

Review of Novel Catalysts for Biomass Tar Cracking and Methane Reforming

M. A. Gerber

October 2007



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Executive Summary

A review of the literature was conducted to examine the performance of catalysts, other than conventional nickel catalysts and alkaline earth and olivine based catalysts, for treating hot raw product gas from a biomass gasifier to convert methane and tars into synthesis gas. Metal catalysts other than Ni included precious metals Rh, Ru, Ir, Pt, and Pd, as well as Cu, Co, and Fe in limited testing. Nickel catalysts promoted with Rh, Zr, Mn, Mo, Ti, Ag, or Sn were also examined, as were Ni catalysts on Ce_2O_3 , TiO_2 , ZrO_2 , SiO_2 , and La_2O_3 . In general, Rh stood out as a consistently superior metal catalyst for methane reforming, tar cracking, and minimizing carbon buildup on the catalyst. Ru and Ir also showed significant improvement over Ni for methane reforming. Ceria stood out as good support material and particularly good promoter material when added in small quantities to another support material such as alumina, zirconia, or olivine. Other promising supports were lanthana, zirconia, and titania.

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1.0 Introduction

Biomass gasification technology converts lignocellulosic materials such as wood, corn stover, and switchgrass into a medium-Btu gas that can be used in a number of energy applications such as fuel for process heat, steam, cogeneration of electricity, and the synthesis of liquid products that can be used in producing transportation fuels such as gasohol and diesel fuel. The U.S. Department of Energy (DOE) is particularly interested in its potential for producing a synthesis gas suitable for producing ethanol and other mixed alcohols.

The product gas from a biomass gasifier mainly consists of CO, H₂, CO₂, CH₄, H₂O, and smaller amounts of N₂. In addition, it contains small quantities of hydrocarbon gases such as ethane, organic vapors broadly classified as tars (in this report tars are considered to be organic compounds with a molecular weight greater than or equal to benzene), and trace amounts of inorganic impurities such as H₂S, CS₂, COS, AsH₃, PH₃, HCl, NH₃, HCN, and alkali salts. The tars consist of a range of hydrocarbons and oxygenated hydrocarbons, typically containing aromatic, polyaromatic, and furanic backbone structures, with aliphatic and oxygenated functional groups (acids, aldehydes, ketones, and alcohols) attached to the backbone structures. These tars are notorious for condensing and subsequently polymerizing on downstream equipment such as compressors and gas turbine surfaces if the gas is sufficiently cooled. They also potentially contribute to significant carbon deposition on catalyst surfaces for processes involved in adjusting the raw gas composition to a synthesis gas suitable for ethanol synthesis, such as water-gas-shift and methane reforming.

The ideal synthesis gas consists of H₂ and CO in an appropriate ratio with a small quantity of CO₂ also allowed. Nitrogen and methane behave as inert gases in alcohol synthesis and are not desirable in the synthesis gas. Furthermore, methane in the raw product gas can tie up a significant quantity of the biomass carbon and hydrogen potentially available for alcohol synthesis. Nitrogen, an impurity mainly associated with air, is minimized by gasifying biomass indirectly or by using purified oxygen to supply heat to the gasifier. Methane is reduced by reforming it with steam and/or CO₂ in the product gas to produce additional CO and H₂.

Tars can be removed from the gas by wet scrubbing and condensation to simultaneously remove water from the raw product gas. However, this produces a wastewater stream that must be further treated and also removes a portion of the biomass carbon and hydrogen potentially available for alcohol synthesis. Alternatively, the tars can be thermally decomposed by operating the gasifier at significantly higher temperatures, increasing the heat requirements for the process and potentially vaporizing alkali metals in the gas, making their subsequent removal more difficult.

A preferred method for reducing tars is to catalytically decompose them at or near the preferred gasifier temperature. This would improve recovery of the carbon and hydrogen in the synthesis gas and reduce the organic loading of waste water produced when the raw gas is cooled to remove steam from the raw product gas. Similarly, it would be preferable to reform methane in the raw gas before cooling the gas, so that any CO₂ resulting from the methane reforming process can be removed in a single step along with the other inorganic gas impurities.

The concept of catalytically treating the biomass gasification hot raw product gas to convert biomass tar into additional H₂ and CO has been of considerable interest since the early 1980s. This effort, as it applies to biomass gasification, has been well documented (Dayton 2002, Stevens 2001, Milne and Evans 1998). Most research has focused on the use of dolomite [CaMg(CO₃)₂] and individual alkaline earths and olivine [(Mg,Fe)₂SiO₄] to reduce the concentration of tars and nickel containing catalysts to both reform methane and reduce the concentration of tars. Both types of catalysts have been examined either in the gasifier or downstream of the gasifier in a separate process. Dolomite as a catalyst is of interest because it is relatively cheap, making it suitable for disposal when its catalytic properties have been spent, although it is not generally considered suitable in a fluidized bed gasifier because of attrition problems. Olivine appears to be preferable to dolomite because of its increased attrition resistance. However, both materials alone are only partially effective in reducing tars to acceptable levels.

Nickel catalysts, including those consisting of nickel impregnated olivine, are much more efficient at converting biomass tars and reforming methane in the hot product gas. However, nickel catalysts are poisoned by coke formation and by inorganic impurities in the raw gas such as H₂S, alkali, and chlorine-containing compounds. Earlier research by industry to improve nickel-based reforming catalysts with respect to coke deposition has resulted in several commercial catalysts that typically include nickel on an alumina and/or alkaline earth silicate/spinel support with alkali promoters to reduce carbon deposition.

The primary purpose of this review is to examine previous research on catalysts other than conventional nickel catalysts and alkaline earth and olivine based catalysts for treating hot raw product gas from a biomass gasifier to convert methane and tars into synthesis gas. Several other metals have been mentioned in the literature as being suitable either biomass or coal tar destruction or methane reforming. These metals include the precious metals Rh, Ru, Pt, Pd, and Ir, and other metals Cu, Co, and Fe. They are examined in this review as well as nickel catalysts used in conjunction with these metals and with other less conventional support and promoter materials.

2.0 Methane Reforming over Precious Metal Catalysts

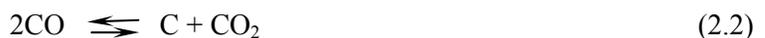
Much of the research since 1995 involving precious metal catalysts has examined methane reforming in steam, CO₂, and mixtures of these two gases to compare the relative performance of Rh, Ru, Pt, Pd, and Ir with respect to each other and with respect to nickel based catalysts. Research has also compared the relative performance specific precious metal catalysts with respect to different catalyst supports.

Rostrup-Nielsen and Hansen (1993) conducted research on both steam and CO₂ reforming catalysts containing Ni, Ru, Rh, Pd, Ir, or Pt on MgO and Ni on MgAl₂O₄. Catalysts were prepared by impregnation of 4.3 x 4.3-mm cylinders of alumina-stabilized magnesia support (Mg:Al ratio of 7:1), with precious metal content ranging from 0.9 to 1.4%. The nickel containing catalyst consisted of 16% Ni on a spinel (MgAl₂O₄) support. All catalysts were reduced in hydrogen at 550°C for 4 hours. Tests were conducted at atmospheric pressure at 500° and 650°C. Reacting gases consisted of 74% CO₂ or H₂O and 18.5% CH₄ and 7.5% H₂. In general, the activity trend for the different metals was Rh, Ru > Ir > Ni, Pt, Pd. All catalysts experienced significantly higher reforming rates with steam than with CO₂. For example, both nickel catalysts tested had turnover frequencies 1.4 to 1.6 times greater in steam than in CO₂ atmospheres at 550°C. Rh, Ru, Ir, Pd, and Pt had respective turnover frequencies 4.3, 3.1, 10.2, 8.9, and 5.6 times greater in steam than in CO₂ at the same temperature. In tests using only CO₂ and H₂, all of the catalysts were active for the water-gas shift reaction. In thermo-gravimetric analysis (TGA) tests conducted with a gas mixture of 4.55% CH₄, 45.5% CO₂, 2% H₂, and 7% N₂ up to temperatures as high as 847°C to examine the simultaneous methane reforming and carbon deposition reactions, all of the precious metals had lower carbon deposition rates than the nickel catalysts due to methane decomposition:



Specifically, no carbon deposition occurred on the Rh and Ru catalysts. Rapid carbon deposition occurred on Pd only above 650°C, and slow deposition occurred on the Ir and Pt catalysts above 750°C. Carbon deposition rates were most rapid on the Ni catalysts. Only Ni and Pd formed whisker carbon during these tests.

Qin et al. (1996) and Qin and Lapszewicz (1994) conducted tests to compare partial oxidation (POX), steam, CO₂, and mixed steam/CO₂ reforming using Rh, Ru, Pd, Pt, and Ir on MgO supports to examine the reaction mechanism for POX. All catalysts were prepared by the incipient wetness technique, using aqueous solutions of the appropriate metal chlorides. The catalysts were reduced in hydrogen at 500°C for 10 hours. Metal content on the all of the catalysts catalysts was 5%. Mixed steam/CO₂ reforming took place between 600° and 900°C in a feed gas consisting of 21.4% CH₄, 14.3% H₂O, 7.1% CO₂, and 57.1 N₂ (the N₂ serving as the diluent). They found the same order of reactivity as Rostrup-Nielsen and Hansen (1993), although they noted that all of the reactions were lower than had been observed when CO₂ or H₂O were used alone. They attributed the loss of activity to an enhanced inhibiting effect of steam and CO₂ on methane conversion rates when they are used together rather than the rates observed when these gases are used alone. They also found very little carbon buildup on the Ru, Rh, and Ir catalysts during the experiments due to methane decomposition (Eq. 2.1) and the Boudouard reaction:



Kusakabe et al. (2004) examined steam reforming of methane using 10 wt% Ni on γ -Al₂O₃, ZrO₂ and Ce-ZrO₂ supports with Ce:Zr ratios of 1:100, 15:85, 25:75, and 50:50. The ZrO₂ and Ce-ZrO₂ supports were prepared by adding a urea solution to an aqueous solution containing ZrOCl₂ · 8 H₂O and Ce(NO₃)₃ · 6 H₂O in the appropriate ratios. The mixture was maintained at 100°C for 50 hours, filtered at room temperature, rinsed with ethanol, and calcined at 500°C for 4 hours. Nickel was added to the supports by the incipient wetness technique using an aqueous solution of Ni(NO₃)₂, dried in a vacuum at 50°C for 2 hours, and calcined in air at 500°C for 2 hours. The calcined catalysts were reduced in H₂ at 500°C for 2 hours.

Kusakabe et al. (2004) also examined steam reforming of methane using Rh, Ru, and Pt catalysts on Ce-ZrO₂ supports with Ce:Zr ratios of 15:85. A catalyst consisting of 10% nickel on the same Ce-ZrO₂ support was also examined for comparison. The Ce-ZrO₂ support was prepared by adding a urea solution to an aqueous solution containing ZrOCl₂ · 8 H₂O and Ce(NO₃)₃ · 6 H₂O in the appropriate ratio. The mixture was maintained at 100°C for 50 hours, filtered at room temperature, rinsed with ethanol, and calcined at 500°C for 4 hours. The appropriate metal was added to the supports by the incipient wetness technique using an aqueous solution of H₂PtCl₆, RhCl₃, RuCl₃, or Ni(NO₃)₂. The impregnated catalysts were dried in a vacuum at 50°C for 2 hours and calcined in air at 500°C for 2 hours. The calcined catalysts were reduced in H₂ at 500°C for 2 hours.

Tests were performed between 500° and 800°C in a gas stream consisting of 16.6% CH₄, 33.3% H₂O, and 50% Ar. After testing the Pt/Ce-ZrO₂ catalyst with different metal loadings at 600°C, a preferred metal loading of 3% was chosen for tests to examine all of the catalysts over the entire temperature range. All of the precious catalysts with 3% metal concentration were more active than the 10% Ni catalyst over the entire temperature range. However, the Rh/Ce_{0.15}Zr_{0.85}O₂ was significantly more active than the Ru and Pt based catalysts. No carbon deposition was noted on any of the noble metal-based catalysts after 5 hours of testing.

Fereira-Aparicio et al. (1998) compared the performance of Co, Ni, Ru, Rh, Ir, and Pt catalysts on silica and γ -alumina supports for CO₂ reforming of methane. Catalysts were prepared by impregnation of the supports with aqueous solutions of the appropriate precursor salts (nitrate salts of Co and Ni, chloride salts of Ir, and Pt, and hydrated chloride salts of Ru and Rh). The impregnated catalysts were dried overnight, calcined in air at 500°C for 3 hours, and reduced in hydrogen at 400°C for 4 hours following a 5°C/min heat-up rate to that temperature. The metal concentrations for the different catalysts ranged from 0.63 to 1.21 wt % for the silica-supported catalysts and from 1.0 to 4.88 wt % for the γ -alumina supported catalysts. However, the concentration of each precious metal was the same on both catalyst supports for Rh and Ir. The Ru concentration on the SiO₂ support was about 12% higher than that on the γ -alumina support, while the Pt concentration on the SiO₂ support was about half of that on the γ -alumina support. The metal concentrations for Ni and Co on the SiO₂ supports were about 20% of that on the γ -alumina supports. Tests were conducted from 400° to 750°C in a gas stream consisting of 10% CO₂, 10% CH₄, and 80% He. In general, they found that the alumina supported catalysts were more reactive over the temperature range than the silica supported catalysts. However, they noted that the Ir catalyst on both supports deactivated during the first 2 hours of testing. The general trend in methane turnover frequencies at 450°C for the alumina-supported catalysts was Rh > Ni > Ir > Pt, Ru > Co, and the trend for the silica supported catalyst was Ni >> Ru >> Rh, Ir, (trends could not be determined for Pt and Co catalysts due to low hydrogen chemisorption). They also showed, using temperature-programmed reforming reaction tests, that alumina supported Pt and Ru deactivated due to sintering at 750°C. Ru on

silica also appeared to undergo deactivation due to both sintering and carbon deposition, while Ir on both supports underwent rapid deactivation due to carbon deposition. The Rh, Ni, and Co catalysts were thermally stable.

Bradford and Vannice (1999) conducted research to investigate the interaction between titania supports and the catalyst metal during CO₂ reforming of methane by characterizing and measuring the activities of select precious metals on silica and titania. All catalysts were prepared by incipient wetness technique using aqueous solutions of the appropriate metal salt hydrated chloride salts of Ru, Rh, and Ir; PdCl₂ and H₂PtCl₆ · H₂O (Ir/SiO₂ and Ru/SiO₂ catalysts were not prepared). Metal loadings ranged from 1.1 to 6.8 wt% on the SiO₂ supports and from 0.3 to 1.2 wt% on the TiO₂ supports. All catalysts were dried in air over night at 150°C and sieved to -70/+120 mesh. All catalysts except the Rh/SiO₂ catalyst were reduced in hydrogen first at 150°C for 30 minutes followed by heating up to and maintaining at 500°C for 1 hour. The Rh/SiO₂ catalyst was reduced in a 20% H₂ in He gas mixture at 500°C for 2 hours. Tests were conducted over a temperature range of 400°–500°C in a gas mixture with a CO₂:CH₄:He ratio of 1:1:1.8. Their results indicated that Pt, Pd, and Rh were much more reactive on titania than on silica in terms of CO and CH₄ turnover frequencies.

Hennings and Reimert conducted research on CO₂ reforming of methane using 2.5 wt% Rh, Ru, or Pt on Ce₂O₃ and on Gd-doped Ce₂O₃ with a Ce:Gd ratio of 4:1. The catalysts were prepared by dissolving Ce₂(NO₃)₃ · 6 H₂O, and the appropriate quantity of Gd(NO₃)₃ · 6 H₂O; Ru(NO)(NO₃)₃, Rh(NO₃)₃, or Pt(NH₃)₃(NO₃)₃; and a stoichiometric amount of glycine in a small quantity of water. The mixture was evaporated in an open pressure vessel followed by heating to ignition in the closed vessel. The resulting powders were calcined in air at 550°C for 2 hours. Tests were conducted from ~ 500° to ~ 850°C using a gas stream consisting of 14% CH₄, 43% CO₂, and 43% N₂. They found that at temperatures between about 550° and 700°C the Rh/CeO₂ catalyst was the most active; followed by the Ru/CeO₂, Ru/Gd/CeO₂, and Rh/Gd/CeO₂ catalysts, which had similar activities; followed by the Pt/CeO₂ and Pt/Gd/CeO₂ catalysts, which were significantly less reactive. These general trends held above 700°C except that the Ru/CeO₂ catalyst became less active above 700°C and the Ru/Gd/CeO₂ catalysts became less active above 800°C. The two Rh catalysts and the Pt/CeO₂ catalysts were able to achieve 100% CH₄ conversion at 850°C under the flow conditions tested. There were, however, significant differences in the deactivation rates of the catalysts. The Rh/Gd/CeO₂ catalyst did not show signs of deactivation after 24 hours of testing. The times to achieve 50% deactivation for the Rh/CeO₂ and Pt/Gd/CeO₂ catalysts were 10.5 and 13.5 hours, respectively, while the other catalysts achieved 50% deactivation in 3.2 hours or less. The authors determined that catalyst deactivation was not due to coke deposition, which was not observed on any of the catalysts under the conditions tested, and was consistent with the test conditions that were not favorable to carbon deposition. Instead they attributed deactivation due to decoration of the catalyst particles with the support (also referred to as strong metal-support interaction, in which some of the support covers exposed noble metal particles over time at the higher temperatures), as evidenced by high-resolution transmission electron microscopy images of the spent catalysts showing mineral coatings on noble metal particles for all but the Rh particles on the Gd/CeO₂ support. Hennings and Reimart also examine the sulfur resistance of the Rh/Gd/CeO₂ catalyst to sulfur in the gas feed in comparison to a commercial nickel-based catalyst. While the nickel-based catalyst completely deactivated after less than 4 hours in a gas stream containing 5.2 mg S/m³, the Rh based catalyst only lost about 20% of its activity after 5 hours. The Rh-based catalyst still retained ~50% of its initial activity after an additional 5 hours in a gas containing 12.34 mg S/m³ and about 20% of its initial activity after yet an additional 3.5 hours in a gas stream containing 26.5 mg S/m³. The fact that the Rh-based catalyst maintained much of its activity

even after more than enough sulfur had passed over the catalyst to deactivate all of the Rh on the catalyst indicates sulfur tolerance by the catalyst. However, the authors pointed out that the CeO₂ support may be acting as a getter for the sulfur, forming Ce(SO₂)₃ and/or Ce₂O₂S species, and the Rh/Gd/CeO₂ catalyst would become deactivated once the sulfur capacity of the cerium was achieved.

Wisniewski et al. (2005) investigated CO₂ reforming of methane over 0.16 wt% iridium on a Ce_{0.9}Gd_{0.1}O_{2-x} (CGO) catalyst support that was being considered for use as an anode material for a solid oxide fuel cell. The CGO support was obtained from Praxair Specialty Ceramics, Inc., Woodinville, Washington. It was added to the support using wet impregnation with an aqueous solution of H₂IrCl₆·4H₂O. The aqueous solution and support were stirred at room temperature for 30 minutes, evaporated under reduced pressure at 70°C, and dried at 120°C overnight. The dried catalyst was calcined in air for 6 hours at 800°C (following a 2°C/min heatup rate to 800°C). Tests were conducted 600° to 800°C in a gas mixture consisting of 25% CH₄, 12.5–37.5% CO₂, and the balance N₂ (CH₄:CO₂ ratios from 2–0.67). Total gas space velocity was 35,000 L/L_{cat}/hr. They found that CH₄ conversion peaked at a CH₄:CO₂ ratio of ~1 at all temperatures tested with a maximum CH₄ conversion of 73% at 800°C. The authors noted that carbon deposition was not observed after long-term testing (at least 20 hours) below 800°C regardless of the CH₄:CO₂ ratio tested. Even at 800°C, the only time carbon deposition was observed was when the CH₄:CO₂ ratio was 2 and the carbon deposition was calculated to be 0.13%.

Noronha et al. (2003) examined CO₂, steam, and combined CO₂ and steam reforming of Pt/ZrO₂ and Pt/Ce-ZrO₂ catalysts. Zirconium hydroxide and ceria-doped zirconium hydroxide supports were obtained from a commercial supplier and were calcined at 800°C for 4 hours in air. Platinum was added to the catalysts by the incipient wetness technique using aqueous solutions of H₂PtCl₆·6H₂O. Impregnated supports were dried and calcined at 400°C for 2 hours. Platinum loading was 1.5 wt%. Catalysts were reduced at 500°C for 1 hour in hydrogen. CO₂ reforming experiments were conducted from 800°C in a gas mixture of CH₄ and CO₂ with CH₄:CO₂ of 1 and 2. The authors found that while methane conversion during CO₂ reforming with the fresh Pt/ZrO₂ catalyst was higher than the fresh Pt/Ce-ZrO₂ catalyst (42% versus 37%), the rate decreased by about 40 and 60% over a 22-hour period using gas mixtures with CH₄:CO₂ ratios of 1, and 2, respectively, while the Pt/Ce-ZrO₂ catalyst did not experience any decrease for either condition. As a result, the conversion efficiency after 22 hours was greater for the Pt/Ce-ZrO₂ catalyst. During combined CO₂ and steam reforming, methane conversion with the fresh Pt/ZrO₂ catalyst was ~42% versus 27% with the fresh Pt/Ce-ZrO₂ catalyst. The conversion with the Pt/ZrO₂ catalyst decreased by about 75% over a 22-hour period, while conversion with the Pt/Ce-ZrO₂ catalyst decreased by about 7%. temperature-programmed oxidation (TPO) measurements showed carbon buildup on all of the catalysts with carbon buildup greatest for both catalysts during combined CO₂ and steam reforming, followed by CO₂ reforming with a gas mixture with a CH₄:CO₂ ratio of 2. However, there was no clear trend between the amount of carbon deposited and the catalyst activities.

3.0 Alternative Nickel Based Reforming Catalysts

Several researchers have examined the potential for improvements to nickel-based catalysts, either by adding promoters other than alkali and alkaline earths to the alumina-supported nickel catalysts or by using other catalyst supports besides alumina.

3.1 Promoted Nickel/Alumina Catalysts

Becerra et al. (2002) examined the promoting effect of rhodium on Ni/Al₂O₃ catalysts using supports prepared from two different commercially available aluminas. One was impregnated with 18.1 wt% Ni and the other with 10.2 wt% Ni added as nickel nitrate solution. The catalysts were dried at 120°C for 5 hours and calcined at 550°C for 3 hours in air. Rhodium was impregnated on both Ni-catalysts as rhodium nitrate solution to produce catalysts with 0.0, 0.05, 0.1, and 0.2 wt% Rh on the catalysts. The catalysts were then redried and calcined as before. Catalyst activity tests were conducted at 550°C in a gas mixture consisting of 41.67% CH₄, 41.67% CO₂, and 16.67% H₂. The hydrogen was reported added to avoid catalyst reoxidation. The methane flow rate was 2 mole/g_{cat}/hr. Test data were collected after a 4- to 6-hour catalyst break-in period where the catalyst activities decreased by about 30%. No further deactivation was observed after 50 hours of testing. Tests results showed that catalyst activity increased with increasing rhodium content, achieving near-equilibrium conversions at the highest Rh loading. Other catalysts prepared with only Rh on the alumina had very low activities. The authors also conducted similar tests, but with steam reforming (57.1% steam, 29.1% CH₄, and 23.8% H₂ gas mixture at 525°C) instead of CO₂ reforming to examine the influence of Rh addition to Ni/Al₂O₃ catalysts and found similar results (Luna et al. 1999). The authors concluded that the addition of rhodium increased the dispersion of the nickel on the catalysts resulting in more exposed metal and in turn higher activity for both CO₂ and steam reforming of methane.

Hou and Yashima (2003) examined the effect of adding Rh to Ni/ α -Al₂O₃ on CO₂ on both reforming of methane and carbon deposition. Catalysts were prepared by co-impregnation method using aqueous solutions containing Ni(NO₃)₂ · 6 H₂O and/or Rh(NO₃)₃. Catalysts were reduced in hydrogen at 800°C for 1 hour. Tests were conducted at 800°C in a gas mixture consisting of 50% CH₄ and 50% CO₂. They found that, while a 5% Rh on α -Al₂O₃ was less reactive than a 10% Ni on α -Al₂O₃, the addition of small quantities of Rh to the 10% Ni on α -Al₂O₃ catalyst resulted in slightly increasing reforming rates, achieving a maximum at a Rh/Ni mole ratio of 0.05. Furthermore, the carbon deposition rate decreased by a factor of 16. At a Rh/Ni mole ratio of 0.10, the catalyst reforming rates were similar to the catalysts containing only nickel, while the carbon deposition rate was negligible. The authors attributed the synergistic reforming behavior to increased dispersion of the Ni with the addition of Rh, while the Rh was a superior CO₂ activation site providing surface oxygen for oxidation of deposited carbon. The lower activity of the catalyst containing only rhodium on α -Al₂O₃ was due to its inferior activity for methane decomposition compared to Ni.

Choi et al. (1998) examined CO₂ reforming of methane over a commercially available Ni/Al₂O₃ catalyst modified with 2 wt % Co, Cu, Zr, Mn, Mo, Ti, Ag, or Sn. The Ni catalyst was ICI-46-1, reported to contain 22% NiO, 13% CaO, 6.5% K₂O, 15% SiO₂, 12% MgO, and the balance alumina. All metal promoters except Sn were impregnated on the catalyst using aqueous solutions of the metal nitrates. Sn was also added in the same manner except that the aqueous solution contained SnCl₂. The impregnated

catalysts were dried at 120°C for 12 hours and calcined at 500°C for 6 hours followed by reduction with H₂ at 800°C for 2 hours. Tests were carried out over a 450°–750°C temperature range using a gas mixture consisting of equal concentrations of CH₄ and CO₂ diluted by varying amounts of He. Total gas flow rate was held constant at 81.7 μmol/sec (also reported as a GHSV of 72,000 L/kg/hr). They found that the order of methane conversion efficiency was Co, Cu, Zr, none > Mn > Ti >> Ag >> Sn, according to their data. The performance of the nickel catalysts promoted with Co, Cu, and Zr was very slightly higher than that for the unpromoted catalyst. They also found that the unpromoted catalyst and catalysts promoted with Co, Cu, and Zr all had very high carbon deposition rates over a 2-hour period, while Mn and Mo promoted catalysts had very little carbon deposition and maintained most of their activity. They noted research done by Borowiecki and Golebiowski (1994) that showed that adding small amounts of W or Mo to a Ni/ α -Al₂O₃ catalyst considerably reduced carbon deposition in steam reforming of methane. Scanning electron microscope images of selected catalysts tested by Choi et al. (1998) showed that filamentous carbon formed on the Co- and Ti-promoted catalysts, but there was no observable coke on the Mo- and Mn-promoted catalysts. Further tests using different loadings of Mn on the ICI-46-1 catalyst showed that adding 3–6% of Mn to the catalyst significantly reduced the carbon deposition to less than 0.2 wt% over a 5-hour period without significantly decreasing the methane conversion rate. Higher manganese loading (10%) achieved slightly lower carbon deposition, but also caused a significant decrease in the methane conversion rate. The authors also examined the effect of the calcining temperature on ICI-46-1 catalyst containing 3 wt% Mn during CO₂ reforming of methane. They found that increasing the calcination temperature from 300° to 700°C resulted in increased methane conversion with less than 0.2% carbon over 20 hours of testing. The 3% manganese promoted catalyst was further tested at 650°C for a 100-hour period in a gas mixture containing equal concentrations of CH₄, CO₂, and He and a space velocity of 18,000 L/kg/hr. It lost about 17% of its initial CO₂ conversion efficiency over that period while experiencing a 0.23% carbon deposition. For comparison, the test was repeated using a 3% Mo-promoted catalyst. The Mo-promoted catalyst experienced a ~34% decrease in CO₂ conversion efficiency in only 30 hours.

Zhuang et al. (1991) conducted experiments using a TGA balance reactor and a temperature-programmed reaction technique to examine the effect of Ce₂O₃ addition to a nickel/MgAl₂O₄ catalyst on carbon deposition during steam-heptane reforming and methane conversion during steam-methane reforming, respectively. TGA tests were conducted with three catalysts prepared by step-wise incipient impregnation on a commercial MgAl₂O₄ spinel support. Preparation consisted of incipient impregnation of nickel nitrate on the support followed by calcining for 2 hours at 700°C and reduction at the same temperature for 3 hours. Next, cerium was added in different quantities to two of the catalysts as an aqueous solution of cerium nitrate followed by calcination at 400°C for 3 hours and reduction at 700°C for 2 hours. All three catalysts contained 11.5 wt% NiO, and Ce₂O₃ loadings were 0.0, 3.3, and 13.3 wt%, respectively. Carbon deposition was studied in steam-heptane reforming tests conducted in a TGA balance reactor in a gas mixture consisting of steam, heptane, and nitrogen at 550°C such that the heptane concentration was 0.04 atm and the steam:carbon ratio was 0.35 mole/atom. They found that the rate of carbon deposition decreased with increasing cerium oxide content in the catalyst, with the catalyst containing 13.3% CeO₂ having about half the carbon deposition rate of the catalyst not containing any CeO₂. Temperature-programmed steam-methane reforming experiments were carried out using two catalysts in a stainless steel flow reactor. These two catalysts were prepared using coprecipitation of Ni and Ce and calcined at 800°C. Both catalysts contained 15% NiO and 3% CeO₂, respectively, and the balance was MgAl₂O₄. Catalysts were reduced in hydrogen at 750°C for 1½ hours. Reforming took place over a 350°–800°C temperature range at a 6°C/min heat-up rate in a gas mixture of steam and

methane at a 1.5 steam:methane ratio. They found that the catalyst containing cerium oxide began reacting at a lower temperature and had a higher reaction rate than the catalyst not containing cerium oxide. The authors concluded that the cerium promoted steam reforming by dissociatively adsorbing water and transferring either $-O$ or $-OH$ to the nickel site to react with the adsorbed carbon species resulting from methane adsorption to form carbon monoxide, carbon dioxide, and hydrogen. As a result, the deposition of carbon was reduced.

Besenbacher et al (1998) studied surface alloy catalysts for methane steam reforming using gold-promoted Ni catalysts as an example of a class of two-component metal systems that do not mix in the bulk. However, such metals can form stable alloys in the outermost surface layer. Density functional theory calculations based on using small amounts of Au on a Ni slab showed that the energy barrier to methane dissociation was greater (lower dissociation rate) when an Au atom was near a Ni atom. However, when Au atoms were near a Ni atom, the adsorption energy for carbon was significantly reduced. The effect of Au on carbon adsorption (and subsequent graphitization) was expected to be more pronounced than that on methane dissociation, and tests were conducted to confirm this. Two catalysts were prepared, both consisting of 16.5 wt% Ni on a $MgAl_2O_4$ catalyst support. One of them also contained 0.3% Au. The specifics of the catalyst preparation were not provided. Tests were conducted at $550^\circ C$ in a gas mixture consisting of 3% butane, 3% steam, 7% H_2 , and 87% He (butane was selected because it has a greater tendency to form graphite on catalysts than methane). The gas space velocity was 1.2/hr. They found that the catalyst containing Ni experienced rapid deactivation while the catalyst Ni and Au did not. Furthermore, the catalyst containing Ni and Au did not show any evidence of graphite formation. These results were consistent with their predictions.

3.2 Alternative Supports for Nickel Catalysts

Kusakabe et al. (2004) examined steam reforming of methane using 10 wt% Ni on $\gamma-Al_2O_3$, ZrO_2 , and Ce- ZrO_2 supports with Ce:Zr ratios of 1:100, 15:85, 25:75, and 50:50. The ZrO_2 and Ce- ZrO_2 supports were prepared by adding a urea solution to an aqueous solution containing $ZrOCl_2 \cdot 8 H_2O$ and $Ce(NO_3)_3 \cdot 6 H_2O$ in the appropriate ratios. The mixture was maintained at $100^\circ C$ for 50 hours, filtered at room temperature, rinsed with ethanol, and calcined at $500^\circ C$ for 4 hours. Ni was added to the supports by the incipient wetness technique using an aqueous solution of $Ni(NO_3)_2$, dried in a vacuum at $50^\circ C$ for 2 hours, and calcined in air at $500^\circ C$ for 2 hours. The calcined catalysts were reduced in H_2 at $500^\circ C$ for 2 hours. Tests were performed between 500° and $800^\circ C$ in a gas stream consisting of 16.6% CH_4 , 33.3% H_2O , and 50% Ar. Between 500° and $600^\circ C$ the Ni/ $Ce_{0.15}Zr_{0.85}O_2$ catalyst was the most active—about twice as reactive as the Ni/ ZrO_2 and Ni/ $Ce_{0.25}Zr_{0.75}O_2$ catalysts, which had similar activities. The Ni/ Al_2O_3 and the Ni/ $Ce_{0.5}Zr_{0.5}O_2$ catalysts were not active over this temperature range. However, the activities of the latter two catalysts increased more rapidly above $600^\circ C$ than the other catalysts so that they were the most active catalysts at $800^\circ C$, although the Ni/ Al_2O_3 catalyst was only slightly better than the Ni/ $Ce_{0.15}Zr_{0.85}O_2$ and Ni/ $Ce_{0.25}Zr_{0.75}O_2$ catalysts. Differences in the activity of the mixed oxide supports was attributed to differences in the crystalline structure of the supports that ranged from a predominantly monoclinic phase when there was little to no Ce in the support, a predominantly tetragonal phase at the intermediate cerium concentrations, and a predominantly cubic phase at the highest Ce concentration. They noted that there was no carbon deposition on the supports containing Ce during these tests.

Bradford and Vannice (1999) conducted research to investigate the interaction between titania supports and the catalyst metal during CO₂ reforming of methane by characterizing and measuring the activities of select base metals on silica and titania. All catalysts were prepared by incipient wetness technique using aqueous solutions of the appropriate metal nitrate salts of Cu, Fe, Co, and Ni (Co/SiO₂ and Cu/SiO₂ were not prepared). All catalysts were dried in air over night at 150°C, sieved to -70/+120 mesh, and then reduced in hydrogen, first at 150°C for 30 minutes followed by heating to and maintaining at 500°C for 1 hour. Tests were conducted over a temperature range of 400° to 500°C in a gas mixture with a CO₂:CH₄:He ratio of 1:1:1.8. Their results indicated that Ni and Fe were more reactive on the titania catalysts but to a much lesser degree than the precious metals (previously discussed). They also noted that the activity of the catalysts containing Fe, Co, or Cu were not much higher than the support material without the metals present and much lower than the catalysts containing nickel irrespective of the support used.

Zhang and Verikios (1996), and Verikios (2003) conducted research on CO₂ reforming of methane on Ni/La₂O₃, Ni/ γ -Al₂O₃, and Ni/CaO catalysts. Catalysts were prepared by wet impregnation of each support with an aqueous solution of nickel nitrate. The resulting slurries were evaporated at 80°C and dried at 110°C for 24 hours. The dried catalysts were calcined at 500°C for 2 hours and then reduced at 500°C for 5 hours in hydrogen flow. A second Ni/La₂O₃ catalyst was prepared by physically mixing NiO and La₂O₃ and reducing the mixture at 750°C in hydrogen. Tests were conducted at temperatures ranging from 550°–750°C in a gas mixture consisting of 20% CH₄, 20% CO₂, and 60% He. Catalysts were diluted in α -alumina, and flow conditions were set to obtain conversions well below equilibrium values. The authors found that the Ni/Al₂O₃ catalyst was significantly more active than the Ni/CaO catalyst. Furthermore, the activity of both the Ni/Al₂O₃ and the Ni/CaO catalysts containing 17 wt% Ni decreased from 32 to 58% and from 41 to 57%, respectively, during the first 5 hours of testing, depending on the reaction temperature. The Ni/La₂O₃ catalyst containing 17% Ni was initially less reactive than either of the other two catalysts, but its activity increased by 38 to 300% during the 5-hour period and then remained relatively stable for 100 hours. Consequently, the activity of the Ni/La₂O₃ catalyst after 5 hours of testing was about the same as the Ni/Al₂O₃ catalyst at 550°C, but was about 2x and 1.5x higher at 650° and 750°C, respectively. Further testing of the Ni/La₂O₃ catalyst showed that an increase in activity to a stable level also occurred with a catalyst containing 10% Ni, while the activity initially increased and then slowly decreased when the nickel loading was 3%. However, after more than 20 hours of testing, the activity of the catalyst containing 3% Ni was still about double that of the catalyst containing 10% Ni and more than double that of the catalyst containing 17% Ni. The authors also showed that equilibrium conversion could be obtained at all temperatures tested using the catalyst with 17% Ni and at contact times of 0.06 g-sec/mL. Examination of catalyst performance after treatment with different gases, and characterization of the Ni/La₂O₃ catalyst before and after testing using a variety of techniques suggested that the initial behavior of the catalyst could be attributed to the conversion of some of the La₂O₃ to La₂O₂CO₃ that decorated the nickel particles. Catalytic activity occurred at the Ni-La₂O₂CO₃ interface, while the oxycarbonate reacted with deposited carbon, thereby removing carbon from the Ni.

4.0 Tar Cracking over Alternative Catalysts

As was discussed, most earlier research focused on the use of dolomite, individual alkaline earths, and olivine to reduce the concentration of tars and nickel-containing catalysts to both reform methane and reduce tars. More recent research has examined alternative catalysts, examining both precious metal catalysts and catalyst promoters as well as other support materials. The scope of research has ranged from examining catalysts in the gasifier (catalytic gasification) and downstream of the gasifier using wood and cellulose feedstocks, to conducting tests using model compounds to represent selected tar components in a tar cracking reactor.

Tomishige et al. (2003) investigated the reforming of tars produced from cedar wood gasification over catalysts containing Ni, Ru, Rh, Pd, or Pt on a support consisting of 60 wt% CeO₂ on SiO₂. The concentrations of the active metals were maintained at 1.2 (10)⁻¹ mole/g_{cat} (0.7, 1.21, 1.23, 1.26, and 2.34 wt%, respectively). The CeO₂-SiO₂ support was prepared by the incipient wetness technique using an aqueous solution of Ce(NH₄)₂(NO₃)₆ and silica (Aerosil 3 80 m²/g). After impregnation, the silica was dried at 110°C for 12 hours followed by calcining in air at 500°C for 3 hours. The precious metal catalysts were prepared from the calcined CeO₂-SiO₂ support by impregnation with an acetone solution of Rh(C₅H₇O₂)₃, Pd(C₅H₇O₂)₂, Pt(C₅H₇O₂)₂, or Ru(C₅H₇O₂)₃. Acetone was evaporated from the solids at ~60°C with constant stirring, followed by drying at 110°C for 12 hours. The dried catalyst was pelletized, crushed, and sieved to a +45/-150 μm particle size range. The nickel catalyst was prepared from the calcined CeO₂ -SiO₂ support by impregnation with an aqueous solution of Ni(NO₃)₂ · 6H₂O, followed by drying at 110°C for 12 hours. All catalysts were calcined at 500°C for 3 hours and reduced in hydrogen at 500°C for 30 minutes. The fluidized bed gasifier was indirectly heated by a furnace surrounding the gasifier vessel. The fluidizing medium was nitrogen and the wood feed contained 10% moisture. The catalyst reactor was also a fluidized bed enclosed in a separate chamber within the gasifier and separated from the gasifier by a distributor plate. In this arrangement, the product gas from the gasifier was passed through the distributor plate and into the second catalytic bed. Char and ash were retained within the biomass fluidized bed gasifier. A small quantity of oxygen was also introduced into the catalyst bed during tests, corresponding to approximately 0.25 mole of oxygen/mole of carbon in the wood fed to the gasifier.

Tests were conducted over a temperature range of 550°–650°C. The Rh catalyst was the best tar cracking catalyst, leaving no reported tars in the product gas over the entire temperature range. Coke deposits remained at constant at 1% of the catalyst weight over this temperature range. None of the other catalysts were particularly effective in tar removal at temperatures up to 600°C, and the Pt catalyst was the only other catalyst able to achieve complete tar conversion at 650°C. The Ru catalyst appeared to become deactivated above 600°C. Similarly, all of the other catalysts obtained higher coke deposits than the rhodium catalyst up to 600°C, with only the Pt catalyst achieving a comparable 1 wt% carbon deposit at 650°C. Examination of the reported methane formation rates based on the gas composition leaving the catalyst bed showed that methane formation increased with increasing temperature for both the Ni and Ru catalysts over the entire temperature range, while the rate decreased for the Pd catalyst. Methane formation rates decreased above 600°C for the Pt and Rh catalysts, with the Pd and Pt catalysts achieving comparable methane formation rates of ~80–85 μmol/min and the Rh catalyst achieving a higher rate of ~160 μmol/min at 650°C. Using a maximum reported methane formation rate of ~390 μmol/min for all of the catalysts and temperatures tested (maximum methane formation rates reported for the Rh catalyst at

550° and 600°C and for Ru at 650°C), the apparent reduction in methane by the Pt and Pd catalysts was ~80%, while the reduction for Rh was ~60%. While the gasifier was operated at relatively low temperatures (550°–650°C) and would produce larger quantities of less stable tar constituents than a gasifier operating at higher temperatures, these results do provide an indication of the ability of the different catalysts to remove more refractory tars, and reform methane.

Asadulla et al. (2001) conducted semi-continuous gasification tests to examine the catalytic gasification of cellulose in an air fluidized bed. Several catalyst supports were evaluated (none, CeO₂, MgO, TiO₂, ZrO₂, Al₂O₃, and SiO₂) as well as several noble metals (Rh, Ru, Pd, Pt, and Ni) on CeO₂. The metal catalysts on CeO₂ were prepared by conventional impregnation method using the appropriate metal acetate in an acetone solution. The metals were all added at a metal loading of $1.2(10)^{-4}$ mol /g_{cat}. A commercially available catalyst from TOYO CCI (G-91) was also tested for comparison. The G-91 catalyst reportedly contained 14% Ni, 65–70% Al₂O₃, 10–14% CaO, and 1.4–1.8% K₂O. Catalysts were reduced in hydrogen at 500°C for 30 minutes prior to testing. Tests were conducted at 823°C using air as the fluidizing medium. A fixed quantity of cellulose was fed to the gasifier. The product gas was passed through an ice bath and collected in a gas bag. Each test lasted for about 7 minutes. Catalyst performance was determined by measuring the yields of CO, CO₂, CH₄, and H₂ in the product gas. They found that only ~50% of the carbon in the feed was converted to the carbon-containing gases with Al₂O₃ and SiO₂ supports or with no catalyst used in the fluidized bed, with the unconverted carbon presumed to be char and tar produced during gasification. CeO₂, MgO, TiO₂, and ZrO₂ supports all converted ~70% of the feed cellulose carbon to carbon containing gases. Coke deposition was more severe on the Al₂O₃ and SiO₂ supports than on the other supports. Cellulose carbon conversion to carbon containing gases ranged from 80–100% when the metals were added to the CeO₂ support. The order of conversion efficiency for the noble metals was Rh > Ru > Pd > Pt > Ni. The G91 catalyst had a conversion efficiency of 87%, which was the same as the Pd-containing catalyst.

Asadulla et al. (2002a) conducted further research on catalytic gasification of cellulose in a continuously fed air/steam fluidized bed using a catalyst consisting of $1.2(10)^{-4}$ mol Rh/g_{cat} (1.2 wt% Rh) on a support containing 35wt % CeO₂ on SiO₂ as the fluidized bed material. The CeO₂ /SiO₂ support was prepared by incipient wetness impregnation of an aqueous solution of Ce(NH₄)₂(NO₃)₆ on silica, drying the catalyst at 120°C for 12 hours and calcining the catalyst in air at 500°C for 2 hours, followed by an additional hour at 600°C. Rh was added to the catalyst by incipient wetness impregnation using an acetone solution of Rh(acac)₃. The catalyst was dried at 120°C for 12 hours, ground, and sieved. The catalyst was reduced in hydrogen at 500°C for 30 minutes prior to the tests. Tests were conducted from 500°–700°C. They also examined a commercial reforming catalyst (G-91) that contained 14% Ni, 65–70% Al₂O₃, 10–14% CaO, and 1.4–1.8% K₂O and dolomite (21% MgO, 30% CaO, 0.7% SiO₂, 0.1% Fe₂O₃, and 0.5% Al₂O₃). They determined that the Rh/CeO₂ /SiO₂ catalyst produced lower methane and tar in the product gas and lower levels of char in the bed than either the nickel-based catalyst or the dolomite. Furthermore, the Rh-based catalyst showed no evidence of deactivation over 7 hours of testing, while the Ni-based catalyst experienced a significant deactivation after 25 minutes. The authors also reported having tested Rh/CeO₂ catalysts using Al₂O₃ and ZrO₂ in place of the SiO₂ and with different levels of Rh loading in the gasifier using air as the gasifying agent. The Rh/CeO₂/SiO₂ catalyst containing 1.2% Rh and 35% CeO₂ was found to be the best catalyst with respect to formation of syngas. When they tested a Rh/CeO₂ catalyst they found deactivation problems with CeO₂ aggregation resulting in a four-fold reduction in the catalyst surface area. Loading the CeO₂ on the SiO₂ inhibited CeO₂ aggregation and

maintained catalyst activity. Similar tests were conducted using a catalyst containing 1.2% Rh and 60% CeO₂ on SiO₂ to air gasify cedar wood, with similar results (Asadullah et al. 2002b).

Zhang et al. (2007) investigated the reforming of the model compounds, benzene and toluene, over Ni/olivine catalysts doped with CeO₂. Olivine used in the tests had a nominal composition of 49% MgO, 4% SiO₂, 8% Fe₂O₃, 0.5% Al₂O₃, and 0.5% CaO. Nickel and cerium were added to the olivine support by wet impregnation with aqueous solutions of nickel and cerium nitrate, respectively, followed by drying in a vacuum at 105°C for 8 hours. Dried catalysts were calcined at a low ramping rate to 800°C and maintained there for 2 hours. The three catalysts that were tested contained 3 wt% NiO, 6 wt% NiO, and 3 wt% NiO, plus 1 wt% CeO₂ on olivine, respectively. Catalysts were reduced at 700°C in a gas mixture consisting of 50% H₂ in N₂ for 2 hours. Baseline tests were conducted from 700° to 830°C in a steam/model compound gas mixture with a steam/carbon ratio of 5 and a model compound space velocity of ~860 L/L_{cat}/hr. They found that the catalyst containing both Ni and Ce achieved consistently higher benzene and toluene conversions than the two catalysts containing two different Ni loadings over the temperature range of 700°–800°C. At 830°C, all three catalysts had similar conversions, which the authors attributed to achieving equilibrium conditions. Catalyst surface elemental analysis of the spent catalysts showed the catalyst with both nickel and cerium on the olivine had significantly lower quantities of carbon indicating superior carbon deposition resistance.

5.0 Conclusions

The purpose of this review was to examine the potential performance of catalysts other than conventional nickel catalysts and alkaline earth and olivine based catalysts for treating hot raw product gas from a biomass gasifier to convert methane and tars into synthesis gas. Metal catalysts other than Ni included precious metals Rh, Ru, Ir, Pt, and Pd, as well as Cu, Co, and Fe in limited testing. Nickel catalysts promoted with Rh, Zr, Mn, Mo, Ti, Au, Ag, or Sn were also examined, as were Ni catalysts on Ce_2O_3 , TiO_2 , ZrO_2 , SiO_2 , and La_2O_3 supports.

Most of the studies involved reaction environments that are much simpler than expected for biomass derived product gas that contains the reactive gases (H_2O , CO , CO_2 , and H_2); unacceptably high concentrations of methane, which ties up biomass carbon and hydrogen in an unreactive form during alcohol synthesis; tar, which can foul downstream equipment, such as compressors; and inorganic impurities that can poison catalysts. More specifically, only a few studies used raw product gas from a biomass gasifier, as the reacting medium for evaluating catalysts. Most of the studies examined methane reforming in simple gas environments containing methane, steam, and/or CO_2 , while one study examined tar cracking using model compounds such as benzene and toluene.

Even though most of the studies involved simple reaction environments, they do provide some performance trends that would apply to some extent in more complex reaction environments. For example, Rh generally stood out as a consistently superior metal catalyst for methane reforming, tar cracking, and minimizing carbon buildup on the catalyst. Ru and Ir also showed significant improvement over Ni for methane reforming. Ceria stood out as good support material and particularly good promoter material when added in small quantities to another support material such as alumina, zirconia, or olivine. Other promising supports were lanthana, zirconia, and titania.

While several catalyst compositions show promise, additional research is needed to evaluate them in the context of a biomass gasifier product gas. Tests using simplified environments should more accurately represent the gasifier product gas in terms of the major gases to evaluate methane reforming and tar conversion using model compounds, with the introduction of selected inorganic impurities, such as H_2S , to screen promising catalysts for resistance to poisoning. Ultimately, tests need to be conducted using hot raw product gas from a gasifier using representative feedstocks, such as wood, switchgrass, and corn stover.

6.0 References

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