Heterogeneous Catalysts Used in Hydrothermal Gasification

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Supercritical water gasification has emerged as a promising technology to sustainably convert waste residues into clean gaseous fuels rich in combustible gases such as hydrogen and methane. The composition and yield of gases from hydrothermal gasification depend on process conditions such as temperature, pressure, reaction time, feedstock concentration, and reactor geometry. However, catalysts also play a vital role in enhancing the gasification reactions and selectively altering the composition of gas products. Catalysts can also enhance hydrothermal reforming and cracking of biomass to achieve desired gas yields at moderate temperatures, thereby reducing the energy input of the hydrothermal gasification process.

Keywords: biofuels ; biomass ; catalysts ; cellulose ; gasification ; hemicellulose ; hydrogen ; lignin ; methane ; supercritical water

1. Introduction

Heterogeneous catalysts applied in the SCWG process can be broadly divided into two categories, namely metal oxides and transition metals. The recovery and recycling of heterogeneous catalysts are relatively easier compared to those of homogeneous catalysts [1]. Heterogeneous catalysts are more active, resulting in efficient and improved gasification efficiency [2]. They are also more selective for specific products by promoting desired reactions.

1.1. Transition Metals

1.1.1. Nickel-Based Catalysts

Nickel-based catalysts are the most widely used heterogeneous catalysts in SCWG because of their high activity compared to other expensive transition metal catalysts. Ni-based catalysts require comparatively lower temperatures and promote biomass gasification with higher efficiency. However, Ni-based catalysts can also consume the produced H_2, CO, and CO_2 due to their high methanation activity, producing CH_4 [3]. Furusawa et al. [4] used the Ni/MgO catalyst in the SCWG of lignin. They studied its regenerative capabilities by recovering and reusing the catalyst thrice. The catalyst showed satisfactory regenerative capability before suffering from deactivation due to the formation of carbon and $Mg(OH)_2$.

Zhang et al. [5] studied the SCWG of glucose and compared the activities and H_2 selectivities of Ni, Co, Ru, and Cu transition metals on γ-Al_2O_3, AC, and ZrO_2 supports. Both 10%Ni/γ-Al_2O_3 and 10%Ru/Al_2O_3 demonstrated the highest catalytic activities and H_2 selectivities. The order of activity of the supports for the Ni catalyst was: γ-Al_2O_3 > ZrO_2 > AC. Due to satisfactory results with 10%Ni/γ-Al_2O_3, further enhancement with Na, K, Mg, and Ru promotors was also studied. The addition of the 0.5%K promoter on 10%Ni/γ-Al_2O_3 significantly increased the H_2 yield by favoring the water–gas shift reaction.

Azadi et al. [6] studied the SCWG of various lignocellulosic feedstocks (e.g., glucose, fructose, cellulose, pulp, xylan, bark, and lignin) using five transition metals catalysts (e.g., Ni/Al_2O_3, Ru/C, Raney nickel, Ni/hydrotalcite, and Ru/Al_2O_3). The activities of Ni/Al_2O_3 and Ni/hydrotalcite catalysts for SCWG demonstrated the highest H_2 selectivities. In contrast, Raney nickel showed the lowest H_2 selectivity. Ni/α-Al_2O_3 and Ni/hydrotalcite also demonstrated low CH_4 yields at high temperatures and longer reaction times. The high H_2 selectivities of Ni/α-Al_2O_3 and Ni/hydrotalcite were attributed to the lower nickel dispersion and large crystallite sizes of Ni/α-Al_2O_3 and Ni/hydrotalcite catalysts compared to Raney nickel. The high nickel dispersion of Raney nickel strongly favored C–O bond cleavage compared to Ni/Al_2O_3 and Ni/hydrotalcite catalysts, thus explaining the low H_2 selectivity of Raney nickel. The authors also reported that among all feedstocks, lignin was the most resistant to SCWG because of its branched polymeric structure. The lowest gas yield obtained from lignin was attributed to potential deactivation of the catalysts due to its sulfur content.

Azadi et al. [7] compared Ni catalysts on different support materials, including γ-Al_2O_3, α-Al_2O_3, activated carbon, carbon nanotubes (CNT), hydrotalcite, MgO, SiO_2, silica gel, TiO_2, ZrO_2, and various zeolites in the SCWG of glucose. The 20%Ni/α-Al_2O_3 catalyst showed the highest H_2 selectivity, and Ni/CNT demonstrated high H_2 yields (17–24 mmol/g) and high stability with maximum carbon gasification efficiency. On the other hand, Ni/MgO demonstrated a better H_2 yield (26 mmol/g) and satisfactory carbon gasification efficiency. Due to its low cost and high stability, the authors further investigated the Ni/α-Al_2O_3 catalyst by varying Ni loading and using promoters. Tin increased the H_2 selectivity but decreased the catalytic activity, whereas alkali promoters increased the carbon gasification efficiency but decreased the H_2 selectivity. Lu et al. [8] also studied Ni-based catalysts with various promoted Al_2O_3 supports (e.g., CeO_2/Al_2O_3, MgO/Al_2O_3, La_2O_3/Al_2O_3, and ZrO_2/Al_2O_3) in the SCWG of glucose. CeO_2/Al_2O_3 showed the highest H_2 yield, followed by La_2O_3/Al_2O_3, ZrO_2/Al_2O_3, Al_2O_3, and MgO/Al_2O_3.

Onwudili and Williams [9] investigated the catalytic SCWG of various plastic wastes with Ru and Ni catalysts. By increasing RuO_2 loading up to 5 wt% in the SCWG of low-density polyethylene, the H_2 yield rose from 1 to 9.9 mol/kg at 450 °C in 1 h. However, the subsequent increase in RuO_2 loading from 5 wt% to 20 wt% decreased the H_2 yield to 4.9 mol/kg while increasing the hydrogen gasification and carbon gasification efficiency. By using a 20 wt% RuO_2-γ-Al_2O_3 catalyst, polypropylene produced a high H_2 yield and the highest carbon gasification efficiency of 99%. High- and low-density polyethylenes also showed similar gas yields, whereas polystyrene produced the lowest yields of C_2-C_4 gases. Low-density polyethylene demonstrated the highest H_2 yield, followed by polystyrene, polypropylene, and high-density polyethylene.

Adamu et al. [10] studied Ce-mesoAl_2O_3 support impregnated with Ni in the SCWG of glucose. Ce-mesoAl_2O_3 had superior support properties compared to γ-Al_2O_3, such as moderate acidity, which helped to reduce coke formation and enabled high metal loading with low agglomeration. The Ni(20)/Ce-Al_2O_3 catalyst exhibited a very high H_2 yield of 10.2 mol/mol of glucose. The meso-form led to the cracking of large intermediates such as tar compounds. Furthermore, Ce helped to improve the thermal stability of the alumina support.

Lu et al. [11] compared Ni, Cu, and Fe transition metals supported on MgO in the SCWG of wheat straw. The H_2 yields varied with the application of different catalysts in the following order: Ni/MgO > Fe/MgO > Cu/MgO. Due to excellent H_2 selectivity with Ni, the authors explored various supports, such as basic oxides (MgO and ZnO), acidic oxide (Al_2O_3), and amphoteric oxide (ZrO_2). The H_2 selectivities of Ni-supported catalysts varied in the order of Ni/MgO > Ni/ZnO > Ni/ Al_2O_3 > Ni/ZrO. Although the type of support had a minimal effect on H_2 yield, a significant effect was observed on the decrease in CO yield. Basic oxide supports such as MgO and ZnO favored water–gas shift reactions, thus increasing H_2 yields. The acidic support such as Al_2O_3 did not enhance the water–gas shift reaction. Hence, Ni/Al_2O_3 showed nearly double the CO yield as compared to the Ni/ZnO and Ni/MgO catalysts.

Okolie et al. [12] performed the SCWG of soybean straw using different Ni-based catalysts, catalyst supports, and promoters. ZrO_2 and Al_2O_3 proved to be the most effective supports for Ni-based catalysts. Both 10%Ni-ZrO_2 and 10%Ni-Al_2O_3 demonstrated higher H_2 yields than other catalyst supports (e.g., CNT, SiO_2/Al_2O_3, SiO_2, and AC). Therefore, the authors further studied the effects of K, Na, and Ce promotors on Ni-based catalysts supported by ZrO_2 and Al_2O_3. The 10%Ni-1%Ce/ZrO_2 catalyst demonstrated the highest H_2 yield of 10.9 mmol/g, followed by 10%Ni-1%K/ZrO_2 and 10%Ni-1%Na/ZrO_2. The relative increment in H_2 yield and total gas yield without using any promoters was more substantial with the Ce and K promotors than with the Na promotor. However, the Na promotor showed the highest H_2 yield with the Al_2O_3 support compared to the K and Ce promotors. The 10%Ni-1%Na/Al_2O_3 catalyst demonstrated the highest H_2 yield (10.8 mmol/g) compared to 10%Ni-Ce/Al_2O_3 and 10%Ni-1%K/Al_2O_3. The 10%Ni-1%Ce/ZrO_2 catalyst demonstrated an improved H_2 yield and excellent catalytic performance. Further analysis revealed that the Ce promotor could store oxygen species and eliminate coke formation and sintering of the catalysts, resulting in its high performance.

Su et al. [13] investigated the effects of La_2O_3 in promoting the Ni-La_2O_3/θ-Al_2O_3 catalyst in the SCWG of food waste. La enhanced the water–gas shift reaction, resulting in a high H_2 yield. La also inhibited the methanation reaction, which is a major limitation of Ni-based catalysts. La also improved the metal dispersion, which increased the catalytic activity. Chowdhury et al. [14] also reported that Ni/Al_2O_3 with an La promoter can lead to excellent catalytic activity in the SCWG of food waste. Ni/9%La-Al_2O_3 showed high H_2 and gas yields. La improved the mesoporous structure and increased the dispersion of Ni, which enhanced the water–gas shift reaction and increased the H_2 yield. Ni/9%La-Al_2O_3 also demonstrated high stability, which could be attributed to its better anti-carbon deposition property.

Mastuli et al. [15] compared doped and supported Zn and Ni catalysts on MgO support in the SCWG of oil palm frond. The doped catalysts had high surface areas, high stability, and high-activity basic sites, resulting in high H_2 yields compared to supported catalysts. Zn-based catalysts showed higher H_2 yields than Ni-based catalysts for both supported and doped catalysts. Mastuli et al. [16] further investigated the structural and catalytic effects of $Mg_{1-x}Ni_xO$ nanomaterial as a catalyst. They synthesized $Mg_{1-x}Ni_xO$ nanomaterial via a self-propagating combustion method in the SCWG of oil palm frond. As the Ni content increased, the cell volume decreased linearly. This increased the specific surface area and improved the basic properties of the catalyst. The $Mg_{0.8}Ni_{0.2}O$ catalyst with the highest Ni content demonstrated the highest gas and H_2 yields.

Li et al. [17] demonstrated that the formation of the char layer could be minimized using co-precipitated Ni-Mg-Al catalysts. They varied the Mg-Al molar ratio in the catalyst and investigated its effects in the SCWG of glucose. The catalysts favored H_2 production, resulting in high H_2 selectivity. Furthermore, Mg inhibited graphitic carbon formation because of its neutralizing action on alumina acidic sites, thus increasing the lifespan of the catalysts. However, the subsequent increase in Mg loading formed the $MgNiO_2$ complex, which limited the activity of Ni metal.

Li et al. [18] also studied the stability and activities of various wet-impregnated Mg-promoted Ni catalysts on Al_2O_3 and CNT supports in the SCWG of glycerol. The stability studies showed the loss of Al, which resulted in deactivation of the Mg-promoted Ni-Al_2O_3 catalysts. Both the Ni/α-Al_2O_3 and Ni/γ-Al_2O_3 catalysts showed poorer stability and regenerability over repeated use than the Ni/CNT catalyst.

Li and Guo [19] compared the catalytic action of Mg-promoted Ni/Al_2O_3 catalysts synthesized via the co-precipitation and wet impregnation methods for a variety of feedstocks, such as glycerol, cellulose, glucose, poplar leaf, corncob, phenol, and sawdust. The results showed that the co-precipitated Ni-Mg-Al catalysts were more stable than the wet-impregnated Ni-Mg-Al catalysts. This was due to the growth of the crystal size of the wet-impregnated Ni-Mg-Al catalysts in SCW. Among different feedstocks, the co-precipitated Ni-Mg-Al catalysts were more active for the gasification of water-soluble organics as compared to real lignocellulosic biomasses.

Kang et al. [20] explored and proposed a detailed catalytic mechanism of Ni-Co supported on Mg-Al in the SCWG of lignin. The 2.6%Ni-5.2%Co/2.6%Mg-Al catalyst prepared via the co-precipitation method demonstrated high total gas and H_2 yields due to significant improvement in its coke resistance ability. They also concluded that the co-precipitation method was more efficient than the wet-impregnated method. Norouzi et al. [21] showed that the addition of Ru on Fe-Ni/γ-Al_2O_3 could enhance gas yields while minimizing char formation. Another study by Lu et al. [8] showed that the addition of the Ce promoter on Ni/γ-Al_2O_3 was also capable of reducing coke and carbon deposition.

Catalysts synthesized in SCW have demonstrated high stability through their ability to reduce sintering. The supercritical water synthesis (SCWS) method for catalyst design provides better control over the size and shape of the nanoparticle without any requirement for organic solvents or precipitants. A few studies on SCWS synthesis of Ni-based catalysts on various supports (e.g., ZrO_2, Ce-ZrO_2, Al_2O_3, Mg-Al_2O_3, CNT and AC) have been reported for the SCWG of biomass [22] [23]. SCWS-synthesized Ni/MgO-Al_2O_3 catalysts demonstrated the highest activities and stability. Despite their increased specific surface areas and pore volumes, SCWS-synthesized Ni/CeO_2-ZrO_2 catalysts showed no promotional effects when Ce was used. This was because of the low Ni particle dispersion in the Ni/CeO_2-ZrO_2 catalysts. However, as compared to sol-gel prepared catalysts, which have bigger bulk NiO particles, the SCWS-synthesized catalysts showed high dispersion and stable crystalline structures. After multiple use cycles, the SCWS-synthesized catalysts retained their high dispersion, whereas sol-gel-prepared catalysts experienced growth in size. This allowed the SCWS-prepared catalysts to maintain their high activities over repeated use, as opposed to catalysts prepared using conventional methods that may lose their activity over repeated use. Additionally, SCWS-synthesized catalysts are also synthesized in an environmentally friendly way as they do not require any organic solvents or robust chemical compounds.

Li et al. [24] studied and proposed a catalytic mechanism in the SCWG of dewatered sewage sludge and various model compounds using $AlCl_3$ combined with Ni, KOH, or K_2CO_3 catalysts and oxidants (e.g., H_2O_2, $K_2S_2O_8$, and CaO_2). $AlCl_3$-H_2O_2 demonstrated the highest gas yields, followed by $AlCl_3$-$K_2S_2O_8$. $AlCl_3$ combined with Ni, KOH, CaO, or K_2CO_3 catalysts resulted in low H_2 yields as compared to $AlCl_3$ alone. However, using $K_2S_2O_8$ or H_2O_2 alone decreased the H_2 yield. The H_2 yield decreased, and gasification efficiency increased with a rise in the addition of oxidants. Interestingly, $AlCl_3$-H_2O_2 (8:2) showed the highest gas yield, followed by $AlCl_3$-$K_2S_2O_8$ (8:2) and $AlCl_3$. For the $AlCl_3$-catalyzed SCWG of the model compound, glycerol resulted in the highest H_2 yield, followed by guaiacol, glucose, alanine, and humic acid. Al_2Cl_3-H_2O_2 increased the H_2 yield of humic acid by 17% but decreased the H_2 yields of glucose and glycerol by 20% and 12%, respectively, compared to the $AlCl_3$ catalyst. The authors also proposed a catalytic mechanism in the SCWG of dewatered sewage sludge with an $AlCl_3$-H_2O_2 catalyst. They proposed that $AlCl_3$ promoted the cleavage of the C–C bond with Al_3^+ ions. The Al_3^+ ions increased the acidity of SCW by reacting with water and forming $Al(OH)_3$ and H^+ ions. $Al(OH)_3$ further underwent dehydration to form AlO(OH), which formed precipitates in water. The H^+ and Cl^- ions enhanced the gasification of intermediate compounds to produce H_2, thus increasing the H_2 yield. H_2O_2 further enhanced the gasification of benzene-containing monomers by favoring the steam reforming reaction. In the case of sewage sludge, H^+ generated via Al_3^+ deposition further enhanced the ring-opening activity of H_2O_2 to promote the decomposition of benzene-containing monomers into small molecules. These small organic molecules were further gasified by the combined catalytic effects of Cl^- and H^+ ions to increase H_2 yields.

Although Ni-based catalysts demonstrate improvement in gasification efficiency, they suffer from deactivation mainly because of tar formation and coke deposition [25]. Despite the high activity of Ni/γ-Al_2O_3-based catalysts, they still suffer from various issues, such as sintering, formation of Ni/Al_2O_4 complexes, and transformation of the γ-Al_2O_3 phase to the α-Al_2O_3 phase. These issues significantly hamper the catalysts' stability. This is a severe issue for alumina-supported catalysts due to the ready conversion of intermediate products adsorbed on the acidic site into carbon, which deactivates Ni-based catalysts. The addition of alkali promoters can suppress cracking and polymerization reactions. Alkali promoters can also neutralize the acidic sites of alumina supports. Thus, alkali promotors can significantly reduce carbon formation.

1.1.2. Ruthenium-Based Catalysts

Ru-based catalysts with promising metal dispersion are more reactive at low temperatures than Ni-based catalysts [26]. Ru-based catalysts have higher surface areas and distribution than Ni-based catalysts. Therefore, high surface area and more metal distribution can be achieved with relatively low Ru metal loading on the support material. Nguyen et al. [27] also confirmed that Ru-based catalysts show higher catalytic activities per metallic mass than Ni-based catalysts. Additionally, Ru-based catalysts are highly resistant to oxidation and hydrothermal conditions compared to Ni-based catalysts. Ru-based catalysts have higher activities toward hydrogenation and C–C bond cleavage [28]. When compared to other expensive transition metals, Ru-based catalysts exhibit the highest activity and H_2 selectivity.

As opposed to Ni-based catalysts, Ru-based catalysts are more susceptible to deactivation by sulfur poisoning [29]. To overcome sulfur sintering, a sacrificial agent with a relatively high affinity towards sulfur can be used to protect Ru from sulfur sintering. Peng et al. [30] used ZnO as a sacrificial agent with Ru/C catalysts to study the SCWG of microalgae (*Chlorella vulgaris*). ZnO showed high mechanical stability and sulfur adoption performance, which minimized Ru metal sintering. Despite Ru-based catalysts having high surface areas, high dispersion, and high catalytic performance, the relatively low cost of Ni-based catalysts makes them preferable for large-scale industrial applications over Ru-based catalysts.

Kang et al. [31] also observed that Ru/Al_2O_3 showed the highest metal dispersion compared to Ni-based catalysts. They concluded that 5%Ru/Al_2O_3 demonstrated a higher H_2 yield than the 5%Ni/Al_2O_3 catalyst in the SCWG of cellulose and lignin. Therefore, for the same metal loading, Ru-based catalysts had higher H_2 yields than Ni-based catalysts. Nanda et al. [32] compared Ru/Al_2O_3 with Ni/Si-Al_2O_3, K_2CO_3, and Na_2CO_3 catalysts in the SCWG of waste cooking oil. The order of H_2 yield was Ru/Al_2O_3 > Ni/Si-Al_2O_3 > K_2CO_3 > Na_2CO_3. The effects of metal loading showed that 5 wt% Ru/Al_2O_3 resulted in the maximum H_2 yield.

The superior catalytic performance of Ru/Al_2O_3 catalysts has also been reported in the SCWG of glucose and guaiacol [28][33]. In the SCWG of glucose, the Ru/Al_2O_3 catalyst inhibited the production of furfural and 5-hydroxymethylfurfural while favoring the degradation of intermediates such as phenols, ketones, acids, and arenes [28]. Enhanced gasification of intermediates improved process efficiency and increased total gas and H_2 yields while preventing the formation of char. During the SCWG of guaiacol, Ru/Al_2O_3 catalysts enhanced the conversion of phenol to cyclohexanol by favoring the hydrogenation reaction and the conversion of cyclohexanol to hexanone or hexenol by favoring ring-opening reactions [33]. Hexanone and hexenol can further decompose into small gaseous molecules, including H_2. Thus, Ru/Al_2O_3 improved H_2 and total gas yields while minimizing char and tar formation.

Zhang et al. [5] observed the effects of Ni and Ru bimetallic catalysts supported on γ-Al_2O_3. They recommended the use of Ni and Ru bimetallic catalysts supported on γ-Al_2O_3 in the SCWG of glucose to achieve high activity and H_2 selectivity. Hossain et al. [34] further investigated various bimetallic Ni-Ru/Al_2O_3-supported aerogel catalysts. Ni-Ru/Al_2O_3 aerogel catalysts demonstrated 1.3- and 1.6-times higher H_2 yields than mesoporous and wet-impregnated synthesized Ni-Ru/Al_2O_3 catalysts for the same amount of metal loading. The aerogel catalysts showed high and uniform metal particle dispersion with strong interaction between the support and active metal. The high catalytic performance of the aerogel catalysts was due to the supercritical CO_2 drying step during aerogel catalyst synthesis, which improved the surface area and reactant diffusivity. A significant decrease in coke formation was also observed with the aerogel catalysts due to their low acidity. This resulted in high stability and activities of the aerogel catalysts.

Tushar et al. [35] confirmed the catalytic effects of Ni and Ru catalysts. They investigated ten different combinations of Ni and Ru catalysts on various supports, such as γ-Al_2O_3 and ZrO_2. Overall, Ni-Ru/γ-Al_2O_3-ZrO_2 demonstrated the maximum H_2 yields and high carbon gasification efficiency. Ni-Ru/γ-Al_2O_3-ZrO_2 also demonstrated high stability and activities over repeated use. In another study, dual-component catalysts having equal amounts of Ru/C-Ru/C demonstrated better catalytic activities than single-component catalysts [36].

Yang et al. [37] investigated the kinetics and intermediate products of Ni-Ru/Al_2O_3 bimetallic catalysts for the SCWG of phenol. They proposed that phenol converted into an enol intermediate via a partial hydrogenation reaction. Furthermore, enol rapidly formed cyclohexanone. This observation was different from the mechanism proposed by Zhu et al. [33] where cyclohexanone was considered as an intermediate product for the formation of cyclohexanol. The kinetic study revealed that phenol was more difficult to gasify than the intermediate compounds. Interestingly, steam reforming of cyclohexanone was not the main contributor to H_2 production due to its lower concentration than phenol.

1.1.3. Other Heterogeneous Catalysts

Apart from Ni and Ru, other transition metals such as Pt, Co, and Rh (supported or unsupported) are also used as heterogeneous catalysts in the SCWG process. Karakuş et al. [38] investigated Pt/Al_2O_3 and Ru/Al_2O_3 catalysts in the SCWG of 2-propanol. Their results showed that the H_2 selectivity of Pt/Al_2O_3 was relatively higher than that of Ru/Al_2O_3 due to enhancement of the methanation reaction, which produced CH_4 at the expense of H_2. Pairojpiriyakul et al. [39] used Co-based catalysts on a variety of supports, such as α-Al_2O_3, ZrO_2, γ-Al_2O_3, La_2O_3, and yttria-stabilized zirconia (YSZ), in the SCWG of glycerol. The highest H_2 yield was obtained with Co/YSZ. In addition, increasing the Co loading up to 10% improved the gasification efficiency of glycerol and H_2 production. However, a further increase in the Co loading decreased both H_2 yield and glycerol conversion.

Deactivation, sintering, and poisoning of heterogeneous catalysts by sulfur or coke is still a major challenge. Additionally, heterogeneous catalysts oxidize the elemental sulfur and chlorine in biomass to acids. Retention of these acids in the liquid products of SCWG poses a serious challenge for its disposal and/or recycling. The non-polar nature of SCW dissolves the organic compounds during hydrothermal gasification but the inorganic components, including the active metal (catalyst) and mineral matter (catalyst support), can precipitate and form agglomerates in the reactor if not removed properly. The gradual deposition of these precipitates and agglomerates can corrode the reactor during high-temperature and high-pressure operations [40]. Nevertheless, more advancements are needed to address these challenges to synthesize suitable heterogeneous catalysts with high activity, regenerability, and stability, with resistance to sintering and deactivation.

2. Metal Oxide Catalysts

Metal oxide catalysts are rarely used in the SCWG process and very little literature is available on their catalytic performance in SCWG processes. They are generally used as supports to improve the stability and activities of metal-supported catalysts. The most common metal oxides used in SCWG processes are RuO_2, ZrO_2, and CeO_2. Cao et al. [41] compared different metal oxides catalysts such as V_2O_5, MnO_2, Cr_2O_3, Fe_2O_3, CuO, Co_2O_3, ZnO, MoO_3, ZrO_2, SnO_2, CeO_2, and WO_3 in SCWG of glucose. Among all metal oxide catalysts, Cr_2O_3, CuO, and WO_3 showed high gasification efficiencies compared to Fe_2O_3, ZnO, and ZrO_2. The H_2 yields decreased with almost all metal oxide catalysts, except Cr_2O_3, which improved the H_2 yield.

Various co-precipitated binary metal oxide catalysts, such as CeO_2-ZrO_2, CuO-ZnO, and Fe_2O_3-Cr_2O_3, have demonstrated high catalytic performance in SCWG [42][43]. Cao et al. [42] showed that in the SCWG of lignin, the CuO-ZnO catalyst demonstrated high catalytic performance with a high H_2 yield and better gasification efficiency, followed by Fe_2O_3-Cr_2O_3 and CeO_2-ZrO_2. However, in the SCWG of cellulose, Fe_2O_3-Cr_2O_3 showed a greater H_2 yield and high carbon gasification efficiency, followed by CuO-ZnO and CeO_2-ZrO_2. This was due to the higher oxygen content of cellulose compared to lignin. Thus, oxygen released by metal oxide catalysts had less pronounced effects in the SCWG of cellulose. Additionally, the H_2 yield from cellulose was less than that from lignin, which also decreased the reducibility of the reaction medium. The catalytic mechanism of binary metal oxide catalysts showed that CeO_2 was the main active component in the CeO_2-ZrO_2 catalyst [43]. CeO_2 distributed on ZrO_2 released active oxygen via redox reactions to enhance the SCWG process. ZrO_2 also absorbed active H_2 and small intermediates to increase contact between the intermediates and CeO_2 for improved catalytic performance. In CuO-ZnO, Cu was the main active component, which released oxygen species. ZnO acted as a structural stabilizer, promotor and absorbent for sulfur in the CuO-ZnO supported catalyst.

Onwudili [44] studied the detailed catalytic mechanism of $RuO_2/\gamma-Al_2O_3$ in the SCWG of municipal solid waste. $RuO_2/\gamma-Al_2O_3$ drastically increased H_2, CH_4, and CO_2 yields while significantly improving gasification efficiency. The high yield of H_2 was due to enhancement of the water–gas shift reaction by the catalytic action of $RuO_2/\gamma-Al_2O_3$. In addition, the enhancement of methanation of CO or CO_2 and hydrogenolysis of C–C hydrocarbons resulted in a high CH_4 yield. Improvement in the yields of the reduction product (CH_4) and oxidation product (CO_2) indicated the involvement of the $RuO_2/\gamma-Al_2O_3$ catalyst in Ru(IV) and Ru(0) cyclic redox reactions. Reduction of Ru(IV) into Ru(0) was essential for the SCWG process, whereas oxidation of Ru(0) into Ru(IV) was necessary for the catalytic process. The primary synergetic effects were due to the improvement of the dispersion of RuO_2 on $\gamma-Al_2O_3$, which resulted in enhanced carbon gasification efficiency.

Samiee-Zafarghandi et al. [45] compared MnO_2/SiO_2 and NiO/SiO_2 catalysts in the SCWG of microalgae *Chlorella*. MnO_2/SiO_2 demonstrated the highest H_2 yield (1.1 mmol/g) compared to NiO/SiO_2 (0.6 mmol/g) and non-catalytic SCWG (0.2 mmol/g). Therefore, NiO/SiO_2 was less active than the supported MnO_2/SiO_2. Borges et al. [46] investigated the Ni/Fe_2O_4 catalyst in the SCWG of *Eucalyptus* wood chips. Ni/Fe_2O_4 enhanced the H_2 yield and decreased the char yield. Further investigation showed that Ni/Fe_2O_4 favored the water–gas shift and steam reforming reactions, thus increasing H_2 yield and decreasing CH_4 yield. It also demonstrated good stability and recyclability despite the coke deposit [47].

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