15 and 13%, respectively, comparing with the Ni/CGA-1d catalyst. The high performance of the Mo-Ni/CGA-1d catalyst should be attributed to the formation of Mo-Ni alloy, which is probably as a result of electron transfer from the Mo to Ni, increasing the electron density of the catalytic site and hence the catalytic activity. In the case of the Mn addition, the interaction between Mn and Ni, even Fe was involved, resulted the migration of Mn species to the surface of the metallic Ni particles. Due to their synergy effect, the Mn-Ni/CGA-1d catalyst also exhibited better catalyst activity and only slightly lower than the performance of the Mo-Ni/CGA-1d catalyst. Among all catalysts added promoters, the Co-Ni/CGA-1d catalyst exhibited the worst performance. It was known from XRD and TPR analyses that the interaction between the active species (Co and Ni) and support was ignorable. This may be the cause of the Co-Ni/CGA-1d catalyst with little improvement in activity because this kind of interaction can help to minimize the metal-bond (M-O-M) strength in a certain degree that can promote the production of lattice oxygen. Only the crystal phase of the Ce promoter did not change before and after reduction. It has been reported that CeO2 acting as an oxygen donor on the catalyst surface can promote relative reactions due to its oxygen vacancies with high mobility. Based on the advantage, the toluene conversion of the Ce-Ni/CGA-1d catalyst was only slightly up to 80%, which is probably because of the cover of Ni active sites by Ce species. The observed result of the Fe-Ni/CGA-1d catalyst was very interesting. Its toluene conversion could reach to 85.7%, but corresponding H2 yield was lowest among five modified catalysts with the value of 52.3%, which was slightly higher than that for the Ni/CGA-1d catalyst. It suggests that the existence of Fe species can promote the cleavage of the C–C bond in toluene, but it also can inhibit the steam reforming reactions, especially for water-gas shift reaction (eq 6). This behavior should be caused by the excess of Fe species including the Fe promoter and Fe element in support, and which had been claimed in the previous report.

Figure 5b presents the gas production rate and H2/CO on these catalysts. It could be seen that the main product stream consists of H2, CO, CO2 and trace amounts of CH4 during the toluene reforming process. The production of these gases can be explained by eqs 4–11. In the case of the Ni/CGA-1d catalyst, corresponding production rates of H2, CO, CO2, and CH4 were only 17,488, 5494, 4485, and 193 μmol/min, respectively. It was observed that the production rate of CH4 was low and comparable for all catalysts (<300 μmol/min), which means that the methane reforming reactions (eqs 8 and 9) were very thorough and most CH4 was converted to CO and H2. Therefore, one could see that the content of H2 and CO was very high in syngas. Especially for the Mo-Ni/CGA-1d catalyst, its H2 and CO product rates were 22,000 and 7928 μmol/min, respectively. The corresponding total H2 consumption is shown in Table 4. The catalytic performance of all as-prepared catalysts in toluene steam reforming. (a) Toluene conversion and H2 yield. (b) Gas production rate and H2/CO ratio. Reaction condition: T = 800 °C, h = 60 min.

Table 4. Total H2 Consumption of Support and Catalysts

| catalyst | CGA-1d | Ni/CGA-1d | Co-Ni/CGA-1d | Ce-Ni/CGA-1d | Mn-Ni/CGA-1d | Mo-Ni/CGA-1d | Fe-Ni/CGA-1d |
|----------|--------|-----------|--------------|--------------|--------------|--------------|--------------|
| total H2 consumption (cm3/g) | 8.64   | 54.59     | 75.30        | 59.17        | 73.60        | 90.81        | 72.36        |
μmol/min, respectively, and they were 87.7% of syngas. The change of H₂ and CO product rates was relative with that of the H₂ yield and toluene conversion, respectively, for all catalysts. After the addition of promoters, the CO₂ product rate fell slightly. Although the addition of promoters could increase the toluene conversion, it also could enhance the reverse WGS reaction (eq 6) under the higher reaction temperature of 800 °C, which should be due to the exothermic reaction represented by WGS reaction (eq 6). Therefore, the reverse WGS reaction (eq 6) and the Boudouard reaction (eq 10) are appropriate to explain the increase of CO and H₂ and the decrease of CO₂ after the addition of promoters. Additionally, the Boudouard reaction (eq 10) represents the removal of carbon deposition on these catalysts during reforming. For the H₂/CO ratio, it was contrary to catalyst activity because the H₂/CO ratios of Fe-Ni/CGA-1d, Mn-Ni/CGA-1d, and Mo-Ni/CGA-1d catalysts were lower than Ni/CGA-1d, Co-Ni/CGA-1d, and Ce-Ni/CGA-1d catalysts. First, it was easy to find that the lower H₂/CO ratio over the Fe-Ni/CGA-1d catalyst was due to the low H₂ production rate. Second, for Mn-Ni/CGA-1d and Mo-Ni/CGA-1d catalysts, the H₂ production rate was higher than other catalysts, but the CO production rate was also very high, which resulted in the lower H₂/CO ratio. This phenomenon can be explained by Boudouard reaction (eq 10) and coke gasification reaction (eq 11), which can further achieve the removal of coke deposition and enhance the CO production rate. It should be the key reason for better catalytic performance over Mn-Ni/CGA-1d and Mo-Ni/CGA-1d catalysts.

Toluene was often selected as the tar model compound to test the catalyst activity. Relative studies have been done by many researchers. Claude et al. synthesized a series Ni/γ-Al₂O₃-SiO₂ catalysts for reforming toluene. The results showed that the Ni/γ-Al₂O₃-SiO₂ catalyst (450 m²/g) had higher performance than Ni/γ-Al₂O₃, and corresponding toluene conversion was 94% because the Ni/γ-Al₂O₃ catalyst modified by the silicon precursor showed high resistance against the sintering of Ni particles. This means that composite support has more advantages than single support due to its complex chemical and structure. Meanwhile, similar results about the advantage of composite support were also claimed by Liu et al. In our work, the CGA-1d also could be related to a kind of composite support, but its low surface area still was a defect. Therefore, the performance of Ni/CGA-1d was lower than the Ni/γ-Al₂O₃-SiO₂ catalyst, even the Mo-Ni/CGA-1d after modification was only comparable with it because the Mo promoter could increase the toluene conversion and enhance the selection of CO and H₂ as reported. However, for the Mn-Ni/CGA-1d catalyst, its catalytic activity was better than the Mn-Ni/dolomite catalyst as reported, which suggests that the CGA-1d support possess certain advantage contrasting with natural minerals such as dolomite. In addition, Zhou et

Figure 6. Stability test of Mn-Ni/CGA-1d for toluene steam reforming. Reaction condition: T = 800 °C, h = 300 min. (a) Toluene conversion and H₂ yield. (b) Gas production rate and H₂/CO ratio.

Figure 7. Stability test of Mo-Ni/CGA-1d for toluene steam reforming. (a) Toluene conversion and H₂ yield; (b) Gas production rate and H₂/CO ratio. Reaction condition: T = 800 °C, h = 300 min.
al.\(^2\) also investigated the effect of different promoters (Ce, Zr, Fe) on Ni-Mg-Al hydrotalcite-derived catalysts. The results show that the addition of promoters can enhance the activity and stability of catalysts. They considered that it should be due to the reducibility improvement of Ni species by adding more Lewis acid–base pairs (intermediate) and low coordinated species (O species) after the introduction of Ce species and the strong support-metal interaction and generation of Fe-Ni alloys after the introduction of Fe species.\(^4\) Relative results were consistent with our work about the function of metal promoters and composite support.

### 3.2.2. **Stability of the Catalyst**

According to above results, it can be seen that the Mn-Ni/CGA-1d and Mo-Ni/CGA-1d catalysts exhibit the best catalytic activities. Hence, the two kinds of catalysts were selected to investigate their resistance to deactivation for toluene reforming at 800 °C for 300 min. The variations of the toluene conversion, H\(_2\) yield, gas production rate, and H\(_2\)/Co ratio with time on-steam over Mn-Ni/CGA-1d and Mo-Ni/CGA-1d catalysts are shown in Figures 6 and 7. During the runtime, the toluene conversion and H\(_2\) yield showed a decrease trend of catalytic performance over Mn-Ni/CGA-1d and Mo-Ni/CGA-1d catalysts. The toluene conversion decreased from 90 to 80%, and the H\(_2\) yield decreased from 66 to 53% over the Mn-Ni/CGA-1d catalyst (Figure 6a). Meanwhile, the toluene conversion decreased from 93 to 87%, and the H\(_2\) yield decreased from 64 to 56% over the Mo-Ni/CGA-1d catalyst (Figure 7a). It indicated that the stability of the Mo-Ni/CGA-1d catalyst was better than the Mn-Ni/CGA-1d catalyst because the decrease of the toluene conversion and H\(_2\) yield over the Mo-Ni/CGA-1d catalyst was less than that over the Mn-Ni/CGA-1d catalyst. In addition, the toluene conversion could keep above 90% within 200 min of reforming reaction for the Mo-Ni/CGA-1d catalyst, but it fell to 84% for Mn-Ni/CGA-1d on the same conditions. This decrease in catalytic performance with time is primarily due to the deposition of carbon species over the catalysts during the steam reforming process. This deposited carbon can encapsulate the active metal species, resulting in a decrease in the amount of catalytically active species.\(^1\) The crystal phase of carbon species deposited over the spent catalyst was observed by XRD (Figure 8), and it will be discussed later.

In terms of gas production, the H\(_2\) and CO\(_2\) product rates slightly decreased, whereas the variation trend of CO product rate was opposite, and it slightly decreased over Mn-Ni/CGA-1d and increased over Mo-Ni/CGA-1d. The CH\(_4\) product rate was at a low level throughout the whole time on-steam reaction (Figures 6b and 7b). Commonly, the decrease of H\(_2\), CO\(_2\), and CO product rates was easy to understand because it was due to the decrease of the toluene conversion and H\(_2\) yield. Under this circumstance, the increase of the CO product rate should be attributed to the combined action among reverse WGS (eq 6), Boudouard reaction (eq 10) and coke gasification reaction (eq 11). It also suggests that the carbon resistance ability of the Mo-Ni/CGA-1d catalyst is better than that of the Mn-Ni/CGA-1d catalyst. After 5 h steam reforming, the H\(_2\) product rate basically could keep at 20000 \(\mu\)mol/min over Mn-Ni/CGA-1d and Mo-Ni/CGA-1d catalysts, and its volume content was higher than 60% of the syngas. Therefore, these catalysts all exhibited better H\(_2\) selectivity. For the Mn-Ni/CGA-1d catalyst, the same variation trend of H\(_2\) and CO product rates resulted from the relatively stable H\(_2\)/CO ratio around 3.0. However, the contrary variation trend of them was observed over the Mo-Ni/CGA-1d catalyst, which led to the decrease of H\(_2\)/CO from 2.9 to 2.3.

After 300 min steam reforming reaction, the Mn-Ni/CGA-1d and Mo-Ni/CGA-1d catalysts were characterized by XRD (Figure 8). The phase of the Mn-Ni/CGA-1d catalyst was similar before and after reaction except for the formation of graphene, which was related to the shoulder peak at 26.2°. However, the active component phase changed significantly for the Mo-Ni/CGA-1d catalyst. The Mo-Ni alloy was destroyed, the new peaks at 34.4°, 37.9°, 39.4°, 52.1°, 61.5°, 69.6°, 74.6°, and 75.5° could be attributed to the presence of Mo\(_2\)C (PDF: 11-0680), and without obvious, peaks for MoO\(_3\) or Mo-Ni alloy were observed, meaning that the phase structure of Mo\(_2\)C was very stable. The graphene phase was also observed with the peak at 26.2°, but its peak intensity for Mo-Ni/CGA-1d was lower than that for Mn-Ni/CGA-1d. In addition, according to Table 2, the crystallite size of Ni\(_0\) increased to 95.35 and 37.70 nm for spent Mn-Ni/CGA-1d and Mo-Ni/CGA-1d catalysts, respectively. It indicated that the sintering phenomenon between Ni\(_0\) particles occurred during catalytic reforming, which may be one of the reasons for the deactivation of above two catalysts during the toluene reforming process. Shi et al.\(^5\) suggested that the Ni-Mo\(_2\)C was a typical bifunctional catalyst, and the dissociation of CH\(_4\) is catalyzed by Ni, while the activation of CO\(_2\) takes place on Mo\(_2\)C during CH\(_4\)/CO\(_2\) dry reforming. This is single reaction only involving CH\(_4\) and CO\(_2\) as reactants. While in steam reforming, H\(_2\)O is a reactant and oxidant dominating the oxygen mobility and coke gasification. Some researchers claimed that Mo\(_2\)C also was easy to be oxidized by H\(_2\)O and form MoO\(_2\), which could continue to be carbonized by hydrocarbons during reforming.\(^3\)-\(^5\) It means that the conversion process of Mo\(_2\)C was Mo\(_2\)C-MoO\(_2\)-Mo\(_2\)C, which suggests that the presence of Mo\(_2\)C can achieve the fixation and transfer of carbon deposition. Thus, the formation of Mo\(_2\)C is greatly helpful to the enhancement of Mo-Ni/CGA-1d catalytic performance because the carbon can be removed by free oxygen species that are originated from CO\(_2\) or H\(_2\)O dissociation (eqs 10 and 11). It may be the key reason that the Mo-Ni/CGA-1d catalyst performed most efficient among all catalysts. Meanwhile, to accurately reflect the carbon deposition on Mo-Ni/CGA-1d and Mn-Ni/CGA-1d catalysts, the results of TG analysis are shown in Figure 9. The TG test results showed that the amount of carbon deposition on Mo-Ni/CGA-1d was about 12 wt %, which was obviously lower than that on the Mn-Ni/CGA-1d catalyst with
respectively. Smaller Lₐ carbon sp2 bonds of highly ordered carbon, respectively.⁵⁶ carbonaceous aromatic structure and the stretching mode of carbon atoms with dangling bonds in the disordered reaction.

Figure 10. As shown, D- and G-bands were obvious, located at 1,352 and 1,577 cm⁻¹, attributed to the vibrations of carbon atoms with dangling bonds in the disordered carbonaceous aromatic structure and the stretching mode of carbon sp2 bonds of highly ordered carbon, respectively.⁵⁶ According to Tuinstra and Koenig’s law, the microcrystalline planar size (Lₐ), used to quantify the degree of carbon species in disorder, was measured by equation as follow⁵⁷

\[ Lₐ (nm) = 4.4 \times \frac{I_D}{I_G} \]

where \( I_D \) and \( I_G \) are the peak heights of the D- and G-bands, respectively. Smaller \( Lₐ \) represents the higher disordering degree of the carbon species deposited on the surface of catalysts. \( Lₐ \) (3.57 nm) for Mn-Ni/CGA-1d was lower than \( Lₐ \) (4.26 nm) for Mo-Ni/CGA-1d. It indicated that the carbon deposition on the Mn-Ni/CGA-1d catalyst surface was easier to be removed. But the intensities of D- and G-bands were far higher than that for the Mo-Ni/CGA-1d catalyst because the formation of Mo₂C species can remove the carbon deposition efficiently. Therefore, the carbon resistance ability of the Mo-Ni/CGA-1d catalyst was better than the Mn-Ni/CGA-1d catalyst.

4. CONCLUSIONS

Coal gangue ash after acid pretreatment was chosen as catalyst support. The Ni/CGA-1d catalyst was prepared for steam reforming of toluene as a biomass tar model compound. Then, it was modified by five promoters (Co, Ce, Fe, Mn, and Mo) and corresponding catalysts were tested. The results demonstrated that all promoters could improve the performance of the Ni/CGA-1d catalyst. Furthermore, The Mo-Ni/CGA-1d catalyst showed the best steam reforming performance in terms of the toluene conversion and H₂ yield with an S/C = 2, at 800 °C, followed by Mn-Ni/CGA-1d, Fe-Ni/CGA-1d, Ce-Ni/CGA-1d, and Co-Ni/CGA-1d catalysts. The superior catalytic performance of Mo-Ni/CGA-1d was mainly due to the formation of Mo-Ni alloy particles. Meanwhile, comparing with the Mn-Ni/CGA-1d catalyst, the Mo-Ni/CGA-1d catalyst exhibited higher stability for the formation of Mo₂C, which can effectively remove carbon deposition by free oxygen species originated from CO₂ or H₂O dissociation.

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REFERENCES
(1) Qian, K.; Kumar, A. Catalytic reforming of toluene and naphthalene (model tar) by char supported nickel catalyst. Fuel 2017, 187, 128–136.
(2) Mei, D.; Liu, S.; Wang, Y.; Yang, H.; Bo, Z.; Tu, X. Enhanced reforming of mixed biomass tar model compounds using a hybrid gliding arc plasma catalytic process. Catal. Today 2019, 337, 225–233.
(3) Claude, V.; Mahy, J. G.; Geens, J.; Courson, C.; Lambert, S. D. Synthesis of Ni/γ-Al2O3-SiO2 catalysts with different silicon precursors for the steam toluene reforming. Microporous Mesoporous Mater. 2019, 284, 304–315.
(4) Yang, X.; Liu, X.; Guo, T.; Liu, C. Effects of Cu and Fe additives on low-temperature catalytic steam reforming of toluene over Ni/AC catalysts. Catal. Surv. Asia 2019, 23, 54–63.
(5) Adnan, M. A.; Hidayat, A.; Ajiwobi, O. O.; Adamu, S.; Muraza, O.; Hossain, M. M. Fluidizable Fe-Co/ZeoliteZrO2 catalysts for steam reforming of toluene as a tar surrogate in biomass gasification. Energy Fuels 2018, 32, 12833–12842.
(6) Zhao, X.; Xue, Y.; Lu, Z.; Huang, Y.; Guo, C.; Yan, C. Encapsulating Ni/Co-ZrO2-SiO2 with SiO2 layer to improve its catalytic activity for steam reforming of toluene. Catal. Commun. 2017, 101, 138–141.
(7) Artetxe, M.; Nahil, M. A.; Olazar, M.; Williams, P. T. Steam reforming of phenol as biomass tar model compound over Ni/Al2O3 catalyst. Fuel 2016, 184, 629–636.
(8) Oh, G.; Park, S. Y.; Seo, M. W.; Ra, H. W.; Mun, T. Y.; Lee, J.-G.; Yoon, S. J. Combined steam-dry reforming of toluene in syngas over CuNiRu/Al2O3 catalysts. Int. J. Green Energy 2019, 16, 333–349.
(9) Oh, G.; Park, S. Y.; Seo, M. W.; Kim, Y. K.; Ra, H. W.; Lee, J.-G.; Yoon, S. J. Ni/Ru-Co/Mn/Al2O3 catalysts for steam reforming of toluene as model biomass tar. Renewable Energy 2016, 86, 841–847.
(10) Adamu, S.; Xiong, Q.; Bakare, I. A.; Hossain, M. M. Ni/Co-Al2O3 for optimum hydrogen production from biomass/tar model compounds: role of support type and ceria modification on desorption kinetics. Int. J. Hydrogen Energy 2019, 44, 15811–15822.
(11) Yang, X.; Xu, S.; Xu, H.; Liu, X.; Liu, C. Nickel supported on modified olivine catalysts for steam reforming of biomass gasification tar. Catal. Commun. 2010, 11, 383–386.
(12) Zhang, R.; Wang, H.; Hou, X. Catalytic reforming of toluene as tar model compound: Effect of Ce and Ce-Mg promoter using Ni/olivine catalyst. Chemosphere 2014, 97, 40–46.
(13) Heo, D. H.; Lee, R.; Hwang, J. H.; Sohn, J. M. The effect of addition of Ca, K and Mn over Ni-based catalyst on steam reforming of toluene as model tar compound. Catal. Today 2016, 265, 95–102.
(14) Ahmed, T.; Xin, S.; Wang, L.; Shahbazi, A. Investigation of Ni/Fe/Mg zeolite-supported catalysts in steam reforming of tar using simulated-toluene as model compound. Fuel 2018, 211, 566–571.
(15) Bao, X.; Kong, M.; Lu, W.; Fei, J.; Zheng, X. Performance of Co/MgO catalyst for CO2 reforming of toluene as a model compound of tar derived from biomass gasification. J. Energy Chem. 2014, 23, 795–800.
(16) Ashok, J.; Kathiraser, Y.; Ang, M. L.; Kawi, S. Ni and/or Ni-Cu alloys supported over SiO2 catalysts synthesized via phyllosilicate structures for steam reforming of biomass tar reaction. Catal. Sci. Technol. 2015, 5, 4398–4409.
(17) Chen, J.; Sun, J.; Wang, Y. Catalysts for steam reforming of bio-oil: a review. Ind. Eng. Chem. Res. 2017, 56, 4627–4637.
(18) Koike, M.; Ishikawa, C.; Li, D.; Wang, L.; Nakagawa, Y.; Tomishige, K. Catalytic performance of manganese-promoted nickel catalysts for the steam reforming of tar from biomass pyrolysis to synthesis gas. Fuel 2013, 103, 122–129.
(19) Chen, M.; Li, X.; Wang, Y.; Wang, C.; Liang, T.; Zhang, H.; Yang, Z.; Zhou, Z.; Wang, J. Hydrogen generation by steam reforming of tar model compounds using lanthanum modified Ni/sepelite catalysts. Energy Convers. Manage. 2019, 184, 315–326.
(20) Santanamia, L.; Artetxe, M.; Lopez, G.; Cortazar, M.; Amutio, M.; Bilbao, J.; Olazar, M. Effect of CeO2 and MgO promoters on the performance of a Ni/Al2O3 catalyst in the steam reforming of biomass pyrolysis volatiles. Fuel Process. Technol. 2020, 198, 106223.
(21) Higo, T.; Saito, H.; Ogo, S.; Sugiyara, Y.; Sekine, Y. Promotive effect of Ba addition on the catalytic performance of Ni/LaAlO3 catalysts for steam reforming of toluene. Appl. Catal., A 2017, 530, 125–131.
(22) Zhou, F.; Pan, N.; Chen, H.; Xu, X.; Wang, C.; Du, Y.; Guo, Y.; Zeng, Z.; Li, L. Hydrogen production through steam reforming of toluene over Ce, Zr or Fe promoted Ni-Mg-Al hydrotalcite-derived catalysts at low temperature. Energy Convers. Manage. 2019, 196, 677–687.
(23) Hu, S.; He, L.; Wang, Y.; Su, S.; Jiang, L.; Chen, Q.; Liu, Q.; Chi, H.; Xiang, J.; Sun, L. Effects of oxygen species from Fe addition on promoting steam reforming of toluene over Fe-Ni/Al2O3 catalysts. Int. J. Hydrogen Energy 2016, 41, 17967–17975.
(24) Wang, L.; Li, D.; Koike, M.; Watanabe, H.; Xu, Y.; Nakagawa, Y.; Tomishige, K. Catalytic performance and characterization of Ni-Co catalysts for the steam reforming of biomass tar to synthesis gas. Fuel 2013, 112, 654–661.
(25) Li, Z.; Li, M.; Ashok, J.; Sibudjing, K. NiCo@NiCo phyllosilicate/CoO hollow core shell catalysts for steam reforming of toluene as biomass tar model compound. Energy Convers. Manage. 2019, 180, 822–830.
(26) Marafi, A.; Hauser, A.; Stanislaus, A. Deactivation patterns of Mo/Al2O3, Ni-Mo/Al2O3 and Ni-Mo/P/Al2O3 catalysts in atmospheric residue hydrodesulphurization. Catal. Today 2007, 125, 192–202.
(27) Malaiabar, Z. O.; Croiset, E.; Amin, A.; Epling, W. Effect of interactions between Ni and Mo on catalytic properties of a bimetallic Ni-Mo/Al2O3 propane reforming catalyst. Appl. Catal., A 2015, 490, 80–92.
(28) Wang, S.; Zhang, F.; Cai, Q.; Li, X.; Zhu, L.; Wang, Q.; Luo, Z. Catalytic steam reforming of bio-oil model compounds for hydrogen production over coal ash supported Ni catalyst. Int. J. Hydrogen Energy 2014, 39, 2018–2025.
(29) Guo, F.; Dong, Y.; Fan, P.; Lv, Z.; Yang, S.; Dong, L. Catalytic decomposition of biomass tar compound by calcined coal gauze: A kinetic study. Int. J. Hydroenergy 2016, 41, 13380–13389.
(30) Al-Rahbi, A. S.; Williams, P. T. Waste ashes as catalysts for the pyrolysis-catalytic steam reforming of biomass for hydrogen-rich gas production. J. Mater. Cycles Waste Manage. 2019, 21, 1224–1231.
(31) Hussain, M.; Tuf, L. D.; Yusup, S.; Zabiri, H. Characterization of Coal Bottom Ash & Ash Potential to be used as Catalyst in Biomass Gasification. Mater. Today: Proc. 2019, 16, 1886–1893.
(32) Tian, Y.; Zhou, X.; Yang, Y.; Nie, L. Experimental analysis of air-steam gasification of biomass with coal-bottom ash. J. Energy Inst. 2020, 93, 25–30.
(33) Gao, Y.; Huang, H.; Tang, W.; Liu, X.; Yang, X.; Zhang, J. Preparation and characterization of a novel porous silicate material from coal gauze. Microporous Mesoporous Mater. 2015, 217, 210–218.
(34) Han, J.; Ha, Y.; Guo, M.; Zhao, P.; Liu, Q.; Liu, C.; Song, C.; Ji, N.; Lu, X.; Ma, D.; Li, Z. Synthesis of zeolite SSZ-13 from coal gauze via ultrasonic pretreatment combined with hydrothermal growth method. Ultrason. Sonochem. 2019, 59, 104703.
(35) Li, H.; Cheng, B.; Liu, Z.; Du, C. Waste control by waste: Fenton-like oxidation of phenol over Cu modified ZSM-5 from coal gauze. Sci. Total Environ. 2019, 683, 638–647.
(36) Lu, M.; Xiong, Z.; Fang, K.; Li, X.; Li, J.; Li, T. Steam reforming of toluene over nickel catalysts supported on coal gauze ash. Renewable Energy 2020, 160, 385–395.
(37) Lakhapatri, S. L.; Abraham, M. A. Deactivation due to sulfur poisoning and carbon deposition on Rh-Ni/Al2O3 catalyst during steam reforming of sulfur-doped n-hexadecane. Appl. Catal. A, 2009, 364, 113–121.

(38) Huang, F.; Wang, R.; Yang, C.; Driss, H.; Chu, W.; Zhang, H. Catalytic performances of Ni/mesoporous SiO2 catalysts for dry reforming of methane to hydrogen. J. Energy Chem. 2016, 25, 709–719.

(39) Bereketidou, O. A.; Goula, M. A. Biogas reforming for syngas production over nickel supported on ceria-alumina catalysts. Catal. Today 2012, 195, 93–100.

(40) Mo, L.; Zheng, X.; Huang, C.; Fei, J. A novel catalyst Pt/CoAl2O4/Al2O3 for combination CO2 reforming and partial oxidation of CH4. Catal. Lett. 2002, 80, 165–169.

(41) Wang, L.; Hisada, Y.; Koike, M.; Li, D.; Watanabe, H.; Nakagawa, Y.; Tomishige, K. Catalyst property of Co-Fe alloy particles in the steam reforming of biomass tar and toluene. Appl. Catal., B 2012, 121-122, 95–104.

(42) Osorio-Vargas, P.; Flores-González, N. A.; Navarro, R. M.; Fierro, J. L. G.; Campos, C. H.; Reyes, P. Improved stability of Ni/Al2O3 catalysts by effect of promoters (La2O3, CeO2) for ethanol steam-reforming reaction. Catal. Today 2016, 259, 27–38.

(43) Ashok, J.; Kawi, S. Nickel-iron alloy supported over iron-alumina catalysts for steam reforming of biomass tar model compound. ACS Catal. 2013, 4, 289–301.

(44) Wang, L.; Li, D.; Koike, M.; Kosu, S.; Nakagawa, Y.; Xu, Y.; Tomishige, K. Catalytic performance and characterization of Ni-Fe catalysts for the steam reforming of tar from biomass pyrolysis to synthesis gas. Appl. Catal., A 2011, 392, 248–255.

(45) Laosiripojana, N.; Sutthinripok, W.; Charojrochkul, S.; Assabumrungrat, S. Development of Ni-Fe bimetallic based catalysts for biomass tar cracking/reforming: effects of catalyst support and co-fed reactants on tar conversion characteristics. Fuel Process. Technol. 2014, 127, 26–32.

(46) Tian, D.; Liu, Z.; Li, D.; Shi, H.; Pan, W.; Cheng, Y. Bimetallic Ni-Fe total-methanation catalyst for the production of substitute natural gas under high pressure. Fuel 2013, 104, 224–229.

(47) Claude, V.; Mahy, J. G.; Tilkin, R. G.; Lambert, S. D. Enhancement of the catalytic performances and lifetime of Ni/γ-Al2O3 catalysts for the steam toluene reforming via the combination of dopants: inspection of Cu, Co, Fe, Mn, and Mo species addition. Mater. Today Chem. 2020, 15, 100229.

(48) Maluf, S. S.; Assaf, E. M. Ni catalysts with Mo promoter for methane steam reforming. Fuel 2009, 88, 1547–1553.

(49) Savuto, E.; Navarro, R. M.; Mota, N.; Di Carlo, A.; Bocci, E.; Carlini, M.; Fierro, J. L. G. Steam reforming of tar model compounds over Ni/Mayenite catalysts: effect of Ce addition. Fuel 2018, 224, 676–686.

(50) Liu, Y.; Yu, H.; Liu, J.; Chen, D. Catalytic characteristics of innovative Ni/slag catalysts for syngas production and tar removal from biomass pyrolysis. Int. J. Hydrogen Energy 2019, 44, 11848–11860.

(51) Mitran, G.; Mieritz, D. G.; Seo, D. K. Steam reforming of toluene as model of tar compound over Mo catalysts derived from hydrotalcites. J. Saudi Chem. Soc. 2019, 23, 916–924.

(52) Shi, C.; Zhang, A.; Li, X.; Zhang, S.; Zhu, A.; Ma, Y.; Au, C. Ni-modified Mo2C catalysts for methane dry reforming. Appl. Catal., A 2012, 431, 164–170.

(53) LaMont, D. C.; Thomson, W. J. Dry reforming kinetics over a bulk molybdenum carbide catalyst. Chem. Eng. Sci. 2005, 60, 3553–3559.

(54) Marin Flores, O. G.; Ha, S. Study of the performance of Mo2C for iso-octane steam reforming. Catal. Today 2008, 136, 235–242.

(55) Darujati, A. R. S.; Thomson, W. J. Kinetic study of a ceria-promoted Mo2C/γ-Al2O3 catalyst in dry-methane reforming. Chem. Eng. Sci. 2006, 61, 4309–4315.

(56) Xu, T.; Xu, F.; Moyo, G. G.; Sun, Y.; Chen, Z.; Xiao, B.; Wang, X.; Hu, Z. Comparative study of MxOy (M = Cu, Fe and Ni) supported on dolomite for syngas production via chemical looping reforming with toluene. Energy Convers. Manage. 2019, 199, 111937.