# Heterogeneous Catalysts Used in Hydrothermal Gasification

#### Subjects: Energy & Fuels

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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.

biofuels	biomass	catalysts	cellulose	gasification	hemicellulose	hydrogen
lignin	methane	supercritical wa	ater			

# 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 <sup>[1]</sup>. Heterogeneous catalysts are more active, resulting in efficient and improved gasification efficiency <sup>[2]</sup>. 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<sub>2</sub> due to their high methanation activity, producing CH<sub>4</sub> <sup>[3]</sup>. Furusawa et al. <sup>[4]</sup> 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)<sub>2</sub>.

Zhang et al. <sup>[5]</sup> studied the SCWG of glucose and compared the activities and  $H_2$  selectivities of Ni, Co, Ru, and Cu transition metals on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, AC, and ZrO<sub>2</sub> supports. Both 10%Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 10%Ru/Al<sub>2</sub>O<sub>3</sub> demonstrated the

highest catalytic activities and H<sub>2</sub> selectivities. The order of activity of the supports for the Ni catalyst was:  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> > ZrO<sub>2</sub> > AC. Due to satisfactory results with 10%Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, further enhancement with Na, K, Mg, and Ru promotors was also studied. The addition of the 0.5%K promoter on 10%Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> significantly increased the H<sub>2</sub> yield by favoring the water–gas shift reaction.

Azadi et al. <sup>[6]</sup> 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<sub>2</sub>O<sub>3</sub>, Ru/C, Raney nickel, Ni/hydrotalcite, and Ru/Al<sub>2</sub>O<sub>3</sub>). The activities of Ni/Al<sub>2</sub>O<sub>3</sub> and Ni/hydrotalcite catalysts for SCWG demonstrated the highest H<sub>2</sub> selectivities. In contrast, Raney nickel showed the lowest H<sub>2</sub> selectivity. Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Ni/hydrotalcite also demonstrated low CH<sub>4</sub> yields at high temperatures and longer reaction times. The high H<sub>2</sub> selectivities of Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and Ni/hydrotalcite were attributed to the lower nickel dispersion and large crystallite sizes of Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> and Ni/hydrotalcite catalysts, thus explaining the low H<sub>2</sub> 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. <sup>[7]</sup> compared Ni catalysts on different support materials, including  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, activated carbon, carbon nanotubes (CNT), hydrotalcite, MgO, SiO<sub>2</sub>, silica gel, TiO<sub>2</sub>, ZrO<sub>2</sub>, and various zeolites in the SCWG of glucose. The 20%Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst showed the highest H<sub>2</sub> selectivity, and Ni/CNT demonstrated high H<sub>2</sub> yields (17–24 mmol/g) and high stability with maximum carbon gasification efficiency. On the other hand, Ni/MgO demonstrated a better H<sub>2</sub> yield (26 mmol/g) and satisfactory carbon gasification efficiency. Due to its low cost and high stability, the authors further investigated the Ni/ $\alpha$ -Al<sub>2</sub>O<sub>3</sub> catalyst by varying Ni loading and using promoters. Tin increased the H<sub>2</sub> selectivity but decreased the catalytic activity, whereas alkali promoters increased the carbon gasification efficiency but decreased the H<sub>2</sub> selectivity. Lu et al. <sup>[8]</sup> also studied Ni-based catalysts with various promoted Al<sub>2</sub>O<sub>3</sub> supports (e.g., CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, MgO/Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, and MgO/Al<sub>2</sub>O<sub>3</sub>.

Onwudili and Williams <sup>[9]</sup> investigated the catalytic SCWG of various plastic wastes with Ru and Ni catalysts. By increasing RuO<sub>2</sub> loading up to 5 wt% in the SCWG of low-density polyethylene, the H<sub>2</sub> yield rose from 1 to 9.9 mol/kg at 450 °C in 1 h. However, the subsequent increase in RuO<sub>2</sub> loading from 5 wt% to 20 wt% decreased the H<sub>2</sub> yield to 4.9 mol/kg while increasing the hydrogen gasification and carbon gasification efficiency. By using a 20 wt% RuO<sub>2</sub>- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, polypropylene produced a high H<sub>2</sub> 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<sub>2</sub>-C<sub>4</sub> gases. Low-density polyethylene demonstrated the highest H<sub>2</sub> yield, followed by polystyrene, polypropylene, and high-density polyethylene.

Adamu et al. <sup>[10]</sup> studied Ce-mesoAl<sub>2</sub>O<sub>3</sub> support impregnated with Ni in the SCWG of glucose. Ce-mesoAl<sub>2</sub>O<sub>3</sub> had superior support properties compared to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, such as moderate acidity, which helped to reduce coke formation and enabled high metal loading with low agglomeration. The Ni(20)/Ce-Al<sub>2</sub>O<sub>3</sub> catalyst exhibited a very high H<sub>2</sub> 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. <sup>[11]</sup> compared Ni, Cu, and Fe transition metals supported on MgO in the SCWG of wheat straw. The H<sub>2</sub> yields varied with the application of different catalysts in the following order: Ni/MgO > Fe/MgO > Cu/MgO. Due to excellent H<sub>2</sub> selectivity with Ni, the authors explored various supports, such as basic oxides (MgO and ZnO), acidic oxide (Al<sub>2</sub>O<sub>3</sub>), and amphoteric oxide (ZrO<sub>2</sub>). The H<sub>2</sub> selectivities of Ni-supported catalysts varied in the order of Ni/MgO > Ni/ZnO > Ni/ Al<sub>2</sub>O<sub>3</sub> > Ni/ZrO. Although the type of support had a minimal effect on H<sub>2</sub> 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<sub>2</sub> yields. The acidic support such as Al<sub>2</sub>O<sub>3</sub> did not enhance the water–gas shift reaction. Hence, Ni/Al<sub>2</sub>O<sub>3</sub> showed nearly double the CO yield as compared to the Ni/ZnO and Ni/MgO catalysts.

Okolie et al. <sup>[12]</sup> 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<sub>2</sub> and 10%Ni-Al<sub>2</sub>O<sub>3</sub> demonstrated higher H<sub>2</sub> yields than other catalyst supports (e.g., CNT, SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, 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<sub>2</sub> catalyst demonstrated the highest H<sub>2</sub> yield of 10.9 mmol/g, followed by 10%Ni-1%K/ZrO<sub>2</sub> and 10%Ni-1%Na/ZrO<sub>2</sub>. The relative increment in H<sub>2</sub> 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<sub>2</sub> yield with the Al<sub>2</sub>O<sub>3</sub> support compared to the K and Ce promotors. The 10%Ni-1%Na/Al<sub>2</sub>O<sub>3</sub> catalyst demonstrated the highest H<sub>2</sub> yield (10.8 mmol/g) compared to 10%Ni-Ce/Al<sub>2</sub>O<sub>3</sub> and 10%Ni-1%K/Al<sub>2</sub>O<sub>3</sub>. The 10%Ni-1%Ce/ZrO<sub>2</sub> catalyst demonstrated an improved H<sub>2</sub> 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. <sup>[13]</sup> investigated the effects of  $La_2O_3$  in promoting the Ni- $La_2O_3/\theta$ -Al<sub>2</sub>O<sub>3</sub> catalyst in the SCWG of food waste. La enhanced the water–gas shift reaction, resulting in a high H<sub>2</sub> 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. <sup>[14]</sup> also reported that Ni/Al<sub>2</sub>O<sub>3</sub> with an La promoter can lead to excellent catalytic activity in the SCWG of food waste. Ni/9%La-Al<sub>2</sub>O<sub>3</sub> showed high H<sub>2</sub> 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<sub>2</sub> yield. Ni/9%La-Al<sub>2</sub>O<sub>3</sub> also demonstrated high stability, which could be attributed to its better anticarbon deposition property.

Mastuli et al. <sup>[15]</sup> 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<sub>2</sub> yields compared to supported catalysts. Zn-based catalysts showed higher H<sub>2</sub> yields than Ni-based catalysts for both supported and doped catalysts. Mastuli et al. <sup>[16]</sup> further investigated the structural and catalytic effects of Mg<sub>1-x</sub>Ni<sub>x</sub>O nanomaterial as a catalyst. They synthesized Mg<sub>1-x</sub>Ni<sub>x</sub>O 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. <sup>[17]</sup> 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<sub>2</sub> complex, which limited the activity of Ni metal.

Li et al. <sup>[18]</sup> 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/ $\alpha$ - $Al_2O_3$  and Ni/ $\gamma$ - $Al_2O_3$  catalysts showed poorer stability and regenerability over repeated use than the Ni/CNT catalyst.

Li and Guo <sup>[19]</sup> compared the catalytic action of Mg-promoted Ni/Al<sub>2</sub>O<sub>3</sub> catalysts synthesized via the coprecipitation 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 wetimpregnated 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. <sup>[20]</sup> 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<sub>2</sub> 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. <sup>[21]</sup> showed that the addition of Ru on Fe-Ni/y-Al<sub>2</sub>O<sub>3</sub> could enhance gas yields while minimizing char formation. Another study by Lu et al. <sup>[8]</sup> showed that the addition of the Ce promoter on Ni/y-Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>, Ce-ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Mg-Al<sub>2</sub>O<sub>3</sub>, CNT and AC) have been reported for the SCWG of biomass <sup>[22][23]</sup>. SCWS-synthesized Ni/MgO-Al<sub>2</sub>O<sub>3</sub> catalysts demonstrated the highest activities and stability. Despite their increased specific surface areas and pore volumes, SCWS-synthesized Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts showed no promotional effects when Ce was used. This was because of the low Ni particle dispersion in the Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts. However, as compared to sol-gel prepared catalysts, which have bigger bulk NiO particles, 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. <sup>[24]</sup> studied and proposed a catalytic mechanism in the SCWG of dewatered sewage sludge and various model compounds using AICl<sub>3</sub> combined with Ni, KOH, or K<sub>2</sub>CO<sub>3</sub> catalysts and oxidants (e.g., H<sub>2</sub>O<sub>2</sub>, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and CaO<sub>2</sub>). AlCl<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> demonstrated the highest gas yields, followed by AlCl<sub>3</sub>-K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. AlCl<sub>3</sub> combined with Ni, KOH, CaO, or K<sub>2</sub>CO<sub>3</sub> catalysts resulted in low H<sub>2</sub> yields as compared to AlCl<sub>3</sub> alone. However, using K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> or H<sub>2</sub>O<sub>2</sub> alone decreased the H<sub>2</sub> yield. The H<sub>2</sub> yield decreased, and gasification efficiency increased with a rise in the addition of oxidants. Interestingly, AlCl<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> (8:2) showed the highest gas yield, followed by AlCl<sub>3</sub>-K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (8:2) and AlCl<sub>3</sub>. For the AlCl<sub>3</sub>-catalyzed SCWG of the model compound, glycerol resulted in the highest H<sub>2</sub> yield, followed by guaiacol, glucose, alanine, and humic acid. Al<sub>2</sub>Cl<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> increased the H<sub>2</sub> yield of humic acid by 17% but decreased the H<sub>2</sub> yields of glucose and glycerol by 20% and 12%, respectively, compared to the AlCl<sub>3</sub> catalyst. The authors also proposed a catalytic mechanism in the SCWG of dewatered sewage sludge with an AlCl<sub>3</sub>-H<sub>2</sub>O<sub>2</sub> catalyst. They proposed that AICl<sub>3</sub> promoted the cleavage of the C–C bond with Al<sub>3</sub><sup>+</sup> ions. The Al<sub>3</sub><sup>+</sup> ions increased the acidity of SCW by reacting with water and forming AI(OH)<sub>3</sub> and H<sup>+</sup> ions. AI(OH)<sub>3</sub> further underwent dehydration to form AIO(OH), which formed precipitates in water. The H<sup>+</sup> and Cl<sup>-</sup> ions enhanced the gasification of intermediate compounds to produce H<sub>2</sub>, thus increasing the H<sub>2</sub> yield. H<sub>2</sub>O<sub>2</sub> further enhanced the gasification of benzenecontaining monomers by favoring the steam reforming reaction. In the case of sewage sludge, H<sup>+</sup> generated via  $Al_3^+$  deposition further enhanced the ring-opening activity of  $H_2O_2$  to promote the decomposition of benzenecontaining monomers into small molecules. These small organic molecules were further gasified by the combined catalytic effects of  $CI^-$  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 <sup>[25]</sup>. Despite the high activity of Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-based catalysts, they still suffer from various issues, such as sintering, formation of Ni/Al<sub>2</sub>O<sub>4</sub> complexes, and transformation of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> phase to the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> 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. <sup>[27]</sup> 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 <sup>[28]</sup>. 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 <sup>[29]</sup>. 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. <sup>[30]</sup> 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. <sup>[31]</sup> also observed that Ru/Al<sub>2</sub>O<sub>3</sub> showed the highest metal dispersion compared to Ni-based catalysts. They concluded that 5%Ru/Al<sub>2</sub>O<sub>3</sub> demonstrated a higher H<sub>2</sub> yield than the 5%Ni/Al<sub>2</sub>O<sub>3</sub> catalyst in the SCWG of cellulose and lignin. Therefore, for the same metal loading, Ru-based catalysts had higher H<sub>2</sub> yields than Ni-based catalysts. Nanda et al. <sup>[32]</sup> compared Ru/Al<sub>2</sub>O<sub>3</sub> with Ni/Si-Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, and Na<sub>2</sub>CO<sub>3</sub> catalysts in the SCWG of waste cooking oil. The order of H<sub>2</sub> yield was Ru/Al<sub>2</sub>O<sub>3</sub> > Ni/Si-Al<sub>2</sub>O<sub>3</sub> > K<sub>2</sub>CO<sub>3</sub> > Na<sub>2</sub>CO<sub>3</sub>. The effects of metal loading showed that 5 wt% Ru/Al<sub>2</sub>O<sub>3</sub> resulted in the maximum H<sub>2</sub> yield.

The superior catalytic performance of Ru/Al<sub>2</sub>O<sub>3</sub> catalysts has also been reported in the SCWG of glucose and guaiacol <sup>[28][33]</sup>. In the SCWG of glucose, the Ru/Al<sub>2</sub>O<sub>3</sub> catalyst inhibited the production of furfural and 5-hydroxymethylfurfural while favoring the degradation of intermediates such as phenols, ketones, acids, and arenes <sup>[28]</sup>. Enhanced gasification of intermediates improved process efficiency and increased total gas and H<sub>2</sub> yields while preventing the formation of char. During the SCWG of guaiacol, Ru/Al<sub>2</sub>O<sub>3</sub> 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 <sup>[33]</sup>. Hexanone and hexenol can further decompose into small gaseous molecules, including H<sub>2</sub>. Thus, Ru/Al<sub>2</sub>O<sub>3</sub> improved H<sub>2</sub> and total gas yields while minimizing char and tar formation.

Zhang et al. <sup>[5]</sup> observed the effects of Ni and Ru bimetallic catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. They recommended the use of Ni and Ru bimetallic catalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the SCWG of glucose to achieve high activity and H<sub>2</sub> selectivity. Hossain et al. <sup>[34]</sup> further investigated various bimetallic Ni-Ru/Al<sub>2</sub>O<sub>3</sub>-supported aerogel catalysts. Ni-Ru/Al<sub>2</sub>O<sub>3</sub> aerogel catalysts demonstrated 1.3- and 1.6-times higher H<sub>2</sub> yields than mesoporous and wetimpregnated synthesized Ni-Ru/Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> 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. <sup>[35]</sup> confirmed the catalytic effects of Ni and Ru catalysts. They investigated ten different combinations of Ni and Ru catalysts on various supports, such as  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>. Overall, Ni-Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> demonstrated the maximum H<sub>2</sub> yields and high carbon gasification efficiency. Ni-Ru/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> 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 <sup>[36]</sup>.

Yang et al. <sup>[37]</sup> investigated the kinetics and intermediate products of Ni-Ru/Al<sub>2</sub>O<sub>3</sub> 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. <sup>[33]</sup> 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<sub>2</sub> 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. <sup>[38]</sup> investigated Pt/Al<sub>2</sub>O<sub>3</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> catalysts in the SCWG of 2-propanol. Their results showed that the H<sub>2</sub> selectivity of Pt/Al<sub>2</sub>O<sub>3</sub> was relatively higher than that of Ru/Al<sub>2</sub>O<sub>3</sub> due to enhancement of the methanation reaction, which produced CH<sub>4</sub> at the expense of H<sub>2</sub>. Pairojpiriyakul et al. <sup>[39]</sup> used Co-based catalysts on a variety of supports, such as  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, and yttria-stabilized zirconia (YSZ), in the SCWG of glycerol. The highest H<sub>2</sub> yield was obtained with Co/YSZ. In addition, increasing the Co loading up to 10% improved the gasification efficiency of glycerol and H<sub>2</sub> production. However, a further increase in the Co loading decreased both H<sub>2</sub> 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 <sup>[40]</sup>. 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<sub>2</sub>, ZrO<sub>2</sub>, and CeO<sub>2</sub>.

Cao et al. <sup>[41]</sup> 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<sub>2</sub> yields decreased with almost all metal oxide catalysts, except  $Cr_2O_3$ , which improved the H<sub>2</sub> yield.

Various co-precipitated binary metal oxide catalysts, such as CeO<sub>2</sub>-ZrO<sub>2</sub>, CuO-ZnO, and Fe<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub>, have demonstrated high catalytic performance in SCWG <sup>[42][43]</sup>. Cao et al. <sup>[42]</sup> showed that in the SCWG of lignin, the CuO-ZnO catalyst demonstrated high catalytic performance with a high H<sub>2</sub> yield and better gasification efficiency, followed by Fe<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>-ZrO<sub>2</sub>. However, in the SCWG of cellulose, Fe<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> showed a greater H<sub>2</sub> yield and high carbon gasification efficiency, followed by CuO-ZnO and CeO<sub>2</sub>-ZrO<sub>2</sub>. 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<sub>2</sub> 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<sub>2</sub> was the main active component in the SCWG process. ZrO<sub>2</sub> also absorbed active H<sub>2</sub> and small intermediates to increase contact between the intermediates and CeO<sub>2</sub> 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 <sup>[44]</sup> studied the detailed catalytic mechanism of  $RuO_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> in the SCWG of municipal solid waste.  $RuO_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> drastically increased H<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> yields while significantly improving gasification efficiency. The high yield of H<sub>2</sub> was due to enhancement of the water–gas shift reaction by the catalytic action of  $RuO_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub>. In addition, the enhancement of methanation of CO or CO<sub>2</sub> and hydrogenolysis of C–C hydrocarbons resulted in a high CH<sub>4</sub> yield. Improvement in the yields of the reduction product (CH<sub>4</sub>) and oxidation product (CO<sub>2</sub>) indicated the involvement of the  $RuO_2/\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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. <sup>[45]</sup> compared MnO<sub>2</sub>/SiO<sub>2</sub> and NiO/SiO<sub>2</sub> catalysts in the SCWG of microalgae *Chlorella*. MnO<sub>2</sub>/SiO<sub>2</sub> demonstrated the highest H<sub>2</sub> yield (1.1 mmol/g) compared to NiO/SiO<sub>2</sub> (0.6 mmol/g) and non-catalytic SCWG (0.2 mmol/g). Therefore, NiO/SiO<sub>2</sub> was less active than the supported MnO<sub>2</sub>/SiO<sub>2</sub>. Borges et al. <sup>[46]</sup> investigated the Ni/Fe<sub>2</sub>O<sub>4</sub> catalyst in the SCWG of *Eucalyptus* wood chips. Ni/Fe<sub>2</sub>O<sub>4</sub> enhanced the H<sub>2</sub> yield and decreased the char yield. Further investigation showed that Ni/Fe<sub>2</sub>O<sub>4</sub> favored the water–gas shift and steam reforming reactions, thus increasing H<sub>2</sub> yield and decreasing CH<sub>4</sub> yield. It also demonstrated good stability and recyclability despite the coke deposit <sup>[47]</sup>.

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